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Kyoto University
STUDIES ON THE CATALYSIS BY NEW SOLID ACID CATALYSTS AND THE CHARACTERIZATION

TAKASHI YAMAMOTO

1999
STUDIES ON THE CATALYSIS BY NEW SOLID ACID CATALYSTS AND THE CHARACTERIZATION

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GRADUATE SCHOOL OF ENGINEERING
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1999
Preface

The main themes of the present thesis are to clarify acidic property and the generation mechanism of some new solid acid catalysts. The present thesis consists of three parts. In the first part, acidic properties of siliceous FSM-16 were investigated. The second part describes acidic properties of silica-supported rare earth oxides and their structural characterizations. The generation mechanism has been proposed for a long time, but no one confirmed it. The last part is devoted to clarification of the role of Fe and Mn in Fe-, Mn-SO₄²⁻/ZrO₂. SO₄²⁻/ZrO₂, which promotes superacidic reactions at room temperature, is regarded as a promising catalyst in practice. Recently, it was reported that Fe and Mn promotion onto SO₄²⁻/ZrO₂ enhances a catalytic activity of n-butane isomerization by three orders of magnitude, whereas the structures and roles of the promoters have not been clarified. As an appendix, the author applied X-ray absorption spectroscopy to characterize new-type homogeneous Lewis acid catalyst of ytterbium trifluoromethane-sulfonates.

The clue, which let the author start the series of investigations described in this thesis, is that he paid attention to the narrow pore-size distribution of mesoporous silica FSM-16 as a host of solid base particles. The original aim was to prepare homogeneous rare earth oxide particle inside the mesopore with narrow pore-size distribution, and to examine dependence of the particle size on “solid basicity”. The author prepared mesoporous silica FSM-16 supported ytterbium oxide catalysts with various loading amounts; however, unexpected phenomena that siliceous FSM-16 itself enhances some acid-catalyzed reactions were found. Subsequently, specific acidic and structural characters were found on silica-supported ytterbium oxide catalysts. Therefore, the author focused these new solid acid catalysts and investigated to clarify their acidic properties and the origins.

Catalytic processes are indispensable for modern chemical industry. Above all, the processes, to which catalyses by solid acids and bases are applied, occupy a special place. Petroleum, natural gas and coal are main resources for producing raw materials for almost all chemical products. To convert these resources, solid acid catalysts have been utilized in many important reactions such as cracking of hydrocarbons, conversion of methanol into hydrocarbons, isomerization, alkylation and acylation, oligomerization and polymerization, hydration and dehydration, hydrolysis and so forth. On the other hand, from the scientific point of view, chemistry of catalysis by solid acids and bases is considerably intriguing subject: developing new catalysts and catalysis systems, analyzing the states of catalysts and elucidating the new mechanisms and innovating the new catalysts and catalysis systems. Acid-base catalysis is always one of the main themes in International Congresses on Catalysis held every four years, and conferences on catalysis held somewhere in the world every year. Furthermore, a series of congresses focused on acid-base catalysis have been held every three years.

In 1795, Humphry Davy found that alcoholic vapor changed to other kind of a flammable gas over a heated natural clay. This phenomenon is one of the oldest discovery of catalysis by solids, and now is interpreted that ethanol was dehydrated to ethene over the clay.
A surface of solid material usually exhibits acid property. The first direct discovery of surface acid was reported by Kobayashi in 1901. Kobayashi found that the natural clay produced at Kita-Kabahara in Niigata Prefecture, Japan changed the blue color of wet Litmus paper to red. Natural clay minerals consist of mainly hydrated magnesium silicate and aluminosilicates, and the both are now generally accepted to be solid acids. The first solid acid catalyst industrially used on a large scale was activated natural clay, as a cracking catalyst in Houdry's process in 1936 (fixed-bed catalytic cracking; developed by Socony Vacuum Oil Co.). After 7 years, the moving-bed catalytic cracking process was developed by Socony Mobil Oil Company & Houdry Process Company. Almost at the same time, the first fluid catalytic cracking (FCC) process was realized by Standard Oil of Louisiana in 1942. In the cracking process, gasoline is produced from light oil distillates. Sulfuric acid-treated natural clay (mainly montmorillonite) was used for the first catalytic cracking process, however, iron impurity lowered selectivity to gasoline. It had already been known that co-precipitate of silica and alumina, and mixture of wet silica-gel and alumina-gel exhibit solid acidity. Then, amorphous silica-alumina (Al₂O₃: ca 14 wt%) catalyst was applied to the process in 1944. In 1954, Breck and Milton (Union Carbide Corp.) succeeded to synthesize A- and X-type zeolite; a family of crystalline aluminosilicates. Union Carbide Corp. and Socony Mobil Oil Co. reported in 1960 an excellent paraffin cracking ability of cation exchanged zeolite. In 1962, rare earth-exchanged hydrogen-Faujasite (RE-H-FAU) was firstly used for the cracking process by Socony Mobile Oil Company. This is an epoch-making progress in FCC processes because of highly superior of RE-H-FAU to amorphous silica-alumina in both activities and selectivities. And old type catalysts had been replaced by the zeolite-based catalysts. High performances of zeolite-catalysts drastically changed the facilities of catalytic cracking process as well. Since then, zeolite-based catalysts used for FCC process have been improved; to enhance selectivities, hydrothermal stability, stability to poisons such as SOx, Ni and V; to obtain high octane number; to decrease carbon-deposition.

Besides FCC catalysts, a large number of solid acids have been investigated and applied to industrial processes; e.g., heteropoly acids, clay minerals, MFI-type zeolites, ion-exchange resins, metal sulfates and phosphates, sulfate-ion treated zirconia, mixed metal oxides, and so forth. On the other hands, generation mechanisms of the acidic properties have not been postulated, and many questions still remain unsolved. Even nowadays, novel solid acid catalysts have been found. The chemistry of solid acid catalyst has been in progress.

The present thesis is a summary of the author's studies on the catalysis and characterization of new solid acid catalysts, which have been carried out under the supervision of Professor Satohiro Yoshida at Department of Molecular Engineering, Graduate School of Engineering, Kyoto University during 1996-1999.

The author wishes to express his sincerest gratitude to Professor Satohiro Yoshida for his helpful guidance, valuable discussions and continual encouragement throughout this work. The author is deeply grateful to Professor Takuzo Funabiki for his instructive discussions and
heartily encouragement. Special acknowledgments should be made to Professor Tsunehiro Tanaka for his fruitful discussions and suggestions, helpful advises, continual encouragement. Thanks are made to Professor Sadao Hasegawa at Tokyo Gakugei University for the collaboration about Fe-, Mn-SO$_4^{2-}$/ZrO$_2$, which is described in Chapter 6. The author is owing to Professor Shu Kobayashi at Tokyo University and Dr. Tomoko Yoshida at Nagoya University for the collaboration and instructive discussions about Yb(OTf)$_3$ complexes, which is described in Chapter 7. Dr. Shinji Inagaki at Toyota Central R & D Labs., Inc. is acknowledged for his useful and lively discussions about FSM-16, and elemental analysis. The author is delightful to express his thanks to Dr. Ryuichiro Ohnishi at Hokkaido University for his helpful advises for carrying out $\alpha$-pinene isomerization. Heartily thanks are made to Professor Masaharu Nomura at High Energy Accelerator Research Organization for the advise for recording XAFS spectra and to the staffs of Photon Factory at KEK for making the beam line available. Acknowledgments are made to Drs. Tomoya Uruga and Hajime Tanida at SPring-8 for their technical assistances for XAFS spectra measurements. The author would like to express his gratitude to the staffs at SPring-8 and the members of Broad Energy Band XAFS (BEB-XAFS; Drs. Shuichi Emura, Makoto Harada, Yoshiyuki Nakata, Masao Takahashi at Osaka University, Hidekazu Kimura at NEC, Osamu Kamishima, Yoshihiro Kubozono, Hironobu Maeda at Okayama University, and Yasuo Nishihata at JAERI) for making the beamline BL01B1 at SPring-8 available.

The author is deeply grateful to Mr. Takahiro Matsuyama for his collaboration and instructive discussions about supported rare-earth oxide catalysts, which are described in Chapters 3, 4, 5. Professor Hiromi Yamashita at Osaka Prefecture University, Drs. Yasuo Nishimura at Osaka National Research Institute, and Hisao Yoshida at Nagoya University are acknowledged for useful discussions and hearty encouragement. Thanks are made to Drs. Hirofumi Aritani at Kyoto Institute of Technology for his lively discussions and computational assistance, and Sakae Takenaka at Tokyo Institute of Technology for his useful discussions and assistance for measurements of FTIR, Raman and XAFS spectra, and glass work of apparatus. The author acknowledges Messrs. Yoshiumi Kohno for his fruitful discussions and computational assistance, and Ryoji Kuma for his assistance with TPD measurements. Thanks must be made to Secretary Miss Akiko Nakano for her kind official support. The author is indebted to all the members of the group of catalysis research led by Professor Yoshida.

Finally, the author would like to thank his parents, Masao and Kyoko, his grand mother Matsue, and his brothers Hiroshi and Takahiro for their understanding and encouragement.

Takashi Yamamoto

Kyoto,
June, 1999
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General Introduction

History of Acid and Base 1-6

Since ancient times, catalysis itself has been familiar with the life of human kinds. Without special consciousness, people had been making use of catalyses for brewage of alcoholic beverages, vinegars and so forth. Catalyses began to be utilized on purpose in the early 13th century, and diethylether synthesis from ethanol had been carried out with sulfuric acid. In 1781, Parmentier found that starch decomposes to glucose by inorganic acids in those days. The first man that recognized the "catalysis" from a scientific point of view is Kirchhoff. In 1811, he found that starch in heated water decomposes to sugars by addition of inorganic acids, whereas the inorganic acids remain unchanged. The word of "catalysis" was firstly proposed by J. J. Berzelius in 1836. W. Ostwald defined an improved definition about catalysis in 1901, i.e., a catalyst is substance that never appears on the final products in a chemical reaction, but changes the reaction rate. So far, the concept proposed by Ostwald is recognized as the definition of catalyst.

The history of chemistry began with alchemy in medieval times of Europe. Accompanied by alchemy, chemistry about acid-base had improved because alchemists tried to alchemize common metals to gold, and inorganic acids were used to separate mixed metals. In the early 15th century, B. Valentinus firstly succeeded in fractional precipitation of metal ions with acids and bases, and detected iron in tin, copper in iron, silver in copper, and gold in silver. In the early 16th century, G. Agricola achieved to separate a mixture of gold and silver with nitric acid. Until the middle 17th century, character of acid had been recognized as follows; it tastes sour, is water soluble, and exhibits high solvation ability. In 1663, R. Boyle found that blue color of litmus paper changes to red by acids, and confirmed heat of neutralization. In 1774, Raoult first proposed a definition of bases. The proposed concept was that a base is a matter which produces a salt with an acid. H. Cavendish assumed a concept of equilibrium relationship among acids and bases in 1766. W. Lewis utilized plant pigments as acid-base indicators in the middle of 18th century. From 17th through late 19th century, many concepts about acid-base and their origins had been proposed by many scientists. A. L. Lavoisier named the substance, which was called as flame air (Feuerluft), as oxygen in 18th century, and insisted that oxygen is the origin of all acids. On the other hand, P. L. Dulong insisted that hydrogen is the common source of all acids, because hydrochloric acid had been proved to be non-oxygen acid by H. Davy. J. L. Gay-Lussac and P. L. Dulong newly proposed two kinds of acid-concepts in the early 18th century; one is oxygen-acid, the other is hydrogen-acids. The refined concept was proposed by J. Liebig in 1838. He stated as follows; acids are compounds containing hydrogen atoms, which could be replaced by metal ions. S. A. Arrhenius proposed a theory of electrolytic dissociation in 1886, and furthermore an ionic
theory and ionic product in 1887. This ionic theory is defined as that an acid dissociates to proton and acid residue, and a base dissociates to hydroxide ion and metal ion in aqueous solution. In 1888, W. Ostwald established the dilution law, by which strengths of many weak acids and bases can be determined. Then a concept of pH was introduced by S. P. L. Sørensen in 1909. However, these concepts were restricted within aqueous solution systems, and could not apply to non-aqueous solution systems.

The memorial year about acid-base is 1923 when two important definitions were proposed. T. M. Lowry and J. N. Brønsted proposed independently a new acid-base definition; acids are substances that release proton, and bases are ones that accommodate proton. However, this new definition by Lowry-Brønsted could not explain the acidity of well-known acidic compounds such as of SOCl2, AlCl3, SO3, BF3 and so forth. Another definition was proposed by G. N. Lewis. According to his definition, acids shall accept a lone electron pair, and bases shall donate a lone electron pair. This definition includes the definition proposed by Lowry and Brønsted. After 1923, some definitions have been proposed. A definition proposed by H. Lux in 1939 was one focusing on donor-acceptor of O2-. In 1947, H. Flood and T. Förland expanded the definition proposed by Lux. The Lux-Flood definition is often applied to molten salts and oxides, i.e., acid acts as network former and base acts as network modifier.

At the present time, two acid-base definitions proposed by Lowry-Brønsted and Lewis are utilized for explanation acid-base phenomena. The Lewis's definition includes that of Lowry-Brønsted. All Brønsted base sites are also Lewis base sites. In a field of catalysis, a clarification of acid-base site is judged whether the corresponding site transfers a proton or an electron pair. Now, these two definitions used to make use of together in almost all cases.

**Solid Acid and Acidity**

Since Benesi measured acid strengths of many clays and cracking catalysts with Hammett indicators in 1956, Hammett function \( (H_0) \) and Hammett indicators have been utilized to evaluate acid strength and the distribution of solid acids (acidity), the method of which was established by Benesi.\(^7\)\(^-\)\(^9\) The acid strength of a solid surface is defined as an ability of the surface to convert an adsorbed neutral base into its conjugate acid, quantitatively expressed by Hammett and Derup's \( H_0 \) function.\(^10\) If a reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is expressed by \( H_0 \),

\[
H_0 \equiv -\log \frac{a_{H^+} f_B}{f_{BH^+}} \quad \text{or} \quad H_0 = pK_a + \log[B]/[BH^+]
\]

where \( a_{H^+} \) is the activity of proton \([B]\) and \([BH^+]\) are respectively the concentrations of neutral base (basic indicator) and its conjugate acid and, and \( f_B \) and \( f_{BH^+} \) the corresponding activity.
coefficients. If a reaction takes place by means of electron pair transfer from the adsorbate to the surface, $H_0$ is expressed by

$$H_0 = -\log \frac{a_A f_B}{f_{AB}} \quad \text{or} \quad H_0 = pK_a + \log[B] / [AB]$$

where $a_A$ is the activity of a Lewis acid or electron pair acceptor, $[AB]$ is the concentration of neutral base coupled with electron acceptor A. The indicators used for a determination of acid strengths and amounts are listed in Table 1. The amounts of acid sites on a solid surface could be estimated by amine titration after determination of acid strength. For a titrant, $n$-butylamine is recommended. Combining with Hammett indicators and amine titration method, the acid strength distribution of a solid surface could be evaluated.

After Hammett and Derup proposed $H_0$ function for homogeneous systems in 1932, Hauser and Leggett observed a color reaction on aluminosilicate minerals attendant upon adsorption of various substances. Weil-Malherbe and Weiss firstly recognized such the color reactions on aluminosilicates as phenomena related to acid. The first scientist that expressed surface of solid with $H_0$ function is Walling. Walling evaluated surface properties of some inorganic compounds besides aluminosilicates, and found that metal sulfates such as copper(II) and iron(III) exhibit solid acidity. Tamele performed a quantitative analysis of acid sites of alumina-silica cracking catalyst with $n$-butylamine, using $p$-dimethylaminoazobenzene as an indicator. He found a linear relationship between catalytic activity for propylene polymerization and the number of acid sites.

Nowadays, the estimation of acidity on catalyst surfaces has been widely performed with Hammett indicators and amine-titration method. However, some limitations and problems about these techniques are pointed out. One problem is the difficulty to determine a point where the protonation equilibrium of an indicator attains. The most serious problem is the fact that it takes a very long time to achieve equilibrium, and it is rarely achieved. Both of them result in the wrong estimation of the number of corresponding acid sites. Other serious problem is the possibility that the color arising from an acid form is produced by surface sites which are not catalytically active. For example, the evaluated maximum acid strengths with Hammett indicator were $H_0 = -12.7$ or $-14.52$ for ZrO$_2$. The evaluated acid strength of ZrO$_2$ is enough to catalyze $n$-butane skeletal isomerization, however, the reaction is never promoted. Although SO$_4^{2-}$/ZrO$_2$ is truly super-acid which catalyzes $n$-butane isomerization at room temperature, some spectroscopic characterizations indicate that the real maximum acid strength of SO$_4^{2-}$/ZrO$_2$ is comparable to that of HY or 100% H$_2$SO$_4$. Nevertheless the evaluated acid strength of SO$_4^{2-}$/ZrO$_2$ was $H_0 = -16.04$. There are some limitations and exceptions for applying Hammett indicator to determine acid strength on solids. However, Hammett indicators still play an important role to characterize acid properties of solids combining with other characterizing methods, especially in qualitative analysis.
TABLE 1. Basic Indicators Used for the Measurement of Acid Strength

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Color Base-form</th>
<th>Color Acid-form</th>
<th>$pK_a$</th>
<th>Equivalent (H₂SO₄) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral red</td>
<td>yellow</td>
<td>red</td>
<td>+6.8</td>
<td>8 x 10⁻⁸</td>
</tr>
<tr>
<td>Methyl red</td>
<td>yellow</td>
<td>red</td>
<td>+4.8</td>
<td></td>
</tr>
<tr>
<td>Phenylazonaphthylamine</td>
<td>yellow</td>
<td>red</td>
<td>+4.0</td>
<td>5 x 10⁻⁵</td>
</tr>
<tr>
<td>$p$-(Dimethylamino)azobenezene</td>
<td>yellow</td>
<td>red</td>
<td>+3.3</td>
<td>3 x 10⁻⁴</td>
</tr>
<tr>
<td>2-Amino-5-azotoluene</td>
<td>yellow</td>
<td>red</td>
<td>+2.0</td>
<td>5 x 10⁻³</td>
</tr>
<tr>
<td>Benzeneazodiphenylamine</td>
<td>yellow</td>
<td>purple</td>
<td>+1.5</td>
<td>2 x 10⁻²</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>blue</td>
<td>yellow</td>
<td>+0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>$p$-Nitrobenzeneazo(p'-nitro-diphenylamine)</td>
<td>orange</td>
<td>purple</td>
<td>+0.43</td>
<td></td>
</tr>
<tr>
<td>Dicinnamalacetone</td>
<td>yellow</td>
<td>red</td>
<td>-3.0</td>
<td>48</td>
</tr>
<tr>
<td>Benzalacetophenone</td>
<td>colorless</td>
<td>yellow</td>
<td>-5.6</td>
<td>71</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>colorless</td>
<td>yellow</td>
<td>-8.2</td>
<td>90</td>
</tr>
<tr>
<td>2,4,6-Trinitroaniline</td>
<td>colorless</td>
<td>yellow</td>
<td>-10.10</td>
<td>98</td>
</tr>
<tr>
<td>$p$-Nitrotoluene</td>
<td>colorless</td>
<td>yellow</td>
<td>-11.35</td>
<td></td>
</tr>
<tr>
<td>(100 % H₂SO₄)</td>
<td></td>
<td></td>
<td></td>
<td>11.93</td>
</tr>
<tr>
<td>m-Nitrotoluene</td>
<td>colorless</td>
<td>yellow</td>
<td>-11.99</td>
<td></td>
</tr>
<tr>
<td>$p$-Nitrofluorobenzene</td>
<td>colorless</td>
<td>yellow</td>
<td>-12.44</td>
<td></td>
</tr>
<tr>
<td>$m$-Nitrochlorobenzene</td>
<td>colorless</td>
<td>yellow</td>
<td>-13.16</td>
<td></td>
</tr>
<tr>
<td>2,4-Dinitroaniline</td>
<td>colorless</td>
<td>yellow</td>
<td>-13.75</td>
<td></td>
</tr>
<tr>
<td>2,4-Dinitrofluorobenzene</td>
<td>colorless</td>
<td>yellow</td>
<td>-14.52</td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trinitroaniline</td>
<td>colorless</td>
<td>yellow</td>
<td>-16.04</td>
<td></td>
</tr>
</tbody>
</table>

Novel Solid Acid Catalyst

Discovery of new catalysts and new reactions are desired at all times. A large number of various solid-acid catalysts are used for more than 100 industrial processes. ZSM-5 and sulfated zirconia ($SO₄^{2-}/ZrO₂$) are representatives of the greatest discovery of solid acid catalysts in recent years. ZSM-5 is practically utilized and has replaced with other conventional catalysts. $SO₄^{2-}/ZrO₂$ is regarded as a promising catalyst in practice. In 1990s', there are plenty of reports about newly prepared catalysts and/or materials. The author believes that the most excellent discovery (preparation) of catalyst in 1990s' is mesoporous silica such as MCM-41 and FSM-16. The materials possess a variety of availability.
References

Part I

Acidic Property of Mesoporous Silica FSM-16
Introduction of Part I

Mesoporous Silica

Before 1990s', there were no mesoporous materials having narrow pore size distributions. Porous gels, pillared clays and USY zeolites possess large pores in a mesopore range, however, their sizes are not uniform and the distributions are very wide. Because newly synthesized mesoporous silicas, FSM-16 and MCM-41, possess large and uniform mesopores with extremely high surface areas (ca. 1000 m²g⁻¹), much attentions have been paid for application of it, i.e., catalysts, hosts for nano-structured compounds, absorbers, models to clarify of absorption properties in nano-ranges, and so forth. The structure of FSM-16 is almost identical to that of MCM-41. Both of them possess uniform one dimensional pores which are hexagonally arrayed to form two dimensional structure. In general, qualities of mesoporous materials, and uniformities and regularities of the mesopores are characterized with XRD, nitrogen adsorption-desorption isotherm measurements and TEM micrograph observations. A TEM micrograph and an XRD pattern do not always reflect the whole structure of a sample. The disposition and/or coexistence of amorphous gels onto mesoporous materials often occurs, however, it can not be detected with XRD characterization. The deposited silica gel little affects an evaluated surface area of mesoporous materials. Typical features in the nitrogen adsorption-desorption isotherm, which are accompanied with capillary condensation and the hysteresis loop, are the most sensitive to the morphology and porosity. It is desirable to examine a structure of mesoporous materials with nitrogen adsorption isotherm experiments, accompanied by XRD characterizations.

In 1990, Kuroda et al. reported the first preparation of mesoporous silica with narrow pore size distribution and high specific surface area. It was prepared from kanemite of layered polysilicate by an application of intercalation technique. The pore diameter was able to be controlled by changing alkyl-chain length of intercalates (CₙH₂ₙ₊₁(CH₃)₃N⁺Cl⁻, n = 12, 14, 16, 18). At that time, the experimentally confirmed information about the structure of the mesoporous compounds is 1) its layered structure by TEM, and 2) three dimensional SiO₂ networks by XRD and ²⁹Si-MAS NMR. In 1993, hexagonal regular array of channels was confirmed for this new material with TEM micrograph, and a folding sheets' formation mechanism was proposed by Inagaki. In fact, formation of intermediate lamellar silicate-surfactant intercalate phase was detected with real-time in situ X-ray diffraction measurements. On the basis of the model of folding silicate sheets of kanemite, this new material was named to FSM-16. The addition of mesitylene in the mother suspension results in an expansion of the pore diameter.

The pore wall thickness of FSM-16 was estimated to be 0.8-0.9 Å with XRD simulations, indicating that the wall consists of double SiO₄ layers.
mechanism indicates that the wall consists of both single and double silicate layers, indicating FSM-16 possesses two kinds of walls with different thickness. However, recent TEM characterization revealed that there are no differences in the wall thickness of any sides, the value of which is 12 Å. At the present stage, any spectroscopic differences between FSM-16 and amorphous silica gel were not confirmed with 29Si-MAS NMR, FTIR, and Raman characterizations. The precise mechanism of formation and pore wall structure of FSM-16 remain unknown.

In 1992, Mobile researchers reported a preparation of ordered mesoporous silica named MCM-41 (MCM; Mobile Composition of Matter) which possesses regular hexagonal arrays of uniform channels. TEM micrographs and Ar physisorption measurements of MCM-41 revealed that the pore size can be regulated in a very narrow distribution ranging 16 to 100 Å. The pore size of MCM-41 was varied with alkyl-chain length of surfactants (alkyltrimethylammonium salt), and further addition of 1,3,5-trimethylbenzen or 1,3,5-triisopropylbenzene, as well as the case of FSM-16. On the other hand, the pore size and wall thickness of MCM-41 could be controlled by a proper choice of synthesis temperature and/or time, even if it was synthesized from one kind of surfactant (hexadecyltrimethyammonium bromide). Namba reported that a pore size of MCM-41 are able to be finely controlled by changing in a template mixture of hexadecyltrimethyammonium bromide / dodecyl trimethyl-ammonium bromide. The long-range structural order and textural uniformity of MCM-41 are markedly improved if MCM-41 was synthesized with repeated pH adjusting.

As a formation scheme of MCM-41, liquid-crystal templating mechanism was proposed. The proposed mechanism was as follows: hexagonal arrays of cylindrical micelles form with the polar groups of the surfactants to the out side. Silicate species then occupy the spaces between cylinders and the final calcination step burns off the original organic material, leaving hallow cylinders of inorganic material. In contrast, another formation mechanism of MCM-41 was proposed by Stucky et al. In their formation mechanism, firstly formed surfactant-silicate system of lamellar phase transforms to hexagonal mesophase. In fact this phase transformation was confirmed with TEM microscopy, and 14N-NMR characterization. However, a time resolving in situ XRD experiment revealed that no intermediate phases are observed during a formation of the silica-surfactant mesophase that leads to MCM-41. The reason why two kinds of different MCM-41 synthesis mechanisms have been demonstrated is the remarkable difference in their synthesis conditions. After all, the two quite different formation pathways of hexagonal mesophase give the same compound of MCM-41.

As other kinds of mesoporous silica molecular sieves, HMS and MSU-1 have been synthesized. HMS is synthesized with neutral primary amine surfactants (C8-C18: S0) and neutral inorganic precursors (T0), and MSU is synthesized with tetraethyl-orthosilicate and polyethylene oxide surfactant [C11.15H23.31O-(CH2CH2O)31H]. In contrast to HMS and
MSU, MCM-41 is synthesized with long-chain quaternary ammonium cation surfactant (S⁺) and anionic inorganic precursors (I⁻). HMS and MSU-1 possesses high surface area of ca. 1000 m² g⁻¹, and relatively narrow pore size distributions. Both of MSU-1 and HMS exhibit only one d₁₀₀ reflection in their XRD patterns, and capillary condensation over wide range of pressure in the nitrogen adsorption isotherms. XRD patterns and nitrogen adsorption-desorption isotherms indicate that the crystallinities and pore size uniformities and/or distributions seem to be inferior to those of MCM-41.

It is known that the value of thin pore wall thickness estimated with HRTEM is affected by a focus at a sample position. The wall structure of MCM-41 was investigated with molecular dynamics (MD) and simulations of XRD patterns. The experimentally obtained XRD pattern was reproduced by a simulation when model MCM-41 structure possessed 44.6 Å of a₀ value and 10.9 Å of pore wall thickness. Under the condition, MD simulation demonstrated that the pore wall mainly consists of four and five membered rings, whereas the bulk silica mainly consists of six membered ring. When computational simulation is applied to reproduction of experimentally recorded XRD pattern of MCM-41, regularly arrayed hexagonal model structure has been usually assumed. However, recent investigation revealed that a special structure with a destroying hexagonal pore-arrays or a broader pore size distribution, effects only a minor influence on the simulated diffraction patterns against to the regular structure. This result indicates a possibility that hexagonally arrayed pore structures of MCM-41 and FSM-16 are disordered. On the other hand, Elder et al. proposed a two-layered wall structure. They recorded X-ray diffraction patterns of MCM-41 using synchrotron radiation, and simulated the recorded patterns with a model which consists of both dense and less dense walls, the thickness of which are 15.0-16.0 and 5.5-6.4 Å, respectively. Based on the results, the real pore diameter of calcined MCM-41 was estimated to be 13.9-14.8 Å, which was much smaller than those reported by the other research groups (ca. 30 Å). About large differences in pore wall thickness, they claimed that these earlier methods measured only an average wall thickness, which was assumed a simple two-region hole/wall model. As well as FSM-16, there are no evidences about structural differences among amorphous silica and MCM-41. Chen et al. reported that IR, Raman, Si MAS- and CP- NMR spectra of MCM-41 are quite similar to those of amorphous silica. The real structure of mesoporous silica such as MCM-41 and FSM-16 remains unknown, in particular in the pore-structure and pore-wall thickness.

FSM-16 and MCM-41 exhibit high thermal stability up to 1273 K in the absence of moisture. In contrast, mesoporous silicas are mechanically unstable compared to zeolites, and the crystallinity is reduced by pressing. Compared to FSM-16, MCM-41 exhibits low hydrothermal stability and the crystallinity is easily reduced. To improve its hydrothermal stability, addition of cations into synthesis gels, post-synthesis water treatment, and postsynthesis sililation were carried out. The reason for differences in the hydrothermal stability among FSM-16 and MCM-41 might be due to the pH values in the preparation step. MCM-41 is synthesized in an autoclave around pH = 12. In contrast, pH adjustment was
carried out in FSM-16 preparation procedure, pre- and post-adjusted values of which are 12 and 8.5, respectively. Two Si-OH condense to form Si-O-Si linkage at a lower pH at a preparation of FSM-16. The different pH values at the synthesis procedures might cause differences in the degree of Si-OH condensation, which reflects their structural stabilities.

Amorphous silica deposits easily on the surface of FSM-16 at the pH adjustment procedure. Prior to the pH adjustment from 12 to 8.5, removal of solved silicate species is indispensable for FSM-16 synthesis to obtain silica gel free FSM-16.\(^8\) Nitrogen adsorption-desorption isotherm of MCM-41 scarcely shows hysteresis at high P/P\(_0\) (P\(_0\): saturated vapor pressure) region,\(^{16,43}\) whereas that of FSM-16 exhibits small hysteresis above P/P\(_0\) = 0.5 due to deposition of amorphous silica.\(^9,44\) SEM characterizations revealed that the morphology of MCM-41 is a hexagonal prism,\(^{16,17}\) while that of FSM-16 retains that of kane main which does not possess regular morphology.\(^6\) The differences in morphology might be affected by the preparation condition. MCM-41 crystallizes in an autoclave under a static condition. On the other hand, mother suspension of FSM-16 synthesis is in stirring all the time. As a result, secondary granular of FSM-16 might not reflect the hexagonally arrayed pore structure, in contrast to the case for MCM-41. Other possible reason is the deposition of amorphous silica. Although the secondary granular of FSM-16 and MCM-41 are quite different, XRD characterization has never revealed differences among them. There are no data reflecting differences in physical properties among them at the present stage.

Silica is generally a catalytically inert material, and the surface silanol groups are very weakly acidic in nature.\(^{45}\) Therefore, FSM-16 and MCM-41 themselves are considered to be catalytically inactive. To generate catalytic activity of mesoporous silicas, introduction of other elements such as Al\(^{17,23,46,47}\) and Ti\(^{26,48,49}\) to the framework was performed by many researchers.\(^1,2,50\) As other attempts to generate active sites on mesoporous silicas, grafting of organometallic compounds,\(^{51-56}\) or supporting of transition metal oxides (Mn\(^{57}\) Mn\(^{58}\) Cs\(^{59}\) Cs and/or La,\(^{60}\) Ge, Sn, Ti\(^{61}\) Fe\(^{62}\)) and novel metal particles (Ru\(^{63}\) Rh\(^{64,65}\) Pt\(^{66-69}\) Au\(^{70}\)) and Pt wires\(^{71,72}\) were examined. Using a large pore of FSM-16, ship-in-bottle synthesis of platinum carbonyl cluster, the size of which was too large to be accommodated into pores of conventional zeolites such as FAU, was carried out.\(^{68, 69, 73,74}\) Al-contained mesoporous silica was applied for production of fine chemicals such as dimethylacetals and Jasminaldehyde.\(^{76}\) Shinoda \textit{et al.} reported that Al-loaded FSM-16 exhibits excellent shape selectivity for meso-tetraarylporphyrin synthesis.\(^{77}\)

In contrast to these efforts, catalyses over pure siliceous mesoporous silicas were found in 1997. The selective dehydration of 2-methylbut-3-yn-2-ol to 2-methylbut-3-yn-1-ene proceeded at 453 K over MCM-41.\(^{78}\) Cumene cracking was catalyzed over FSM-16 at 673 K.\(^{79}\) These two works did not focus the catalysis over siliceous mesoporous silicas, but those were used as reference samples or for a blank test. Nakajima \textit{et al.} found that silicious FSM-16 catalyzes Beckmann rearrangement of cyclohexanone oxime at 523-623 K without deactivation for 5 h.\(^{80}\) The activities are higher than those of silica-alumina, HZSM-5, Na-ZSM-5, HX and
Silica gel enhances this reaction with the same selectivity as that for FSM-16. Although the activity for silica gel was quite lower than that for FSM-16, differences in activities between FSM-16 and silica gel were not discussed. On the contrary, Sakata et al. found that siliceous FSM-16 accelerates a rate of degradation of plastic polymers into liquid hydrocarbons.\textsuperscript{81,82} They concluded that non-acidic mesoporous silica acts as a radical-flask.

Although these significant data have been reported within recent several years, still the neutrality of FSM-16 and MCM-41 has been generally believed. In 1998, the present author found that FSM-16 enhances acid-catalyzed reactions and proposed that siliceous FSM-16 possesses acid sites.\textsuperscript{14} Soon after our discovery, a similar catalytic behavior for acetalization of carbonyl groups was confirmed on siliceous MCM-41 by Iwamoto \textit{et al.}\textsuperscript{83} Their proposed active sites and the activity generation mechanism\textsuperscript{84} were almost the same as ones proposed by the present author. Furthermore, photocatalyses over dehydrated FSM-16 were confirmed by Yoshida. FSM-16 evacuated at 1073 K catalyzes metathesis\textsuperscript{85} and oxidation\textsuperscript{86} of propene under photolysis, active sites of which are proposed to be produced by removal of hydroxyl groups. Amorphous silica itself catalyzes photomethathesis of alkenes\textsuperscript{87,88} and photooxidation of propene,\textsuperscript{89} however, FSM-16 exhibits higher activities than amorphous silica. They speculated that much amounts of surface silanol groups due to its large surface area and/or the wall structure of FSM-16 relate to higher catalytic activities than amorphous silica.

Until 1997, no one took in account for acid properties of siliceous mesoporous silicas. We opened and shed light to the new intrinsic properties of mesoporous silicas. The present part describes the discovery of the acid sites of FSM-16 and discusses its acid properties. In chapter 1, catalyses of but-1-ene and \(\alpha\)-pinene isomerizations over siliceous FSM-16 were examined and the change of acidic property upon thermal treatment are reported. Relations among Brønsted acidic property of FSM-16, the surface silanol groups, and the structure were discussed. Chapter 2 describes a formation of Lewis acid sites on FSM-16 accompanied with a high-temperature treatment. Generation of Lewis acid sites and their acidic properties, and catalytic properties were examined with catalyses for methylamine synthesis and pyridine-adsorption-desorption experiments.

References

Chapter 1

Characterization of Brønsted Acid Sites on FSM-16

Abstract

Siliceous FSM-16 possesses acid sites to catalyze but-1-ene isomerization to produce but-2-ene ($\text{cis} / \text{trans} = 1.4 - 1.7$) at 323 K and 2,6,6- trimethylbicyclo[3.1.1]hept-2-ene (α-pinene) isomerization at 303 K. Catalytic activity was dependent upon heat treatment and reached a maximum at 673 K. The maximum acid strength was invariably $H_0 = -3.0$ independent of the pretreatment temperatures. The acidity was much reduced by calcination at higher temperatures, but restored by water treatment at 353 K as long as the FSM-16 retained its structure.
Introduction

FSM-16, MCM-41, and HMS are mesoporous silicas with narrow pore size distribution, high specific surface area, and high thermal stability up to 1273 K. These materials, synthesized with cetyltrimethylammonium salts, have a quite similar structure, a unique adsorption isotherm of nitrogen, high BET specific surface area, a narrow pore size distribution, and a high pore volume, although the XRD pattern of HMS is slightly different from the others. While XRD patterns of FSM-16 and MCM-41 may exhibit up to four well-defined peaks, that of HMS exhibits only one broad peak attributed to the 100 reflection. The main difference between FSM-16 and MCM-41 is the synthesis procedure and formation mechanism. Mobil researchers proposed the formation mechanism of M41S materials, such as MCM-41, based on a liquid crystal templating model. The folding sheets mechanism was proposed for FSM-16: intercalation of surfactants to layered polysilicate kanemite with a primary d spacing of 10 Å and then the folding of layers to form the specific hexagonal structure. On the other hand, Monnier et al. proposed a layered intermediate with a primary d spacing of 31 Å for the formation of MCM-41. In fact, an in situ XRD study showed that the intermediate lamellar silica-surfactant intercalate was formed during the synthesis of FSM-16 from kanemite, whereas no intermediate phases were observed during the formation of MCM-41.

Silica is a generally catalytically inert material, and the surface silanol groups are very weakly acidic in nature. Therefore, FSM-16 and MCM-41 themselves are considered inactive catalytically, and the introduction of Al to the framework was often performed to generate acidity. Other metals or cations are also added to FSM-16 and MCM-41 to generate catalytic activity, as exemplified by incorporation of transition metal cations such as Ti to the framework, introduction of metal cations by ion exchange, direct incorporation of novel metals via synthesis gel, and introduction of catalytically active species into pores.

Here, we report that siliceous FSM-16 catalyzes isomerization of but-1-ene and 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α-pinene) at 323 and 303 K, respectively. Isomerizations of terpenes such as the rearrangement of α-pinene to 2,2-dimethyl-3-methylenebicyclo[2.2.1]-heptane (camphene) and the migration of olefinic bonds of 1-methyl-4-(1-methylethynyl)cyclohexene (limonene) were known to be acid catalyzed reactions. In contrast, solid bases such as CaO and SrO catalyze isomerization of α-pinene to produce 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene), selectively. Therefore, isomerization of α-pinene is an excellent test reaction for acid-base properties of a catalyst.

Recently, catalysis by siliceous mesoporous materials was reported. The selective dehydration of 2-methylbut-3-yn-2-ol to 2-methylbut-3-yn-1-ene proceeded at 453 K over MCM-41. Cumene cracking was catalyzed over FSM-16 at 673 K. Furthermore, Yoshida et al. reported that FSM-16 evacuated at 873 K catalyzes metathesis of propene under
photoirradiation. However, the first two papers did not focus on the catalytic properties of siliceous mesoporous materials. There have been no reports discussing the acidic properties of siliceous mesoporous materials.

**Experimental Section**

**Materials**

FSM-16 was synthesized according to Inagaki's method. Prior to calcination, the Si/Na atomic ratio of water glass (Osaka Keiso Co., LTD; SiO₂ = 31.93, Na₂O = 15.37, Al = 0.0098, Fe = 0.0028 wt %; Si/Al = 1463 atomic ratio) was adjusted to 1.00 by addition of NaOH solution (Wako Pure Chem. Ind., LTD). During synthesis, water glass successively changed to β-Na₂Si₂O₅, kanemite (NaHSi₂O₅·3H₂O), and finally FSM-16 via three steps. [C₁₆H₃₃(CH₃)₃N]Br (Tokyo Chem. Ind. Co., LTD) was used as a template. The ion exchange of kanemite to produce FSM-16 was carried out as follows. At the beginning of ion exchange of kanemite, the concentration of template was 0.10 M and a molar ratio of the template to Si of kanemite was adjusted to 0.2. The ion exchange was carried out at 343 K for 3 h with stirring. After cooling to room temperature, the solid was filtered off and then dispersed in distilled water again. After adjustment of pH to the 8.5 with 2 M HCl, it was heated up to 343 K and stirred for 6 h while maintaining the pH at 8.5. Finally, ion-exchanged kanemite (FSM-16) was calcined in a dry air stream at 823 K for 6 h. The yield of FSM-16 based on SiO₂ was 24%. After calcination, FSM-16 was ground to powder under 100 mesh. The XRD pattern (d₁₀₀; 38 Å), the BET specific surface area (1078 m² g⁻¹), the N₂ adsorption isotherm, the pore volume (0.73 cm³ g⁻¹; estimated by t-plot), and the pore diameter (27.6 Å; estimated by the Clanston-Inkley method) were quite similar to those reported in the literature. Calcined and rehydrated FSM-16 was also prepared because a hydration state of FSM-16 is closely related to catalytic activities, as would be described below. Rehydrated catalysts were prepared via two steps. Before rehydration, FSM-16 was calcined once in a dry air stream at 1173 or 1373 K for 2 h (FSM-1173, FSM-1373). At the next step, the calcined FSM-16 was treated with water at 353 K for 4 h with stirring, followed by calcination at 773 K for 5 h (FSM-1173H, FSM-1373H).

Silicon oxide hydrate (H₂Si₂O₅) was synthesized from kanemite, which was the same material as used for FSM-16 synthesis. Kanemite dispersed in distilled water was converted to H₂Si₂O₅ keeping the pH at 1.2 at room temperature. Adjustment of the pH was performed with 2 M HCl, and the condition was maintained for 24 h with stirring. The precipitate was washed with distilled water until Cl⁻ was free based on AgNO₃ test. It was dried at 343 K for 12 h followed by calcination at 773 K for 5 h. Formation of H₂Si₂O₅ crystal was confirmed by XRD (JCPDS file No. 27-606) for the dried sample, which became
amorphous upon calcination at 773 K. TG-DTA analysis showed that H$_2$Si$_2$O$_5$ released the interlayer water molecules around at 473 K, and the loss of interlayer water should account for the loss of crystallinity. This phenomenon was consistent with previous works. Al-doped $\delta$-Na$_2$Si$_2$O$_5$ and H$_2$Si$_2$O$_5$ were also synthesized. To adjust the Si/Al atomic ratio to be 16, whose value was to form 5 wt % of Al$_2$O$_3$ containing SiO$_2$-Al$_2$O$_3$ as a starting material, NaAlO$_2$ was added to water glass.

SiO$_2$ gel was synthesized from tetraethyl orthosilicate (Nacalai tesque, EP-grade, once distilled) by hydrolysis in a water-ethanol mixture at boiling point followed by calcination at 773 K for 5 h in a dry air stream. Before calcination, a dried sample was ground to powder under 100 mesh. No crystalline phases of SiO$_2$ were detected by XRD analysis.

Other silicas used were Japan Reference Catalyst (JRC-SIO-5, JRC-SIO-7), supplied by the Committee on Reference Catalyst, Catalysis Society of Japan. JRC-SIO-5 contains 134 ppm Na, 122 ppm Al, 40 ppm Ca, 57 ppm Fe, and 100 ppm Mg. JRC-SIO-7 contains 135 ppm Na, 195 ppm Al, 36 ppm Ca, 72 ppm Fe, and 117 ppm Mg. The BET specific surface area of JRC-SIO-5 and JRC-SIO-7 is 192 and 86 m$^2$ g$^{-1}$, respectively. They were precalcined in dry air at 773 K for 3 h.

Reference catalysts used for $\alpha$-pinene isomerization were HZSM-5 (JRC-Z5-25H, -70H, -1000H; Si/Al atomic ratio are 12.3, 40.0, 623, respectively), NaY (JRC-Z-1), $\gamma$-Al$_2$O$_3$ (JRC-ALO-4), ZrO$_2$ (JRC-ZRO-1), TiO$_2$ (JRC-TIO-4), Mg(OH)$_2$ (Rare Metallic Co., 99%), Ca(OH)$_2$ (Nacalai, GR), Nb$_2$O$_5$-nH$_2$O (CBMM) and NiSO$_4$-nH$_2$O (Nacalai, GR).

**Characterization**

NH$_3$-TPD measurements were carried out by a quadrupole-type mass spectrometer at a heating rate of 5 K min$^{-1}$. Before TPD measurements, each 100 mg of sample was evacuated at 673 K for 0.5 h and calcined under 6.66 kPa of O$_2$ for 1 h, followed by evacuation at the same temperature for 1 h. The sample was exposed to 500 $\mu$mol of NH$_3$ at room temperature for 0.5 h followed by evacuation at the same temperature for 1 h. The amount of desorbed gases (NH$_3$; $m/e = 16$) was normalized with that of introduced Ar ($m/e = 40$) as an internal standard.

FTIR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer in a transmission mode at room temperature. IR spectra of adsorbed pyridine were recorded with a resolution of 4 cm$^{-1}$. Each sample (20-80 mg) was pressed into a self-supporting wafer (20 mm in diameter) with a pressure of 100 kg cm$^{-2}$ for 10 s, and was mounted in an in situ IR cell equipped with BaF$_2$ windows. The wafer was pretreated in the same way as that for NH$_3$-TPD measurements and exposed to 27 Pa of pyridine vapor at 423 K for 5 min followed by evacuation at the same temperature for 1 h. The other spectra were recorded with a resolution of 2 cm$^{-1}$.

Thermogravimetric analysis was carried out with Rigaku Thermoflex TG 8110 in a dry N$_2$ stream at a heating rate of 5 K min$^{-1}$.
X-ray diffraction patterns of samples were obtained with a Rigaku Geigerflux diffractometer using Ni-filtered Cu Kα radiation (1.5418 Å).

The acid strength of catalysts was measured by various Hammett indicators. The indicators used for the titration method were 0.1 wt % benzene solution of methylred ($H_0 = +4.8$), $p$-dimethylaminoazobenzene (+3.3), benzenazodiphenylamine (+1.5), dicinnamalacetone (-3.0) and benzalacetophenone (-5.6).

**Catalysis**

But-l-ene isomerization was carried out in a closed circulation system (dead volume, 200 cm$^3$). Prior to each run, 50 mg of FSM-16 was evacuated at a prescribed temperature for 0.5 h and calcined under 6.66 kPa of O$_2$ for 1 h, followed by evacuation at the same temperature for 1 h. The amount of substrate was 400 μmol, and the reaction temperature was 323 K.

α-Pinene isomerization was carried out under dry N$_2$ atmosphere using a stirred batch reactor at 303 or 353 K. The pretreatment procedure was the same as mentioned above. In a typical experiment, the reactor was loaded with 2 mL (12.6 mmol) of α-pinene (Nacalai, EP, 99.8%) and 50 mg of catalyst.

Products were analyzed by GC and GC-MS (Shimadzu, GCMS-QP5050).

**Results and Discussion**

**Elemental Analysis**

Table 1 summarizes elemental analysis of prepared catalysts. Although the Si/Al atomic ratio of water glass was 1463, that of synthesized FSM-16 was 735. This result shows that Al was slightly concentrated but the concentration was still quite low. Results of FSM-1173H and FSM-1373H show that no treatment changes the original elemental composition except for Na. Because H$_2$Si$_2$O$_5$ was treated with water of pH = 1.2 during synthesis, almost all of the trace elements were extracted off. SiO$_2$ gel contained little other elements.

**Acidic Property**

Figure 1 shows initial rates for but-l-ene isomerization over FSM-16 pretreated at various temperatures and BET specific surface areas of the FSM-16 samples. The initial rate strongly depended on the pretreatment temperature. Samples pretreated at temperatures from 473 through 673 K showed similar initial rates. Once pretreatments were performed at temperatures higher than 873 K, the initial rate drastically decreased although BET specific
TABLE 1: Elemental Analysis of Catalysts<sup>a</sup>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Na</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Ti</th>
<th>Si/Al atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSM-16</td>
<td>0.008</td>
<td>0.061</td>
<td>0.012</td>
<td>0.023</td>
<td>0.003</td>
<td>0.032</td>
<td>735</td>
</tr>
<tr>
<td>FSM-1173H&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.017</td>
<td>0.062</td>
<td>0.012</td>
<td>0.021</td>
<td>0.003</td>
<td>0.029</td>
<td>723</td>
</tr>
<tr>
<td>FSM-1373H&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.021</td>
<td>0.071</td>
<td>0.014</td>
<td>0.031</td>
<td>0.004</td>
<td>0.035</td>
<td>631</td>
</tr>
<tr>
<td>FSM-16&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.01</td>
<td>0.14</td>
<td>0.02</td>
<td>0.003</td>
<td>0.003</td>
<td>0.004</td>
<td>320</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;Si&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.005</td>
<td>0.008</td>
<td>0.006</td>
<td>0.002</td>
<td>0.001</td>
<td>0.007</td>
<td>5612</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; gel</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Analyzed by ICP (inductively coupled plasma) and atomic absorption spectroscopy.

<sup>b</sup> Hydrated at 353 K for 4 h followed by calcination at 773 K for 5 h. Before hydration, FSM-16 was calcined in a dry air stream at 1173 K for 2 h.

<sup>c</sup> Hydrated at 353 K for 4 h followed by calcination at 773 K for 5 h. Before hydration, FSM-16 was calcined in a dry air stream at 1373 K for 2 h.

<sup>d</sup> Supplied by Toyota Central R&D Labs., Inc. (Lot No. NG78-550).

TABLE 2: Results of α-Pinene Isomerization at 303 K<sup>a</sup>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment Temperature / K</th>
<th>Conversion (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSM-16</td>
<td>373</td>
<td>16.0</td>
<td>1</td>
<td>42</td>
<td>6</td>
<td>42</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>27.1</td>
<td>1</td>
<td>40</td>
<td>5</td>
<td>44</td>
<td>7</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>44.6</td>
<td>tr</td>
<td>40</td>
<td>4</td>
<td>43</td>
<td>9</td>
<td>2</td>
<td>2</td>
<td>tr</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>29.5</td>
<td>tr</td>
<td>39</td>
<td>3</td>
<td>48</td>
<td>7</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>6.6</td>
<td>1</td>
<td>37</td>
<td>3</td>
<td>48</td>
<td>7</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1273</td>
<td>1.5</td>
<td>4</td>
<td>37</td>
<td>3</td>
<td>46</td>
<td>7</td>
<td>1</td>
<td>2</td>
<td>tr</td>
</tr>
<tr>
<td>FSM-16&lt;sup&gt;c&lt;/sup&gt;</td>
<td>673</td>
<td>52.9</td>
<td>tr</td>
<td>39</td>
<td>4</td>
<td>43</td>
<td>8</td>
<td>2</td>
<td>2</td>
<td>tr</td>
</tr>
</tbody>
</table>

<sup>a</sup> α-pinene, 2 mL; catalyst, 50 mg; reaction time, 0.5 h.

<sup>b</sup> 1, β-pinene; 2, camphene; 3, α-fenchene; 4, limonene; 5, terpinolene; 6, α-terpinene; 7, γ-terpinene; 8, others.

<sup>c</sup> Supplied by Toyota Central Lab., Inc. (lot no. NG78-550).

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Figure 1. Plots of initial rates for but-1-ene isomerization over FSM-16 and BET specific surface area vs. pretreatment temperatures. Dead volume, 200 cm$^3$; catalyst, 50 mg; but-1-ene, 400 μmol; reaction temperature, 323 K.
Figure 2. Scheme of $\alpha$-pinene isomerization.
surface areas remained high. No correlation between initial rates and surface areas was observed. For example, only a 5% difference in surface area was observed for the samples pretreated at 873 and 1073 K, but the initial rates differed by 1.5 orders of magnitude. In all cases, the ratios of the cis-isomer to the trans-isomer in produced but-2-enes were 1.4 - 1.7, indicating that this reaction was catalyzed by acids. No reaction proceeded over SiO2 gel pretreated at 673 K.

A similar catalytic behavior was exhibited in isomerization of α-pinene (Figure 2), as summarized in Table 2. It should be noted that the selectivity did not change at all, whereas the catalytic activity was drastically changed depending upon pretreatment temperature. Main products were camphene and limonene, and the selectivity to these two products was around 40%. Products of α-pinene isomerization can be classified into three groups. The first group is β-pinene. Over solid base catalysts, only equilibrium between α-pinene and β-pinene would be observed. The second group consists of bicyclic (camphene, α-fenchene, etc.) and tricyclic (tricyclene, etc.) products. The last group is composed of monocyclic products (limonene, terpinolene, α-terpinene, γ-terpinene, etc.). One remarkable result of the present study is that the formation of β-pinene was negligible over FSM-16. This result also revealed that few basic sites existed on FSM-16, and this reaction was catalyzed by acids. It was reported that monocyclic products were formed more preferentially than bi- or tricyclic products over strong acid catalysts. The independence of selectivity for this reaction indicates that the maximum acid strengths were not changed by pretreatment temperatures.

As shown in Table 3, over SiO2 gel, δ-Na2Si2O5, H2Si2O5, JRC-SIO-5, and JRC-SIO-7, α-pinene isomerization hardly took place even at 353 K. As-calcined H2Si2O5 pretreated at 373 and 473 K, which remained as a crystal structure, was also inactive. The result of JRC-SIO-7 shows that silica containing 195 ppm of Al is not enough to catalog this reaction at the temperature of 353 K. Furthermore, Al-doped H2Si2O5 showed very low activity. Typical acid catalysts were also tested (Table 3). γ-Al2O3, TiO2, Nb2O5·nH2O, and NiSO4·nH2O were active for this reaction at 353 K, but activities were quite low compared to that of FSM-16. In the case of NiSO4·nH2O, a selectivity for bi- or tricyclic products was particularly high, 88%, which coincides with the previous reports. It is very intriguing that HZSM-5, the Si/Al atomic ratio of which was 12.3, known as a strong acid catalyst, was less active than FSM-16 at least at a temperature of 303 K. It may be due to its small pore size. Although FSM-16 has a large mesopore of 28 Å, the MFI type zeolite has a micropore in which the three-dimensional channel system has straight 10-ring 5.2 x 5.7 Å channels connected by a zigzag structure like 5.3 x 5.6 Å channels. In the case of HZSM-5, a diffusion of substrates or products was suppressed especially at a low temperature of 303 K. These results indicate that the effective surface area of MFI type zeolite for α-pinene isomerization is much lower than that of FSM-16. FSM-16 could provide a reaction field for large molecules such as α-pinene. In addition, HZSM-5 of Si/Al = 623 was almost inactive at 303 K and showed low activity even at 353 K, although the Si/Al atomic ratios of the HZSM-5 and FSM-16 were almost the same.
<table>
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<th>Catalyst</th>
<th>Pretreatment Temp/K</th>
<th>Conversion (%)</th>
<th>Selectivityb (%)</th>
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<td></td>
<td>1073</td>
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<tr>
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</table>

\* α-Pinene, 2 mL; catalyst, 100 mg; reaction time, 3 h. 
\* 1,β-pinene; 2, camphene; 3, α-fenchene; 4, limonene; 5, terpinolene; 6, α-terpinene; 7, γ-terpinene; 8, others. 
\* Catalyst: 50 mg; reaction temperature, 303 K. 
\* Si/Al atomic ratio was 16.1 as a starting material. 
\* Tricyclene: 8%. 
\* Catalyst: 300 mg as M(OH)₂ (M = Mg, Ca).
### TABLE 4: Results of β-Pinene Isomerization

<table>
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<tr>
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</thead>
<tbody>
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<td>873</td>
<td>873</td>
</tr>
<tr>
<td>Reaction Temperature /K</td>
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<td>423</td>
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<tr>
<td>Weight /mg</td>
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<td>300$^b$</td>
<td>300$^b$</td>
</tr>
<tr>
<td>Time /h</td>
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<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Conversion (%)</td>
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<td>3.5</td>
<td>9.3</td>
</tr>
<tr>
<td>Selectivity (%)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
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<td>98</td>
<td>99</td>
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<td>Camphene</td>
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<td>2</td>
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<tr>
<td>Limonene</td>
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<tr>
<td>Terpinolene</td>
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<tr>
<td>Others</td>
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</tr>
</tbody>
</table>

$^a$ β-Pinene: 2 mL.

$^b$ As M(OH)$_2$, (M = Mg, Ca).

![NH3-TPD profiles](image-url)

**Figure 3.** NH3-TPD profiles of FSM-16 (a), SiO$_2$ (b), and H$_2$Si$_2$O$_5$ (c) pretreated at 673 K.
The second intriguing point is that the selectivity for formation of α-fenchene was particularly high. It results from restricted transition state selectivity. Another HZSM-5 of different Si/Al atomic ratio also showed high selectivity for α-fenchene formation. In the small pore of the MFI type zeolite, it is difficult for α-pinene isomerization to bulky transition states to produce terpinolene, α-terpinene, γ-terpinene, and so forth, compared to that of limonene. In contrast, the FAU type zeolite has larger supercages of 13 Å, and this restriction was no longer observed. It was reported that NaY had acid sites, the maximum acid strength of which range from $H_0 = +1.5$ to $+4.0$. Although NaY is a very weak acid in nature, its specific surface area was estimated to be $973 \text{ m}^2 \text{ g}^{-1}$ by Langmuir plot. The high activity of NaY was due to the large surface area in comparison with other catalysts. Furthermore, over Brønsted acid catalysts, catalytic activity was strongly related to the mobility of protons. From IR experiments, Ward observed the delocalization of protons on HY in the range 473 - 700 K. Baba et al. observed changes of the line width of the $^1 \text{H}$ MAS NMR signal of acidic OH groups of HZSM-5 with temperature and found a relation between line widths and catalytic activities. They discussed that the mobility of protons depended on temperature and the same amounts of protons would not necessarily exhibit the same activities.

MgO and CaO were also active for α-pinene isomerization. The selectivities for β-pinene formation were almost 100%, while they exhibited low conversion at 353 K (Table 3). The selective isomerization between α-pinene and β-pinene is one of the characteristics of solid base catalyst, and the low conversions were due to the low equilibrium constant of β-pinene to α-pinene. Table 4 summarizes isomerization of β-pinene over FSM-16, MgO, and CaO. Over solid base catalysts, only transformation between β-pinene and α-pinene was selectively catalyzed, and formation of other products was negligible. In contrast, the reaction continuously proceeded via α-pinene, and many kinds of secondary products were observed over FSM-16. The result of β-pinene isomerization also strongly suggests that not basic but acidic sites were the main active sites on FSM-16. The lack of basic sites over FSM-16 was supported by the result of but-1-ene isomerization discussed above. In general, solid base catalyzes but-1-ene and the cis/trans ratio of produced but-2-ene is very large. In the case of FSM-16, however, that ratio was between 1.4 and 1.7.

Figure 3 shows NH3-TPD profiles of FSM-16, SiO2 gel, and H2Si2O5 pretreated at 673 K. SiO2 gel and H2Si2O5 exhibited a single peak around at 370 and 360 K respectively. The profile of FSM-16 shows a peak above 400 K besides a peak around 355 K; however the peak around at 473 K is not due to strong acid sites. It clearly shows that the acid sites of FSM-16 pretreated at 673 K are different from those of the others. This was supported by IR spectra. Figure 4 shows IR spectra of adsorbed pyridine on SiO2 gel and FSM-16 pretreated at 673 K. Assignment of pyridine adsorption peaks was as follows. Peaks due to hydrogen-bonded pyridine were 1448 and 1598 cm$^{-1}$, those due to pyridine adsorbed on Brønsted acid sites were 1546 and 1638 cm$^{-1}$, and those on Lewis acid sites were 1456 and 1624 cm$^{-1}$.
Figure 4. FTIR spectra of adsorbed pyridine at 423 K. FSM-16 (21 mg) evacuated at 423 K (a), 473 K (b), 573 K (c), and 673 K (d) and SiO2 gel (80 mg) evacuated at 423 K (e).
A peak at 1493 cm\(^{-1}\) was due to pyridine adsorbed on both Brønsted and Lewis acid sites. SiO\(_2\) gel possessed only hydrogen-bonded sites, whereas FSM-16 possessed both Brønsted and Lewis acid sites besides hydrogen-bonded sites. When FSM-16 adsorbing pyridine was evacuated at 473 K, hydrogen bonded pyridine and pyridine adsorbed on Brønsted sites were desorbed. Almost all of the pyridine was desorbed at 673 K with increasing evacuation temperature. IR spectra of pyridine adsorbed on Al-containing MCM-41 were measured by many researchers.\(^9\) - 11, 41 Although Corma et al. observed Brønsted acid sites on MCM-41 of Si/Al = 100,\(^9\) Jentys et al. observed only Lewis acid sites on the same Si/Al ratio's material.\(^11\) Further, Jentys et al. and Mokaya et al.\(^10\) observed only hydrogen-bonded species on pure siliceous MCM-41. While the Si/Al atomic ratio of synthesized FSM-16 was 735, both Lewis and Brønsted acid sites were observed on FSM-16. The spectrum was quite similar to those of Al-MCM-41 (Si/Al = 100). Although we have not compared directly the acidic property between FSM-16 and MCM-41, IR spectra of adsorbed pyridine suggest that the acidic property of FSM-16 is higher than, or at least equal to, those of MCM-41. Zhao et al. performed pyridine TPD of siliceous MCM-41 and observed two desorption peaks in the temperature range 323 - 523 K.\(^42\) They claimed that two peaks were due to desorbed pyridine from hydrogen-bonded SiOH and free SiOH groups, and both activation energies of desorption sites were similar to those of amorphous silica. In fact, the reported pyridine desorption profile for silica gel (Kieselgel 60; Merk NV) was quite similar.\(^43\) The pyridine desorption profile for MCM-41 was also quite similar to the NH\(_3\) desorption profile for FSM-16, although it is very difficult to compare with the results of pyridine and NH\(_3\)-TPD experiment. Because the NH\(_3\)-TPD profile for SiO\(_2\) gel was different from that for FSM-16, it could be possible that the property of siliceous MCM-41 is similar to that of FSM-16 demonstrated in the present work.

**Contribution of Aluminum to Acidic Property**

FSM-16 employed in the present work contains a trace amount of Al (Si/Al = 320, 735), which might be associated with the acid sites. Van Roosmalen et al. reported the catalysis of but-1-ene isomerization over silica gel.\(^44\) They concluded that activities of silica gel were directly proportional to the concentration of Al being present as a trace impurity at 600 - 700 K. In their report, silica gel (Rhône-Propel; Spherosil XOA-400, 361 m\(^2\) g\(^{-1}\), Si/Al = 100 - 1000) showed a rate constant of 31 nmol m\(^{-2}\) s\(^{-1}\) at 600 K and 1.1 x 10\(^5\) Pa for but-1-ene, whereas in the case of FSM-16, the activity comparable to that reported was exhibited at a low temperature of 323 K and a low pressure of 4.7 x 10\(^3\) Pa for but-1-ene. Furthermore, we confirmed that the amorphous silica prepared from the same water glass was inactive. West et al. reported that many reactions catalyzed by silica gel took place at impurity sites.\(^45\) They observed improvement of activity more than 100 times for hex-1-ene isomerization over Al(NO\(_3\))\(_3\) added to silica gel (120 ppm as Al) than the original silica gel. However, the original silica gel (Davison Grade 59 or Grade 70) contains 0.1% Al\(_2\)O\(_3\), 0.01% Fe\(_2\)O\(_3\), 0.02% TiO\(_2\),
0.07% CaO, 0.06% Na2O, and 0.03% ZrO2, and the rate of hex-1-ene isomerization was reported to be 0.2 mmol h⁻¹ g⁻¹ at 373 K. This value was about 60 times smaller than the rate of but-1-ene isomerization over FSM-16 at 323 K. Although it is hard to compare them, we should suppose that the acidity of FSM-16 is much higher than that of silica gel containing 0.1% Al2O3.

In the case of ZSM-5, it was reported that catalytic activities of many reactions were directly proportional to the concentration of Al and the proportional relations were applicable down to 10 ppm. The reported reactions were propylene polymerization, n-hexane cracking, hex-1-ene isomerizations, and so forth. However, all reactions were performed over 700 K. On the other hand, isomerization of but-1-ene and α-pinene proceeds over FSM-16 even at 323 K. There have been no reports that butene isomerization proceeds at ambient temperature on silica including such a trace amount of impurity at measurable rates. In α-pinene isomerization, activities of FSM-16 whose Si/Al atomic ratio was 320 and 735 were almost the same. We emphasize again that the acidity of FSM-16 exhibited by the present sample is not due to Al impurity.

Dehydroxylation

As shown in Figure 1 and Table 2, FSM-16 pretreated at 673 K showed maximum catalytic activity. The activity was drastically reduced when FSM-16 was pretreated at higher than 873 K. Sintering or the change of surface property is thought to be the reason for deactivation. The possibility that sintering causes deactivation can be excluded from the result of BET measurements. Therefore, the change of surface property should be the main reason for deactivation. Dehydration and condensation of SiOH groups should relate closely to the change of specific property.

Figure 5 shows a thermogravimetric analysis and H2O-TPD profile of FSM-16. The weight loss completely corresponded to desorption of H2O. Since large part of physisorbed H2O was eliminated below 373 K, a TPD experiment was performed after preevacuation at 373 K for 1 h. Because FSM-16 was once calcined at 823 K in a synthesis step, the signal intensity of m/e = 18 below 773 K was small. Dehydroxylation continuously proceeded over 773 K. A large quantity of H2O evolution over 773 K was due to dehydroxylation of a silanol group to form a siloxane bridge, and catalytic activities were drastically lowered in this region.

IR spectra of FSM-16 showed similar behavior, as shown in Figure 6. With increasing evacuation temperature, a very broad band around 3500 cm⁻¹ gradually decreased and a new window around 900 cm⁻¹ appeared. The band around 3500 cm⁻¹ is due to strongly hydrogen bonded silanol groups. Figure 6b shows spectra of isolated silanol groups. In the case where the evacuation temperature was below 773 K, positions of the peak maximum were 3742 cm⁻¹. As evacuation temperature increases, the peak position was shifted to higher frequency. When FSM-16 was evacuated at 1073 K, the peak position was finally reached at 3745 cm⁻¹.
Figure 5. Thermogravimetric analysis and H2O-TPD profile of FSM-16. Prior to TPD measurement, 20 mg of FSM-16 was evacuated at 373 K for 1 h.
Morrow et al. reported that observed bands of isolated silanol groups were a combination of two species.52 One was truly isolated silanol (ν(SiO-H) of species I: 3750 cm\(^{-1}\)), and the other was weakly perturbed vicinal pairs of silanols (ν(SiO-H) of species II: 3740 cm\(^{-1}\)). Morrow et al. also reported that fumed silica and precipitated silica have different peak frequencies and bandwidths of isolated silanol because different preparation methods caused the ratio of the two isolated silanols to differ. If the concentration of weakly perturbed vicinal pairs of silanol is high, the peak position should be near 3740 cm\(^{-1}\). On the contrary, if the concentration of truly isolated silanol is high, the peak position should be near 3750 cm\(^{-1}\). From the band position of FSM-16, we conclude that isolated silanol groups on FSM-16 are rich in species II (weakly perturbed vicinal pairs of silanol). Ishikawa et al. observed a silanol band at 3740 cm\(^{-1}\) over FSM-16 and estimated the surface concentration.53 The wavenumber also indicates that almost all the silanol groups are weakly perturbed, although their concentration was lower than that of ordinary silica gel. Over siliceous MCM-41, the band due to isolated silanol groups was confirmed at 3738 cm\(^{-1}\), which was also close to the band of species II.42

When FSM-16 was evacuated at above 773 K, weakly perturbed vicinal pairs of silanol (species II) were selectively dehydroxylated to form truly isolated silanol (species I). The blue shift of the isolated silanol band on FSM-16 was due to a change of their ratio. These phenomena were more clearly shown in difference spectra, as shown in Figure 7. Below 673 K, broad bands of strongly hydrogen bonded silanol groups were mainly weakened. The difference spectrum between 573 and 673 K has the largest band area. It corresponded to the first peak of the H\(_2\)O-TPD profile and a gravimetric decrease (Figure 5). Above 773 K, the position of the weakened band was shifted to higher frequency. The most typical case was the difference spectra between 873 and 1073 K. The positions of weakened and strengthened peaks were 3741 and 3748 cm\(^{-1}\), respectively. In this region, elimination of silanol groups occurred. We observed a new band generation around 892 cm\(^{-1}\) in accordance with blue shift of isolated silanol bands (Figure 6c). Morrow et al. observed generation of new two bands at 908 and 888 cm\(^{-1}\) on fumed silica. New bands appeared when silica was evacuated at temperatures higher than 873 K, and these intensities reached a maximum at 1473 K.54-56 They assigned these peaks to a reactive strained siloxane bridge formed by condensation of isolated silanol groups. Further, Bunker et al. assigned them to an edge-shared silicate tetrahedral ring.57 In the second derivative of the IR spectrum, a trace peak and a distinct peak were observed on FSM-16 at 912 and 892 cm\(^{-1}\), respectively. IR behavior exhibited by FSM-16 resembles that previously reported on fumed silica, although the new band on FSM-16 was almost single. The IR result suggests that weakly perturbed vicinal pairs of silanols on FSM-16 condensed to produce siloxane bridges, similar to those on fumed silica and silica gel.51 Therefore the dehydroxylation of surface silanol groups of FSM-16 was responsible for the deactivation. The temperature of 673 K is the point where catalytic activity of FSM-16 decreased. Matsumura et al. reported that silica gel pretreated above 1000 K was active for selective ethanol dehydrogenation and the active site was an active siloxane bridge formed by the dehydration of
Figure 6. FTIR spectra of FSM-16 evacuated at various temperatures.
Figure 7. Difference IR spectra of FSM-16 evacuated at various temperatures: between 373 K and room temperature (a), 473 and 573 K (b), 573 and 673 K (c), 673 and 773 K (d), 773 and 873 K (e), and 873 and 1073 K (f).
silanol groups.\textsuperscript{58,59} In contrast, the siloxane bridge on FSM-16 did not concern the isomerization because no increase in activity was observed for FSM-16 evacuated at higher temperatures. The isolated silanol band observed on FSM-16 was only one and the wavenumber was around 3742 cm\(^{-1}\), so called neutral. We conclude that the active sites were surface silanol groups of species II themselves and/or silanol-related sites, although they were not so called acidic silanol bands around 3600 cm\(^{-1}\). This presumably results from the synthesis method and the crystal structure of FSM-16, on which the silanol groups were supposed to be regularly arrayed. There are very few reports in which neutral silanol groups are active sites for any reactions. Sato et al. claimed that Beckmann rearrangement of cyclohexanone oxime was catalyzed by neutral silanol groups, whose wavenumber was 3740 cm\(^{-1}\), on the external surface of highly siliceous MFI type zeolites.\textsuperscript{60} Although they did not discuss the silanol groups in detail, we suspect that the silanol groups should be weakly perturbed vicinal pairs.

\textit{Regeneration of Acid Sites}

In the previous section, we mentioned that catalytic activity of the highest FSM-16 was exhibited by pretreatment at 673 K and deactivation was due to dehydroxylation of silanol groups. To examine whether silanol groups of FSM-16 participate in acidic property or not, we prepared calcined and rehydrated FSM-16. If only silanol groups were the active sites, rehydrated FSM-16 should exhibit the same activity as fresh catalyst. Table 5 summarizes results of \(\alpha\)-pinene isomerization over variously treated FSM-16. Pretreatments were performed at 673 K in all cases. The catalyst noted simply as FSM-16 in Table 5 was the fresh catalyst, which was the same catalyst as listed in Table 2. FSM-16 calcined at 1173 K (FSM-1173) was less active than the fresh catalyst, but the activity was slightly higher than that pretreated at 1073 K. As expected, the activity of the less active catalyst was completely restored by hydration of the catalyst at 353 K followed by calcination at 773 K (FSM-1173H). The selectivity was not changed. These results indicate that hydration to restore silanol groups on FSM-16 regenerates acidic sites. The reason FSM-1173 was more active than FSM-16 pretreated at 1073 K was explained as follows. By moisture in atmospheric air, partial rehydration proceeded on FSM-1173 during the storage. Rehydrated FSM-16 having been calcined at 1373 K (FSM-1373H) did not catalyze isomerization of \(\alpha\)-pinene, in contrast to the result of FSM-1173H. This indicates that FSM-1373H no longer had the same properties as fresh FSM-16. The reason for the difference of catalytic activity between FSM-1173H and FSM-1373H is considered as follows. The possible first reason may be that the active elements such as Al and Ti on FSM-16 were lost during various treatments. The first reason can be excluded because no change of elemental composition was found (Table 1). The second is the fundamental structural change of FSM-16. This is only sintering.
TABLE 5: Change of the Activity of $\alpha$-Pinene Isomerization over FSM-16$^a$

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<th>Catalyst</th>
<th>Pretreatment</th>
<th>Conversion</th>
<th>Selectivity$^b$ (%)</th>
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</thead>
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<td>Temp./K</td>
<td>(%)</td>
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<td>FSM-1373H</td>
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<td>&lt;0.1</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $\alpha$-Pinene: 2 mL. catalyst: 50 mg. reaction temperature: 303 K. reaction time: 0.5 h.

$^b$ 1, $\beta$-Pinene; 2, camphene; 3, $\alpha$-fenchene; 4, limonene; 5, terpinolene; 6, $\alpha$-terpinene; 7, $\gamma$-terpinene; 8, others.

**Figure 8.** FTIR spectra of adsorbed pyridine at 423 K: fresh FSM-16 (21 mg) (a), FSM-1073pre (20 mg) (b), FSM-1173H (30 mg) (c), and FSM-1373H (80 mg) (d).
To investigate the difference of acidic properties more in detail, IR spectra of adsorbed pyridine were recorded. Figure 8 shows those of four typical variously treated FSM-16. The four catalysts are the fresh one, FSM-16 pretreated at 1073 K (FSM-1073pre), FSM-1173H, and FSM-1373H. Brønsted pyridine was observed on the fresh FSM-16, while not on FSM-1073pre. Although as many Lewis acid sites existed on the surface as on fresh FSM-16, FSM-1073pre was inactive for but-1-ene and α-pinene isomerization. The band around 1492 cm\(^{-1}\) was assigned to overlapping 19a bands of both Lewis and Brønsted pyridine. The intensity ratio of the band at 1492 cm\(^{-1}\) to a 19b band of Lewis pyridine at 1456 cm\(^{-1}\) was quite different from fresh FSM-16 and FSM-1073pre. The ratio of Lewis and Brønsted acid sites ([L]/[B] ratio) can be calculated from the band area of adsorbed pyridine at 1455 and 1492 cm\(^{-1}\).63 The calculated [L]/[B] ratio of fresh FSM-16 was 2.6, and that of FSM-1073pre was 5.6. This suggests that the fraction of Brønsted sites was decreased by pretreatment at 1073 K. The majority of acid sites were Lewis acid; however, Lewis acid sites are inactive for the catalysis of the isomerization of α-pinene and but-1-ene. The IR spectrum of adsorbed pyridine on FSM-1173H was quite similar to that on fresh FSM-16, and the [L]/[B] ratio of FSM-1173H was 2.6. This is in good accordance with the results of the catalysis. In other words, the surface property of FSM-1173H was the same as that of fresh FSM-16. On the other hand, FSM-1373H was quite different. Only hydrogen-bonded pyridine was observed in the IR spectrum of adsorbed pyridine on FSM-1373H, and it was quite similar to that of SiO\(_2\) gel (Figure 4). This strongly suggests that FSM-1373H was fundamentally different from that of fresh FSM-16 and FSM-1173H. From the results of catalytic activities and IR spectra, we conclude that the surface property of FSM-1373H is similar to that of ordinary silica gel rather than that of FSM-16.

To clarify the difference of each structure, we measured the XRD pattern of these samples. Figure 9 shows those of variously treated FSM-16 listed in Table 5. The XRD pattern of fresh FSM-16 exhibited four peaks, and the primary \(d\) spacing was 38 Å. This profile is identical with that reported previously. All peaks observed on FSM-1173 were shifted to higher degree. This was due to shrinkage of the lattice, and the shrunk primary \(d\) spacing was 32 Å. FSM-1173 and FSM-1173H still kept the structure of FSM-16, although the fourth peak disappeared. The result of XRD measurements shows that a series of rehydration procedures scarcely influenced the structure of FSM-1173. In the case of FSM-16 calcined at 1373 K, peaks below 10 degrees completely disappeared and no peaks were observed in all regions. This clearly shows that FSM-1373H became amorphous. From XRD results, we conclude that acidic properties appeared on only the crystal FSM-16. This result strongly suggests that the active site of FSM-16 was not due to impurity.

Over FAU type zeolites, Severino et al. reported that the change of the [L]/[B] ratio around 1.0 caused an abrupt change of selectivity to camphene in α-pinene isomerization. They concluded that the reaction rate catalyzed by Brønsted sites was higher than that by Lewis sites and that Lewis sites preferentially catalyzed to produce bicyclic products such as...
Figure 9. Cu Kα XRD patterns of fresh FSM-16 (a), FSM-1173 (b), FSM-1173H (c), and FSM-1373 (d).
camphene. In the case of FSM-16, selectivity for camphene was independent of pretreatment temperature. Further, low-temperature-treated niobic acid, known to be a typical Brønsted acid, gave a high selectivity for camphene. The suggestion by Severino et al. was not applicable to our experiments. The majority of acid sites on FSM-16 were Lewis sites, but Lewis sites did not participate in the catalysis of both but-1-ene and α-pinene isomerization. Therefore, we concluded that Brønsted acid sites were active sites for both reactions and that the sites were weakly perturbed vicinal pairs of silanol groups (species II).

Survey of Catalyst Property

It was reported that reversible dehydroxylation of silanols occurred below 673 K and irreversible dehydroxylation of isolated silanols occurred above 923 K. On the other hand, silanol groups of FSM-1173 were completely restored by rehydration procedures. This was supported by results of α-pinene isomerization, as shown in Table 5. The difference between our experiments and reported results was due to rehydration processes. The rehydration has been attempted at ambient temperature with 100% relative humidity, whereas FSM-16 was rehydrated in water at 353 K. To investigate the property of catalysts further, we measured the maximum of acid strength of catalysts by Hammett indicators. Table 6 summarizes maximum acid strength and BET specific surface area. Once SiO2 gel (BET specific surface area was 650 m² g⁻¹) was calcined at 1173 K, the surface area was reduced to 445 m² g⁻¹. Even if calcined silica gel was rehydrated in water at 353 K, complete regeneration of silanol groups was impossible because of its sintering. In contrast, the surface area of FSM-1173 was maintained at 965 m² g⁻¹. FSM-16 was stable at temperatures up to 1273 K and possessed high surface area even for a rehydrated sample calcined at 1173 K (Table 6). The rigid structure of FSM-16 made it possible to complete reversible dehydroxylation of isolated silanols.

FSM-16 pretreated at 673 and 1073 K exhibited medium acid strength of H0 = -3.0. This value is almost the same as those for SiO2-MgO, and NiSO4·nH₂O, but much weaker than that of SiO2-Al₂O₃ which is stronger than H₀ = -8.2. FSM-16, with Si/Al atomic ratios of both 735 and 320, showed the same value of maximum acid strength. The maximum acid strengths of SiO2 gel were much weaker than those for FSM-16. Werner et al. reported that crystalline silicates have much stronger acid sites than those of silica gel. For example, H₂Si₂O₅ and H₂Si₁₄O₂₉·5H₂O exhibited a maximum acid strength of H₀ = +2.3 to +3.3 and -5 to -3, respectively. They discussed that the high acidity resulted from regular and extended hydrogen-bonding systems including the surface water molecules. The maximum acid strength of synthesized H₂Si₂O₅ was the same as the reported value of H₀ = +3.0, although calcined H₂Si₂O₅ became amorphous. From elemental analysis, The Al concentration of H₂Si₂O₅ was estimated to be only 80 ppm (Table 1); however, its maximum acid strength of H₀ = +3.3 was higher than that of SiO2 gel of +4.8. These results show that almost pure siliceous materials have the possibility to exhibit acidic properties. Thus, we conclude that but-
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment Temp. /K</th>
<th>Surface Area /m² g⁻¹</th>
<th>$H_0$ max</th>
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<td>1078</td>
<td>-3.0 c</td>
</tr>
<tr>
<td></td>
<td>673</td>
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<td></td>
<td>873</td>
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<td></td>
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</tr>
<tr>
<td>FSM-16 a</td>
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<td>965</td>
<td>-3.0</td>
</tr>
<tr>
<td>FSM-1173H</td>
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<td>874</td>
<td>-3.0</td>
</tr>
<tr>
<td>FSM-1373H</td>
<td>673</td>
<td>37</td>
<td>-3.0 c</td>
</tr>
<tr>
<td>FSM-16 b</td>
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<tr>
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<tr>
<td></td>
<td>1073</td>
<td>490</td>
<td>+3.3</td>
</tr>
<tr>
<td>H₂Si₂O₅</td>
<td>673</td>
<td>144</td>
<td>+3.3 c</td>
</tr>
</tbody>
</table>

*a* Calcined in a dry air stream at 1173 K for 2 h.

*b* Supplied by TOYOTA Central R & D Labs., Inc. (lot no. NG78-550).

*c* Hammet indicator was faintly colored.
1-ene and α-pinene isomerizations were catalyzed by Brønsted acid sites with an acidic strength of $H_0 < +3.3$. In the case of FSM-16, the selectivity of α-pinene isomerization and the maximum acid strength were independent of the pretreatment temperature. This result indicates that the change of catalytic activity of FSM-16 does not depend on the change of the acid strength but on the number of acid sites. IR and H$_2$O desorption experiments showed that active sites on FSM-16 were blocked by hydrogen-bonded adsorbed water when FSM-16 was pretreated at below 673 K. This was supported by the result that addition of water to pretreated FSM-16 drastically lowered catalytic activity. Although FSM-16 pretreated at 1273 K showed the maximum acid strength of $H_0 = -5.6$, the number of the strongest acid sites was quite small because no change of selectivity for α-pinene isomerization was observed and activities for α-pinene and but-1-ene isomerization were quite low. Although FSM-1373H was amorphous, it still possessed a small number of acid sites whose $H_0_{\text{max}}$ was -3.0. As shown in Table 5, the activities of FSM-1373H and fresh FSM-16 were different from each other by over 400 times. On the other hand, the BET specific surface area of FSM-1373H was about 3% of the fresh one. The reduction of catalytic activity was far from that of the surface area. Therefore, the possibility that sintering was the main reason for deactivation is excluded. The structure of FSM-16 is indispensable to acidic property, although the mechanism of generation of acid sites is not clear. This is supported by the fact that FSM-16 having became amorphous, could not regenerate the acidic property by the rehydration process.

We suppose that the structure of FSM-16 is indispensable to acidic property, especially to its thin wall and regularly arrayed silanol groups.

Conclusion

FSM-16 catalyzes but-1-ene isomerization at 323 K and α-pinene isomerization at 303 K in the liquid phase. Catalytic activity of FSM-16 was dependent upon pretreatment temperatures and showed a maximum at 673 K. The activity of FSM-16 calcined at higher than 773 K was much reduced, but it could be restored by rehydration procedures as long as the samples maintained the crystal structure. The active sites were weakly perturbed silanol groups and a trace amount of Al of FSM-16 did not effect acidic property. Maximum acid strength was invariably $H_0 = -3.0$, independent of pretreatment temperatures. These properties are related to the regular structure of FSM-16.

References

Chapter 2

Generation of Lewis Acid Sites on FSM-16

Abstract

Catalysis over Lewis acid sites on siliceous mesoporous FSM-16 was confirmed. Acidic property of FSM-16 was studied by pyridine-TPD measurements and catalyses of α-pinene isomerization and methylamine synthesis. FSM-16 posses both Brønsted and Lewis acid sites, and another Lewis acid site formed on FSM-16 when a catalyst was pretreated above 873 K. α-Pinene isomerization was catalyzed over Brønsted acid sites, the activity of which is the highest when FSM-16 is pretreated at 673 K. Lewis acid sites on FSM-16 catalyze methylamine synthesis and the initial rates enhanced with increasing pretreatment temperature up to 1273 K. The structure of FSM-16 was completely retained throughout a pretreatment at 1273 K and a reaction procedure for methylamine synthesis at 673 K.
Introduction

Since the discovery of highly ordered mesoporous silica, mesoporous silica such as MCM-41, HMS, and FSM-16 have been investigated extensively. All the three materials exhibit a similar structure to each other, and possess high surface area, narrow pore size distributions, and high pore volume. Because siliceous mesoporous materials have been believed to be catalytically inert, preparation of Al-containing mesoporous materials has been attempted for the application to solid-acid catalysis. Most commonly, Al-source was added into the starting materials before synthesis of mesoporous materials. Impregnation methods of AlCl₃ or Al(OiPr)₃ to synthesized mesoporous silica were also performed. In another way, preparation of heteropoly acid introduced MCM-41 was reported.

In contrast to the efforts, catalyses of acid-catalyzed reaction over siliceous mesoporous materials were reported by some researchers in 1997. However, they did not pay attention to catalyses by mesoporous silicas. In their reports, results over siliceous mesoporous silicas were dealt with one of the reference catalysts or blank test. Sakata found thermal degradation of polyethylene proceeds over siliceous FSM-16 as fast as silica-alumina. The yield of liquid products over FSM-16 was higher than that for silica-alumina. They concluded that the mesopore surrounded by silica sheets act as a radical flask.

We have first reported the acid property of mesoporous silica in detail. FSM-16 catalyzes but-1-ene isomerization and α-pinene isomerization at 323 and 303 K, respectively. Subsequently our results were confirmed and supported by a report of the catalyses over siliceous MCM-41 about acetalization of aldehydes and ketones. The activities of FSM-16 depend on pretreatment temperatures and exhibit the highest when the catalyst was pretreated at 673 K. The acidity of FSM-16 is much reduced by calcination temperature at higher temperature, but restores by water treatment at 353 K as long as the FSM-16 retains its structure. We have concluded from IR characterizations that the active sites for the two reactions are weakly perturbed silanol groups which act as Brønsted acid sites. However, FTIR characterization of adsorbed pyridine on FSM-16 revealed that majority of the acid sites was Lewis acid sites. Furthermore, the peak intensity assigned to 8a mode of Lewis pyridine (1624 cm⁻¹) on FSM-16 pretreated at 1073 K was stronger much more than that on FSM-16 pretreated at 673 K. In the previous work, no evidence was obtained about catalyses over Lewis acids.

In the present study, we focused on the Lewis acid property of FSM-16. The property was evaluated with pyridine-TPD measurement and a catalysis for methylamine synthesis. Methylamine synthesis from methanol and ammonia is known to typical acid-catalyzed reaction, which proceeds over many solid acid catalysts having Lewis and/or Brønsted acid sites. Segawa et al. reported that γ-Al₂O₃ (JRC-ALO-4) catalyzes methylamine synthesis from methanol and ammonia, and the initial rate was higher than those of amorphous silica-alumina (JRC-SAL-2; Al₂O₃ = 13 wt%) and HZSM-5 (Si/Al = 12.5). It has been concluded from IR
spectra of adsorbed pyridine that the acid site of $\gamma$-Al$_2$O$_3$ is only Lewis acid sites. Therefore, the reaction catalyzed over $\gamma$-Al$_2$O$_3$ is considered to be a Lewis acid promoted reaction, and is expected to proceed over FSM-16 pretreated above 1073 K.

Experimental

Materials

FSM-16 was synthesized according to the literature, and the procedure was previously reported in detail. The grade of water glass used for FSM-16 synthesis is as follows; Fuji Silysia Co., LTD: SiO$_2$ = 15.3 wt%, Na$_2$O = 6.1 wt%, Al = 0.6 ppm, Fe = 0.4 ppm; Osaka Keiso Co., LTD: SiO$_2$ = 31.93 wt%, Na$_2$O = 15.37 wt%, Al = 98 ppm, Fe = 28 ppm. The Cu-K$\alpha$ XRD pattern of synthesized FSM-16 exhibits typical $d_{100}$, $d_{110}$, $d_{200}$ and $d_{210}$ reflections at $2\theta$ = 2.3, 4.1, 4.7 and 6.3°, respectively.

SiO$_2$ gel was synthesized from tetraethyl orthosilicate (Nacalai tesque, EP-grade, singly distilled) by hydrolysis in a water-ethanol mixture at boiling point, followed by calcination at 773 K for 5 h.

Precipitated silica was prepared from silicic acid, by calcination at 773 K for 5 h. Silicic acid was obtained by mixing of water glass (Fuji Silysia Co. LTD) and 2 M HCl at room temperature, followed by washing with 0.2 M HNO$_3$ until Cl$^-$ was free based on AgNO$_3$ test.

Reference catalysts used were Japan Reference Catalyst (JRC-ALO-4, JRC-SAL-2), supplied by the Committee on Reference Catalyst, Catalysis Society of Japan. JRC-ALO-4 is $\gamma$-Al$_2$O$_3$ which contains 0.01% of Fe$_2$O$_3$, SiO$_2$ and Na$_2$O. JRC-SAL-2 is amorphous silica-alumina which contains 0.02% Fe, 0.012% Na$_2$O, 0.33% SO$_4$, and 13.75% Al$_2$O$_3$. The BET specific surface areas of JRC-ALO-4 and JRC-SAL-2 are 177 and 560 m$^2$ g$^{-1}$, respectively.

Characterization

Elemental analysis was carried out by inductively coupled plasma (ICP) with Shimadzu ICPS-2000, and the results are shown in Table 1. The N$_2$ adsorption-desorption isotherm measurement was carried out with BELSORP 28SA (BEL JAPAN, Inc.) at 77 K. The specific surface area was calculated by BET method. The pore sized distribution was estimated by the Clanton-Inkley method. The pore volume and outer surface area were estimated by t-plot using a N$_2$ adsorption isotherm of non-porous silica as a standard.

Pyridine temperature-programmed desorption (TPD) experiments were performed at a heating rate of 10 K min$^{-1}$ and quadrupole-type mass spectrometer (MASSMATE-100, ULVAC) was used as a detector. Before TPD measurements, each 100 mg of sample was pre-evacuated at 673 K for 0.5 h and calcined under 6.66 kPa of O$_2$ for 1 h, followed by evacuation at the same temperature for 1 h. The pretreated sample was exposed to 80 µmol of
pyridine at 373 or 423 K for 10 min, followed by evacuation at the same temperature for 1 h. The amount of desorbed pyridine was normalized to that of introduced Ar (m/z = 40) as an internal standard. Because the most intense signal for pyridine-mass spectrum was that of m/z = 52, we adopted profiles of m/z = 52 for acid properties of catalyst.

FTIR spectra were recorded using a Perkin-Elmer Paragon 1000 spectrometer with a resolution of 2 cm\(^{-1}\). The 20 mg of FSM-16 was pressed into a self supporting wafer (20 mm in diameter) with a pressure of 100 kg cm\(^{-2}\) for 10 s, and was mounted in an in situ IR cell equipped with BaF\(_2\) windows. A wafer was evacuated at 673 or 1073 K for 1 h. After cooling to room temperature, each spectrum was recorded in a transmission mode.

Catalysis

\(\alpha\)-Pinene isomerization was carried out under dry N\(_2\) atmosphere using a stirred batch reactor at 303 or 353 K.\(^{18}\) Methylamine synthesis was carried out with a closed circulation system (dead volume, 200 cm\(^3\)) at 673 K. The pretreatment procedure for both reactions was the same as TPD experiment. In a typical experiment for \(\alpha\)-pinene isomerization, the reactor was loaded with 2 mL (12.6 mmol) of \(\alpha\)-pinene (Nacalai, EP, 99.8%) and 50 mg of catalyst. The amounts of substrates used for methylamine synthesis were 200 or 800 \(\mu\)mol of ammonia and 400 \(\mu\)mol of methanol. Products were analyzed by FID gas-chromatography (GC-14A, Shimadzu) with a CBP20-M25-025 capillary column (Shimadzu) for \(\alpha\)-pinene isomerization, and by GC-8A (Shimadzu) with an Unicarbon B-2000 column (GL Sciences, 2.6 \(\phi\) x 2 m) for methylamine synthesis.

Results and Discussion

Catalysis over Brønsted Acid Sites

From FTIR characterization, we have concluded that the active sites for but-1-ene and \(\alpha\)-pinene isomerizations are Brønsted acid sites of weakly perturbed silanol groups. The 19b mode of Brønsted pyridine (1546 cm\(^{-1}\)) was observed on FSM-16 pretreated at 673 K, whereas not on FSM-16 pretreated at 1073 K.\(^{18}\) A trace amount of Al of FSM-16 did not affect the acidic property at all. To confirm this conclusion again, \(\alpha\)-pinene isomerization was carried out with two kinds of FSM-16 which contain different concentration of Al. Results of catalytic test are summarized in Table 2. The selectivity was independent on Al concentrations as well, and camphene (ca. 39%) and limonene (ca. 43%) were produced. A rate for successive isomerization of limonene was low over FSM-16 even at 353 K. If Al-related sites on FSM-16 participate in the acidity, obvious difference in the activity should have been observed between sample No. 1 and No. 2. As shown in Table 2, any evident relations between the catalytic
### TABLE 1: Elemental Analysis of Catalysts

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Catalyst</th>
<th>Na (mass%)</th>
<th>Al (mass%)</th>
<th>Ca (mass%)</th>
<th>Fe (mass%)</th>
<th>Mg (mass%)</th>
<th>Ti (mass%)</th>
<th>Si/Al a</th>
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</tr>
</tbody>
</table>

*a* Atomic ratio  
*b* Precipitated silica

### TABLE 2: Results of α-Pinene Isomerization a

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>Reaction temperature/K</th>
<th>Conversion (%)</th>
<th>Selectivity b (%)</th>
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</table>

*a* α-Pinene: 2 mL (12.6 mmol). Catalyst: 50 mg. Reaction time: 0.5 h. Pretreatment temperature: 673 K.  
*b* 1, β-pinene; 2, camphene; 3, α-fenchene; 4, limonene; 5, terpinolene; 6, α-terpinene; 7, γ-terpinene; 8, others.  
*c* Taken from reference (18).  
*d* Catalyst: 100 mg. Reaction time: 3 h.  
*e* Pretreatment temperature: 1073 K.
activity and Al concentration in FSM-16 were not observed. It strongly suggests that the acid property of FSM-16 is not due to contamination of Al.

Over silica-alumina of strong solid acid, consecutive isomerization of limonene proceeded and dehydrogenate product (p-cymene) and polymerized products were observed even at 303 K for 30 min. Effective acid strength for α-pinene isomerization was proposed to $\text{H}_0 \leq +3.3,18,29$ Although γ-Al$_2$O$_3$ possesses certain amounts of strong Lewis acid sites (580 μmol g$^{-1}$), the maximum strength of which is over pKa $\leq -5.6,23,30$ the activity was much less than that of FSM-16. It was proposed the reaction rate for α-pinene isomerization over Lewis acid site is lower than that over Brønsted acid site.$^{31}$ Low activity of γ-Al$_2$O$_3$ is due to scarce existence of Brønsted acid sites. Other silicas were inert for α-pinene isomerization at 353 K.

**Temperature Programmed Desorption Measurements of Pyridine**

To clarify a change of acidic property of FSM upon thermal treatment, pyridine TPD experiment was carried out. It was reported that strained siloxane bridge was formed on silica evacuated above 673 K. The site reacts with NH$_3$ to produce SiNH$_2$ and SiOH even at room temperature, whereas the sites do not react with pyridine.$^{32,33}$ Therefore, we adopted pyridine as a base molecule to evaluate the acidic property. The results of pyridine TPD experiments, each adsorption temperature of which was 373 K, are shown in Figure 1. TPD profiles of FSM-16 pretreated at 673 K exhibited a large desorption peak around 473 K and a faint peak around 800 K. With increasing pretreatment temperatures, the peak intensity around 473 K drastically reduced, whereas that around 800 K was almost constant. In the desorption profiles of FSM-16 pretreated at 1073 and 1273 K, a new desorption peak appeared around 510 K. The behavior of the desorption peak around 473 K upon pretreatment temperature is consistent with that of catalytic activities for but-1-ene and α-pinene isomerization. This pyridine adsorption site may be conjectured to be the active sites of FSM-16, which have been proposed to Brønsted acid. However, a pyridine TPD profile of SiO$_2$ gel pretreated at 673 K, which was inert for the two reactions, exhibited a large desorption peak around 473 K. When pyridine-adsorption procedure was carried out at 373 K, a large amount of hydrogen bonded pyridine adsorbed onto residual water molecules of both the catalysts. Therefore, the peak observed around 473 K is desorption pyridine from both hydrogen-bonded and Brønsted acid sites.

To reduce the effect of hydrogen-bonded pyridine in TPD experiments, pyridine adsorption procedure was then performed at 423 K. The TPD profiles are shown in Figure 2. The TPD profile of FSM-16 pretreated at 673 K exhibited a small broad desorption peak around 600 K and a shoulder over 773 K. With increasing pretreatment temperature, a new desorption peak grew around 550 K. It is obvious that somewhat new acid sites generate, the amount of which increased on FSM-16 by thermal treatment. When pyridine was adsorbed at 373 K,
Figure 1. Pyridine TPD profiles of FSM-16 pretreated at 673 K (a), 873 K (b), 1073 K (c) and 1273 K (d), and SiO$_2$ gel pretreated at 673 K (e) and 1073 K (f). Adsorption temperature: 373 K. Rate: 10 K min$^{-1}$. 
Figure 2. Pyridine TPD profiles of FSM-16 pretreated at 673 K (a), 873 K (b), 1073 K (c) and 1273 K (d), and SiO₂ gel pretreated at 673 K (e) and 1073 K (f). Adsorption temperature: 423 K. Rate: 10 K min⁻¹.
FSM-16 pretreated at 673 K desorbed the largest amounts of pyridine. In contrast, FSM-16 pretreated at 1273 K desorbed the largest amounts when pyridine was adsorbed at 423 K. Similar phenomena were observed in pyridine TPD profiles of SiO2 gel adsorbed at 423 K. Little pyridine adsorbed on SiO2 gel pretreated at 673 K. A new desorption peak was observed in that of SiO2 pretreated at 1073 K as well, however, the intensity was much smaller than that of FSM-16. No desorption peaks were observed in those of SiO2 gel above 673 K, in contrast to those of FSM-16.

When FSM-16 was pretreated above 1073 K, desorbed amounts of pyridine from FSM-16 were almost the same among the two different adsorption temperatures. IR spectra indicated that hydrogen-bonded silanol groups were absent on the surface of FSM-16 evacuated at 1073 K. As a result, hydrogen-bonded pyridine was absent on FSM-16 pretreated above 1073 K, and differences of TPD profiles were not observed among different adsorption temperatures. Pyridine TPD experiment of siliceous MCM-41 pretreated at 573 K was performed by Zhao. Unfortunately, because the adsorption temperature on MCM-41 was 325 K, the difference of acidic property between FSM-16 and MCM-41 is not able to compare with. In conclusions, another kind of acid sites generate on FSM-16 pretreated above 873 K, and effects of hydrogen-bonded pyridine are free if pyridine adsorption was carried out at 423 K.

*Generation of Lewis Acid Sites*

We have measured IR spectra of adsorbed pyridine on FSM-16, and estimated the ratio of Lewis and Brønsted acid sites ([L]/[B] ratio). Total amount of Lewis acid sites was much more than that of Brønsted acid sites. The [L]/[B] ratio of FSM-16 pretreated at 673 K was estimated to 2.9, and that of FSM-16 pretreated at 1073 K was 5.6. In these spectra, the peak intensity assigned to 8a mode of Lewis pyridine (1624 cm⁻¹) enhanced by high-temperature pretreatment. The peak area on FSM-16 pretreated at 1073 K was 1.4 times as large as that on FSM-16 pretreated at 673 K. In cases of TPD experiments, cumulated amounts of desorbed pyridine in the range of 423-873 K differed by 2.2 times between the two FSM-16 samples of different evacuation temperatures. The tendency of pyridine TPD profile adsorbed at 423 K is consistent with the results of IR spectra.

Figure 3 shows IR spectra of FSM-16 evacuated at 673 and 1073 K. In the range around 900 cm⁻¹, a new peak appeared at 892 cm⁻¹ when FSM-16 was treated at 1073 K. In the second derivative spectra, an additional peak was confirmed at 912 cm⁻¹. On the other hand, any peaks were not present in the IR spectrum of FSM-16 treated at 673 K. This phenomena observed on FSM-16 are quite similar to those for amorphous silica. It is well known that isolated surface silanol groups of silica are dehydroxylated to form strained siloxane bridge over 900 K. Such the dehydroxylated silica, two defect bands are observed at 888 and 908 cm⁻¹ in the range of 800-1000 cm⁻¹ which were assigned to edge-shared disiloxane ring. They are produced by dehydroxylation of isolated silanol groups, and can
Figure 3. FTIR spectra of FSM-16 evacuated at 673 K (a) and 1073 K (b), and their second derivatives.
be classified to be Lewis acid.\textsuperscript{38} In fact, dehydrogenation of ethanol was catalyzed over highly dehydrated silica, the active site of which was proposed to be Si-O-Si oxygen bridge.\textsuperscript{39} However, the acid strength of SiO\textsubscript{2} pretreated at 1073 K was not very strong, so that only hydrogen bonded pyridine was detected with FTIR spectroscopy.\textsuperscript{40} The newly formed acid sites on FSM-16 pretreated above 873 K are possibly due to silicon atoms of strained siloxane bridge as well as amorphous silica. If one of the silicon-oxygen bond of siloxane bridge was prolonged, the silicon atom could be regarded as pseudo-coordination unsaturated site and strength of the Lewis acidity remarkably should be enhanced. We speculate that such the pseudo-coordination unsaturated silicon species formed on FSM-16 pretreated at higher temperature. The rigid structure of FSM-16 permits the existence such unstable species like them. This might be the reason for the difference in acidity between FSM-16 and SiO\textsubscript{2} gel.

\textit{Catalysis over Lewis Acid Sites}

As shown in Figure 2, amounts of Lewis acid sites on FSM-16 increase with raising pretreatment temperatures. As a test reaction for Lewis acid sites on FSM-16, methylamine synthesis was examined. If the Lewis acid sites on FSM-16 are effective for this reaction, the catalytic activity should be enhanced with increasing pretreatment temperatures.

Figure 4 shows a time course of methylamine synthesis over FSM-16. As expected, the initial rate for methanol conversion exhibited the highest when FSM-16 was pretreated at 1273 K. Figure 4b shows the selectivity for methylamine synthesis over 1273 K pretreated FSM-16. At the initial step, a selectivity to monomethylamine (MMA) was 90\% and that for trimethylamine (TMA) was 10\%. Formation of dimethyl ether was not observed. Ammonia was rapidly methylated to MMA over FSM-16, however, a rate for consecutive methylated was very slow. The amount of dimethylamine (DMA) formation was very small even when reaction time was 180 minutes. The selectivities to each methylamine unchanged by pretreatment temperatures, and no induction periods were observed in all cases. Figure 5 summarizes initial rates for methylamine synthesis and activities of \textalpha-pinene isomerization over FSM-16 versus pretreatment temperature. Catalytic activity for \textalpha-pinene isomerization was dependent upon heat treatment and reached maximum at 673 K, and the activity was drastically reduced when FSM-16 was pretreated above 1073 K. In contrast, methylamine synthesis was catalyzed by FSM-16 pretreated at 1273 K, the activity of which was higher than that of FSM-16 pretreated at 673 K. It clearly shows that methylamine synthesis proceeds over Lewis acid sites on FSM-16. These two reactions should be catalyzed by the different active sites on FSM-16.

Lewis acid sites on FSM-16 might change to Brønsted acid sites with water which formed by dehydration among methanol and ammonia. Hence, it is doubtful whether Lewis acid sites really participate in a catalysis for methylamine synthesis. If Brønsted acid sites were active sites, which were converted from the Lewis acid sites, induction period should have been observed. Furthermore, the reaction rate over FSM-16 pretreated at 1273 K should never
Figure 4. Time course of methylamine synthesis over FSM-16 pretreated at various temperatures. Methanol: 400 μmol. Ammonia: 200 μmol. Catalyst: 100 mg. Reaction temperature: 673 K. Dead volume: 200 cc.

Figure 5. Effects of pretreatment temperature on catalytic properties of FSM-16. Dotted line: α-Pinene isomerization at 303 K. Reproduced from reference (18). Solid line: Methylamine synthesis at 673 K. N/C = 0.5.
exceed one over FSM-16 pretreated at 673 K. However, present results of catalysis did not agree with these postulates. Therefore, it is obvious that the Lewis acid sites formed on FSM-16 acts as active sites.

From the results that H-type MFI, Y and Mordenite zeolites exhibit higher activities for methylamine synthesis than those of each Na-type zeolite, not only Lewis but also Brønsted acid sites catalyze this reaction. In addition, reaction mechanisms catalyzed by Brønsted acid sites have been proposed. We cannot conclude whether the active sites of FSM-16 for methylamine synthesis were Brønsted and/or Lewis acid sites. However, we say again that Lewis acid sites on FSM-16 participate in this catalysis.

When the reaction was carried out with 400 μmol of methanol and 200 μmol of NH₃, evident difference in initial rates was observed on FSM-16 pretreated various temperatures. In contrast, the differences in activities to pretreatment temperatures were small when the reaction was performed with 400 μmol of methanol and 800 μmol of NH₃. The reaction rates for methanol conversion were not so different by N/C (ammonia to methanol) ratios, however, the rate of TMA formation increased in a case N/C = 2. FSM-16 catalyzed methylamine synthesis to produce MMA readily, but the rate of consecutive methanation was relatively slow in all reaction conditions. As a result, reaction rates for methanol consumption were not influenced by the reaction condition of different N/C ratios.

To compare the catalytic activity of FSM-16 with other catalysts, methylamine synthesis was carried out with various reference catalysts. No products other than methylamines were formed in all cases. The time courses of methanol consumption are shown in Figure 6. Activities of silica-alumina and γ-Al₂O₃ were higher by one order of magnitude than that of FSM-16. γ-Al₂O₃ exhibited the largest initial rates in the catalysts. SiO₂ gel pretreated at 1073 K were not active for this reaction at all. The activity of FSM-16 (sample no. 1) was slightly lower than that of FSM-16 (sample no. 2). The amounts of contained Al were 610 ppm for FSM-16 (sample no. 1) and 1100 ppm for FSM-16 (sample no. 2). The difference of catalytic activities between FSM-16 (no. 1) and FSM-16 (no. 2) was much less than that of contained amounts of Al impurities. Although FSM-16 were less active than silica-alumina and γ-Al₂O₃, the point we emphasize is that not only Brønsted but also Lewis acid sites on FSM-16 participate in certain kinds of catalyses.

The results of methylamine synthesis are summarized in Table 3. Consecutive methylation over FSM-16 was accelerated in a reaction condition of N/C = 2 more than N/C = 0.5. The equilibrium concentrations of methylamines (MMA/DMA/TMA) are 5/25/70 for N/C = 0.5, and 31/38/31 for N/C = 2 at 673 K. It suggests that FSM-16 possesses the acid sites to catalyze methylation of ammonia, the acid strength of which is not sufficient to reach the equilibrium of methylamines rapidly. In an initial period of methylamine synthesis over γ-Al₂O₃, MMA was selectively produced and the formation of TMA was scarce. In contrast, TMA was produced in an initial step over silica-alumina of strong solid acid.
### TABLE 3: Results of Methylamine Synthesis at 673 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment Temperature / K</th>
<th>N/C&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Conversion (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Selectivity (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>MMA</th>
<th>DMA</th>
<th>TMA</th>
</tr>
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<tbody>
<tr>
<td>FSM-16&lt;sup&gt;d&lt;/sup&gt;</td>
<td>673</td>
<td>0.5</td>
<td>78.7</td>
<td>88</td>
<td>-</td>
<td>12</td>
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<tr>
<td></td>
<td>873</td>
<td>0.5</td>
<td>80.3</td>
<td>88</td>
<td>-</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>0.5</td>
<td>84.2</td>
<td>87</td>
<td>-</td>
<td>13</td>
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<tr>
<td></td>
<td>1273</td>
<td>0.5</td>
<td>83.4</td>
<td>88</td>
<td>-</td>
<td>12</td>
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</tr>
<tr>
<td>FSM-16&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>84.1</td>
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<td>4</td>
<td>38</td>
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<tr>
<td></td>
<td>1073</td>
<td>2</td>
<td>83.8</td>
<td>62</td>
<td>4</td>
<td>34</td>
<td></td>
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<tr>
<td></td>
<td>1273</td>
<td>2</td>
<td>86.9</td>
<td>69</td>
<td>3</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>FSM-16&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1073</td>
<td>2</td>
<td>74.3</td>
<td>71</td>
<td>3</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>SiO₂ gel</td>
<td>1073</td>
<td>2</td>
<td>1.3</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>γ-Al₂O₃&lt;sup&gt;f&lt;/sup&gt;</td>
<td>673</td>
<td>2</td>
<td>83.5&lt;sup&gt;g&lt;/sup&gt;</td>
<td>90</td>
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<td></td>
<td>2</td>
<td>91.7</td>
<td>51</td>
<td>21</td>
<td>51</td>
<td>28</td>
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<tr>
<td>silica-alumina&lt;sup&gt;f&lt;/sup&gt;</td>
<td>673</td>
<td>2</td>
<td>81.3&lt;sup&gt;h&lt;/sup&gt;</td>
<td>68</td>
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<td></td>
<td>2</td>
<td>95.3</td>
<td>50</td>
<td>8</td>
<td>42</td>
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</tbody>
</table>

<sup>a</sup> Catalyst, 100 mg; Methanol, 400 μmol; Ammonia, 200 or 800 μmol.

<sup>b</sup> Molar ratio of ammonia to methanol.

<sup>c</sup> Reaction time, 1 h.

<sup>d</sup> Sample No. 1.

<sup>e</sup> Sample No. 2.

<sup>f</sup> Catalyst, 10 mg.

<sup>g</sup> Reaction time, 10 min.

<sup>h</sup> Reaction time, 20 min.
We have estimated the maximum acid strength of catalysts with Hammet indicators. When pretreatment procedure was performed below 1073 K, FSM-16 exhibits medium acid strength of $H_0 = -3.0$. In a case that FSM-16 was pretreated at 1273 K, the maximum acid strength was estimated to $H_0 = -5.6$. When FSM-16 was pretreated above 1073 K, catalytic activities for but-1-ene and $\alpha$-pinene isomerization drastically reduced, in spite of the results that FSM-16 still exhibited solid acidity of medium acid strength. Therefore, we conclude that Lewis acid site on FSM-16 possesses medium acid strength of $H_0_{\text{max}}$ = -3.0 to -5.6, which little catalyze but-1-ene and $\alpha$-pinene isomerization at 323 K.

**Thermal and Hydrothermal Stability of FSM-16**

To examine the structural change of FSM-16 throughout a reaction, N$_2$ adsorption isotherms of fresh and reacted samples were measured. The reacted sample measured was FSM-16 (sample no. 2) which was pretreated at 1273 K and the reaction was carried out at 673 K for 3 h (N/C = 2). Prior to measurement, reacted FSM-16 was calcined at 873 K for 2 h in a dry air, followed by evacuation at 673 K for 3 h. Figure 7 shows adsorption/desorption isotherms (a), t-plots (b) and pore size distribution curves (c) of fresh and reacted FSM-16. The estimated pore parameters are summarized in Table 4. The shape of t-plot and estimated parameters for fresh FSM-16 are quite similar to those of FSM-16, and that of MCM-41.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ $^a$ /m$^2$ g$^{-1}$</th>
<th>$V_p$ $^b$ /cm$^3$ g$^{-1}$</th>
<th>$S_t$ $^c$ /m$^2$ g$^{-1}$</th>
<th>$S_{\text{out}}$ $^d$ /m$^2$ g$^{-1}$</th>
<th>$D$ $^e$ /nm</th>
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<tbody>
<tr>
<td>1</td>
<td>FSM-16</td>
<td>1059</td>
<td>0.721</td>
<td>1012</td>
<td>102</td>
<td>2.76</td>
</tr>
<tr>
<td>2</td>
<td>FSM-16</td>
<td>1068</td>
<td>0.762</td>
<td>948</td>
<td>97</td>
<td>2.76</td>
</tr>
<tr>
<td>2</td>
<td>FSM-16$^f$</td>
<td>924</td>
<td>0.642</td>
<td>888</td>
<td>94</td>
<td>2.76</td>
</tr>
<tr>
<td>3</td>
<td>SiO$_2$ gel</td>
<td>637</td>
<td>0.683</td>
<td>582</td>
<td>59</td>
<td>4.26</td>
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<tr>
<td>4</td>
<td>$p$-Silica $^g$</td>
<td>464</td>
<td>0.266</td>
<td>477</td>
<td>14</td>
<td>(3.76)</td>
</tr>
</tbody>
</table>

$^a$ BET specific surface area.

$^b$ Pore volume estimated by t-plot.

$^c$ Total surface area estimated by t-plot.

$^d$ Outer surface area estimated by t-plot.

$^e$ Tentative pore diameter estimated by Clanston-Inkley method.

$^f$ After methylamine synthesis at 673 K for 3h. The catalyst was pretreated at 1273 K.

$^g$ Precipitated silica.
Figure 7. Results of N₂ adsorption/desorption isotherm measurements at 77 K: Adsorption/desorption isotherms (a), pore size distribution curves (b) and t-plots (c). Circle: Fresh FSM-16 (sample No. 2). Square: Reacted FSM-16, which was pretreated at 1273 K and used for methylamine synthesis at 673 K for 3 h (N/C = 2).
Reacted FSM-16 retained 85% of BET specific surface area (924 m$^2$ g$^{-1}$) and total pore volume (0.642 mL g$^{-1}$), comparing to those of fresh ones. The shape of N$_2$ adsorption/desorption isotherm of reacted FSM-16 was retained to that of fresh one. The ranges of capillary condensation were observed among P/P$_0$ = 0.29 - 0.34 and 0.25 - 0.32, respectively. In the case of reacted FSM-16, the range of pore filling was slightly shifted to lower P/P$_0$ due to shrinkage of the lattice, however, its decay was almost the same as that of fresh FSM-16. It clearly shows that the crystallinity and pore-uniformity of FSM-16 retained in the pretreated and reacted sample. It was supported by the pore size distribution curves.

Under reaction condition of a methylamine synthesis, H$_2$O is produced by dehydrative condensation among methanol and ammonia. As a result, catalysts were exposed to saturated water vapor at 673 K. Nevertheless, scarce reduction of the crystallinity occurred and no increase of outer surface area was observed throughout the reaction. Furthermore, FSM-16 has been pretreated at a high temperature of 1273 K prior to the reaction. The N$_2$ adsorption/desorption isotherm measuring experiments strongly demonstrate the excellent thermal and hydrothermal stability of FSM-16. It was consistent with the result that FSM-16 soaking into 353 K of water for 5 h retained the original structure, without reducing its crystallinity at all.\(^{18}\)

**Conclusion**

Lewis acid site formed on siliceous FSM-16 when a catalyst was pretreated above 873 K. Lewis acid sites on FSM-16 catalyzed methylamine synthesis at 673 K. The activity was enhanced with increasing pretreatment temperature up to 1273 K. The structure of FSM-16 was retained throughout a pretreatment at 1273 K and a reaction at 673 K. When FSM-16 was pretreated at 673 K, reactions catalyzed over Brønsted acid sites exhibit the highest rates. The rates of Lewis acid-catalyzed reactions were enhanced with increasing pretreatment temperature up to 1273 K.

**References**

Tanabe, K. Solid Acids and Bases; Kodansha, Tokyo, 1970, pp. 119-125
Part II

Acidic Property and their Structural Characterization of Silica-Supported Rare Earth Oxide Catalysts
Introduction of Part II

Supported Rare Earth Oxide Catalysts

Rare earth oxides themselves are well-known solid base catalysts, and enhance certain kinds of reactions, which are catalyzed by alkali earth oxides. Rare earth oxides possess not only base sites but also acid sites. In fact, Lewis acid sites are observed on La$_2$O$_3$, CeO$_2$ and Yb$_2$O$_3$ evidenced by IR spectra of adsorbed pyridine. Aurox carried out microcalorimetric study of acidity and basicity of rare-earth oxide. In dehydration of secondary alcohols, it was reported that both acid and base sites on CeO$_2$ act simultaneously to give olefins of E1cB selectivity (Hofmann orientation). Such an acid-base pair was proposed on La$_2$O$_3$, and the pair activates methane to form methyl radicals in an oxidative coupling of methane.

Investigations for catalysis by supported rare earth oxides are very scarce. According to the hypothesis for acidity prediction proposed by Tanabe et al., binary oxides of La$_2$O$_3$-SiO$_2$ and Y$_2$O$_3$-SiO$_2$ are expected to exhibit solid acidity. In fact, the maximum acid strengths estimated with Hammet indicators were $H_0 = -5.6$ for SiO$_2$-Y$_2$O$_3$ and $H_0 = -4.4$ for La$_2$O$_3$-SiO$_2$. Recently, catalysis of monoethanolamine synthesis over SiO$_2$-Y$_2$O$_3$ was reported. To the author's knowledge, this is the only one case for acid catalyzed reactions over supported rare earth oxide catalysts.

In the Ln/γ-Al$_2$O$_3$ systems (Ln = La, Sm, Lu), Captián et al. observed a strong interaction between a supported phase and the Al$_2$O$_3$ support, which affects the vibration frequency of Al-O bonds, binding energy of the Ln(4d) levels, the white line intensities at Ln-L$_{III}$ edge XANES spectra, and the d-orbital electron densities evaluated with ab initio calculations. They proposed that the strong interaction causes a redistribution of the electron density over Al-O-Ln ensembles, which implies a modification of acid-base properties of the surface. On the other hand, Shen et al. investigated acid-base properties of silica- and alumina-supported europium oxide with spectroscopic and calorimetric methods. They found that alumina supported europium oxide possesses basic sites stronger than that of Eu$_2$O$_3$, and silica-supported europium oxide exhibits Lewis acid properties. Connell and Dumesic observed both Lewis and Brønsted acid sites over Sc-loaded silica. Nevertheless, no acid-base catalyzed reactions were not performed over those kinds of La/Al$_2$O$_3$, Eu/Al$_2$O$_3$ and Eu/SiO$_2$.

Soled et al. prepared various kinds of rare earth oxide modified silica-aluminas, and carried out model reactions to evaluate the acid strengths. From the selectivity in 2-methylpent-2-ene isomerization, they concluded that acid strengths of rare-earth modified catalysts, which contain 5-20 wt% of rare earth oxides, were the same level as halide ion-treated aluminas of intermediate acid strength. However, their aim was to control the acidity of...
The addition of weakly basic rare earth oxides in a well dispersed state poisons the stronger acid sites of amorphous silica-alumina. As a result, the acid strength of silica-alumina was lowered.

Vannice et al. reported that dispersed La2O3 on alumina exhibits higher activity for selective reduction of NO to N2 with CH4 in the presence of oxygen at 973 K than unsupported La2O3 and Co/ZSM-5, while the catalytic activity of La/SiO2 was quite lower than that of La2O3. They found the activity was dependent upon the La2O3 precursor used, the pretreatment, and the loading amounts. The most active catalyst was that prepared with γ-Al2O3 and lanthanum acetate, and calcined at 1023 K. The optimum loading amount was 40 %, which corresponds to 1.5 theoretical monolayers of La2O3 on alumina. They concluded that the precursor of lanthanum salt affects the dispersion on alumina, and speculated that the low catalytic ability of La/SiO2 relates to its water sensitivity to form lanthana-silicate. Capitán et al. investigated Sm2O3/Al2O3 catalyst focusing correlations between catalysis for oxidative coupling of methane and the surface Sm-Al-O phases. They concluded that oxide-like structure shows better selectivity toward C2 species than the SmAlO3 phase. When Sm/Al2O3 catalyst was calcined at 873 K, samarium species present as oxide-like structure over alumina surface. If the catalyst was calcined at 1173 K, samarium species formed perovskite-like phase on the surface. The phase transition of samarium species on alumina, which affects the catalytic performance, is quite similar to that for La/Al2O3 proposed by Bettman.

As mentioned above, the study of the supported lanthanides from the view point of acid-base catalysis has just begun and we need more accumulation of the knowledge. In the present part, acid-base properties of silica-supported rare-earth oxides are described on the basis of investigation with various spectroscopic methods and α-pinene isomerization as an acid-base model reaction. The effects of loading elements and amounts, and thermal treatments on their catalytic properties are discussed. Accompanied by structural characterizations, the structures of acid sites on silica-supported rare-earth oxide catalysts were proposed. In Chapter 3, physicochemical properties of silica-supported ytterbium oxide catalysts are reported. The effects of loading amounts and pretreatment temperature on the catalytic activity are discussed. The structure of active species is also proposed. In Chapter 4, XAFS investigation for characterization of Yb/SiO2 catalysts is reported. Differences in the local structure around Yb between Yb/SiO2 catalysts and Yb2O3, and coordination environments around Yb are discussed. In Chapter 5, differences in acid properties of silica-supported rare-earth oxides among supported elements are described. Relations among catalytic properties and the structural environment of each Ln/SiO2 catalyst are discussed.

References
Chapter 3

Silica-Supported Ytterbium Oxide Characterized by Spectroscopic Methods and Acid-Catalyzed Reactions

Abstract

Acid-Base properties of silica-supported ytterbium oxide catalyst, loading amounts of which are 25 μ - 8.4 mmol Yb g(SiO₂)⁻¹, were investigated by TPD experiment and α-pinene isomerization. The relations among acid properties, structures, and catalytic properties are discussed. The catalytic activity depends on loading amounts of ytterbium and pretreatment temperatures, and reached the highest when loading amount were 3.4 mmol g(SiO₂)⁻¹ and pretreatment temperature 1073 K. No crystalline phase was detected with XRD technique. By XAFS spectroscopy, Yb atoms adjacent to Yb were found to be absent, but the presence of Si atoms adjacent to Yb was observed in all the catalysts. XRD and XAFS analyses revealed that Yb atoms are supported on SiO₂ in a highly dispersed form as YbO₆ octahedra. Solid acidity is concluded to be due to strong interaction between a YbO₆ octahedron and a SiO₄ tetrahedron, and the specific activity per Yb-Si unit was independent of loading amounts. When loading amounts of Yb were excess to form two-dimensional ytterbium oxide overlayer, the apparent turn over numbers drastically reduced.
Introduction

The catalysis of rare-earth oxide is well known, and many reactions have been reported.\(^1\)-\(^3\) Rare earth oxide is known as a solid base catalyst, but there are few reports about catalysis over supported rare earth compound. As a general use, rare earth elements are added to catalyst supports to enhance their thermal stability.\(^4\) Binary oxides of \(\text{SiO}_2-\text{La}_2\text{O}_3\) and \(\text{SiO}_2-\text{Y}_2\text{O}_3\) were predicted to exhibit acidity, according to the hypothesis proposed by Tanabe.\(^5\),\(^6\) Shen et al. investigated acid-base property of europium oxides supported on silica and alumina by microcalorimetry and IR spectra of adsorption of ammonia and carbon dioxide.\(^7\) They observed a generation of base sites on alumina-supported europium oxide, whereas a generation of acid sites was observed on silica-supported europium oxide. Connell and Dumesic reported the generation of Lewis and Brønsted acid sites on Sc/\(\text{SiO}_2\) with IR spectra of adsorbed pyridine.\(^8\) However, catalytic reactions have not been performed in these works mentioned above. Recently, Soled et al. reported the catalysis by rare earth oxide loaded on silica-aluminas, acid strength of which was the same level as halide-treated aluminas.\(^9\) However, their aim was to control the acidity of silica-alumina by reduction of acid strength. Therefore, the relations among acid-base properties, structures, and catalytic properties of supported rare earth oxides have left unclear.

In the series of rare earth elements, we paid attention to ytterbium. Kobayashi et al. reported that lanthanide trifluoromethanesulfonate acts as a water-tolerant Lewis acid, and the ytterbium triflate exhibited the highest activities in lanthanide triflates.\(^10\) Imamura et al.\(^11\)-\(^13\) and Baba et al.\(^14\)-\(^16\) prepared various kinds of supported Yb amide complexes, which were prepared by impregnation of support-materials with a liquid ammonia solution of Yb metal, followed by evacuation. They reported that supported Yb(III)-amide complexes successively changed to Yb(II)-imide and finally to Yb(III)-nitride as ramping evacuation temperatures. The catalytic properties exhibited by these complexes were quite different from each other. In the case of Y-type zeolite supported Yb complex, Yb(II)-imide complex promoted base-catalyzed reactions.\(^14\)-\(^16\) In the case of Yb-dosed \(\text{SiO}_2\), the atomic array of \(=\text{Si-O-Yb-NH}_2\) was responsible for hydrogenation property.\(^12\)

However, catalysis by supported ytterbium oxide has not been reported. We prepared silica-supported ytterbium oxide catalysts with various loading amounts of Yb by conventional impregnation method. In this work, we report acid-base property of silica-supported ytterbium oxide catalysts and the results of characterization of their structure. For a model reaction for the acid-base property, \(\alpha\)-pinene isomerization was utilized.

Experimental
SiO₂ gel was synthesized from tetraethyl orthosilicate (Nacalai tesque, EP-grade, singly distilled) by hydrolysis in a water-ethanol mixture at the boiling point, followed by calcination at 773 K for 5 h. Before calcination, a dried sample was ground to a powder under 100 mesh. Silica supported ytterbium oxide catalyst was prepared by impregnation of SiO₂ gel with an aqueous solution of ytterbium nitrate (Mitsuwa Co., 99.9%) at 353 K. The sample was dried at 363 K for 12 h, followed by calcination at 773 K for 5 h. These samples are referred to as \( x \) mmol Yb/SiO₂ (\( x \) stands for loading amounts of Yb atom per one gram of SiO₂). Ytterbium oxide was prepared by thermal decomposition of ytterbium nitrate at 773 or 1273 K for 5 h. They were identified by XRD patterns in comparison with Yb₂O₃ of C-rare earth structure (JCPDS file No. 18-1463).

α-Pinene isomerization was carried out under dry a N₂ atmosphere using a stirred batch reactor at 323 K. Before reaction, each sample was evacuated at 1073 K for 0.5 h and calcined under 6.66 kPa of O₂ for 1 h, followed by evacuation at the same temperature for 1 h. In a typical experiment, the reactor was loaded with 2 mL (12.6 mmol) of α-pinene (Nacalai, EP, 99.8%) and 50 mg of catalyst. Products were analyzed by GC and GC-Mass (Shimadzu, GCMS-QP5050).

The BET specific surface area measurements were carried out with N₂ adsorption isotherms at 77 K. Each sample was pretreated in the same way as α-pinene isomerization.

Temperature-programmed desorption (TPD) experiment was used as a detector for quadrupole-type mass spectrometer. NH₃ and CO₂ TPD measurements were performed at a heating rate of 5 K min⁻¹, and TPD measurement of pyridine was performed at a heating rate of 10 K min⁻¹. The pretreatment procedure was the same as mentioned above. The sample (100 mg) was exposed to 500 μmol of CO₂ or NH₃ at 373 K for 30 min, or 80 μmol of pyridine at 423 K for 10 min, followed by evacuation at the same temperature for 1 h. The amounts of desorbed gases (CO₂; \( m/e = 44 \), NH₃; \( m/e = 16 \), pyridine; \( m/e = 52 \)) were normalized to that of introduced Ar (\( m/e = 40 \)) as an internal standard. Because the most intense signal for pyridine-mass spectrum was that of \( m/e = 52 \), we adopted the profiles of \( m/e = 52 \) for acid properties of the catalyst.

X-ray diffraction patterns of samples were obtained with a Rigaku Geigerflux diffractometer using Ni-filtered Cu Kα radiation (1.5418 Å).

Yb-LIII edge X-ray absorption experiments were carried out at BL10B, Photon Factory in High Energy Accelerator Research Organization (KEK-PF; Tsukuba, Japan) with a ring energy of 2.5 GeV and a stored current, 250 - 280 mA. The X-ray absorption spectra were recorded by the EXAFS facilities installed on the BL10B in transmission mode at room temperature with a Si(311) two-crystal monochromator. X-ray was detected with ion chambers filled with 100% N₂, which are flowing at atmospheric pressure. The lengths of the ion chamber for incident and transmitted X-ray detection were 17 and 31 cm, respectively.
Data reduction was performed using a FACOM M1800 computer of Kyoto University Data Processing Center. The normalization method has been previously reported in detail.\textsuperscript{17} To curve-fitting analysis, the following EXAFS formula was applied.

\begin{equation}
\chi(k) = \sum_j (k^2 N_j / R_j^2) A_j(k) \exp \left( -2 \sigma_j^2 k^2 \right) \sin \left( 2 k R_j + \delta_j(k) \right)
\end{equation}

where $k$ is the wavenumber of photoelectron, $N_j$ the number of scattering atoms of the $j$th shell located at a distance of $R_j$ from an Yb atom, $A_j$ the envelope function which includes backscattering amplitude and damping factor caused by inelastic loss during electron traveling, $\sigma_j$ the Debye-Waller factor and $\delta_j$ the phase shift. For an oxygen atom scatter, $A_j$ and $\delta_j$ were extracted from L\textsc{iii} edge EXAFS spectrum of C-type Yb$_2$O$_3$ crystal, and hence $\sigma_j$ corresponds to the relative Debye-Waller factor derivatived from that of the reference compound. In the extraction of these parameters, EXAFS spectrum of Yb$_2$O$_3$ prepared at 1273 K was used.

**Results and Discussion**

*Catalysis*

It is known that $\alpha$-pinene isomerization was one of the excellent test reactions for acid-base catalyst,\textsuperscript{18-20} and the products of $\alpha$-pinene isomerization can be classified to three groups as shown in Scheme 1. The first group is $\beta$-pinene. The second group consists of bicyclic products (camphene, $\alpha$-fenchene, etc.). The last group is composed of monocyclic products (limonene, terpinolene, $\gamma$-terpinene, etc.). Over solid base catalysts such as MgO and SrO, only equilibrium between $\alpha$-pinene and $\beta$-pinene should be observed.\textsuperscript{21} In contrast, acid catalysts promote the reactions producing all the three groups, and the selectivities depend on the maximum acid strength. Table 1 shows results of $\alpha$-pinene isomerization over silica-supported ytterbium oxide catalyst. Yb/SiO$_2$ catalysts exhibited high activity, however, SiO$_2$ and Yb$_2$O$_3$ were inactive for this reaction at 323 K. Catalytic activities were varied with Yb loading amounts. Catalytic activities per unit weight catalyst were enhanced as increasing Yb loading amounts and reached the highest when those were 3.4 through 5.8 mmol g(SiO$_2$)$^{-1}$. The selectivity was independent of loading amounts. The main products were limonene and camphene, selectivities of which were ca. 70% and 20%, respectively. A selective formation of $\beta$-pinene from $\alpha$-pinene occurs over solid bases, whereas $\beta$-pinene was scarcely produced over Yb/SiO$_2$ catalysts. The selectivities of Yb/SiO$_2$ catalysts for $\alpha$-pinene isomerization indicate that the generated active sites were acid sites. The independence of selectivities to loading amounts was revealed that the acid strength distributions of all Yb/SiO$_2$ catalysts resemble each other. A difference of the selectivity for 280 $\mu$mol Yb/SiO$_2$ catalyst against others was only due to its low conversion of 1.3%. 
Scheme 1. α-Pinene isomerization.
<table>
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<tr>
<th>Yb content / mmol g(SiO$_2$)$^{-1}$</th>
<th>Conversion [%]</th>
<th>Selectivity (%)$^c$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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</table>

$^a$ $\alpha$-Pinene, 2 mL (12.6 mmol); catalyst, 50 mg; pretreatment temperature, 1073 K; reaction time, 3 h.

$^b$ As Yb$_2$O$_3$.

$^c$ 1: $\beta$-Pinene, 2: camphene, 3: $\alpha$-fenchene, 4: limonene, 5: terpinolene, 6: $\alpha$-terpinene, 7: $\gamma$-terpinene, 8: others.

$^d$ Catalyst: 300 mg as Mg(OH)$_2$, pretreatment temperature: 873 K, reaction temperature: 353 K.
To clarify the effect of loading amounts on catalytic activity, we estimated specific activities per an Yb atom from results of Table 1. The calculation is according to an assumption that all Yb-related sites on catalyst participate in the catalysis. As shown in Figure 1, estimated turn over numbers (TONs) per Yb atom are almost equal, except for 280 μmol and 8.4 mmol Yb/SiO₂ catalysts. This shows that each Yb-related site, loading amounts of which were among 1.7 and 5.8 mmol g(SiO₂)⁻¹, exhibits similar catalytic activities. The results, to which specific activity and the selectivity were quite similar, indicate that the structure of active sites resembles each other.

The effect of pretreatment temperature in α-pinene isomerization is shown in Figure 2. We selected 3.4 mmol Yb/SiO₂ catalyst as a representative of silica-supported ytterbium oxide catalysts because the catalyst exhibited the highest catalytic activity. Catalytic activity strongly depends on pretreatment temperature. The highest activity was exhibited when a catalyst was pretreated at 1073 K. When the pretreatment was carried out at 1273 K, the catalytic activity drastically reduced. To clarify the effect of pretreatment temperature to catalysis, concentrations of products versus that of α-pinene during reaction are plotted in Figure 3. Although pretreatment and reaction temperatures were variant for each plot, plots of all products concentrations, except for α-fenchene and cymene, versus that of α-pinene were on lines. The slope of the lines for each product represents the selectivity for α-pinene isomerization. Those of limonene and camphene were 0.62 and 0.19, respectively, and these were almost the same as the results found in Table 1. This shows that the products selectivities of α-pinene isomerization independent of pretreatment temperatures, and these compounds are the primary products. The concentration of cymene rapidly increased when α-pinene was almost consumed. This shows that cymene was the second products formed by dehydrogenation of monocyclic products such as limonene,18 terpinolene and α-, γ-terpinene.22

The independence of selectivities to pretreatment temperatures also revealed that the acid strength distributions resemble each other, the same as effects of loading amounts. The same results were observed in the case of 1.7 mmol Yb/SiO₂ catalyst.

Temperature Programmed Desorption

To examine acid-base property of catalysts, CO₂ and NH₃-TPD were carried out and the profiles are shown in Figure 4. Much amount of CO₂ was desorbed from Yb₂O₃, whereas 3.4 mmol Yb/SiO₂ and SiO₂ did not desorb CO₂ at all. Basicity of ytterbium oxide completely disappeared in Yb/SiO₂ catalyst. In NH₃-TPD profiles, 3.4 mmol Yb/SiO₂ exhibited much larger peak around 473 K than those on Yb₂O₃ and SiO₂. It shows that new acid sites generate over Yb/SiO₂ catalyst. On the other hand, another desorption peak above 573 K was observed on both Yb₂O₃ and SiO₂. It has been reported that rare earth oxide possesses not only basic sites but also acid sites.23,24 The NH₃-TPD profile of Yb₂O₃ had a desorption peak at 473 K and a shoulder peak at 723 K, and the tendency resembles that of previously reported.25 The
Figure 1. Turn over numbers (TONs) of catalysts in α-pinene isomerization. The TON per one Yb atom was calculated from results of TABLE 1.

Figure 2. Dependence of pretreatment temperature in α-pinene isomerization. Catalyst: 3.4 mmol Yb/SiO₂, α-pinene: 2 mL, reaction time: 3 h.
Figure 3. Concentration of products vs substrate in α-pinene isomerization. Plotted data are results of Figure 2. Catalyst: 3.4 mmol Yb/SiO₂. Pretreatment temperature: 473-1273 K. Reaction time: 323, 353 K.
Figure 4. Temperature-programmed desorption profiles of CO₂ (a), NH₃ (b), and pyridine (c). Pretreatment procedure was performed at 1073 K.
NH₃-TPD profiles revealed that Yb₂O₃ possesses both acid and base sites; however Yb₂O₃ pretreated at 1073 K was inactive for α-pinene isomerization at 323 K.

From IR study, Morrow et al. reported that silica evacuated above 673 K has active siloxane bridge that reacts with NH₃ to produce SiNH₂ and SiOH at room temperature, whereas it did not react with pyridine. In the present study, each the catalyst was pretreated at 1073 K, the temperature of which is enough to form such the active siloxane bridge. Therefore, the desorption peak around 623 K observed on silica was due to decomposition of surface SiNH₂ species. To clarify acidic property in more detail, pyridine TPD was also performed. Results were shown in Figure 4c. The 3.4 mmol Yb/SiO₂ catalyst exhibited the largest peak around 573 K in all the catalysts. The desorption peak of pyridine was observed on Yb₂O₃ and SiO₂, as the same as those of NH₃-TPD measurements. However the quantity of desorbed pyridine from Yb/SiO₂ catalysts extremely exceeded those of SiO₂ and Yb₂O₃. Results of pyridine TPD measurements corresponded to catalytic results. In our case, pyridine TPD measurement is more suitable method for an explanation of the acidic property of the catalysts pretreated at 1073 K than that of NH₃. In addition, the profile of SiO₂ exhibited only a single peak in contrast to that of NH₃. It is in agreement with IR study described above.

X-ray Diffraction

Figure 5 shows Cu Kα XRD patterns of catalysts pretreated at 1073 K. Yb₂O₃ exhibited strong d222 and d400 reflections at 29.7 and 34.4°. SiO₂ gel exhibited only halo around 22°. With increasing loading amounts of Yb, a new halo grew around 30°. This halo was due to amorphous phase of Yb₂O₃ or ytterbium silicate. Any distinct peak was not observed over all the catalysts, although loading amounts of ytterbium as Yb₂O₃ went up to 5 - 60 wt%. This clearly shows that long-range ordering structures not formed. A trace peak was observed on 8.4 mmol Yb/SiO₂ at 29.8°, which might be due to the d222 reflection of Yb₂O₃. However, large parts of Yb atoms of 8.4 mmol Yb/SiO₂ were present on SiO₂ in an amorphous phase because this peak was very faint overlapping with large halo.

In the phase diagram of Yb₂O₃-SiO₂ system, it is reported that Yb₂O₃ and SiO₂ does not form solid solutions but form crystals of Yb₂O₃-SiO₂ and/or Yb₂O₃·2SiO₂. On the other hand, no crystalline phases were detected in all the catalysts. Therefore, it is concluded that ytterbium oxide on silica available for α-pinene isomerization is not in a crystal state but in an amorphous one.

X-ray Absorption Fine Structure

Figure 6 shows k⁴-weighted EXAFS spectra and their Fourier transforms of Yb₂O₃. In the Fourier transform (FT) of EXAFS, peaks due to six O atoms and twelve Yb atoms were
Figure 5. Cu-Kα XRD patterns of catalysts.
Figure 6. XAFS spectra of Yb$_2$O$_3$ prepared by calcination of ytterbium nitrate at 773 K (dotted curve), and 1273 K (solid curve).
observed at 1.9 and 3.3 Å, respectively. These calculated distances from crystallographic data (a₀ = 10.436 Å), are 2.259 Å for Yb-O, and 3.690 Å for Yb-(O)-Yb. The dotted curves in Figure 6 are the spectra of the sample that was prepared by thermal decomposition of ytterbium nitrate at 773 K. The k³-weighted EXAFS spectrum was quite similar to that of Yb₂O₃ prepared at 1273 K, although the amplitude was lower. It shows that the temperature of 773 K is enough to decompose ytterbium nitrate salt to form Yb₂O₃ crystal, although the crystallinity was relatively low. Therefore, all Yb atoms of catalysts were present on SiO₂ as oxide.

Figure 7 shows Yb-L₃ edge k³-weighted EXAFS spectra of Yb/SiO₂ catalysts calcined at 773 K. The amplitudes and phases of all spectra were quite similar to each other. The amplitude decayed with k increasing, and no oscillations were observed beyond 12 Å⁻¹. The similarity of each EXAFS spectrum indicates that the local structures around Yb were almost the same. The oscillation frequencies of one EXAFS spectrum were not constant, and it shows that the EXAFS spectrum consists of some sine waves, as noted in EXAFS formula (1). It is clear that neighboring atoms of Yb were not a single kind. Teo et al. calculated that backscattering amplitude functions of lanthanides which have two peaks in low and high k region, and that of Yb has a large peak above 10 Å⁻¹.⁲⁹ On the other hand, those of light elements such as O and Si are monotonously decreasing with k, and become very small above 10 Å⁻¹. Because the amplitude of EXAFS spectra of catalysts monotonously decayed with k, it is concluded that any Yb atoms did not present around an Yb atom, in contrast to Yb₂O₃.

The k³-weighted Fourier transformation was carried out against EXAFS of catalysts in the k range of 3.0 - 15.0 Å⁻¹, to obtain the radial structure function (RSF). The results are shown in Figure 8. In analogy with EXAFS spectra, all RSF were quite similar, and two peaks were observed around 1.8 and 2.9 Å. The peak around 1.8 Å was due to O atoms, the distance of which was similar to that of Yb₂O₃. The distance of second peak (indicated by an arrow) was much shorter than the peaks due to Yb atoms in Yb₂O₃ crystal. From the envelope functions of corresponding EXAFS spectra, it is obvious that the second peaks are not due to Yb atoms but due to light elements. As shown in Figure 6, ytterbium nitrate was decomposed to Yb₂O₃ crystal even at 773 K. Then, we assigned the second peaks due to Si atoms of supports. The distance was similar to previously reported ones between Si and transition metal atoms, such as Ti,³⁰ Ni,³¹ and Nb.³²⁻³⁵

The curve-fitting results of catalysts and the crystallographic datum of Yb₂O₃ are summarized in Table 2. The first coordination spheres of all the catalysts could be fitted by one shell, and the estimated parameters were almost identical to each other. All the estimated parameters are consistent with those of Yb₂O₃ within an experimental error. The inter-atomic distances between Yb and O atoms strongly supported that Yb atoms of all the catalysts are in an octahedral coordination. From the results that no Yb-(O)-Yb contribution was observed and that of Yb-(O)-Si were observed, it is concluded that Yb atoms were supported on SiO₂ in a highly dispersed form as a YbO₆ octahedron, and a YbO₆ octahedron connected with SiO₄ tetrahedron through bridging oxygen. It is well known that coordination environments of
Figure 7. $k^3$-Weighted Yb-LIII edge EXAFS spectra of silica-supported ytterbium oxide.
Figure 8. Fourier Transforms of $k^3$-weighted Yb-L$_{III}$ edge EXAFS spectra of silica-supported ytterbium oxide.
<table>
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<th>Sample</th>
<th>CN $^b$</th>
<th>R / Å $^c$</th>
<th>$\Delta \sigma^2 / \AA^2$ $^d$</th>
<th>Refinement (%) $^e$</th>
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$^a$ Inverse-Fourier range, $\Delta R = 1.2 - 2.2$ Å; fitting range, $\Delta k = 4.0 - 12.0$ Å$^{-1}$.

$^b$ Coordination number.

$^c$ Distance between Yb and O atoms.

$^d$ Relative Debye-Waller factor against that of reference sample (Yb$_2$O$_3$).

$^e$ $\sqrt{\frac{\Sigma (k^3 \chi_{obvious} - k^3 \chi_{calculated})^2}{\Sigma (k^3 \chi_{obvious})^2}} \times 100$. 
supported metal oxide often change by loading amounts and/or various treatments, and the changes of coordination cause the change of catalysis. On the other hand, the coordination environments around Yb were independent of its loading amounts. This is the reason of the result of α-pinene isomerization that no changes of its selectivity was observed.

Structure of Active Sites

Table 3 summarized the estimated BET specific surface areas. The areas of catalysts include the SiO2 carrier. The  is a surface area g(SiO2)⁻¹ carrier, which was calculated from BET specific surface area and Yb content. The  is estimated occupied area by YbO6 unit according to three assumptions described below. The first assumption is that all Yb atoms exist as a YbO6 octahedron. The second is that all YbO6 units have the same cross section. The third assumption is that the cross section is 16.0 Å² per YbO6 unit, which is calculated by the following equation; 2.26 x 2.26 x π.

The surface area pretreated at 1073 K kept 85% of that pretreated at 673 K (fresh catalyst), whereas that pretreated at 1273 K was reduced to 50% of the original by sintering. This abrupt decrease of surface area between 1073 and 1273 K is one of the reasons for deactivation of catalyst, as shown in Figure 2. Because the extent of deactivation significantly exceeded that of sintering, another factor for deactivation should be considered although it is not clear now.

As shown in Figure 1, the high catalytic activities per Yb atom were demonstrated when loading amounts of Yb were among 1.7 and 5.8 mmol g(SiO2)⁻¹. In cases of these loading amounts, the areas occupied by YbO6 units ( ) were calculated to 162 - 559 m² g(SiO2)⁻¹. These values were comparable to the surface areas of g(SiO2)⁻¹ carriers and the area of SiO2 pretreated at 1073 K. It shows that two dimensional thin-layers of ytterbium oxide formed on SiO2 surface, and local interaction between a YbO6 octahedron and a SiO4 tetrahedron generate solid acidity. In the case of 8.4 mmol Yb/SiO2, the calculated  is 812 m² g(SiO2)⁻¹, which exceeds the area of carrier. The excess Yb atoms deposited on the thin-layer and blocked active sites, as the same as zirconium oxide deposited on TiO2. As a result, the estimated specific activity per Yb atom of 8.4 mmol Yb/SiO2 was quite low. Because the highest activity was exhibited when pretreatment procedure was performed at 1073 K, we propose that the active sites are Lewis acid sites. It was reported that silica monolayer deposited on metal oxide exhibits weak Brønsted acidity, and niobium oxide one-atom-layers on SiO2 catalyzes dehydration of ethanol. In the case of Yb/SiO2 catalysts, it is concluded that the analogous two-dimensional ytterbium oxide overlayers were formed in 5.8 mmol Yb/SiO2. The reason for no Yb-(O)-Yb configuration was observed in XAFS spectra is as follows; the distributions of distances among Yb atoms were wide and the Debye-Waller factor of Yb-Yb bonding due to static structural disorder was extremely large. In the case of 1.7 mmol Yb/SiO2,
### TABLE 3: Physical Properties of Samples

<table>
<thead>
<tr>
<th>Yb content / mmol g(SiO₂)⁻¹</th>
<th>Pretreatment Temp / K</th>
<th>Area b / m² g⁻¹</th>
<th>S₀ c / m²</th>
<th>S occupied d / m² g(SiO₂)⁻¹</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>673</td>
<td>661</td>
<td>661</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>601</td>
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<td>323</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>212</td>
<td>352</td>
<td>323</td>
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<tr>
<td></td>
<td>873</td>
<td>199</td>
<td>331</td>
<td>323</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>1273</td>
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<td>323</td>
</tr>
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<tr>
<td>Yb₂O₃ e</td>
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<td>45</td>
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</tr>
<tr>
<td></td>
<td>1073</td>
<td>16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a As Yb₂O₃.

b BET specific surface area.

c Surface area of g(SiO₂)⁻¹ carrier.

d Occupied area by assumed YbO₆ unit.

e Prepared by thermal decomposition of ytterbium nitrate at 773 K for 5 h.
the loading amount of Yb was much less than a formation of YbO₆ monolayer, but the specific activity per Yb atom was comparable to that of 5.8 mmol Yb/SiO₂. It shows that the formation of ytterbium oxide monolayer was not necessary for the generation of acid sites. It was concluded that the generation of solid acidity over Yb/SiO₂ catalyst was due to the strong interaction between a YbO₆ octahedron and a SiO₄ tetrahedron.

Conclusion

Silica supported ytterbium oxide catalyst exhibit solid acidity and catalyzes α-pinene isomerization at 323 K. The selectivity was independent of loading amounts and pretreatment temperature. The highest activity is exhibited when the pretreatment procedure was performed at 1073 K. Catalytic activity per Yb atom is constant when loading amounts are below 5.8 mmol g(SiO₂)⁻¹. Ytterbium atoms widely spread on SiO₂ surface as a YbO₆ octahedron, and the YbO₆ octahedron strongly interacts with SiO₄ tetrahedra. Local interaction between silica and ytterbium oxide generates solid acidity.

References

28 Levin, E. M.; Robbins, C. R.; McMurdie, H. F. Phase Diagrams for Ceramists; ed. The American Ceramic Society, Columbus: Ohio, 1969, p. 108, Figure 2391.


Chapter 4

Structural Analysis of Silica-Supported Ytterbium Oxide Catalyst by XAFS

Abstract

The structure of silica-supported ytterbium oxide catalyst (1.7, 3.4, 8.4 mmol Yb g(SiO₂)⁻¹) was characterized by X-ray diffraction and Yb LIII-edge XAFS. XANES and EXAFS spectra of all the catalysts were quite similar to each other but different from those of the Yb₂O₃ crystal. The local structure around Yb was not affected by the loading amounts of Yb and thermal treatment up to 8.4 mmol g(SiO₂)⁻¹ and 1273 K, respectively. In the second derivatives of the XANES spectra, Yb₂O₃ exhibited a doublet, while all the Yb/SiO₂ samples gave a singlet. The presence of Yb-O-Si linkage and the absence of Yb-O-Yb contributions were confirmed in all the Yb/SiO₂ catalysts. Yb atoms were supported on SiO₂ in a highly dispersed form as a YbO₆ octahedron, which strongly interacted with SiO₄ tetrahedra.
Introduction

The silica-supported ytterbium oxide catalyst (Yb/SiO₂) exhibits an acid property, although SiO₂ and Yb₂O₃ themselves are inactive for this reaction at 323 K.¹ The Yb/SiO₂ catalyst, loading amounts of which are in the rage of 280 μmol - 8.4 mmol g(SiO₂)⁻¹, catalyzes α-pinene isomerization to produce limonene selectively. The catalytic activity, which depends on loading amounts of ytterbium and pretreatment temperatures, reached its highest level at 3.4 mmol g(SiO₂)⁻¹ and 1073 K, respectively. It is known that the selectivity for α-pinene isomerization changes with acidity.² Loading amounts of Yb and pretreatment temperatures did not affect the selectivity, indicating that all the Yb/SiO₂ catalysts possess similar maximum acid strengths. Furthermore, specific activities per Yb atom were almost equal between 1.7 and 5.8 mmol g(SiO₂)⁻¹. This clearly shows that the structure of active sites have similar structure. In the present study, the local structures of Yb/SiO₂ catalyst samples around Yb are investigated by Yb L₃,Ⅲ-edge XAFS.

Experimental

Silica supported ytterbium oxide catalyst (Yb/SiO₂) was prepared by impregnation of SiO₂ gel (637 m² g⁻¹) with an aqueous solution of ytterbium nitrate at 353 K. The sample was dried at 363 K for 12 h, followed by calcination at 773 K for 5 h. These samples are referred to as x mmol Yb/SiO₂ (x stands for loading amounts of Yb atom per one gram of SiO₂). Pretreated samples were prepared as follows: each sample was evacuated at a prescribed temperature for 0.5 h and calcined under 6.66 kPa of O₂ for 1 h, followed by evacuation at the same temperature for 1 h. A post-reacted sample (3.4 mmol Yb/SiO₂ pretreated at 1073 K) was prepared.³

Yb₂O₃ of C-rare earth structure⁴ was prepared by thermal decomposition of ytterbium nitrate at 1273 K for 5 h. YbPO₄ of xenotime structure⁵ was prepared by calcination of precipitate at 1273 K for 5 h. The precipitate was obtained by addition of phosphoric acid solution (1.6 M) into an aqueous solution of ytterbium nitrate (0.1 M). Yb₃Al₅O₁₂ of garnet structure, which is the same structure as Y₃Al₅O₁₂,⁶ was synthesized by the citric acid process. A mixture of ytterbium nitrate (3 mmol), aluminum nitrate (5 mmol) and citric acid (40 mmol) was dissolved at 348 K in 2 mL of water. The solution was stirred vigorously until it was solidified, followed by aging at 383 K for 48 h. The formed amber foam was precalcined at 623 K for 2 h, followed by calcination at 1273 K for 5 h. After calcination, it was quenched to a room temperature. Each ytterbium atom of YbPO₄ and Yb₃Al₅O₁₂ is surrounded by two kinds of oxygen shells and the total coordination number is eight. The crystalline phases were identified by XRD pattern measurements with JCPDS files (Yb₂O₃: 18-1463, YbPO₄: 26-998,
Yb₃Al₅O₁₂: 23-1476). The reference compound used was YbNbO₄ (Soekawa, Co. LTD: monoclinic distortion of the scheelite structure).

Yb-L₃ edge X-ray absorption experiments were carried out on the BL01B1 at SPring-8 (Hyogo, Japan) with a ring energy of 8 GeV and a stored current from 16 to 20 mA (proposal No. 1997B01100, 1998A0258). The X-ray absorption spectra were recorded in transmission mode at room temperature with a Si(111) two-crystal monochromator. The dispersive X-ray was collimated to be a parallel ray by a total reflection mirror, which locates at an upper stream 32.9 m from an X-ray source. The height of the X-ray size was 1.0 mm. X-ray absorption spectra were recorded every 0.3 eV in XANES region. Data reduction was performed using a FACOM M1800 computer at the Kyoto University Data Processing Center. The normalization method has been previously reported in detail. For curve-fitting analysis, backscattering amplitude and phase shift functions for Yb-O pairs were obtained from k³-weighted EXAFS spectrum of the Yb₂O₃ crystal.

Results and Discussion

X-ray Diffraction

The Cu-Kα XRD pattern of Yb₂O₃ exhibited strong d₂₂₂ and d₄₀₀ reflections at 2θ = 29.7 and 34.4°. The pattern of SiO₂ gel exhibited only a single halo around 22°. No distinct peaks were observed for any of the catalysts pretreated at 1073 K. With increasing loading amounts of Yb, a new halo grew on those of Yb/SiO₂ catalysts around 30°. The origin of this amorphous phase could not be identified as both crystalline ytterbium silicates and Yb₂O₃, which exhibit typical reflections in this region.

XANES

Figure 1 shows the XANES spectra and second derivatives of Yb/SiO₂ catalysts and Yb₂O₃. Absorption edges of all the spectra were identical, indicating all the Yb/SiO₂ catalysts consist of Yb³⁺ species. Each XANES spectrum of the Yb/SiO₂ catalyst exhibited almost the same shape. This shows that the local structure around Yb is quite similar to each other for all the catalysts. A small peak around 8962 eV, which was tentatively ascribed to shake-up transition, were observed on the spectrum of Yb₂O₃, but not on spectra of Yb/SiO₂. Normalized heights of the white line are 2.3 for that of Yb₂O₃, and about 3.0 for those of Yb/SiO₂. Yb-L₃ edge XANES spectra could be deconvoluted with two curves: one is Lorentzian for 2p-5d transition; the other is an arctangent for the continuum absorption. Peak areas and FWHM for the Lorentzian curve of Yb₂O₃ are 56 a.u. and 6.5 eV, and those for 3.4 mmol Yb/SiO₂ pretreated at 1073 K are 71 a.u. and 5.3 eV, respectively.
Figure 1. Yb-L_{III} edge XANES spectra and their second derivatives: (a) 1.7 mmol Yb/SiO_{2}; (b) 3.4 mmol Yb/SiO_{2}; (c) pretreated at 1073 K; (d) after reaction pretreated at 1073 K; (e) pretreated at 1273 K; (f) 8.4 mmol Yb/SiO_{2} pretreated at 1073 K, and (g) Yb_{2}O_{3}. 
The white line of Yb$_2$O$_3$ was a little broader and lower than those of Yb/SiO$_2$. To investigate white lines in more detail, we differentiated the XANES spectra. As shown in Figure 1, the second derivative of Yb$_2$O$_3$ split to a doublet, while all Yb/SiO$_2$ derivatives were singlets. Each doublet peak intensity of Yb$_2$O$_3$ was equivalent. One possible reason for this split is coexistence of Yb$^{2+}$ and Yb$^{3+}$ species; however, this could be excluded. In the Yb-L$_{III}$ edge XANES spectra of Yb$^{2+}$ and Yb$^{3+}$ compounds, the peak positions of each white line differ by 7 eV.$^{10-12}$ In the present study, the energy difference for splitted peaks was only 3.3 eV. This splitting energy is close to the ordinary $d$-orbital splitting energy caused by the crystal field. The 5$d$ orbital of Yb$^{3+}$ is vacant. If the 5$d$ orbital splits to two by a crystal field, the five $d$-orbitals would redistribute two kinds of energy levels, vacant sites of which are two to three. As the split peaks were equivalent in intensity, this split is not caused by the crystal field. The other possible reason is the crystal structure of Yb$_2$O$_3$. There are two kinds of distorted YbO$_6$ octahedra in Yb$_2$O$_3$ of C-rare earth structure. However, Lytle et al. observed a similar doublet structure on second derivatives of Ho$_2$O$_3$ and Eu$_2$O$_3$, but not on Nd$_2$O$_3$ and Lu$_2$O$_3$.\textsuperscript{13} This splitting phenomenon does not arise from C-rare earth structure.

All Yb/SiO$_2$ catalyst samples are amorphous. To examine whether a split of white line results from the crystallinity or not, XANES spectra of other ytterbium oxide crystals were recorded. Figure 2 shows XANES spectra and their second derivatives of Yb$_2$O$_3$ ($Th^7; Ia3$), YbNbO$_4$ ($C2^3; C2$), YbPO$_4$ ($D4h^{19}; Ia/amd$) and Yb$_3$Al$_5$O$_{12}$ ($Oh^{10}; Ia3d$). In the second derivative, the spectrum of YbNbO$_4$ was a triplet, and those of YbPO$_4$ and Yb$_3$Al$_5$O$_{12}$ were singlets. It may be questionable whether the second derivative of YbNbO$_4$ XANES exhibits a triplet, but obviously the second derivative is not a singlet. It shows that a split of white line is not related merely to the crystallinity. Although we do not know the origin of this splitting at the present stage, it can be concluded that local structures around Yb in Yb/SiO$_2$ catalysts are quite different from that of Yb$_2$O$_3$.

The characteristic peak in Yb-L$_{III}$ XANES is a small peak at 8962 eV. The crystal system of YbPO$_4$ is tetragonal, the symmetry of which is the highest in reference compounds. Garnet crystallize of $Ia3d$ is one of the most symmetric space groups of the cubic system.\textsuperscript{14} YbPO$_4$ has not only the highest white line, but also the smallest peak intensity of 8962 eV. In the XANES spectra of all the Yb/SiO$_2$ catalysts, there are no peak around 8962 eV, and there are higher white lines than in spectra of YbPO$_4$ and Yb$_3$Al$_5$O$_{12}$. Therefore, it is possible that a YbO$_n$ unit on SiO$_2$ is highly symmetric.

EXAFS

Figure 3 shows Yb-L$_{III}$ edge $k^3$-weighted EXAFS spectra and their Fourier transforms. The amplitudes and phases of all the spectra of Yb/SiO$_2$ were quite similar, whereas each EXAFS oscillation does not consist of a single frequency. The similarity of each EXAFS spectrum indicates that each of the local structures around Yb was almost the same and
Figure 2. Yb-L_{III} edge XANES spectra and their second derivatives.
Figure 3. $k^3$-weighted Yb-L$_{III}$ edge EXAFS spectra and their Fourier transform: (a) 1.7 mmol Yb/SiO$_2$; (b) 3.4 mmol Yb/SiO$_2$; (c) pretreated at 1073 K; (d) after reaction pretreated at 1073 K; (e) pretreated at 1273 K; (f) 8.4 mmol Yb/SiO$_2$ pretreated at 1073 K, and (g) Yb$_2$O$_3$. 

- 97 -
that none of the treatments affected the structure. In contrast to that of Yb₂O₃, the amplitude of EXAFS functions decayed with increasing wavenumber and no oscillations were observed over 12 Å⁻¹ in the Yb/SiO₂ catalysts. The lack of oscillations above 12 Å⁻¹ indicates that the contributions of Yb-O-Yb pairs are not present in the Yb/SiO₂ catalyst. As in the EXAFS spectra, all radial structure functions (RSFs) were quite similar, and two peaks were observed around 1.8 and 2.9 Å in each spectrum. The distance of the second peak (indicated by an arrow) was much shorter than that of the peak due to Yb atoms of Yb₂O₃.

To clarify the structure of the Yb/SiO₂ catalyst around Yb, an inverse Fourier transformation of RSFs was performed against Yb₂O₃ and 3.4 mmol Yb/SiO₂ catalyst pretreated at 1073 K. Figure 4 shows the inverse Fourier transformed k³-weighted EXAFS spectra and their envelope functions. The envelope function for the second shell of Yb₂O₃, which is due to Yb-Yb pairs, had two peaks around 7 and 13 Å⁻¹. In contrast, those for both the first and second shells of Yb/SiO₂ catalyst monotonically decreased with k. Then, we assigned the peak appeared in the RSFs at 2.9 Å due to not Yb, but Si atoms of support. This was supported by the results that the position of the second peak in the RSF of Yb/SiO₂ was quite different from that of Yb₂O₃, and that the envelope function has a similar tendency to the backscattering amplitude function for Si of theoretical calculations. In each the RSF of Yb/SiO₂ sample, the magnitude of peaks due to Si was the same level in all the catalysts, regardless of loading amounts and pretreatment procedures. It shows that a strong interaction between Yb and Si atoms had formed in the sample preparation step.

The curve-fitting results are summarized in Table 1. Because all the samples are amorphous and the loading amounts of Yb are very large 25 - 62 wt% as in Yb₂O₃, it is presumed that the local structure of each Yb/SiO₂ catalyst sample around Yb should not be uniform. Then, we did not carry out a curve fitting analysis for the second peak, which appeared in the RSF around 2.9 Å.

The first coordination spheres of all the catalysts could be satisfactorily fitted by a single shell. All the estimated parameters were within errors, and were similar to those of Yb₂O₃. The inter-atomic distances between Yb and O atoms strongly supported the hypothesis that Yb atoms of all the catalysts are in a six-fold coordination. The results, that no Yb-O-Yb contribution was observed and that contribution of Yb-O-Si were observed, indicate the presence of an isolated YbO₆ octahedron connected to SiO₄ tetrahedra with sharing oxygen atoms. However, all of an YbO₆ units are not always truly isolated. The distributions of distances among Yb atoms were broad, and the Debye-Waller factor due to static structural disorder was extremely large. Therefore, Yb-Yb contributions were not observed in all the spectra of Yb/SiO₂ catalysts. The interaction between a YbO₆ octahedron and SiO₄ tetrahedra is concluded to be much stronger than that of among the YbO₆ units.
Figure 4. Inverse Fourier transformed EXAFS (solid curves) and their envelope functions (dotted curves); 3.4 mmol Yb/SiO₂ pretreated at 1073 K (a, b), and Yb₂O₃ (c).
TABLE 1: Structural Parameters for Yb-O Shells of Samples $^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>R / Å</th>
<th>$\Delta\sigma^2 / \AA^2$</th>
<th>Refinement (%) $^b$</th>
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<tr>
<td>Yb$_2$O$_3$</td>
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<td>8.4 mmol Yb/SiO$_2$</td>
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<tr>
<td>pretreated at 1073K</td>
<td>6.0</td>
<td>2.27</td>
<td>0.0044</td>
<td>12.2</td>
</tr>
</tbody>
</table>

$^a$ Inverse-Fourier range, $\Delta R = 1.2 - 2.2$ Å; fitting range, $\Delta k = 4.0 - 12.0$ Å$^{-1}$.

$^b$ $\sqrt{\sigma (k^3\chi_{\text{obvious}} - k^3\chi_{\text{calculated}})^2 / \sigma (k^3\chi_{\text{obvious}})^2} \times 100$.

$^c$ Average interatomic distance, calculated from the crystallog datum ($a_0 = 10.436$ Å).

$^d$ Inverse-Fourier range, $\Delta R = 1.4 - 2.4$ Å; fitting range, $\Delta k = 4.0 - 12.0$ Å$^{-1}$.

Conclusion

All the silica-supported ytterbium oxide catalysts (1.7, 3.4, 8.4 mmol Yb g(SiO$_2$)$^{-1}$) retained their amorphous state after thermal treatment at 1073 K. Neither the loading amounts of Yb nor thermal treatment affected on the local structure around Yb. The coordination sphere around Yb was quite similar to each Yb/SiO$_2$ catalyst. Yb atoms were supported on SiO$_2$ in a highly dispersed form as a Yb$_6$ octahedron. The Yb$_6$ octahedron strongly interacted with SiO$_4$ tetrahedra, rather than with other Yb$_6$ octahedra. A definitive difference between Yb$_2$O$_3$ crystal and ytterbium oxide supported on SiO$_2$ was observed in Yb-L$_{III}$ edge XANES spectra.

References

α-Pinene isomerization was carried out under dry N₂ atmosphere at 323 K for 3 h using a stirred batch reactor, which was loaded with 5 mL of α-pinene (32 mmol) and 300 mg of pretreated catalyst. The 99.8% of α-pinene had converted to limonene and camphene, selectivities of which were 66% and 18%, respectively.
Chapter 5

Generation of Acid Sites on Silica-Supported Rare Earth Oxide Catalysts: Structural Characterization and Catalysis for α-Pinene Isomerization

Abstract

Silica-supported rare earth oxide catalysts (Ln/SiO₂; Ln = La, Ce, Pr, Sm, Eu, Tb, Yb and Y), loading amounts of which were 3.4 mmol g(support)-¹, were characterized by α-pinene isomerization, and temperature-programmed desorption (TPD), Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray absorption fine structure (XAFS), thermogravimetric-differential thermal analysis (TG-DTA) and Raman spectroscopy. In the lanthanoid series, the catalytic activity increased with atomic number from 57La to 70Yb, except for Ce. All the Ln/SiO₂ catalysts, except for Ce, were amorphous. On the surface of the catalyst, Ln-O-Si and Ln-O-Ln linkages formed, the ratio of which varied with the loaded element. The ratio of Ln-O-Si linkage increases with stronger affinity among LnOₙ unit and SiO₄ tetrahedra, and the affinity depends on the size of Ln³⁺. With increasing ratio of Ln-O-Si to Ln-O-Ln linkage, the catalytic activity increases. Silica-supported yttrium oxide catalyst, trivalent ion radius of which is quite similar to that of ytterbium, exhibited the same activity as that of Yb/SiO₂. Raman spectroscopic characterization revealed that excess loading of Yb atoms on SiO₂-support block Yb-O-Si linkage to form Yb₂O₃ fine particle. When Yb/SiO₂ was pretreated at 1273 K, fine ytterbium silicate crystallites formed. Ln-O-Si linkage without a long-ranged ordering structure was the active site for α-pinene isomerization.
Introduction

The addition of rare-earth elements to catalysts has been performed mainly to enhance thermal stability of the catalysts themselves. In contrast, there are few studies concerning catalyses of supported rare earth oxides. Capitán et al. investigated the Sm2O3/Al2O3 catalyst for correlations between catalysis for oxidative coupling of methane and the surface Sm-Al-O phases. They concluded that the oxide-like structure shows better selectivity toward C2 species than the SmAlO3 phase. Shi et al. reported that dispersed La2O3 on alumina exhibits higher activity for reduction of NO with CH4 in the presence of oxygen than unsupported La2O3, while the catalytic activity of La/SiO2 was significantly lower than that of La2O3.

According to the hypothesis for acidity prediction proposed by Tanabe et al., binary oxides among silica and rare-earth oxides, such as La2O3-SiO2 and Y2O3-SiO2 are expected to exhibit solid acidity. Shen et al. investigated acid-base properties of silica- and alumina-supported europium oxide with spectroscopic methods. They found that alumina-supported europium oxide possesses basic sites stronger than that of Eu2O3, and silica-supported europium oxide exhibits Lewis acid properties. To our knowledge, this report is the only study so far to investigate acid-base properties of supported rare earth oxides. Recently, the catalysis of monoethanolamine synthesis over SiO2-Y2O3 was reported, while the precise acidity remained unknown.

In a previous study, we reported that silica-supported ytterbium oxides exhibit solid acidity and catalyze α-pinene isomerization at 323 K. The activity depends on the loading amounts of ytterbium and pretreatment temperatures. The maximum activity was exhibited when loading amount was 3.4 mmol Yb g(SiO2)−1, and was pretreated at 1073 K. From X-ray absorption fine structure (XAFS) characterization, we have concluded that Yb atoms are supported on silica in a highly dispersed form as a YbO6 octahedron. A YbO6 octahedron strongly interacts with SiO4 tetrahedra, rather than other YbO6 octahedra. The Yb-O-Si linkage was concluded to be the active sites for α-pinene isomerization.

Following on from this, we prepared several kinds of silica-supported rare earth oxide catalysts to elucidate the specific character of each rare earth element. Here, we will report on the catalytic properties of supported rare earth oxides and their structural characterization. As a model reaction of acid-base properties of each catalyst, α-pinene isomerization was adopted, as in our previous work. It is known that the difference in acidity of each catalyst influences the catalysis for α-pinene isomerization concerning its selectivity. Effective acid strength for α-pinene isomerization was proposed as H0 ≤ +3.3.

Experimental

Material
SiO₂ gel (661 m² g⁻¹) was synthesized from tetraethyl orthosilicate (Nacalai, EP-grade, singly distilled) by hydrolysis in a water-ethanol mixture at the boiling point, followed by calcination at 773 K for 5 h in dry air stream.¹⁷ Before calcination, a dried sample was grounded to a powder under 100 mesh. The silica-supported rare earth oxide catalyst was prepared by impregnation of SiO₂ gel with an aqueous solution of Ln(NO₃)₃·xH₂O at 353 K. The elements used were La (Nacalai, 99.9%), Ce, Eu (Rare Metallic, 99.9%), Pr, Gd, Tb (Rare Metallic, 99.99%), Sm (Wako, 99.5%), Yb (Mitsuwa, 99.9%), and Y (Wako, 99.9%). The impregnated sample was dried at 363 K for 12 h, followed by calcination at 773 K for 5 h. Other supports used were γ-Al₂O₃ (JRC-ALO-4), Mg(OH)₂ (Rare Metallic, 99%), and Zr(OH)₄ (obtained by hydrolysis of ZrOCl₂ ¹⁸, ¹⁹). The loading amount of Ln atom per one gram of support was 3.4 mmol in each catalyst.

**Catalysis**

α-Pinene isomerization was carried out under a dry N₂ atmosphere using a stirred batch reactor at 323 K. Prior to each reaction, the catalyst was evacuated at 1073 K for 0.5 h and calcined under 6.66 kPa of O₂ for 1 h, followed by evacuation at the same temperature for 1 h. For each experiment, the reactor was loaded with 2 mL (12.6 mmol) of α-pinene (Nacalai, EP, 99.8%) and 50 mg of catalyst. Products were analyzed by FID gas chromatography (GC-14A; Shimadzu) with a CBP20-M25-025 capillary column (Shimadzu).

**Characterization**

The BET specific surface area measurement was carried out with BELSORP 28SA (BEL Japan, Inc.) using a N₂ adsorption isotherm at 77 K. Prior to the measurement, each sample was outgassed at 1073 K for 3 h. The analyzed results are summarized in Table 1.

X-ray diffraction (XRD) patterns were obtained with a Rigaku Geigerflux diffractometer using Ni filtered Cu-Kα radiation (averaged as 1.5418 Å).

FTIR spectra of adsorbed pyridine were recorded using a Perkin-Elmer Paragon 1000 spectrometer with the resolution of 4 cm⁻¹. Each sample (42-79 mg) was pressed into a self supporting wafer (20 mm in diameter), and was mounted in an in situ IR cell equipped with NaCl windows. A wafer was pretreated in the same way as for the catalytic reaction. The pretreated wafer was exposed to 1.0 kPa of pyridine vapor at 423 K for 5 min, followed by evacuation at the same temperature for 1 h. After cooling to room temperature, each spectrum was recorded in the transmission mode.

Pyridine temperature-programmed desorption (TPD) experiments were performed at a heating rate of 10 K min⁻¹ and a quadrupole-type mass spectrometer (MASSMATE-100, ULVAC) was used as a detector. Prior to TPD measurement, 200 mg of sample was pretreated.
TABLE 1: Specific Surface Area of Catalysts Pretreated at 1073 K

<table>
<thead>
<tr>
<th></th>
<th>SiO2</th>
<th>3.4 mmol Ln / SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>57La</td>
<td>58Ce</td>
</tr>
<tr>
<td>wt% a</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td>Area / m² g⁻¹ c</td>
<td>601</td>
<td>159</td>
</tr>
<tr>
<td>S₀ / m² g⁻¹ d</td>
<td>601</td>
<td>248</td>
</tr>
</tbody>
</table>

a As Ln₂O₃
b As CeO₂
c BET specific surface area estimated with a N₂ adsorption isotherm at 77 K.
d Surface area of g(SiO₂)⁻¹ carrier.

in the same way as for α-pinene isomerization. The pretreated sample was exposed to 2.0 kPa of pyridine at 473 K for 10 min, followed by evacuation at the same temperature for 1 h. The amount of desorbed pyridine was normalized to that of introduced Ar (m/z = 40) as an internal standard.

Thermogravimetric-differential thermal analysis (TG-DTA) was carried out with a Rigaku Thermoflex TG 8110. Each profile was recorded under a dry N₂ stream (20 mL min⁻¹) at the heating rate of 5 K min⁻¹. α-Al₂O₃ crystal was utilized as the standard material for DTA analysis.

The laser Raman spectra were recorded with a JASCO NRS-2000 spectrometer using the 514.5 nm line of Ar⁺ laser emission. The incident laser power was 20 mW at sample position, and scan time was 60 - 120 s for a single spectrum. The spectral resolution was 4 cm⁻¹.

X-ray absorption experiments were carried out on the BL01B1 at SPring-8 (Hyogo, Japan). The ring energy was 8 GeV, and the stored current was 17 - 20 mA. The X-ray absorption spectra were recorded in the transmission mode with a Si(111) two-crystal monochromator. Higher harmonics were eliminated with Rh-coated mirrors (1.5 mrad for Y-K edge, and 5 mrad for Ln-LIII edge XAFS measurements). The dispersive X-ray was collimated by a total reflection mirror, at an upper stream 32.9 m from an X-ray source as a parallel ray. The height of the X-ray size was 1.0 mm. X-ray absorption spectra were recorded every 0.3 eV in the XANES region of each LIII edge. Data reduction was performed using a FACOM M1800 computer at the Kyoto University Data Processing Center. The normalization method has been previously reported in detail. 20
TABLE 2: Results of α-Pinene Isomerization over 3.4 mmol Ln/SiO₂ at 323 K

<table>
<thead>
<tr>
<th>Element</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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</thead>
<tbody>
<tr>
<td>La</td>
<td>0.4</td>
<td>15.3</td>
<td>10</td>
<td>22</td>
<td>1</td>
<td>50</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Ce</td>
<td>0</td>
<td>1.0</td>
<td>9</td>
<td>27</td>
<td>3</td>
<td>43</td>
<td>7</td>
<td>2</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Pr</td>
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<td>30.1</td>
<td>4</td>
<td>19</td>
<td>1</td>
<td>58</td>
<td>6</td>
<td>4</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Sm</td>
<td>3.7</td>
<td>0</td>
<td>1</td>
<td>18</td>
<td>1</td>
<td>66</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Eu</td>
<td>6.7</td>
<td>0</td>
<td>1</td>
<td>18</td>
<td>1</td>
<td>69</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Tb</td>
<td>8.2</td>
<td>0</td>
<td>1</td>
<td>18</td>
<td>2</td>
<td>67</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Yb</td>
<td>26.5</td>
<td>0</td>
<td>tr</td>
<td>23</td>
<td>2</td>
<td>67</td>
<td>4</td>
<td>2</td>
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<td>tr</td>
</tr>
<tr>
<td>(SiO₂)</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>28.3</td>
<td>tr</td>
<td>17</td>
<td>2</td>
<td>63</td>
<td>4</td>
<td>2</td>
<td>2</td>
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<td></td>
</tr>
</tbody>
</table>

\( a \) α-Pinene, 2 mL (12.6 mmol); Catalyst, 50 mg; Pretreatment temperature, 1073 K; Reaction time, 3 h.

\( b \) 1: β-Pinene, 2: camphene, 3: α-fenchene, 4: limonene, 5: terpinolene, 6: α-terpinene, 7: γ-terpinene, 8: others.

\( c \) Catalyst, 100 mg; Reaction temperature, 353 K.
Results

Catalysis

Table 2 shows results of α-pinene isomerization over 3.4 mmol Ln/SiO₂ catalysts pretreated at 1073 K. Only Ce/SiO₂ was inert for this reaction in the series of Ln/SiO₂ catalysts, and Yb/SiO₂ exhibited the highest activity. The activity of La/SiO₂ was much lower than that of Yb/SiO₂. With increasing atomic number from 57La of light rare earth elements to 70Yb of heavy rare earth elements, the activity increased except for Ce/SiO₂. In all the catalysts, α-pinene was selectively converted to limonene (ca. 68%) and camphene (ca. 20%) when the conversion was above 1%. Because La/SiO₂ and Pr/SiO₂ were poorly active at 323 K, the obtained selectivities were different from those of other catalysts. When the reaction was performed at 353 K, La/SiO₂ and Pr/SiO₂ gave identical selectivities to the others. Ce/SiO₂ exhibited quite low activity for α-pinene isomerization even at 353 K. Y/SiO₂ exhibited almost the same activity and selectivity as those of Yb/SiO₂, although yttrium is not a lanthanoid but an element of the sixth period.

The effect of support was examined with a supported ytterbium oxide catalyst. The supports used were SiO₂, γ-Al₂O₃, MgO and ZrO₂. The pretreatment temperature was 1073 K for each catalyst. As summarized in Table 3, only a silica-supported ytterbium oxide catalyst exhibited catalytic activity. No active sites catalyzing this reaction formed on the other supports.

<table>
<thead>
<tr>
<th>Support</th>
<th>Conversion (%)</th>
<th>( S_{\text{BET}}/\text{m}^2\text{g}^{-1} )</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>26.5</td>
<td>180</td>
<td>amorphous</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>tr</td>
<td>76</td>
<td>γ-Al₂O₃, Yb₂O₃</td>
</tr>
<tr>
<td>MgO</td>
<td>tr</td>
<td>39</td>
<td>MgO, Yb₂O₃</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>tr</td>
<td>25</td>
<td>c-ZrO₂&lt;sub&gt;ss&lt;/sub&gt; c</td>
</tr>
<tr>
<td>(Yb₂O₃)</td>
<td>tr</td>
<td>16</td>
<td>Yb₂O₃</td>
</tr>
</tbody>
</table>

\( a \) Loading amount of Yb; 3.4 mmol g(support)<sup>-1</sup>.
\( b \) α-Pinene, 2 mL; Catalyst, 50 mg; Pretreatment temperature, 1073 K; Reaction temperature, 323 K; Reaction time; 3 h.
\( c \) Cubic-ZrO₂ solid solution.
Figure 1 shows Cu-Kα XRD patterns of 3.4 mmol Ln/SiO₂ catalysts and SiO₂ gel pretreated at 1073 K. SiO₂ gel exhibited only one halo around 2θ = 22°. The other catalysts possess a halo around 2θ = 29-31° beside the halo due to amorphous silica. XRD characterization demonstrates that only Ce/SiO₂ crystallized to form CeO₂, and the other catalysts were amorphous. It shows that all of the other rare-earth oxides were supported on silica as an amorphous state. The origin of amorphous phases could not be identified, because both crystalline rare earth silicates and rare earth oxides exhibit typical reflections in this region where the new halo appeared. The 3.4 mmol Yb/SiO₂ sample pretreated at 1273 K, the catalytic activity of which was significantly lower than that of one pretreated at 1073 K⁹ was amorphous as well.

Ytterbium oxide and zirconium oxide forms a solid solution.²¹ In the XRD pattern of 3.4 mmol Yb/ZrO₂ pretreated at 1073 K, only a cubic solid solution ZrO₂-Yb₂O₃ phase was detected. As shown in Table 3, the supported species crystallized on γ-Al₂O₃ and MgO to form Yb₂O₃ (JCPDS file No. 18-1463). Any binary oxides present were not detected in the XRD patterns of all of the supported ytterbium oxide samples.

Figure 2 shows FTIR spectra of adsorbed pyridine on catalyst samples pretreated at 1073 K. The peak assignments were carried out based on studies by Connell and Dumesic.²²,²³ On 3.4 mmol Yb/SiO₂, pyridine adsorption gave three distinct bands bonded to a Lewis site at 1448, 1492 and 1608 cm⁻¹. The spectrum on Yb₂O₃ displayed five bands at 1442, 1474, 1488, 1574 and 1602 cm⁻¹, and a similar spectrum of adsorbed pyridine was obtained on La₂O₃.²⁴ Bands at 1442, 1488 and 1602 were attributed to pyridine adsorbed on a Lewis acid site (L-pyridine). The residual two peaks at 1474 and 1574 were due to carboxylate species formed as cracking products.²⁴ In contrast, only hydrogen-bonded pyridine (H-pyridine) was observed on SiO₂ pretreated at 1073 K.

The 19b mode of L-pyridine on Yb/SiO₂ (1448 cm⁻¹) and 19b mode of H-pyridine on SiO₂ (1446 cm⁻¹) gave quite similar wavenumbers, and it is difficult to distinguish between H-pyridine and L-pyridine. However, the spectrum of SiO₂ had no peak around 1490 cm⁻¹ (19a mode), and had the typical wavenumber of 8a mode below 1600 cm⁻¹. In addition, it was reported that SiO₂ gave H-pyridine at 1446 and 1598 cm⁻¹.²² Therefore, we conclude that Yb/SiO₂ possesses Lewis acid sites, and pretreated SiO₂ has no acid sites to give L-pyridine. Yb₂O₃ possesses Lewis acid sites of almost as much as 3.4 mmol Yb/SiO₂, however, the acid sites do not catalyze α-pinene isomerization at 353 K.
Figure 1. Cu-Kα XRD patterns of 3.4 mmol Ln/SiO₂ pretreated at 1073 K.
Figure 2. FTIR spectra of adsorbed pyridine at 423 K: 3.4 mmol Yb/\(\text{SiO}_2\) (46 mg) (a), Yb\(\text{O}_3\) (79 mg) (b), and Si\(\text{O}_2\) (42 mg) (c) pretreated at 1073 K.
Figure 3 shows pyridine TPD profiles of catalysts pretreated at 1073 K. The pyridine adsorption procedure was carried out at 473 K to avoid effects of physisorption. SiO₂ seldom desorbed pyridine. The profiles of all Ln/SiO₂ catalysts possessed a single desorption peak around 600 K, indicating that certain amounts of acid sites exist on the surface of Ln/SiO₂. In contrast to the catalytic activity for α-pinene isomerization, the difference in each TPD profile among the supported rare earth elements was relatively small.

The profiles of Yb/SiO₂ and Tb/SiO₂ were quite similar to each other, the tailing of which ranged to slightly higher temperatures than those of the other Ln/SiO₂. Although catalytic activities of La/SiO₂ and Eu/SiO₂ differed by one order of magnitude, their TPD profiles exhibited identical features above 700 K. The total desorbed amount of pyridine from La/SiO₂ was 1.5 times larger than that of Pr/SiO₂. Furthermore, the Ce/SiO₂ catalyst desorbed about half as much pyridine as the Yb/SiO₂ catalyst. It was reported that CeO₂ possesses Lewis acid sites, which was confirmed by the IR spectra of adsorbed pyridine²⁵ and adsorption microcalorimetry of ammonia.²⁶ A large part of desorbed pyridine from the Ce/SiO₂ was due to CeO₂ crystal. An evident difference in acidic properties of Ln/SiO₂ was not found from TPD experiments. It clearly shows that part of the pyridine adsorption sites catalyze α-pinene isomerization, the ratio to total amounts of which were not able to estimate.

XANES

Figure 4 shows X-ray absorption near-edge structure (XANES) spectra of rare earth oxides and 3.4 mmol Ln/SiO₂ catalysts pretreated at 1073 K. In the LIII-edge XANES spectra, a strong white line due to the atomic like transition of 2p-5d appeared. XANES spectra of CeO₂ and Tb₄O₇ exhibit doublet white lines due to the coexistence of Ln³⁺ and Ln⁴⁺.²⁷ The ground state of CeO₂ should be described by a mixing of two electron configurations 4f⁰ and 4fL, where L indicates a hole in the oxygen 2p valence bond,²⁸ the same spectrum was recorded by other research groups.²⁷-²⁹ Those of the other rare earth oxides exhibit a single white line. A double white line was observed for that of Ce/SiO₂, which was identical to that of CeO₂. In contrast, single white lines were observed for those of other Ln/SiO₂ samples. The single white lines and the photon energies of the Ln/SiO₂ catalysts indicate that all Ln species supported on SiO₂ were trivalent. Terbium atoms supported on silica were trivalent only, although the average composition of terbium oxide obtained by calcination of terbium salts at 1073 K is Tb₂³⁺Tb₂⁴⁺O₇.³⁰ The height of the white line for each supported rare earth oxide is higher than that of each rare earth oxide crystal, as well as in the case of Yb/SiO₂,¹⁰ Ln/Al₂O₃ (Ln = La, Sm, Lu),³¹,³² and Si:Er₂O₃.³³ Furthermore, the shapes of Y-K edge XANES spectra of Y₂O₃ and Y/SiO₂ are different from each other. If Y atom (Y³⁺; 4d⁰) was supported on silica
Figure 3. Pyridine TPD profiles of 3.4 mmol Ln/SiO$_2$ and SiO$_2$ pretreated at 1073 K.
Figure 4. XANES spectra of 3.4 mmol Ln/SiO$_2$ pretreated at 1073 K (solid curves) and rare earth oxide crystal (broken curves).
in a tetrahedral coordination, a pre-edge or shoulder peak due to the 1s-4d transition should be observed, as in the case for Nb\(^{34,35}\) and Mo\(^{36,37}\). In the Y-K edge XANES spectra of the catalyst, no pre-edge and/or shoulder peaks were observed. The coordination sphere around Y on silica is concluded not to be tetrahedral. These results indicate that the geometry and electric configuration of each supported rare earth oxide is different from that of the rare earth oxide itself.

**EXAFS**

The extraction of the Ce-L\(^{III}\) edge EXAFS function of Ce/Si\(_2\)O\(_2\) was not carried out because Ce species on silica consist of tri- and tetravalent cations with different threshold energy, and the formation of a crystalline Ce\(_2\)O\(_2\) phase has already been confirmed by XRD characterization. Figure 5 shows \(k^3\)-weighted EXAFS spectra of 3.4 mmol Ln/Si\(_2\)O\(_2\) pretreated at 1073 K. Yb-L\(^{III}\) and Y-K edge EXAFS spectra of the catalysts were quite similar to each other. Because the phase shift of the K and L\(^{III}\) edge EXAFS function is differed by \(\pi\) radian\(^3\), those of Y/Si\(_2\)O\(_2\) and Yb/Si\(_2\)O\(_2\) are fundamentally the same. This result indicates that local structures around the Y and Yb atoms of supported catalysts are similar to each other. The Tb-L\(^{III}\) edge EXAFS spectrum of the Tb/Si\(_2\)O\(_2\) catalyst was quite similar to that of Yb/Si\(_2\)O\(_2\), while the oscillation amplitude of Tb/Si\(_2\)O\(_2\) below \(k = 5 \text{ Å}^{-1}\) was slightly smaller than that of Yb/Si\(_2\)O\(_2\). With decreasing atomic number from \(^{70}\)Yb to \(^{57}\)La, the complicated oscillations of each EXAFS spectrum of the catalyst changed. Furthermore, each amplitude decreased as well. One possible reason for the decrease in the amplitude is that many kinds of scatters with different bond length counteract the EXAFS oscillations.

The radial structure functions (RSFs) obtained by Fourier transformation of \(k^3\)-weighted EXAFS functions are shown in Figure 6. The Fourier-filtered range of each EXAFS spectrum differs by the element because of the different limitation of each L\(^{II}\)-absorption edge. In the RSFs of Y/Si\(_2\)O\(_2\), Yb/Si\(_2\)O\(_2\) and Tb/Si\(_2\)O\(_2\), distinct two peaks were observed around 1.8 and 2.8 Å. In the Yb/Si\(_2\)O\(_2\) catalysts, loading amounts of which were 280 μmol - 8.4 mmol g(Si\(_2\)O\(_2\))\(^{-1}\), we have assigned the peak around 1.8 Å due to oxygen, and that around 2.8 Å due to Si atoms of the supports\(^9\),\(^10\). Analogous with Yb/Si\(_2\)O\(_2\), Ln-O-Si linkage are present on Tb/Si\(_2\)O\(_2\) and Y/Si\(_2\)O\(_2\). On the other hand, another peak was observed above 3 Å in the RSFs of Eu/Si\(_2\)O\(_2\), Sm/Si\(_2\)O\(_2\), Pr/Si\(_2\)O\(_2\), and La/Si\(_2\)O\(_2\). These distances were similar to the second peaks observed in the RSFs of rare earth oxide itself. We assigned the peaks observed in RSFs of the catalysts above 3 Å due to Ln-O-Ln linkages. Therefore, the coexistence of Ln-O-Ln and Ln-O-Si linkages with different bond length was concluded, especially in light rare earth oxides supported on silica.

All the samples remained in the amorphous state and each loading amount of the rare earth element was very large, 30 - 40 wt% as Ln\(_2\)O\(_3\). The complicated EXAFS spectra of Ln/Si\(_2\)O\(_2\) catalysts show that the coordination sphere around each Ln atom does not always
Figure 5. $k^3$-weighted EXAFS spectra of 3.4 mmol Ln/SiO$_2$ pretreated at 1073 K.
Figure 6. Fourier Transforms for $k^3$-weighted EXAFS spectra of 3.4 mmol Ln/SiO$_2$ pretreated at 1073 K.
consist of a single component. Therefore, we did not carry out curve fitting analyses for these Ln/SiO\textsubscript{2} catalysts.

**Thermogravimetric-Differential Thermal Analysis (TG-DTA)**

The preparation of each catalyst was carried out accompanied by calcination of the Ln(NO\textsubscript{3})\textsubscript{3}-SiO\textsubscript{2} precursor at 773 K. We have concluded from XAFS analysis that a strong interaction between Yb and Si atoms, which are the active sites for \(\alpha\)-pinene isomerization, had formed in the sample preparation step.\textsuperscript{10} The transformation of each precursor upon thermal decomposition was examined with TG-DTA up to 1200 K. If some crystalline phase formed or phase transition was brought about upon thermal treatment, exothermic or endothermic heat flow should be observed. Figure 7 shows TG-DTA profiles of Yb(NO\textsubscript{3})\textsubscript{3}-xH\textsubscript{2}O, non-calcined 3.4 mmol Yb/SiO\textsubscript{2}, SiO\textsubscript{2} and Si(OH)\textsubscript{4}. Yb(NO\textsubscript{3})\textsubscript{3}-xH\textsubscript{2}O decomposed to Yb\textsubscript{2}O\textsubscript{3} over many steps, including ytterbium hydroxide nitrate salts.\textsuperscript{39} SiO\textsubscript{2} and Si(OH)\textsubscript{4} desorbed a large amount of water below 373 K, and then continuously released water with ramping temperatures. The exothermic peak was not observed in the DTA profile of SiO\textsubscript{2}, indicating crystallization did not occur below 1200 K. The TG-DTA profile of non-calcined Yb/SiO\textsubscript{2} was quite different from those of Yb(NO\textsubscript{3})\textsubscript{3}-xH\textsubscript{2}O, Si(OH)\textsubscript{4} and SiO\textsubscript{2}. In contrast to the confusing DTA profile of Yb(NO\textsubscript{3})\textsubscript{3}-xH\textsubscript{2}O, that of the non-calcined sample was uncomplicated in the temperature range of 473 - 773 K. This result shows that the decomposition mechanism of the ytterbium nitrate salt on silica was different from that of the nitrate salt only. Any significant heat flow was not observed in the profile of Yb/SiO\textsubscript{2} sample up to 1200 K. The DTA characterization suggests that some ytterbium species, which are different from Yb\textsubscript{2}O\textsubscript{3} crystal, had formed during the catalyst sample preparation step. In addition, excess loading amounts of non-calcined sample (15 mmol Yb loading g(SiO\textsubscript{2})\textsuperscript{-1}) exhibited a similar DTA profile to that of the Yb(NO\textsubscript{3})\textsubscript{3} salt.

**Raman Spectra**

To clarify the structure of each catalyst in more detail, Raman spectroscopy was applied to the Yb/SiO\textsubscript{2} catalysts. Figure 8 shows laser Raman spectra of SiO\textsubscript{2}, Yb\textsubscript{2}O\textsubscript{3}, 3.4 mmol Yb/SiO\textsubscript{2} and 8.4 mmol Yb/SiO\textsubscript{2}. The spectrum of Yb\textsubscript{2}O\textsubscript{3} exhibited strong Raman bands at 360 and 612 cm\textsuperscript{-1}, and a small band at 310 cm\textsuperscript{-1}. That of SiO\textsubscript{2} gel exhibits characteristic Raman bands at 490 and 605 cm\textsuperscript{-1}.\textsuperscript{40,41} The band at 977 cm\textsuperscript{-1} is due to silanol groups.\textsuperscript{42} The Raman spectrum of 3.4 mmol Yb/SiO\textsubscript{2} was quite similar to that of SiO\textsubscript{2} gel, and exhibited no other bands except for those due to SiO\textsubscript{2}. The lack of characteristic Raman bands due to crystalline oxides indicates that the metal oxides were well dispersed and any crystallites did not formed on the support.\textsuperscript{43} Raman spectroscopic characterization shows that the crystalline phase of Yb\textsubscript{2}O\textsubscript{3} was not present on 3.4 mmol Yb/SiO\textsubscript{2}. In the spectrum of 8.4 mmol Yb/SiO\textsubscript{2}, a tiny
Figure 7. TG-DTA profiles of Yb(NO$_3$)$_3$·xH$_2$O, non-calcined 3.4 mmol Yb/SiO$_2$, Si(OH)$_4$, and SiO$_2$. 
but distinct peak appeared at 364 cm$^{-1}$ marked by an arrow, besides the peaks due to SiO$_2$. This tiny peak was assigned to Yb$_2$O$_3$ crystal. Although the Yb-L$_{III}$ edge EXAFS spectrum of 8.4 mmol Yb/SiO$_2$ did not indicate any presence of Yb-O-Yb bonding, quite a small part of the Yb species on 8.4 mmol Yb/SiO$_2$ form the Yb$_2$O$_3$ phase. The loading amount of Yb on 8.4 mmol Yb/SiO$_2$ is very high, 62 wt% Yb$_2$O$_3$. Because EXAFS characterization gave the averaged information against a target element, trace amounts of fine Yb$_2$O$_3$ crystallite could not be detected by EXAFS analysis. We have proposed that a large part of the Yb species in 8.4 mmol Yb/SiO$_2$ constitute Yb-O-Si linkages, and the trace residues deposit over Yb-O-Si linkages to reduce the catalytic activity. The deposited excess Yb species, which were YbO$_6$, formed a fine Yb$_2$O$_3$ crystallite and was detected with Raman spectroscopy.

To examine the structural transformation of catalysts upon pretreatment temperature, in situ Raman spectra of 3.4 mmol Yb/SiO$_2$ pretreated at various temperatures were recorded. The results are shown in Figure 9. The sample pretreated below 1073 K exhibited an identical spectrum to that of SiO$_2$ gel, while many Raman bands appeared on the sample pretreated at 1273 K. The new band positions were quite different from those of the Yb$_2$O$_3$ crystal. One possible assignment of them is due to formation of crystalline SiO$_2$ polymorphism. In the temperature range 1140 - 1743 K, the stable phase of SiO$_2$ is tridymite. It is well known that the phase transition of SiO$_2$ polymorphism occurs rapidly and reversibly. We did not quench the sample immediately after the pretreatment procedure, and we measured the Raman spectra at room temperature. If this was the case, the observed crystalline phase of SiO$_2$, should be α-quartz. However, there were only two observed Raman bands for α-quartz (Nacalai, GR) at 206 and 464 cm$^{-1}$ in the range 200 - 1000 cm$^{-1}$. It was concluded that crystalline SiO$_2$ polymorphism had not formed on Yb/SiO$_2$ pretreated at 1273 K. The other possible assignment of the new Raman bands is due to the formation of crystalline ytterbium silicates. As shown in the phase diagram of the Yb$_2$O$_3$-SiO$_2$ system, Yb$_2$O$_3$·SiO$_2$ and Yb$_2$O$_3$·2SiO$_2$ are stable binary oxides. Although we have not prepared ytterbium silicate crystals and do not have any information about their Raman spectra, we presume that fine crystalline particle of Yb$_2$O$_3$·2SiO$_2$ and/or Yb$_2$O$_3$·SiO$_2$ formed on 3.4 mmol Yb/SiO$_2$ pretreated at 1273 K. The size and proportion of Yb-silicate crystallite to the total contents of Yb were too small to detect by XRD and EXAFS measurements.

Discussion

In a series of lanthanoid oxides supported on silica, Yb/SiO$_2$ exhibited the highest activity for α-pinene isomerization. The catalytic activities of Yb/SiO$_2$ and La/SiO$_2$ were quite different from each other by fifty times. The activities changed by the loaded elements in the order of atomic number, but the selectivities were almost the same for all the catalysts. It is very interesting that Yb/SiO$_2$ and Y/SiO$_2$ exhibited not only the similar catalytic activities but also
Figure 8. Raman spectra of Yb$_2$O$_3$, 8.4 mmol Yb/SiO$_2$, 3.4 mmol Yb/SiO$_2$ and SiO$_2$. 
Figure 9. Raman spectra of 3.4 mmol Yb/SiO$_2$ and SiO$_2$ pretreated at various temperatures. *: laser plasma lines.
similar selectivities. The selectivity for β-pinene was relatively high over La/SiO$_2$ and Pr/SiO$_2$ catalysts when the reaction was carried out at 323 K. The selective isomerization of α-pinene toward β-pinene is one of the characteristic base-catalyzed reactions and other compounds hardly formed over solid base. However, the formation of β-pinene is catalyzed by both acids and bases. The equilibrium constant of β-pinene to α-pinene is quite low and produced β-pinene converting to α-pinene again. The selectivity of β-pinene decreased with decreasing total concentration of α-pinene in the reaction system. The high selectivity for β-pinene observed in the cases of La/SiO$_2$ and Pr/SiO$_2$ was due to the low conversion. In fact, identical selectivity was obtained over La/SiO$_2$ and Pr/SiO$_2$ when each reaction was performed at 353 K. The similarity of each selectivity indicates that the property and structure of active sites is similar among all of the Ln/SiO$_2$ catalysts.

Pyridine and/or ammonia adsorption experiments are general methods to characterize acid properties of catalysts. As shown in Figures 2 and 3, however, no distinct difference in acid properties of Ln/SiO$_2$ catalysts was obtained by characterization with pyridine. Ce/SiO$_2$ and Yb$_2$O$_3$ did not catalyze α-pinene isomerization very effectively. On the other hand, IR spectra of adsorbed pyridine showed that Yb$_2$O$_3$ possesses certain amounts of Lewis acid sites as much as 3.4 mmol Yb/SiO$_2$ catalysts. The difference in TPD profile among supported rare earth elements was small, and the existence of acid sites on Ce/SiO$_2$ was demonstrated. The pyridine TPD profiles and IR spectra of adsorbed pyridine gave information not only about the real active sites, but also pyridine adsorption sites which did not participate in catalyses. It is impossible to distinguish them. Pyridine desorption sites do not always directly reflect on the real active sites for catalyses. From TPD measurements, we could not find out the effective difference in acid strengths and the amounts among Ln/SiO$_2$ catalysts.

XRD characterization shows that all of the Ln/SiO$_2$ catalysts are amorphous, except for Ce/SiO$_2$. It was reported that the monolayer structures of transition metal oxides hardly formed on SiO$_2$ with a simple impregnation method, and the oxides were easily crystallized. However, we could prepare amorphous silica supported rare earth oxides by impregnation with nitrate aqueous solutions, followed by calcination. There are some reports that X-ray amorphous rare earth oxides supported on silica are prepared with the same preparation methods, such as 22 wt% La$_2$O$_3$/SiO$_2$ and 31 wt% Eu$_2$O$_3$/SiO$_2$. Rare earth oxides easily spread on the SiO$_2$ surface, in contrast to other transition metal oxides. Only ceria hardly spread on silica, and the crystalline phase was detected even at a low loading amount of 5.8 wt%.

In the Yb/SiO$_2$ system, the loading amount of which ranged from 280 μmol - 8.4 mmol Yb atom g(SiO$_2$)$^{-1}$, each Yb-L$_{III}$ edge EXAFS spectra were identical and no Yb-O-Yb contributions were observed. We have concluded that ytterbium atoms were widely spread on the SiO$_2$ surface as a Yb$_6$O$_6$ octahedron. Each Yb$_6$O$_6$ octahedron strongly interacted with SiO$_4$ tetrahedra, rather than with other Yb$_6$O$_6$ octahedra. The Yb-O-Si species exhibit solid acidity to catalyze α-pinene isomerization. In a series of Ln/SiO$_2$ catalysts, the selectivity for various
products from α-pinene was similar to each other. The difference in acidity of each catalyst influences the selectivity of the produced compounds from α-pinene. Thus, we propose that the structures of active sites of all the Ln/SiO$_2$ catalysts are Ln-O-Si species with similar acidity.

In the cases of other Ln/SiO$_2$ catalysts, EXAFS spectra indicate that a contribution of Ln-O-Ln appeared, besides that of Ln-O-Si. Especially in case of the light rare earth elements, Ln-O-Si contribution was small. The decrease of Ln-O-Si contribution and the increase of Ln-O-Ln contribution directly related to the catalytic performance. The LnO$_n$ polyhedron connected with other SiO$_4$ tetrahedra and/or LnO$_n$ polyhedra. In the case of the heavy rare earth element of Yb, almost all of the YbO$_6$ units strongly connected with SiO$_4$ tetrahedra only. In the case of the light rare earth element of La, LaO$_n$ units connected with other LaO$_n$ and SiO$_4$ units. The fraction differed in order of atomic number of each element. In the case of CeO$_2$, the interaction among SiO$_4$ tetrahedra and CeO$_n$ polyhedra are particularly weak. We conclude that the Ce/SiO$_2$ catalyst is the mixture of CeO$_2$ and SiO$_2$. The low affinity among ceria and SiO$_2$ might be due to the high redox ability of CeO$_2$. It was reported that Ce silicate formed only if the Ce/SiO$_2$ was reduced by hydrogen at 1073 K in the presence of Rh. $^{51}$ As a result, Ce/SiO$_2$ catalyst was inert for the acid catalyzed reaction, and the specific surface area was much larger than the others, especially in the surface area of g(SiO$_2$)$^{-1}$ carrier.

Quite similar EXAFS spectra were observed at the Y-K and Yb-LIII edge. As shown in Figure 6, Y-O-Si contributions were present in the Y/SiO$_2$ catalyst, whereas Y-O-Y contributions were absent. The similarity of the Y-K edge EXAFS spectrum of Y/SiO$_2$ to that of Yb/SiO$_2$ revealed that all of Y atoms located at a center of oxygen-octahedron connected with SiO$_4$ tetrahedra in sharing oxygen.

Two reasons why the catalysis for α-pinene isomerization changes continually with atomic number are considered. The first possible reason is concerning electronegativity. Tanabe et al. found the correlation between maximum acid strengths of binary metal oxides and the averaged electronegativities of each ion. $^{6,52}$ Maximum acid strengths of La$_2$O$_3$-SiO$_2$ and Y$_2$O$_3$-SiO$_2$ have been estimated to $H_0 \leq -4.0$ and $H_0 \leq -5.6$, respectively. $^{6,52}$ The acid strength of 3.4 mmol Yb/SiO$_2$ was evaluated with Hammet indicators to $-3.0 \geq H_0$ max $> -5.6$. Various definitions of electronegativity have been proposed, such as Pauling, Mulliken, Allred & Rochow, Sanderson, and so on. Because all electronegativities of the rare earth elements are quite similar to each other, the continuum and drastic change in the catalytic activity could not be explained by electronegativity effects. This was supported by the result that each selectivity of produced compounds from α-pinene was independent of the supported elements.

The other possible reason for this continuum change in catalyses is the effects of ion radius. It is well known that the ion radius of lanthanides continually decrease with atomic number from $^{57}$La to $^{71}$Lu. The largest ion radius of the lanthanoid ion employed in this work is 1.061 Å for La$^{3+}$, and the smallest one is 0.858 Å for Yb$^{3+}$. $^{53}$ The second smallest lanthanide ion used in the present study is 0.923 Å for Tb$^{3+}$. The size of Y$^{3+}$ is 0.88 Å, which is close to that of Yb$^{3+}$. It clearly shows that a close relationship between the ion radius of
Ln

3+ and the catalytic activity exists. It is obvious that the size of the LnO

n unit would change with the center element. We propose that a suitable size of LnO

n unit strongly interacts with SiO

4 units rather than the other LnO

n units. As a result, remarkable catalytic activity for α-pine isomerization was exhibited over Yb/SiO

2 and Y/SiO

2 catalysts. Catalytic activity depends on the number of effective Ln-O-Si linkages present on the surface.

We have proposed that YbO

6 units form on the surface of SiO

2 by sharing oxygen atoms regardless of the loading amounts. From results of surface area measurements, the deactivation of the 8.4 mmol Yb/SiO

2 catalyst was due to the blockage of active sites with excess YbO

6 units. As shown in Figure 8, Raman spectroscopy detected the formation of Yb2O

3 fine crystallites over 8.4 mmol Yb/SiO

2, the activity of which (conversion 5.5%) was much lower than that of 3.4 mmol Yb/SiO

2 (conversion 26.5%). When the loading amounts exceed the amounts needed to form the YbO

6 monolayer over a SiO

2 surface, the apparent turnover frequency per one ytterbium atom decreases due to the decrease of effective active sites on the surface.

When 3.4 mmol Yb/SiO

2 was pretreated at 1273 K, α-pine isomerization was scarcely catalyzed under the same conditions as shown in Table 2 (conversion < 0.1%). The BET specific surface areas of 3.4 mmol Yb/SiO

2 pretreated at 1073 and 1273 K were 180 and 104 m

2 g

-1 respectively. Therefore, sintering of the catalyst was not the main reason for deactivation. As shown in Figure 9, many new Raman bands appeared only on the deactivated sample. We presume that fine crystalline particles of Yb2O

3·2SiO

2 and/or Yb2O

3·SiO

2 formed on the catalyst. It indicates that crystallites of ytterbium silicates do not exhibit catalytic activity for α-pine isomerization, and partial crystallization corresponds to deactivation. From spectroscopic characterization and catalysis for α-pine isomerization, the site corresponding to solid acidity is the local Yb-O-Si network without having long-range ordering structure.

Conclusion

Silica-supported rare earth oxides exhibit solid acidity for catalysis of α-pine isomerization, and the activities strongly depend on the supported element. In the lanthanoid series (La, Pr, Sm, Eu, Tb, and Yb), the activity increased continuously with atomic number from La to Yb. Ce/SiO

2 was inert for this reaction, and crystalline CeO

2 formed. Y/SiO

2 exhibited the same activity as Yb/SiO

2. All the Ln/SiO

2 catalysts, except for Ce/SiO

2, are amorphous, and form Ln-O-Si and/or Ln-O-Ln linkages with different compositions in each catalyst. The affinity among the LnO

n unit and SiO

4 tetrahedra depends on the size of Ln

3+. With increasing ratio of Ln-O-Si to Ln-O-Ln linkages, the catalytic activity increases.

Excess loading of Yb atoms to SiO

2 blocks the Yb-O-Si linkages of the active site to form Yb2O

3 fine particles. When Yb/SiO

2 was pretreated at 1273 K, fine ytterbium silicate crystallites formed and the crystalline ytterbium silicate did not exhibit catalysis. The Ln-O-Si
linkage in Ln/SiO2 having no long-ranged ordering structure is the active site for α-pinene isomerization.

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Part III

Characterization of Iron- and Manganese-Promoted Sulfated Zirconia
Sulfated Zirconia and Promoted Sulfated Zirconia

In 1976, Tanabe et al. found that addition of (NH₄)₂SO₄ to TiO₂ causes an increase of the activity for but-1-ene isomerization by two orders of magnitude.¹ Any superacidic characters, however, were not confirmed at that time. In 1979, Arata and Hino found that SO₄²⁻/ZrO₂ catalyzes n-butane skeletal isomerization at room temperature.² The catalytic activity depends on calcination temperatures of SO₄²⁻/Zr(OH)₄, and the maximum activity was exhibited when SO₄²⁻/Zr(OH)₄ was calcined at 848-923 K. The maximum acid strength was estimated to be \(-16.04 \geq H_0\) using Hammet indicators.³ Besides SO₄²⁻/ZrO₂, they found many sulfated oxides such as SO₄²⁻/TiO₂ and SO₄²⁻/Fe₂O₃ catalyze n-butane skeletal isomerization, which is usually employed as a test reaction for super acids.⁴,⁵

In a series of sulfated metal oxides, SO₄²⁻/ZrO₂ exhibits the strongest acidity and is prepared by good reproducibility. Both Brønsted and Lewis acid sites are confirmed on SO₄²⁻/ZrO₂ with IR spectra of adsorbed pyridine, and the Lewis and Brønsted sites are easily inter changeable by adsorption or desorption of water.⁵ A recent ¹H-NMR study ⁶ and quantum chemistry calculations ⁷ indicate that Brønsted acidity of sulfated zirconia is not so strong as estimated by Hino but comparable to that of H₂SO₄ (\(H_0 = -11.93\)). Based on changes in ¹H-NMR and FTIR parameters caused by adsorption of acetonitrile, Sachatler claims that the acid strength of Brønsted acid sites of SO₄²⁻/ZrO₂ and Fe-, Mn-SO₄²⁻/ZrO₂ is similar to that of HY, but weaker than that of HZSM-5.⁸ On the other hand, it is well known that amorphous silica-alumina, H-MOR and H-MFI, maximum acid strengths of which are comparable to that of H₂SO₄, never catalyze n-butane skeletal isomerization at around room temperature. In fact, it was reported that SO₄²⁻/ZrO₂ was more active than H-MOR by two orders of magnitude for pentane isomerization at 308 K.⁹ Strictly to say, sulfated zirconia might not be super acid judging from \(H_0\) function criteria. However, it is newly established that sulfated zirconia catalyzes super acidic reactions.

Main disadvantage of SO₄²⁻/ZrO₂ is the rapid deactivation against alkane skeletal isomerization. In 1988, Hosoi found that the addition of platinum to sulfated zirconia (Pt-SO₄²⁻/ZrO₂) enhances catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction was carried out in the presence of hydrogen.¹⁰ In 1990s, Hsu discovered iron- and manganese-promoted sulfated zirconia (Fe-, Mn-SO₄²⁻/ZrO₂) exhibits higher activity for n-butane isomerization by three orders of magnitude than sulfated zirconia.¹¹ Tábara found that SO₄²⁻/ZrO₂ and Fe-, Mn-SO₄²⁻/ZrO₂ exhibit a steady activity for n-butane isomerization at 323 K, although the rate over Fe-, Mn-SO₄²⁻/ZrO₂ drastically reduced after a characteristic induction period.¹² So far, plenty of reviews have been published about sulfated zirconia and promoted sulfated zirconia.⁵,¹³-¹⁹ Nowadays, SO₄²⁻/Zr(OH)₄, which is a
precursor of \( \text{SO}_4^{2-}/\text{ZrO}_2 \), is commercially supplied by Magnesium Elektron, Inc. The \( \text{SO}_4^{2-}/\text{Zr(OH)}_4 \) was prepared commonly with impregnation of \( \text{Zr(OH)}_4 \) with a dilute sulfuric acid or an ammonium sulfate aqueous solution.

The activity of non-promoted \( \text{SO}_4^{2-}/\text{ZrO}_2 \) decreases as the reaction proceeds, which is generally interpreted to be due to coke deposition. To avoid coke formation, promoted catalysts on which a small amount of Pt, Ni etc. was added, were developed. Over a Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) catalyst, no deactivation was observed for more than 1000 h in the skeletal isomerization of \( n \)-pentane at 423 K under hydrogen atmosphere.\(^1\) In a \( n \)-butane isomerization without hydrogen, however, Tábara and R. J. Davis found that Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) exhibits stable activity at 323 K for 10 h.\(^2\) The optimal loading amount of Pt on \( \text{SO}_4^{2-}/\text{ZrO}_2 \) was found to be 0.5-0.7 wt\%. They proposed that higher loadings result in metal agglomeration and suppression of the activity.\(^3\) These results show that role of platinum on \( \text{SO}_4^{2-}/\text{ZrO}_2 \) is not only to remove coke-deposits. On the other hand, Parera proposed that deactivation of \( \text{SO}_4^{2-}/\text{ZrO}_2 \) results from a decrease in the oxidation state of sulfur in the surface complex.\(^4\) Recently, Stair applied UV-Raman spectroscopy to clarify the deactivation mechanism of \( \text{SO}_4^{2-}/\text{ZrO}_2 \).\(^5\) They concluded that the surface phase of \( \text{SO}_4^{2-}/\text{ZrO}_2 \) is reconstructed from tetragonal to monoclinic phase during the deactivation process, while the bulk remains in the tetragonal phase. It should be noted that Raman spectra bring forth more information from the surface layers of a sample than that from the bulk, the partial phase transformation in the surface region could be detected with the Raman characterization.

Ebitani found that CO is scarcely adsorbed on Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \), and propene hydrogenation ability of Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) at 323 K is lower by two orders than that of Pt/\( \text{ZrO}_2 \) at 273 K.\(^6\) The amount of uptaken hydrogen by Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) is fifty times larger than the equivalent to Pt-content in the catalyst, and Lewis acid site on Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) is reversibly converted to Brønsted acid sites by heating under hydrogen atmosphere.\(^7\) Remarkable promotive effects of hydrogen on Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) were found on pentane isomerization at 523 K and cumene cracking at 423 and 473 K.\(^8\) On the basis of hydrogen effects, Hattori and coworkers proposed a mechanism accompanied by a molecular hydrogen-originated protonic acid site formation on Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \).\(^9\)

The state of platinum on \( \text{SO}_4^{2-}/\text{ZrO}_2 \) has been examined by means of mainly TPR, XPS, and XAIFS. Ebitani reported that Pt is supported on \( \text{SO}_4^{2-}/\text{ZrO}_2 \) mainly in an oxidized state with some metallic phase inside.\(^{10}\) Paál and Iglesia claimed that Pt is supported as sulfied one on the activated catalyst. Sayari and coworkers proposed that Pt is metallic, even after calcination in air.\(^{11}\) In the studies mentioned above, loading amounts of Pt (5-7 wt\%) were ten times as much as those of practically used catalysts (ca. 0.5 wt\%). Tábara and R. J. Davis measured XANES spectrum of Pt (0.74 wt\%) /\( \text{SO}_4^{2-}/\text{ZrO}_2 \) and concluded that platinum is present as PtO2.\(^{12}\) On the other hand, Tanaka and Shishido measured XAFS spectra of 0.5 wt\% Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) in an oxidized and reduced state. They found that state of platinum in Pt-\( \text{SO}_4^{2-}/\text{ZrO}_2 \) is the mixture of metallic platinum and platinum.
oxide in both cases, and metallic platinum particles are covered with the thin layer of platinum oxide.35,36

The transition metal doping of Zn, Ni, Co, Fe, Mn, W, Ir, Pt, Rh, Ru, Os has been found to promote greatly n-alkane rearrangement.15,37 Besides Pt in metal-promoted sulfated zirconia, iron- and manganese-promoted sulfated zirconia (Fe-, Mn-SO$_4^{2-}$/ZrO$_2$) has been a subject of the most recent attention for alkane conversion.19 In 1990’s, Hsu and coworkers discovered Fe-, Mn-SO$_4^{2-}$/ZrO$_2$, the activity of which for n-butane isomerization at room temperature was higher by three orders of magnitude than that of conventional SO$_4^{2-}$/ZrO$_2$.11,38 During n-butane isomerization, Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ exhibits an induction period followed by a fast deactivation.39,40 The deactivation of Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ for skeletal isomerization was somewhat suppressed even in the absence of hydrogen. Táborá observed a steady activity for n-butane isomerization at 323 K over Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ after 5 h, although the activity was quarter as much as the maximum activity at the initial period.12 Phenomenon occurring in the induction period is interpreted as a formation and/or accumulation of unsaturated species such as butenes.12,41-44 The n-butane isomerization over Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ was proposed to proceed predominantly via oligomeric intermediates of C$_8$ species, as well as over SO$_4^{2-}$/ZrO$_2$.45-47 The formed butenes induce the skeletal isomerization of bimolecular mechanism by reacting with C$_4$ carbenium ions, but their accumulation on the surface leads to a formation of coke precursors. In fact, Alvarez found over Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ that the activity under continuous flow operation was much higher than that obtained in the pulse mode.43,48 They proposed that the intermediates are desorbed or decomposed under He stream without n-butane at 423 K, while at 373 K they retain. In the case that the reaction was carried out at 423 K, the activity started from a very low value and a new induction period was observed whenever n-butane flow was stopped. By contrast, the induction period was only observed during the first cycle, when the experiment was performed at 373 K. The similar results were obtained in case over Ni-SO$_4^{2-}$/ZrO$_2$.49

In cases of ethane and propane isomerizations above 473 K, the product distributions show that reactions over Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ are consistent with chemistry analogous to that in superacidic solutions.50-52 Based on results of the catalyses, Gates concluded Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ is a stronger acid than SO$_4^{2-}$/ZrO$_2$, USY and HZSM-5.50,52 From benzene-TPD characterizations, Lin and Hsu reported that catalytic activity deeply depends on the SO$_4^{2-}$content, and acid sites on Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ are stronger than those on SO$_4^{2-}$/ZrO$_2$.38 Morterra measured IR spectra of adsorbed CO over Fe-, Mn-SO$_4^{2-}$/ZrO$_2$, Fe-SO$_4^{2-}$/ZrO$_2$ and Mn-SO$_4^{2-}$/ZrO$_2$. They confirmed one peak at 2200 cm$^{-1}$ and a shoulder at 2170 cm$^{-1}$ on Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ and Fe-SO$_4^{2-}$/ZrO$_2$, while only one peak at 2200 cm$^{-1}$ on Mn-SO$_4^{2-}$/ZrO$_2$.53 The peak at 2200 cm$^{-1}$ was assigned to CO adsorbed onto coordinately unsaturated (CUS) Zr$^{4+}$. They assigned the shoulder at 2170 cm$^{-1}$ to those onto CUS surface Fe$^{n+}$ sites, where $n$ is between 2 and 3. M. E. Davis reported that Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ is much more active for n-butane isomerization than Fe-SO$_4^{2-}$/ZrO$_2$ and Mn-SO$_4^{2-}$/ZrO$_2$; and Mn-SO$_4^{2-}$-
/ZrO2 scarcely catalyzes the reaction at 308 K.\textsuperscript{39} However, they pointed out the possibility that differences of activities among them merely depend on the sulfur content. Benzene TPD characterization did not give any informations about differences of the acidities.\textsuperscript{39} In fact, Gates reported that addition of manganese increases the activity by two or three orders of magnitude.\textsuperscript{37} From CO-FTIR and \(^1\)H-NMR characterizations, Sachtlert insisted that both Lewis and Brønsted acidities on SO\(_4^{2-}/\)ZrO\(_2\) and Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) are as such within experimental errors.\textsuperscript{8} Tábara gave the same CO-FTIR spectra of SO\(_4^{2-}/\)ZrO\(_2\) and Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\), indicating that Lewis acidities of the both are the same level,\textsuperscript{40} in contrast to the work by Morterra.\textsuperscript{53} At the present stage, clear differences in acidity among SO\(_4^{2-}/\)ZrO\(_2\), Mn-SO\(_4^{2-}/\)ZrO\(_2\) and Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) are not obtained.

Tábara and R. J. Davis proposed that the role of Fe and Mn promoters in SO\(_4^{2-}/\)ZrO\(_2\) is to increase the surface concentration of intermediate butenes which subsequently react to form isobutane. They concluded that Fe-, Mn- promoted catalyst forms butene not catalytically whereas the Pt-promoted sample forms butene catalytically.\textsuperscript{12} Wan found an effect of calcination and He-purge pretreatment temperature on the activity of Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\).\textsuperscript{47} With increasing calcination temperature in air, catalytic activity for n-butane isomerization increases. On the other hand, with increasing He-purge temperature of pre-calcined catalyst, the activity decreases at a temperature above 523 K. They speculated that high-valent iron oxy species such as tetrahedral Fe\(^{4+}\) species forms on Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) during calcination in air, and these sites are responsible for the oxidative dehydrogenation of n-butane to butene.

Only a few works were performed to investigate the states of Fe and Mn atoms on Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\), because Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) contains very small amounts of Fe (ca. 1.5 wt\%) and Mn (ca. 0.5 wt\%). Tábara et al. measured Fe K-edge EXAFS spectrum of Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) and no contributions from Fe-Zr and/or Fe-Fe pairs were confirmed in the radial structure functions. They concluded that the Fe atoms are not substituted isomorphously into bulk tetragonal zirconia but instead exist in nanometer-size oxide clusters or rafts which located on the surface or at defects inside the bulk.\textsuperscript{40} However, the quality of the datum and method of datum reduction for the EXAFS spectrum were not adequate. It is quite difficult to obtain the information from the spectrum about the local structure abound Fe. From the fact that a pre-edge peak was not present in the Mn-K edge XANES spectrum, they commented that Mn atom in Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) is not tetrahedral coordination. Milburn carried out in-situ XPS characterization of Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\).\textsuperscript{54} They reported that both Fe and Mn atoms were supported on sulfated zirconia in an oxidized state after hydrogen treatment at 423 K. Unfortunately, their X-ray photoelectron spectra of Fe\(_{2p}\), Mn\(_{2p}\), and S\(_{2s}\) were too noisy to determine the accurate binding energies. Knözinger, Gates and coworkers carried out precise characterization of Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) with UV-vis, ESR, Raman, XPS and XRF.\textsuperscript{55} The UV-vis and Raman characterizations show that iron was present in an aggregated form and not as atomically isolated species, although the ESR spectrum shows the presence of isolated Fe\(^{3+}\) ions. Manganese in Fe-, Mn-SO\(_4^{2-}/\)ZrO\(_2\) and Mn-SO\(_4^{2-}/\)ZrO\(_2\) was identified by the ESR
spectra of Mn$^{2+}$, with the resolved hyperfine structure. Based on the spectroscopic characterizations, they concluded that Fe atoms are present as small Fe$_2$O$_3$ particles (1-2 nm) with some isolated Fe$^{3+}$ ions, and Mn atoms are present as divalent ions in a highly dispersed form.

As mentioned above, property of SO$_4^{2-}$/ZrO$_2$ and SO$_4^{2-}$/ZrO$_2$-based catalysts have been uncovered gradually. However, the physicochemical properties of Fe-, Mn-SO$_4^{2-}$/ZrO$_2$, the most promising catalyst in practice, is still full of controversy. The present part, although it contains only one chapter, is devoted to the clarification of the states of Fe and Mn in Fe-, Mn-SO$_4^{2-}$/ZrO$_2$ catalysts. The use of the XAFS and the other techniques firstly elucidated the states of Fe, Mn precisely and the role of these elements is discussed.

References

Chapter 6

Structural Analysis of Iron and Manganese Species in Iron- and Manganese-Promoted Sulfated Zirconia

Abstract

The structural analyses of Fe, Mn-SO$_4^2$-/ZrO$_2$ (FMSZ), Fe-SO$_4^2$-/ZrO$_2$ (FSZ), Mn-SO$_4^2$-/ZrO$_2$ (MSZ), and Fe-Mn/ZrO$_2$ (FMZ) were carried out by means of XAFS, XRD and Raman spectroscopy. Local structure around Fe and Mn of each catalyst, which were at a working state for $n$-butane isomerization and in vacuo, were studied by in-situ XAFS. The valence of the Fe atom of all the catalysts was invariantly trivalent. Coordination environment around Fe of all the catalysts was quite similar to each other. Fe atoms are present inside the bulk phase of ZrO$_2$, the system of which forms interstitial-type solid solution and located at the center of distorted oxygen octahedra. Reaction gas does not directly make contact with Fe atoms, because the introduction of reaction gas did not cause any change of coordination environment and the valence. Mn species on FMSZ and MSZ were present as MnSO$_4$, and their coordination environment was reversibly affected by exposure to $n$-butane. Without sulfate ions, Mn species are present on the catalyst as $\alpha$-Mn$_2$O$_3$. 

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Introduction

Since Arata et al. discovered $\text{SO}_4^{2-} / \text{ZrO}_2$ (SZ) which catalyzes $n$-butane skeletal isomerization at room temperature, SZ and promoted SZ have been investigated extensively. As a promoter, various transition metals have been added to SZ. In the 1990s, Hsu et al. discovered sulfated Fe-Mn-Zr oxide (FMSZ), the activity of which for $n$-butane isomerization at room temperature was higher by 3 orders of magnitude than that of conventional $\text{SO}_4^{2-} / \text{ZrO}_2$. Furthermore, the deactivation of FMSZ for skeletal isomerization was much suppressed even in the absence of hydrogen. Therefore, much attention has been paid to this new solid acid catalyst. However, the distinct difference in physical property except for catalysis between SZ and FMSZ has not been clarified. Further, the role and structure of promoted elements on FMSZ remained unclear, in contrast to the case of Pt-$\text{SO}_4^{2-} / \text{ZrO}_2$. Only a few studies were performed to investigate the states of Fe and Mn atoms on FMSZ because FMSZ contains no more than very small amounts of Fe (ca. 1.5 wt %) and Mn (ca. 0.5 wt %).

Tábora et al. measured Zr-K edge EXAFS spectrum of FMSZ, and concluded that the phase of $\text{ZrO}_2$ was tetragonal. They also measured Fe K-edge EXAFS spectrum and reported that Fe atoms were supported on $\text{ZrO}_2$ as small clusters or rafts of Fe$_2$O$_3$. However, its quality and the method of datum reduction of the Fe K-edge EXAFS were not adequate, and it is difficult to obtain the information about the local structure around Fe. From XPS investigation, Milburn et al. reported that both Fe and Mn atoms were supported on sulfated zirconia in an oxidized state. Unfortunately, their recorded X-ray photoelectron spectra of Fe$_2p$, Mn$_2p$, and S$_2s$ were too noisy to determine the accurate binding energies. More recently, Gates and co-workers investigated the structure of FMSZ with various spectroscopic methods. From XPS, ESR, UV-VIS, and Raman characterizations, they concluded that Fe atoms are present as small Fe$_2$O$_3$ particles with some isolated Fe$^{3+}$ ions, and Mn atoms are present as divalent ions. In contrast, Wan et al. speculated that high-valent iron oxy species such as tetrahedral Fe$^{4+}$ species had formed on FMSZ, and these sites are responsible for the oxidative dehydrogenation of $n$-butane to butene.

If Fe$^{4+}$ species had formed on FMSZ, Fe ions would have been reduced by exposure of butane and some change of the coordination environment should have occurred. In the present study, we carried out in-situ XAFS measurements to investigate the local structures around Fe and Mn atoms, and studied their changes during $n$-butane isomerization. There are no studies investigating coordination environment of Fe and Mn species at a working state.

Experimental

Material
Fe- and Mn-promoted sulfated zirconia (Fe, Mn-SO$_4^{2-}$/ZrO$_2$; FMSZ) was prepared according to Cheung's method. The sulfate ion-treated Zr(OH)$_4$ (SO$_4^{2-}$/Zr(OH)$_4$) was prepared by the impregnation of Zr(OH)$_4$ with 1 M (NH$_4$)$_2$SO$_4$ aqueous solution at room temperature for 0.5 h with stirring followed by filtration and drying at 383 K for 6 h. The Zr(OH)$_4$ was obtained by hydrolysis of ZrOCl$_2$·8H$_2$O with 25 mass% NH$_3$ aqueous solution at room temperature followed by filtration. The final value of pH was 8.0, and the aging time was 2 h. The obtained gel was washed with distilled water repeatedly until Cl$^-$ was free on the basis of the AgNO$_3$ test. Fe and Mn ions were supported on SO$_4^{2-}$/Zr(OH)$_4$ by stepwise equilibrium adsorption of 0.2 M Fe(NO$_3$)$_3$·6H$_2$O and 0.043 M Mn(NO$_3$)$_2$·9H$_2$O aqueous solutions. Each equilibrium adsorption was performed at room temperature for 0.5 h with stirring followed by filtration. After drying at 383 K for 6 h, it was then calcined at 873 K for 3 h.

Fe-SO$_4^{2-}$/ZrO$_2$ (FSZ), Mn-SO$_4^{2-}$/ZrO$_2$ (MSZ) and Fe-Mn/ZrO$_2$ (FMZ) were prepared the same as FMSZ was prepared, by omitting each step.

Elemental composition was determined by X-ray fluorescence (XRF) with a RIGAKU 3270 spectrometer. The BET specific surface area measurement was carried out with BELSORP 28SA using a N$_2$ adsorption isotherm at 77 K. Results of elemental analysis and surface area measurements are summarized in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area /m$^2$ g$^{-1}$</th>
<th>Elements (wt%)</th>
</tr>
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<tbody>
<tr>
<td>ZrO$_2$</td>
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<td>-</td>
</tr>
<tr>
<td>SO$_4^{2-}$/ZrO$_2$</td>
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<td>0.88</td>
</tr>
<tr>
<td>Fe-, Mn-SO$_4^{2-}$/ZrO$_2$</td>
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<td>0.81 1.7 0.25</td>
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<td>Fe-SO$_4^{2-}$/ZrO$_2$</td>
<td>107</td>
<td>0.96 1.1 -</td>
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<tr>
<td>Mn-SO$_4^{2-}$/ZrO$_2$</td>
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<td>1.5 - 0.27</td>
</tr>
<tr>
<td>Fe, Mn/ZrO$_2$</td>
<td>110</td>
<td>1.9 0.42</td>
</tr>
</tbody>
</table>

TABLE 1: BET Specific Surface Area and Chemical Composition
**X-ray Diffractions (XRD)**

X-ray diffraction patterns of samples were obtained with a RIGAKU RINT 1300 diffractometer using Ni-filtered Cu Kα radiation (averaged as 1.5418 Å).

**Raman Spectra**

The laser Raman spectra were recorded with a JASCO NRS-2000 spectrometer using the 514.5 nm line of an Ar+ laser emission. An incident laser power was 0.5 - 5 mW at sample position, and the scan time was 60 - 180 s for a single spectrum. The spectral resolution was 4 cm^{-1}. All spectra were recorded under ambient conditions at room temperature.

**In Situ XAFS Measurements**

Fe and Mn K-edge X-ray absorption experiments were carried out on the BL7C and BL12C at Photon Factory in High Energy Accelerator Research Organization (KEK-PF; Tsukuba, Japan) with a ring energy of 2.5 GeV and a stored current of 250 - 400 mA (Proposal No. 97G041). The X-ray absorption spectra of catalysts were recorded in a fluorescent mode, and those of reference compounds were recorded in a transmission mode with a Si(111) two-crystal monochromator. The energy was calibrated by the preedge peak position of Cu foil (8980.3 eV).

Data reduction was performed using a FACOM M1800 computer of Kyoto University Data Processing Center. The normalization method has been previously reported in detail.\textsuperscript{17} For curve-fitting analysis, the following EXAFS formula was applied.

\[ k^3 \chi (k) = \sum_j \left( k^2 N_j / R_j^2 \right) A_j (k) \exp (- 2 \sigma_j^2 k^2) \sin (2 k R_j + \delta_j (k)) \]

where \( k \) is the wavenumber of photoelectron, \( N_j \) the number of the scattering atoms of the \( j \) th shell located at a distance of \( R_j \) from a central atom, \( A_j \) the envelope function which includes the backscattering amplitude and damping factor caused by inelastic loss during electron traveling, \( \sigma_j \) the Debye-Waller factor and \( \delta_j \) the phase shift. For curve-fitting analysis, the backscattering amplitude and phase shift functions of Fe-O pair were obtained from a \( k^3 \)-weighted EXAFS spectrum of the CoO crystal (Rock salt type, \( a_0 = 4.260 \text{ Å} \)). For Zr atom scatterers, they were estimated with FEFF (6.0).\textsuperscript{18} EXAFS analysis for Mn K-edge could not be performed because the \( S/N \) ratio of each spectrum was too bad to obtain useful information.

Each catalyst was charged in an in-situ XAFS cell with a Kapton window to prevent exposure to the air. The recorded XAFS spectra of each catalyst were pretreated ones (1), ones
at a working state for n-butane isomerization (2), and ones evacuated after a reaction (3). XAFS experiments and n-butane isomerization were carried out at the same time.

Catalysis

The isomerization of n-butane was performed with an in-situ XAFS cell under static conditions at 293 K, at the same time as the XAFS measurement. The cell was made of Pyrex glass and was connected with a glass balloon filled with n-butane (54.1 mmol). Total dead volume of the cell was 1,300 cm$^3$. The catalyst of FMSZ (700 mg) was evacuated at 673 K for 1 h, followed by contact with n-butane at 293 K. After 24 h in a static condition, Fe and Mn K-edge XAFS spectra were recorded at a working state. Then reaction gases were evacuated at room temperature for 10 min, followed by measurement of Fe and Mn K-edge XAFS spectra. The evacuated gas was stored in another vessel, and the composition was analyzed with TCD gas chromatography.

In the cases of FSZ, MSZ, and FMZ, XAFS measurements and n-butane isomerization were carried out in a manner similar to mentioned above. For these three catalysts, another type of in-situ XAFS cell, the dead volume of which was 60 cm$^3$, was used. The amounts of catalyst and substrate were 200 mg and 99 μmol, respectively. Catalysis over SO$_4^{2-}$/ZrO$_2$ (SZ) was performed under the same reaction conditions, using a closed reaction vessel (60 cm$^3$). In all cases, reaction time and temperature were 24 h and 293 K, respectively.

Results

Catalysis

After 24 h at 293 K under static conditions, 12.5 % of the n-butane had converted to iso-butane over FMSZ. The amount of reacted n-butane was 6.76 mmol. Formation of C$_3$ and C$_5$ species was negligible. The amounts of Fe and Mn contained in 700 mg of FMSZ were 213 and 32 μmol, respectively. The apparent turn over numbers per one Fe and Mn atoms were 32 and 211, respectively.

Over FSZ and MSZ, 25 % and 7.3 % of n-butane were converted to iso-butane, respectively. The conversion over SZ was 5.8 %. FMZ was inert for n-butane isomerization. In the case of FSZ, the amount of reacted n-butane was 24.8 μmol and the amount containing an Fe atom was 39 μmol. In the case of MSZ, the amount of reacted n-butane was 7.2 μmol and the amount containing a Mn atom was 9.8 μmol.

Because the reaction vessels for the FMSZ catalyst and for the others are different, we cannot directly compare the activity between them. But it is obvious that the activity for FMSZ is the highest. FSZ exhibited higher activity than SZ. Lange et al. observed Mn increases the
Figure 1. Cu Kα XRD patterns of samples calcined at 873 K: ○; monoclinic phase, ▲; tetragonal phase.
activity by 2 or 3 orders of magnitude.\textsuperscript{19} Whereas in our case, Mn addition to SZ is not very effective, the same as in the previous report.\textsuperscript{8}

\textbf{XRD}

Figure 1 shows XRD patterns of catalysts calcined at 873 K. ZrO$_2$ consists of a mixture of monoclinic and tetragonal phases. SZ, FMSZ, and FSZ consist of only tetragonal ZrO$_2$ of metastable phase. The ZrO$_2$ phases of FMZ and MSZ are mainly tetragonal. Any peaks, other than ZrO$_2$ phases, were not observed in all the XRD patterns.

\textbf{Raman Spectra}

It has been reported that the tetragonal phase of ZrO$_2$ exhibits typical Raman bands at 148, 263, 325, 472, 608, and 640 cm$^{-1}$,\textsuperscript{19} and that the Raman spectrum of SO$_4^{2-}$/ZrO$_2$ is identical to that of tetragonal ZrO$_2$.\textsuperscript{13,21,22} Raman spectra of the catalysts are shown in Figure 2. Although the XRD pattern of ZrO$_2$ shows that ZrO$_2$ consists of both monoclinic and tetragonal phases, the Raman spectrum of ZrO$_2$ calcined at 873 K is identical to the reported spectrum of 100% monoclinic ZrO$_2$.\textsuperscript{20} The positions of the observed Raman bands were 96, 140, 173, 185, 216, 260, 301, 328, 342, 378, 471, 499, 533, 553, 610, 632, and 752 cm$^{-1}$. Two tiny peaks at 140 and 260 cm$^{-1}$ were due to the tetragonal phase, and the others were due to the monoclinic phase. It shows that the surface region of ZrO$_2$ calcined at 873 K consists of the monoclinic phase only, whereas the bulk is a mixture of two phases. The Raman spectrum of SZ shows that the surface phase of is mainly the tetragonal ZrO$_2$ phase with a trace amount of monoclinic phase. The surface ZrO$_2$ phases of FMSZ, FSZ and MSZ consist mainly of the tetragonal phase as well, corresponding to the results of XRD measurements. The positions of the Raman bands assigned to the tetragonal ZrO$_2$ phase were 140, 261, 310, 450 and 635 cm$^{-1}$. Scheithauer et al. measured the Raman spectra of SZ, FSZ, FMSZ and MSZ. They confirmed that ZrO$_2$ phases of all the catalysts were tetragonal only, and also observed the characteristic Raman bands of \textalpha-Fe$_2$O$_3$ on the spectrum of FMSZ.\textsuperscript{13} In contrast, we did not observe any bands due to \textalpha-Fe$_2$O$_3$ (210, 272, 386, 579 cm$^{-1}$) on all the spectra. \textalpha-Mn$_2$O$_3$ and B-MnO$_2$ exhibit no Raman bands in this region.\textsuperscript{23}

Characteristic hydrated sulfate groups were observed on SZ, FMSZ, FSZ and MSZ at 1029 - 1031 cm$^{-1}$, as well as Scheithauer's results. In the range of 950 - 1050 cm$^{-1}$, sulfate groups of reference compounds exhibit characteristic Raman bands at 1016 cm$^{-1}$ for MnSO$_4$, 973 cm$^{-1}$ for FeSO$_4$, and 1010, 1029, 1034 sh, and 1047 cm$^{-1}$ for Fe$_2$(SO$_4$)$_3$, as shown in Figure 3. These Raman bands of metal sulfates appeared in a region similar to those of the sulfate group of SZ. In addition, Tábara et al. measured IR spectra of activated FMSZ and SZ without exposure to air.\textsuperscript{11} In the sulfate region, IR spectra of both SZ and FMSZ exhibited strong two peaks at 1010 and 1043 cm$^{-1}$. Both wavenumbers are similar to those of
Figure 2. Raman spectra of catalysts: (*) plasma lines.
**Figure 3.** Raman spectra of reference compounds: (*) plasma lines.
characteristic Raman bands of MnSO₄ (1016 cm⁻¹) and Fe₂(SO₄)₃ (1010, 1028, 1047 cm⁻¹). With Raman and IR spectroscopy, it is very difficult to prove the presence of MnSO₄ and to determine the origin of sulfate groups of catalysts.

**Fe K-edge XANES**

Figure 4 shows Fe K-edge XANES spectra and the first derivatives of reference compounds. The chemical shift between Fe²⁺ and Fe³⁺ was observed in the edge position of each spectrum. XANES spectra show that Fe₂(SO₄)₃ had transformed to α-Fe₂O₃ when it was calcined at 873 K. As for the Fe³⁺ species, the preedge peak of α-Fe₂O₃ was split but that of γ-Fe₂O₃ was not.

Fe K-edge XANES spectra and their first derivatives of the samples are shown in Figure 5. It is very interesting that XANES spectra of all the catalysts, including the feature and the height of preedge peaks, the edge positions, and the shapes of all spectra, were almost the same as each other. The edge energy shows that Fe atoms of the three catalysts were in the trivalent state. However, XANES spectra of all the catalysts were quite different from those of reference compounds. It shows that Fe atoms on sulfated zirconia are not present as compounds such as the reference samples shown in Figure 4. Furthermore, the local structure around Fe of all the catalysts is not affected by the presence of sulfate nor Mn ions. As pointed out in the case of FMSZ previously, reaction gas did not affect the edge energy nor the shape of XANES spectra. Similar phenomena were observed in XANES spectra of FSZ and FMZ. Redox of Fe atoms on all the catalysts did not take place under a reaction conditions. Evacuation of reacted gas did not cause any change of XANES spectra of the catalyst samples as well.

The preedge peak of Fe K-edge XANES is assigned to the 1s-3d transition which is formally dipole-forbidden. The peak intensity is closely related to the symmetry around Fe atoms, and this peak becomes more intense as the symmetry is distorted from a regular octahedron. Each preedge peak area of all the catalyst samples was a little larger than that of octahedral Fe³⁺ compounds such as α-Fe₂O₃ and did not change during n-butane isomerization. However, the preedge peak area was smaller than those of Fe-MFI and FePO₄, whose local structure around Fe is an Fe₄ tetrahedron. It shows that the local symmetry around Fe was not tetrahedral, but distorted more than that of α-Fe₂O₃. The symmetrical environment around Fe of each sample was not affected by reaction gas. In addition, the differential XANES spectrum of α-Fe₂O₃ exhibits a doublet preedge peak; however, those of FMSZ have only singlet curves. These results strongly suggest the local structure around Fe is quite different from that of α-Fe₂O₃. We propose that Fe atoms are located at a center of a highly distorted octahedron. Because the reacted amounts of n-butane much exceeded those of Fe atoms contained in FMSZ, it could be concluded that n-butane does not affect the structure or the valence of Fe as well. If any chemical reaction and/or change of coordination...
Figure 4. Fe K-edge XANES spectra of reference compounds and their first derivatives. Spectra of FeO, Fe$_3$O$_4$, γ-Fe$_2$O$_3$ were recorded on the BL10B at KEK-PF with a Si(311) channel-cut monochromator. The others were recorded on the BL7C at KEK-PF with a Si(111) two-crystal monochromator.
Figure 5. XANES spectra and their first derivatives of catalysts evacuated at 673 K (a), at a working state (b), and evacuated at room temperature after reaction (c).
environment had occurred on Fe species, some changes would have been observed in XANES spectra of catalyst samples.

*Mn K-edge XANES*

Figure 6 shows the Mn K-edge XANES spectra of reference compounds and their first derivatives. As previously reported,\textsuperscript{27} the edge positions of manganese oxides shift to higher energy with increasing the oxidation number. The divalent compounds of MnO and MnSO\textsubscript{4} exhibit quite similar edge energies in XANES spectra.

Figure 7 shows the Mn K-edge XANES spectra and their first derivatives of catalyst samples. The edge positions of MSZ and FMSZ evacuated at 673 K indicate that Mn atoms were present as a divalent form. The shapes of these two XANES spectra are quite similar to that of MnSO\textsubscript{4}. In contrast, the Mn K-edge XANES spectrum of FMZ exhibits the identical edge position of the trivalent. The shapes of its XANES spectrum and the first derivative resemble those of $\alpha$-Mn$_2$O$_3$. Although they were noisy because of the low concentration of Mn species, the similarity of XANES spectra between FMZ and $\alpha$-Mn$_2$O$_3$ especially support this deduction. These results indicate that Mn atoms are present as MnSO\textsubscript{4} on sulfated ZrO\textsubscript{2}, whereas Mn atoms are present as $\alpha$-Mn$_2$O$_3$ on sulfate-free ZrO\textsubscript{2}.

At a working state, the postedge peak of the Mn K-edge XANES of FMSZ was sharpened, but the edge position did not change. After evacuation, the shape of the postedge peak had turned back to the original state. This reversible change of XANES spectra corresponds to the change of the coordination environment around Mn. It indicates that the Mn atom is present on the surface and directly makes contact with n-butane. A similar phenomenon was observed in XANES spectra of MSZ. No change was observed on those of FMZ.

*Fe K-edge EXAFS*

Figure 8 shows $k^3$-weighted Fe K-edge EXAFS spectra of Fe$^{3+}$ reference compounds and their Fourier transforms in the $k$-range of 3 - 14 Å\textsuperscript{-1}. An EXAFS spectrum of Fe$_2$(SO\textsubscript{4})$_3$ calcined at 873 K and its Fourier transforms are identical to those of $\alpha$-Fe$_2$O$_3$. Even if supported Fe species on sulfated zirconia had formed Fe$_2$(SO\textsubscript{4})$_3$, it might be decomposed in the calcination step at 873 K.

Figure 9 shows $k^3$-weighted Fe K-edge EXAFS spectra of the catalyst samples. EXAFS spectra of FMSZ, FSZ, and FMZ, which were pretreated, are similar to each other. All spectra of the catalyst samples are quite different from those of reference compounds. Although $S/N$ ratios of EXAFS spectra are not good, we conclude that the three EXAFS spectra of the catalyst samples are identical. These results suggest that short-range structure around Fe was not affected by any additives such as manganese and/or sulfate ions. In the case of FMSZ, the three variously treated EXAFS spectra are also quite similar to each other. It clearly shows that the
Figure 6. Mn K-edge XANES spectra and their first derivatives of reference compounds.
Figure 7. Mn K-edge XANES spectra and their first derivatives of catalysts: evacuated at 673 K (a), at a working state (b), and evacuated at room temperature after reaction (c).
Fe K-edge EXAFS spectra and their Fourier transforms of reference Fe$^{3+}$ compounds.
short-range structure of FMSZ around Fe was not affected by n-butane at all. The exposure to
n-butane also did not affect on the local structure of FSZ and FMZ around Fe as well.

Figure 10 shows Fourier transforms of Fe K-edge $k^3$-weighted EXAFS spectra of the
catalyst samples. Because the noise level of each spectrum is different, Fourier filtered ranges
of EXAFS spectra are not regular. The transformed ranges of pretreated FMSZs and the other
two spectra are 3 - 13 and 3 - 14 Å⁻¹, respectively. The ranges of all FSZs are 3 - 11.5 Å⁻¹.
Those of pretreated FMZs and their working states are 3 - 11.5 and 3 - 10 Å⁻¹, respectively. In
all of their radial structure functions (RSFs) except for that of FMZ at the working state, two
distinct peaks appeared around 1.6 and 3.3 Å. The peak around 1.6 Å is due to oxygen
scatterers. The positions of the peak around 3.3 Å is higher than those of $\alpha$-Fe$_2$O$_3$ and $\gamma$-
Fe$_2$O$_3$, which is due to Fe atoms. Therefore, we assigned the second peak due to scattering not
from Fe but from Zr atoms. In contrast to our results, Tábora et al. did not observe the second
peak in the RSF of FMSZ. The reason for the difference between our results and their work
is the data reduction of EXAFS spectra. In the case of Tábora's work, it seems that the
subtracted background was not adequate, especially over $k = 7$ Å⁻¹. In addition, they adopted
$k^2$-weighted EXAFS, in contrast to our $k^3$-weighted EXAFS spectra.

To obtain further information, we performed curve-fitting analysis. The results are
summarized in Table 2. As examples, the fits of Fourier filtered Fe K-edge EXAFS for
pretreated and at a working state of FMSZ are shown in Figure 11. The first coordination
spheres for all the catalysts could not be fit with a single Fe-O shell, but could be fit with two
shell. Only that of pretreated FMZs gave a satisfactory fit with a single shell. For the first shell
of all the catalyst samples, each estimated parameter is identical within calculation errors. Their
interatomic distances and coordination numbers are similar to those of $\alpha$-Fe$_2$O$_3$, the
coordination environment of which is 6-fold. An Fe atom of $\alpha$-Fe$_2$O$_3$ is surrounded by six
oxygen atoms, but the interatomic distances are not uniform. The bond lengths of three Fe-O
pairs are ca. 1.91 Å, and those of three more Fe-O pairs are ca. 2.06 Å. The estimated
EXAFS parameter strongly suggests that Fe species in all the catalyst samples are present at the
center of oxygen octahedron. An estimated coordination number for the first shell of pretreated
FMZ is 4.6; however, the interatomic distance is 2.02 Å. For 4-fold coordination materials, the
bond length between Fe and O atoms has been reported to be 1.85 Å for Fe-MFI and FePO$_4$,
and to be 1.89 Å for Fe/Na-SiO$_2$. The estimated distance (2.02 Å) of the Fe-O bond in
pretreated FMZ is much longer than those for 4-fold coordination. Therefore, we conclude that
the Fe species on pretreated FMZ is also in 6-fold coordination. From the fact that each height
of the pre-edge peak of the catalysts is higher than those of Fe$_2$(SO$_4$)$_3$ and $\alpha$-Fe$_2$O$_3$, the FeO$_6$
 octahedra of catalyst samples are supposed to be distorted.

The peaks around 3.3 Å observed in RSFs of samples could be assigned to scatterers
from Zr atoms, as shown in Table 2. The estimated interatomic distances are almost the same as
each other (3.60 ± 0.02 Å). These bond lengths are close to the Zr-Zr bonding of tetragonal
ZrO$_2$, and ZS and FMSZ. In our analysis, the estimated coordination number was ranged

- 152 -
Figure 9. Fe K-edge EXAFS spectra of catalysts: evacuated at 673 K (a), at a working state (b), and evacuated at room temperature after reaction (c).
Figure 10. Fourier transforms for $k^2$-weighted Fe K-edge EXAFS of catalysts: evacuated at 673 K (a), at a working state (b), and evacuated at room temperature after reaction (c).
from 1.1 to 4.1. However, we recognize that the estimated coordination number is not very important. Because the noise level of the higher $k$-region of many spectra is not sufficient, the reliability of the absolute value seems not to be high. The important points are the facts that contributions from Zr were observed and that the coordination number was much smaller than 12. The reason will be discussed in the following section. A lack of the second peak in RSF of FMZ of the working state is due to the low quality of its EXAFS spectrum, not really to the lack of contribution from the second neighbors.

**Discussion**

*Structure around Fe*

XRD patterns indicate that ZrO$_2$ phases of all promoted catalysts are tetragonal. The phase of sulfated zirconia calcined at 873 K is reported by many researchers as tetragonal by XRD, Raman, and EXAFS characterizations. In our analysis, the ZrO$_2$ phase of sulfate-ion-free FMZ was also tetragonal. XRD analysis suggests that iron and/or manganese atoms also affect the crystal phase of ZrO$_2$ to form the tetragonal metastable phase as well as sulfate ions. The similar effects were observed in WO$_3$-ZrO$_2$ and MoO$_3$-ZrO$_2$ systems. According to the phase diagram for Fe-Zr-O system, Fe$_2$O$_3$ forms a solid solution with ZrO$_2$ when the content of Fe oxide is up to a few mol%. In the case of FMSZ, an Fe fraction as Fe$_2$O$_3$ is 1.85 mol% for ZrO$_2$. That for FMZ is 2.08 mol%. These concentrations permit formation of a solid solution. Therefore, we conclude that Fe and Zr oxide of all the catalyst samples formed solid solution. Because the ion radius of Fe$^{3+}$ (0.67 Å) is much smaller than that of Zr$^{4+}$ (0.87 Å), the type of solid solution is supposed to be interstitial, not substitutional. If Fe$_2$O$_3$ and ZrO$_2$ formed substitutional type solid solution, Fe atom would be in 8-fold coordination and the coordination number for the Fe-Zr shell should be estimated to be 12. In fact, the Y-K edge EXAFS analysis of 3 mol% Y$_2$O$_3$-ZrO$_2$ revealed that the estimated coordination number for the Y-O and Y-Zr shells were 8 and 12, respectively. In addition, the Zr-O bond length of tetragonal ZrO$_2$ is 2.260 ± 0.208 Å, the coordination number of which is eight, and that for monoclinic ZrO$_2$ is 2.160 ± 0.085 Å, coordination number of which is seven. If the Fe atom was in 7- or 8-fold coordination, the Fe-O bond length is expected to be much longer than that of α-Fe$_2$O$_3$ of 6-fold coordination. In our analysis, however, coordination numbers for the Fe-Zr shell of all the samples were much smaller than 12, and the bond lengths for Fe-O shells were close to those for α-Fe$_2$O$_3$. These coordination numbers for Fe-Zr pairs and the bond length for Fe-O pairs support the deduction that the type of solid solution is interstitial and that Fe atoms are present inside the bulk of ZrO$_2$. Both sulfate and/or manganese ions, which are present on the surface of catalysts, did not affect the
<table>
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<th>C.N. (^a)</th>
<th>R / Å (^b)</th>
<th>(\Delta g^2 / \AA^2) (^c)</th>
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\(^a\) Coordination number.
\(^b\) Interatomic distance.
\(^c\) Debye-Waller factor.
\(^d\) Taken from ref. 28.
coordination environment around Fe. It is consistent with the fact that the local structure around Fe was not affected by the exposure to n-butane.

Formation of Solid Solution

XAFS studies of Fe-Zr-O systems have been performed by Berthet et al. and Ji et al. Berthet et al. prepared a cubic solid solution of Zr$_{0.70}$Fe$_{0.30}$O$_{1.85}$ by calcination of the coprecipitates of hydroxides. They observed two peaks around 1.4 and 3 Å in the RSF of the Fe K-edge EXAFS and assigned the second peak to the Fe-Zr shell. They reported that the coordination number and interatomic distance for the second shell were 4.1 and 3.29 Å, respectively. This bond length was much shorter than those of our results (3.60 Å). In their work, the molar fraction of Fe$_2$O$_3$ was 18 mol% which remarkably exceeds the limit of solid solution formation. At that fraction, a mixture of ZrO$_2$ solid solution and hematite solid solution will be formed, as shown in the phase diagram. Therefore, the second peak they observed around 3 Å in the RSF might not be due to Zr scatterers, but to Fe scatterers.

Ji et al. prepared Fe/ZrO$_2$ by equilibrium adsorption of Fe ions onto ZrO$_2$, in which the loading amount of Fe was 0.5 wt%, followed by calcination at 773 K. They observed the second peak in the RSF of Fe K-edge EXAFS around 2.6 Å and concluded that the second peak was due to Fe-Fe scatterers, the coordination number and interatomic distance of which were 1.1 and 3.11 Å, respectively.

In Ji’s study, the concentration of Fe is possible to form a solid solution with ZrO$_2$; however, the solid solution was not formed. The difference between our result and Ji’s study results from the preparation methods. For the support of Fe species, Li et al. used the ZrO$_2$ crystal (16 m$^2$ g$^{-1}$). In our study, iron was supported onto Zr(OH)$_4$ (391 m$^2$ g$^{-1}$) or SO$_4^{2-}$/Zr(OH)$_4$. We believe that the definitive difference is whether the support was ZrO$_2$ or Zr(OH)$_4$. In the calcination step, Fe/Zr(OH)$_4$ or Fe-SO$_4^{2-}$/Zr(OH)$_4$ had transformed to Fe/ZrO$_2$ or Fe-SO$_4^{2-}$/ZrO$_2$ with formation of solid solutions. In the case of Ji’s study, it seems to be difficult for Fe atoms to form a solid solution with the ZrO$_2$ crystal. It was supported by the results that two kinds of 7 mol% Fe$_2$O$_3$/ZrO$_2$ catalysts, which were prepared by the impregnation method onto the ZrO$_2$ crystal and the coprecipitation method, exhibit a remarkable difference in catalytic property for CO hydrogenation and reducibility of Fe atoms.

Structure of Manganese Species

We have reported that the Mn atom was supported on the surface of FMSZ as MnSO$_4$. From an ESR study, Scheithauer et al. concluded that Mn$^{2+}$ atoms were supported on MSZ and FMSZ in a highly dispersed form, although their structures remained unknown. In the present study, Mn K-edge XANES spectra revealed that the Mn species on MSZ and FMSZ are
Figure 11. Fits of Fourier-filtered EXAFS of FMSZ: pretreated (a, a'); working state (b, b'). The solid curves were obtained experimentally, and the dotted ones were the fits.
present as MnSO\(_4\). The calcination temperature of each sample was 873 K, which is lower than the decomposition temperature of MnSO\(_4\). The decomposition temperature of MnSO\(_4\) is 1123 K, while that of Fe\(_2\)(SO\(_4\))\(_3\) is 753 K.\(^{38}\) Therefore, the assumption that MnSO\(_4\) was present on the catalysts is adequate.

In contrast to the cases of FMSZ and MSZ, manganese species on FMZ were identified as \(\alpha\)-Mn\(_2\)O\(_3\). It was reported that \(\alpha\)-Mn\(_2\)O\(_3\) and \(\alpha\)-Mn\(_3\)O\(_4\) are formed by calcination of manganese salt under air at 873 and 1073 K, respectively.\(^{23}\) Because the sulfate ion was free and the calcination temperature of the precursor was 873 K, \(\alpha\)-Mn\(_2\)O\(_3\) was formed on FMZ. In addition, MnO\(_2\) polymorphism might be formed if the precursor of FMZ was calcined at lower than 773 K.

**Role of Fe and Mn Ion**

Wan et al. speculated that a high-valent iron oxy species such as the tetrahedral Fe\(^{4+}\) species have formed during calcination in air, and the site is responsible for the oxidative dehydrogenation of \(n\)-butane to produce butenes.\(^{14}\) However, our present XANES analysis indicates that the Fe atom on each catalyst sample was invariantly trivalent. Although the reacted amounts of \(n\)-butane much exceeded those of Fe atoms contained in the catalyst, it is obvious that reduction of the Fe atom did not occur during reaction. Tábaro stated that Fe atoms in FMSZ are not substituted isomorphously into bulk tetragonal ZrO\(_2\) but instead are in nanometer-size oxide clusters or rafts located on the surfaces or at defects in tetragonal ZrO\(_2\).\(^{11}\) Scheithauer et al. concluded from ESR analysis that small FeO\(_3\) particles are present in FSZ and FMSZ, with some isolated Fe\(^{3+}\) ions.\(^{13}\) In contrast to their opinions, we conclude that Fe\(^{3+}\) ions of FMSZ, FSZ and FMZ are present inside the bulk of tetragonal ZrO\(_2\) to form interstitial type solid solutions, and each Fe atom is isolated from other Fe atoms. The formation of the FeO\(_3\) particle may depend on the preparation method. As discussed above, Fe atoms of all the catalyst samples are present inside the bulk phases and do not make contact with the reactant gas. It shows that the Fe atom does not directly participate in \(n\)-butane skeletal isomerization. Nevertheless, not only FMSZ but also FSZ exhibit quite higher activity for the isomerization than SZ. We speculate that the role of Fe ions is to influence somewhat the surface energy level of SO\(_4^{2-}\)/ZrO\(_2\), although we do not have any evidence for it.

It is well-known that many metal sulfates exhibit solid acidity.\(^{39,40}\) However, these metal sulfates merely exhibit moderate acid strength, the maximum of which are \(H_0 = -3\). It is impossible to catalyze \(n\)-butane isomerization at around 300 K over these kinds of acid sites. This is supported by the result of catalysis that MSZ exhibited only activity similar to that of SZ. However, local structures around Mn on FMSZ and MSZ were affected by the presence of \(n\)-butane, as shown in XANES spectra. Therefore, it can be concluded that Mn sites on FMSZ are not active sites. Because the coordination environment around Mn was affected by the introduction of reactant gas, we propose that the role of the Mn site on Fe, Mn-SO\(_4^{2-}\)/ZrO\(_2\)
would be to accelerate transformation of reactants to active sites on SO$_4^{2-}$/ZrO$_2$. The rapid transformation of substrates results in a remarkable enhancement of the catalytic activity. The combination of two different kinds of promoters enhances remarkably the catalytic activity of SZ.

Arata et al. reported that iron oxide treated with sulfate ion exhibited solid superacidity and catalyzed $n$-butane isomerization even at 273 K.$^{2,41}$ However, in the present case of Fe, Mn-SO$_4^{2-}$/ZrO$_2$, the so-called SO$_4^{2-}$/Fe$_2$O$_3$ was not formed.

Conclusion

Fe oxide and Zr oxide forms interstitial-type solid solutions, regardless of the presence of sulfate and/or Mn ions. The local structures around Fe atoms in Fe, Mn-SO$_4^{2-}$/ZrO$_2$, Fe-SO$_4^{2-}$/ZrO$_2$ and Fe, Mn/ZrO$_2$ are quite similar to each other. Fe atoms of all the catalysts are trivalent and located at the center of oxygen octahedron. The Fe atom is present inside the bulk of ZrO$_2$, and the local structure and the valence were not influenced by $n$-butane. Mn atoms are present as MnSO$_4$ on the surface of sulfated zirconia and as $\alpha$-Mn$_2$O$_3$ on unsulfated-zirconia. Under reaction conditions, $n$-butane molecules make contact with Mn atoms and are desorbed by evacuation.

References

Appendix

Chapter 7

XAFS Study on the Structure of Ytterbium(III) Trifluoromethanesulfonates as a New Type Catalyst

Abstract

Yb L3-edge XAFS spectroscopy was applied to study on the local structures around Yb atoms in ytterbium(III) trifluoromethanesulfonates (Yb(OTf)3) catalysts. Yb(OTf)3 catalysts employed were ones dissolved in various solution and those chiral catalysts prepared by a choice of two types of achiral ligands. XAFS analyses showed the difference in the coordination number of oxygen atoms among Yb(OTf)3 catalysts dissolved in aqueous and non-aqueous solutions, suggesting the activation of the Yb(OTf)3 catalyst by the hydration. For the two Yb(OTf)3 chiral catalysts in dichloromethane, both the catalysts were found to be present as trivalent ytterbium oligomers. Curve-fitting analysis showed that the Yb-Yb distance of the two catalyst complexes is fairly different from each other, i.e., one is 3.68 Å and the other is 4.04 Å, which is expected to explain the difference of the catalytic performance of the two chiral catalysts.
**Introduction**

Lewis acid-catalyzed reactions are very important in organic syntheses. In general, this type of reaction should be performed under a strict anhydrous condition, because Lewis acid catalysts are often hydrolyzed easily. On the other hand, lanthanoid(III) trifluoromethanesulfonates (Ln(OTf)3) is stable in an aqueous solution. Kobayashi found that Ln(OTf)3 acts as a Lewis acid catalyst in aqueous media, which promote hydroxymethylation and aqueous aldol reactions of silyl enol ethers. In the lanthanoid series, Yb(OTf)3 exhibits the highest activity.1,2 Moreover, Kobayashi et al. found out that chiral catalysts prepared from Yb(OTf)3 catalyze the enantio-selective Diels-Alder reactions of some dienophiles with cyclopentadiene. These chiral catalysts afford both enantiomer of the corresponding cyclic compounds in high enantiometric excesses by using a single chiral source and a choice of achiral ligands.3-5 These unique properties are supposed to be related to the specific coordination number of Yb and the configuration of Yb(OTf)3 in the chiral catalysts.6 To understand the reason for the stability of the Yb(OTf)3 catalyst in aqueous solution, and to clarify the effect of a choice of achiral ligands on the structure of the chiral catalysts, in the present work, we applied the X-ray absorption technique for these new type Lewis acid catalysts.

**Experimental**

The preparation method of Yb(OTf)3 complex (catalyst) is described elsewhere.3 The standard chiral Yb catalyst was prepared in situ from Yb(OTf)3, (R)-(+)-binaphthol 1, MS4A and cis-1,2,6-trimethylpiperidine 2, followed by an addition of 3-acetyl-1,3-oxazolidin-2-one 3 or 3-phenylacetylacetonone 4 in CH2Cl2.3 We refer to the samples concluding the former and the latter additives as chiral catalyst A and chiral catalyst B, respectively, hereinafter. The Yb content in each catalyst was ca. 20 mmol/L. For measurements of the X-ray absorption spectrum, each the catalyst was sealed in a polyethylene bag under N2 atmosphere.
X-ray absorption experiments were carried out at BL-7C station at Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF) with a ring energy of 2.5 GeV and stored current of 250 - 350 mA. XAFS data of the samples were obtained at room temperature with a Si(111) two-crystal monochromator. Yb L3-edge spectra of the catalyst samples and solid reference samples were measured in fluorescence and transmission modes, respectively. The curve-fitting analysis was performed for the Fourier-filtered EXAFS with the empirical parameters (the amplitudes and the phase shifts for Yb-O and Yb-Yb shells) extracted from EXAFS of c-type Yb2O3 by a least-squares method.

Results and Discussion

The Effect of the Kind of Solvent on the Local Structure around Yb Ions in Yb(OTf)3 Catalyst

Figure 1a shows Yb L3-edge XANES spectra of Yb(OTf)3 solid catalyst (Yb(OTf)3·xH2O) and the Yb(OTf)3 catalysts dissolved in water, THF(tetrahydrofuran) and ethanol. Each XANES spectrum shows a similar single sharp white line at ca. 8946 eV, although white lines for Yb(OTf)3 catalysts dissolved in these solutions appear at slightly lower energy position than that of Yb(OTf)3·xH2O solid sample. Since the energy position of the white line is characteristic for Yb3+, reported by some workers,7-9 we can attribute the white line to 2p - 5d electron transitions of Yb3+. This result indicates that Yb ions in the Yb(OTf)3 catalysts are trivalent states regardless of the kind of the solvent. The features of the XANES spectra for the Yb(OTf)3 catalysts in the solutions are fundamentally similar to each other, which is in contrast with the case of the YbCl3 catalyst where the catalyst reacts with water molecule to be hydrolyzed easily (Figure 1b). This result may demonstrate the stability of the Yb(OTf)3 catalyst in water. A detailed comparison of the XANES spectra lead us to notice that the intensity of the white line for the Yb(OTf)3 catalyst dissolved in water is slightly higher than those for the catalyst in non-aqueous solution such as THF or ethanol. Therefore, the kind of the solution would have a little influence on the local structure of the Yb(OTf)3 catalyst.

Figure 2 shows radial structure functions (RSFs) of Yb(OTf)3 catalysts dissolved in various solution which were obtained by Fourier-transformation on k^2-weighted Yb L3-edge EXAFS spectra in 3.0 - 13.0 Å⁻¹ region. Although the pattern of RSFs of these samples is almost similar to each other, the peak around 2 Å attributed to Yb-O bond is slightly higher for the catalyst dissolved in water compared with that in non-aqueous solution. As also indicated by the curve-fitting results (Table 1), the estimated coordination number of the neighboring oxygen is larger for Yb(OTf)3 catalyst in water than that for the catalysts in non-aqueous solutions (water (10.5) > THF (9.4) > ethanol (8.8)). This relation for the coordination number probably correlates with that for the intensity of the white line appeared in XANES (water > THF > ethanol). Taking into account that the reaction rate for some aldol reactions by the
Figure 1. Yb L3-edge normalized XANES spectra of (a) Yb(OTf)3 and (b) YbCl3.
Figure 2. FT of $k^2$-weighted Yb L$_3$-edge EXAFS spectra of Yb(OTf)$_3$. 
Yb(OTf)3 catalyst in water is much faster than that in non-aqueous solution, a hydration of the Yb(OTf)3 catalyst (the coordination of H2O molecules to Yb ions) may activate the catalyst.

In supplement, lanthanoid trifluoromethanesulfonate crystal [Ln(H2O)9](CF3SO3)3 possesses two different kind of Ln-O distances in the coordination polyhedron. The two inter-atomic Yb-O distances of Yb(OTf)3 crystal are expected to 2.310 Å for the three pairs, and to 2.508 Å for the residual six. However, the result of curve-fitting analysis for Yb(OTf)3 solid exhibited single Yb-O shell with 2.33 Å of the inter-atomic distance, which is very close to the bond length for Yb(ClO4)3 aqueous solution (2.317 Å). Because XAFS spectrum measurement for Yb(OTf)3 solid was performed under exposure of air, moisture might change the coordination environment to aquo complex-like structure. As a result, differences in the XANES spectra of Yb(OTf)3 among solid form and each the solvents were relatively little, comparing with cases for YbCl3.

**TABLE 1. Results of Curve-fitting Analyses**

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<th>Solvent</th>
<th>Shell</th>
<th>CN</th>
<th>R/Å</th>
<th>Δσ2  b/Å2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(OTf)3 (solid)</td>
<td>Yb-O</td>
<td>8.7</td>
<td>2.33</td>
<td>0.00079</td>
</tr>
<tr>
<td>H2O</td>
<td>Yb-O</td>
<td>10.5</td>
<td>2.33</td>
<td>0.00176</td>
</tr>
<tr>
<td>THF</td>
<td>Yb-O</td>
<td>9.4</td>
<td>2.33</td>
<td>0.00147</td>
</tr>
<tr>
<td>EtOH</td>
<td>Yb-O</td>
<td>8.8</td>
<td>2.34</td>
<td>0.00070</td>
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<tr>
<td>chiral cat. A</td>
<td>CH2Cl2</td>
<td>Yb-Yb</td>
<td>2.4</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yb-O</td>
<td>7.6</td>
<td>2.33</td>
</tr>
<tr>
<td>chiral cat. B</td>
<td>CH2Cl2</td>
<td>Yb-Yb</td>
<td>3.3</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yb-O</td>
<td>9.5</td>
<td>2.32</td>
</tr>
<tr>
<td>Yb2O3(c) (solid)</td>
<td>Yb-O</td>
<td>6.0</td>
<td>2.26</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>Yb-Yb</td>
<td>12.0</td>
<td>3.69</td>
<td>0.00000</td>
</tr>
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</table>

a The errors in CN(coordination number) and R (interatomic distance) are ± 10% and ± 0.02 Å, respectively.
b Δσ2 is the difference between the Debye-Waller factors of the sample and the reference sample Yb2O3.
c Yb-O and Yb-Yb shells were extracted from EXAFS of Yb2O3.
Figure 3. Yb L₃-edge normalized XANES spectra of a) Yb(OTf)₃·xH₂O, b) chiral cat. A and c) chiral cat. B.
Figure 4. FT of $k^2$-weighted Yb L3-edge EXAFS of a) Yb(OTf)3·xH2O, b) chiral cat. A and c) chiral cat. B.
The Structural Analysis of Yb Chiral Catalysts

Figure 3 shows Yb L3-edge XANES spectra of Yb(OTf)3 solid catalyst, chiral catalyst A and chiral catalyst B. Each XANES spectrum showed a single sharp white line at the same energy position around 8946 eV, indicating that Yb ions in both chiral catalysts are also in a trivalent state in a similar manner as Yb(OTf)3 solid catalyst. However, for the intensity of the white line, that of chiral catalyst A reduces compared with that for chiral catalyst B, suggesting that the surroundings around Yb atoms are different in these two chiral catalysts.

To elucidate the difference in the local structure around Yb atoms, $k^3$-weighted Yb L3-edge EXAFS spectra of these samples were measured. The characteristics of the EXAFS spectra for the two chiral catalysts became clearer when Fourier-transformation was performed on the EXAFS in 3.0 - 13.0 Å⁻¹ region to obtain their RSFs. In RSFs of both chiral catalysts (Figure 4), small but distinct peaks around 3 - 4 Å can be seen. The peaks were attributed to the neighboring Yb atoms, coordination numbers of which were evaluated to be ca. 2 - 3 by the curve-fitting analyses (Table 1). These results should reflect that both Yb chiral catalysts exist as dimer or trimer complexes in dichloromethane solution. As for the difference in the local structure of these chiral catalysts, coordination numbers of neighboring oxygen (Yb-O) and ytterbium (Yb-Yb) for chiral catalyst A are estimated at slightly lower compared with those for chiral catalyst B. On the other hand, the difference in the interatomic distance of Yb-Yb, i.e., 3.68 Å for chiral catalyst A and 4.04 Å for chiral catalyst B is obvious. A choice of achiral ligands should mainly affect the distance of Yb-Yb in a chiral catalyst and control the selectivity of enantiomer of the corresponding cyclic compounds in the Diels-Alder reactions.

References

Summary

The author has investigated catalysis by new solid acid catalysts, and their chemical and physical properties. In Part I, the acidic property of siliceous FSM-16 was described. In Part II, acidic properties of silica-supported rare earth oxides were described and discussed by their detailed structural characterizations. In Part III, the characterization of iron- and manganese-promoted sulfated zirconia (Fe-Mn-SO42-/ZrO2) was described to clarify the role and structure of the promoters. The main results are summarized as follows.

In Chapter 1, the existence of acid sites on siliceous FSM-16 was proposed. The acidic property was characterized with acid-catalyzed reactions, a pyridine-adsorption experiment, IR spectroscopy and H2O desorption experiment. The maximum acid strength was estimated with Hammet indicators. Siliceous FSM-16 catalyzes but-1-ene isomerization at 323 K and α-pinene isomerization at 303 K, selectivities of which indicate that both the reactions are catalyzed over acid sites. Catalytic activity varied with heat treatment, and reached a maximum at 673 K. Maximum acid strength was invariably -5.6 < H0 ≤ -3.0, independent of pretreatment temperatures. Both Brønsted and Lewis acid sites are confirmed on FSM-16 from IR spectra of adsorbed pyridine. Only Lewis acid sites were confirmed on FSM-16 pretreated at 1073 K, which scarcely catalyzes both the reactions. The H2O desorption experiments and IR characterization of silanol groups gave a conclusion that the active sites on FSM-16 for olefin isomerizations are weakly perturbed silanol groups which act as Brønsted acid. When FSM-16 was pretreated at a temperature below 673 K, significant amounts of H2O cover the active sites. If FSM-16 was pretreated higher temperature than 673 K, the active silanol groups are dehydroxylatively eliminated, resulting in a deactivation. The activity was much reduced by calcination at higher temperatures, but restored by water treatment at 353 K as long as FSM-16 retained its structure.

In Chapter 2, formation of Lewis acid sites was confirmed on FSM-16 by high-temperature treatment. The Lewis acid sites on FSM-16 were characterized with pyridine-TPD experiments and a Lewis-acid catalyzed reaction of methylamine synthesis. The structural stability of FSM-16 and/or the transformation upon thermal treatment were investigated with IR and nitrogen adsorption-desorption experiments. The pyridine TPD characterization revealed that new acid sites form on FSM-16 with increasing pretreatment temperatures. It was shown that the temperature of pyridine-adsorption process remarkably influences the desorption profiles. IR characterization demonstrated that surface silanol groups on FSM-16 was dehydroxylatively condensed to form highly strained siloxane bridges, which act as Lewis acids. The Lewis acid sites formed on FSM-16 catalyze methylamine synthesis, and the initial rates is enhanced with increasing pretreatment temperatures up to 1273 K. The structure of
FSM-16 completely retained throughout a pretreatment at 1273 K as well as a reaction for methylamine synthesis at 673 K.

Acidic property of siliceous mesoporous silica described in Part I was discovered by the author. Both Lewis and Brønsted acid sites on FSM-16 exhibit mild acid strength of \(-5.6 < H_0 \leq -3.0\). When FSM-16 was pretreated at 673 K, activity of Brønsted acid-catalyzed reactions were exhibited the highest. On the other hand, the activity of Lewis acid-catalyzed reactions were enhanced at higher pretreatment temperature than 873 K. The regularly ordered mesopore of FSM-16 with medium acid strength opens the possibility that FSM-16 is promising for the application to synthetic processes of fine-chemicals.

Chapter 3 dealt with silica-supported ytterbium oxide catalysts (Yb/SiO\(_2\)), loading amounts of which ranged from 25 \(\mu\)mol - 8.4 mmol g(SiO\(_2\))\(^{-1}\). Various loading amounts of ytterbium oxides supported on silica catalyzed \(\alpha\)-pinene isomerization at 323 K. The main products were limonene and camphene, the selectivities to which were 67 and 20\%, respectively. The catalytic activity depended on a loading amount and pretreatment temperature, and reached the highest when the loading amount and pretreatment temperature were 3.4 mmol g(SiO\(_2\))\(^{-1}\) and 1073 K, respectively. On the other hand, the selectivity was independent of the loading amount and pretreatment temperature. Structural characterizations revealed that each ytterbium atom is widely spread over silica as a YbO\(_6\) octahedron which connects with SiO\(_4\) tetrahedra with forming Yb-O-Si linkage. The acid strength and catalytic activity per one active site are independent on loading amount. When loading amount of Yb exceeded the amount where YbO\(_6\) unit can form monolayer on SiO\(_2\), the apparent turn over frequency decreased.

In Chapter 4, local structure around Yb on Yb/SiO\(_2\) catalysts was analyzed by X-ray absorption spectroscopy, in comparison with four kinds of crystalline ytterbium oxides. XANES and EXAFS spectra of all the Yb/SiO\(_2\) catalysts were identical to each other, regardless of the loading amount and various procedures of treatment. It was concluded that amorphous Yb-O-Si species of the active sites had formed in a sample preparation step. The first coordination sphere around Yb was quite similar to those for Yb\(_2\)O\(_3\) and all the Yb/SiO\(_2\) catalysts. On the other hand, the second derivatives of Yb-L\(_{III}\) edge XANES spectra for all the Yb/SiO\(_2\) showed that the XANES is comprised of a single peak, while that for Yb\(_2\)O\(_3\) is double peaks. Referring to the XANES spectra of YbNbO\(_4\), YbPO\(_4\) and Yb\(_3\)Al\(_5\)O\(_{12}\), the coordination environment around Yb species on SiO\(_2\) was supposed to be highly symmetric.

Chapter 5 dealt with various kinds of rare earth elements (Ln/SiO\(_2\); Ln = La, Ce, Pr, Sm, Eu, Tb, Yb and Y) to elucidate a general feature of rare earth supported on silica. The loading amount of each catalyst was adjusted to be 3.4 mmol Ln g(support)\(^{-1}\). The reason for decrease of catalytic activity of Yb/SiO\(_2\), resulting from excess loading and high temperature-treatment, was clarified by Raman spectroscopy. In the series of lanthanide, the activity for \(\alpha\)-pinene isomerization increases monotonously with the atomic number from 57La through 70Yb, except 58Ce. Although the catalytic activity over each Ln/SiO\(_2\) catalyst was significantly
varied with the lanthanide elements, the selectivity of each the catalyst was almost the same. Although cerium was present as crystallites on silica, the other rare earth elements were supported on silica in an amorphous state. From XAFS characterizations, it was concluded that the acidity of Ln-O-Si linkage is independent of the lanthanide species, and only the number of Ln-O-Si species affects the activity. The affinity of LnOₙ unit to SiO₄ tetrahedra depends on the size of Ln³⁺, and influenced the number of Ln-O-Si linkages. Y/SiO₂ catalyst, (the ion radius of Y³⁺ is similar to that of Yb³⁺), exhibited the same activity and EXAFS spectrum as Yb/SiO₂ catalyst. In the Raman spectrum of 3.4 mmol Yb/SiO₂ catalyst pretreated below 1073 K, no bands other than the typical ones to amorphous SiO₂ were detected, whereas many bands were observed on that pretreated at 1273 K. In a case of 8.4 mmol Yb/SiO₂ catalyst, a weak band assigned to Yb₂O₃ crystal was confirmed, in addition to that for silica gel. Excess Yb atoms loaded on SiO₂ block the active Yb-O-Si linkage by forming inactive Yb₂O₃ fine crystallites. The thermal treatment of Yb/SiO₂ catalyst at 1273 K changes the active amorphous Yb-O-Si structure to inactive ytterbium silicate crystallite.

Followings are conclusions of Part II. Each rare earth element is easily spread on SiO₂ to form amorphous Ln-O-Si and/or Ln-O-Ln linkages. The maximum acid strengths and the structure of active sites were independent of the kind of rare earth elements. The differences in catalytic activity among the elements are due to the ion radii of Ln³⁺, which relates to the number of Ln-O-Si units on the surface of each catalyst. The geometry and electric configuration of each supported rare earth oxide are quite different from that of the rare earth oxide crystal itself.

In Chapter 6, in situ XAFS, XRD and Raman techniques were applied to the characterization of Fe-Mn-SO₄²⁻/ZrO₂, Fe-SO₄²⁻/ZrO₂, Mn-SO₄²⁻/ZrO₂, Fe-Mn/ZrO₂ and ZrO₂ catalyst samples. The in situ XANES spectra at Fe-K edge of Fe-Mn-SO₄²⁻/ZrO₂ did not change throughout n-butane isomerization, while those at Mn-K edge were reversibly affected by introduction of reaction gas. According to the XRD and Raman results, it was concluded that Fe³⁺ ions in Fe-Mn-SO₄²⁻/ZrO₂ are present inside the ZrO₂ as an interstitial ions and the ions do not directly participate in the super acidic reaction. The redox of iron ions in the catalyst, which has been speculated by other research groups, does not take place throughout the reaction. Even in the absence of sulfate and/or manganese ions, iron and zirconium oxide form interstitial-type solid solution as well, and the local structure around iron is quite similar to each other and to Fe-Mn-SO₄²⁻/ZrO₂. Mn ions are present on the surface as MnSO₄, and are the sites of adsorption of reactant gas molecules. Without sulfate ions, manganese species is present as Mn₂O₃.
List of Publications

Part I

Chapter 1.
1 Acidic Property of FSM-16
Takashi Yamamoto, Tsunehiro Tanaka, Takuzo Funabiki, Satohiro Yoshida

Chapter 2.
2 Acidic Property of FSM-16 (2): Generation of Lewis Acid Sites and Catalysis
Takashi Yamamoto, Tsunehiro Tanaka, Shinji Inagaki, Takuzo Funabiki, Satohiro Yoshida

Part II

Chapter 3.
3 Silica-Supported Ytterbium Oxide Characterized by Spectroscopic Methods and Acid-Catalyzed Reactions
Takashi Yamamoto, Takahiro Matsuyama, Tsunehiro Tanaka, Takuzo Funabiki, Satohiro Yoshida

Chapter 4.
4 XAFS Study of the Structure of Silica-Supported Ytterbium Oxide Catalyst
Takashi Yamamoto, Tsunehiro Tanaka, Takahiro Matsuyama, Takuzo Funabiki, Satohiro Yoshida
*Solid State Communications*, **1999**, *111*, 137-142.

Chapter 5.
5 Generation of Acid Sites on Silica-Supported Rare Earth Oxide Catalysts: Structural Characterization and Catalysis for α-Pinene Isomerization
Takashi Yamamoto, Takahiro Matsuyama, Tsunehiro Tanaka, Takuzo Funabiki, Satohiro Yoshida
*Physical Chemistry Chemical Physics*, **1999**, *1*, 2841-2849.
Part III

Chapter 6.

6 XAFS Study of Fe- and Mn- Promoted Sulfated Zirconia
Takashi Yamamoto, Tsunehiro Tanaka, Sakae Takenaka, Satohiro Yoshida, Tsutomu Onari, Yoshiaki Takahashi, Tomomi Kosaka, Sadao Hasegawa

7 Structural Analysis of Iron and Manganese Species in Iron- and Manganese- Promoted Sulfated Zirconia
Takashi Yamamoto, Tsunehiro Tanaka, Sakae Takenaka, Satohiro Yoshida, Tsutomu Onari, Yoshiaki Takahashi, Tomomi Kosaka, Sadao Hasegawa, Masataka Kudo

Appendix

Chapter 7.

8 XAFS Study of Ytterbium Complexes as New Type Lewis Acid Catalysts
Tomoko Yoshida, Tsunehiro Tanaka, Takashi Yamamoto, Satohiro Yoshida, Haruro Ishitani, Shu Kobayashi

9 XAFS Study on the Structure of Ytterbium(III) Trifluoromethanesulfonates as a New Type Catalyst
Tomoko Yoshida, Tsunehiro Tanaka, Takashi Yamamoto, Satohiro Yoshida, Haruro Ishitani, Shu Kobayashi
The following papers are not included in this thesis.

10 Ship-in-Bottle Synthesis of $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ Encapsulated in Ordered Hexagonal Mesoporous Channels of FSM-16 and Their Effective Catalysis in Water-Gas Shift Reaction
Takashi Yamamoto, Takafumi Shido, Shinji Inagaki, Yoshiaki Fukushima, Masaru Ichikawa

11 Ship-in-Bottle Synthesis of Pt and Ru Carbonyl Clusters in NaY Zeolite Micropore and Ordered Mesoporous Channels of FSM-16; XAFS/FTIR/TPD Characterization and Their Catalytic Behaviors
Masaru Ichikawa, Takashi Yamamoto, Wei Pan, Takafumi Shido

12 XAFS Characterization of Platinum Carbonyl Clusters Synthesized in the Channel of Mesoporous Zeolite
Takafumi Shido, Takashi Yamamoto, Masafumi Harada, Masaru Ichikawa

13 A Robust Platinum Carbonyl Cluster Anion $[\text{Pt}_3(\text{CO})_6]^{5-}$ Encapsulated in an Ordered Mesoporous Channel of FSM-16: FTIR/EXAFS/TEM Characterization and Catalytic Performance in the Hydrogenation of Ethene and 1, 3-Butadiene
Takashi Yamamoto, Takafumi Shido, Shinji Inagaki, Yoshiaki Fukushima, Masaru Ichikawa

14 Performance of the YB66 Soft-X-ray Monochromator Crystal at the Wiggler Beamline of the UVSOR Facility
15 Templating Fabrication of Platinum Nanoparticles and Nanowires Using the Confined Mesoporous Channels of FSM-16 - Their Structural Characterization and Catalytic Performances in Water Gas Shift Reaction
Makoto Sasaki, Mai Osada, Naonori Higashimoto, Takashi Yamamoto, Atsushi Fukuoka, Masaru Ichikawa

16 The XAFS Beamline BL01B1 at SPring-8

17 Application of XANES Spectra to Supported Catalysts
Tsunehiro Tanaka, Takashi Yamamoto, Yoshiumi Kohno, Tomoko Yoshida, Satohiro Yoshida

Reviews

1 Present Status of SPring-8 (Japanese)
Tsunehiro Tanaka, Takashi Yamamoto