

THE KODAMA LABORATORY

Head: Prof. Dr. Shinjiro Kodama

This laboratory came into existence primarily as a section which was mainly engaged in research of Fischer-Tropsch gasoline synthesis in the Kita Laboratory (Head: Prof. Dr. Gen-itsu Kita). Immediately after the retirement of Prof. Kita in March 1943, the section was newly organized into an independent laboratory under the direction of Prof. Kodama.

The following summaries include, therefore, some of the achievements made or begun at the Kita Laboratory.

I. Research of Synthesis of Gasoline from Carbon Monoxide and Hydrogen

1. Synthesis of Hydrocarbons, Especially with Iron Catalysts under Ordinary Pressure

By G. Kita, S. Kodama, S. Tsuneoka, W. Funasaka, S. Yuasa and others

In this laboratory various investigations were carried out on catalysts and reaction conditions for synthesis of petroleum hydrocarbons from CO and H₂ under the ordinary pressure in a wider scope, and a number of notable results were obtained.

Iron catalysts had been generally regarded as inadequate for industrial use owing to their inferior activity until our research began, but through efforts of the above mentioned persons some iron catalysts was discovered whose activity was comparable to that of the cobalt catalysts.

In October 1937 it was found that the iron catalysts which was prepared by precipitation from nitrate together with copper on kieselgur and contained appropriate alkali had high activity.

Further addition of promoters such as boron compounds, especially boric acid, besides manganese, magnesia and alumina, was found to be highly effective. Namely, with Fe+10~25% Cu+2~5% Mn+100~150% kieselgur+10~20% H₃BO₃+3~4% K₂CO₃ catalysts 130~150 cc/m³ oil was obtained from raw gas of CO:H₂=1:1 at 240~250°C and 90~100 cc/m³ from the raw gas of 1:2 at 240~250°C.

The durability of the iron catalysts was extremely inferior when raw gas of CO:H₂=1:1 was used, but it was improved definitely by using raw gas rich in hydrogen and also by lowering the reaction temperature suitably. These results obtained on the iron catalysts were published in 24 reports for the J. Soc. Chem. Ind., Japan, 1939-1951.

On the other hand, in 1937 a pilot plant was constructed to obtain necessary information for the design of a plant on an industrial scale for synthesis with iron catalysts. At first a small plant (treating 100 l/hr gas) with a inner-catalyst-type reactor, provided with a cooling device by hot oil circulation, was erected and operated, and subsequently the scale of the plant was gradually enlarged, and at the same time various types of the reactor were tested.

In July 1940, a plant dealing with 100 m³ raw gas per hour with an outer-catalyst-type reactor, which was cooled with hot water circulation, was constructed, and continuous runs with CO+10 % Cu+5 % ThO₂+2.5 % U₃O₈+125 % kieselgur catalyst were carried out with gas of CO:H₂=1:2 in which average effective gas content was 84.5 % at 202-211°C for 18 days, and 2288 litres of oil were obtained from 26729 m³ gas. This yield corresponds to 102 cc per 1 m³ of effective gas or 139 cc/m³ for consumed gas, and coincides with the results obtained in laboratory scale experiments.

Also, with the same plant the continuous with Fe+12.5~25% Cu+2% Mn+123 % kieselgur+20 % H₃BO₃+4 % K₂CO₃ catalysts were carried out with gas of CO:H₂=1:2 (average effective gas content 87.2 %) at 235-238°C for a month, and 56255 m³ of gas yielded 4203 litres of oil (the oil yield corresponds to 86 and 180 cc per 1 m³ of effective gas and of consumed gas respectively).

During these experiments decrease in the activity of catalyst was small, and so it was ascertained that by the circulation of excess hydrogen the Fe-catalyst could be used industrially.

The results of semi-industrial experiments were published in form of ten reports in the Bulletin of the Institute for Chemical Research during 1938-1941.

2. Synthesis under Medium Pressures

By G. Kita, S. Kodama and S. Tahara

On this subject eleven papers were published in the J. Soc. Chem. Ind., Japan, 1942-1948.

Advantages of the medium pressure (10~20 atm) synthesis are: (1) remarkable improvement in the durability of catalyst; (2) increase of H₂ consumption in comparison with that of CO, which results in the more effective conversion of raw gas and the better yield in products; (3) lowering of reaction temperature under 210°C (under normal pressure more than 230°C is required).

Besides, the following results were found.

- (1) The optimum pressure is 15 atm.
- (2) As promoter Cu (ca. 20 %) and some K₂CO₃ must be added, and the amount of potassium carbonate must be increased as the reaction pressure rises.
- (3) Particularly effective promoter other than potassium carbonate is not found, but magnesia has some good effect; as a carrier the use of kieselgur (125 %) is suitable.
- (4) The better yield is attained when the catalyst is reduced, before use, under the normal pressure and higher temperature with raw gas.

In the best condition, the catalyst of the composition Fe+25 % Cu+125 % kieselgur+6% K₂CO₃ can yield 119 g./m³ raw gas) of products under 15 atm and 210°C.

3. Synthesis of Gaseous Hydrocarbons

By S. Kodama and K. Tarama

The synthesis of gaseous hydrocarbons except CH₄, the so-called "gasol", from CO and H₂ were investigated from 1940 to 1944 in order to produce raw materials.

for the synthesis of high grade aviation fuel.

At first, under atmospheric pressure the effects of the reaction temperature and the flow rate of gas were studied with the catalyst (Fe+25% Cu+2% Mn+125% kieselgnr+20% H₃EO₃+3% K₂CO₃), and the yield of gasol could be increased without increasing the methane formation by elevating the reaction temperature and increasing the flow rate more than in the case of gasoline synthesis.

Actions of the promoters (Cu, Mn, K₂CO₃, H₃EO₃, etc.) and of the carriers (kieselgur, acid clay etc.) on the Fe-catalyst were precisely investigated, and it was made clear that the mean molecular weight of products was increased by addition of K₂CO₃ or of Cu, but was decreased by adding H₃EO₃ or Mn, and the above results obtained under atmospheric pressure could be satisfactorily explained by the mechanism of the synthetic reaction which will be described later.

Subsequently, synthesis under the pressure from 5 to 40 kg/cm² was investigated and the following results were obtained.

Under high pressure the durability and the reactivity of catalysts are remarkably improved. The most suitable conditions for gasol synthesis are 15-20 kg/cm² and 270-320°C. The maximum yield in gasol (37.5l/m³) was realized under the condition of 15 kg/cm² and 280°C with the catalyst (Fe+25% Cu+125% acid clay+3% K₂CO₃).

As, in these condition of our gaseous hydrocarbon synthesis a fairly good quantity of oil are also formed besides gasol, this process can also be regarded as a process of gasoline synthesis from CO and H₂.

Fifteen papers were reported for the J. Soc. Chem. Ind., 1941-1945.

4. Removal of Organic Sulfur from Raw Gas and Other Industrial Gases

By W. Funasaka

Under Fischer-Tropsch's gasoline synthesis it is required to refine sulfur in raw gas down to 0.2 g/100 m³. Though removal of inorganic sulfur is relatively easy, it is almost impossible to remove organic sulfur by ordinary methods such as adsorption, extraction and washing, then the catalytic conversion or fixation of organic sulfur at a comparatively high temperature becomes necessary.

Many experiments were carried out, with several kinds of gases containing various kinds and quantities of organic sulfur on different catalyst or fixing materials, and the following results were obtained.

(1) Ni, Pb, Sn, Cr, Al and Mg convert organic sulfur in some extent into H₂S, while Fe, Cu and Mn fix them chemically almost quantitatively.

(2) Organic sulfur in water gas chiefly consists of thiocarbonyl, and can be easily removed until the required content is gained (0.2 g/100 m³) by fixing action of Japanese yellow ocher or goethit at 250°C and with the space velocity 400. On the other hand this is converted into H₂S by Al or Sn.

(3) CS₂ in hydrogen, water gas or natural gas can be easily removed, but complete removal is difficult.

(4) Thiophene in hydrogen, water gas or natural gas can be removed almost completely, especially by Ni or Cu to a satisfactory extent.

(5) Precise purification of town gas is very difficult owing to the presence of heavy hydrocarbon gases.

(6) Acidic gases such as CO_2 and HCN promote the action of catalysts to convert the organic substance into H_2S at high temperatures.

(7) Natural gas can be refined highly by Fe, Cu, Mn, Al or Mg catalysts.

(8) H_2S is fixed on Fe, Cu or Mn even at higher temperatures, and can be removed over 90% from gases.

These results were reported in three papers for the J. Soc. Chem. Ind. Japan (1947).

5. Physico-chemical Studies on the Mechanism of Synthetic Process

By S. Kodama, S. Matsumura and H. Kadota

Activated adsorption of H_2 , CO , H_2O and CO_2 on the various catalysts containing CO and Fe were studied. On the basis of these studies the following mechanism for hydrocarbon synthesis was proposed.

At first CO reacts with metals in the catalyst forming carbide.

The carbide thus formed is reduced to CH_2 radical by the action of the atomic hydrogen which is present on the catalyst as the result of the activated adsorption of H_2 .

The CH_2 radicals suffer polymerization and reduction, and hydrocarbons are formed in the adsorbed state on the catalyst, and afterwards they evaporate. These changes, polymerization, reduction and evaporation, proceed sustaining a kind of equilibrium, and hydrocarbons of various molecular sizes are formed.

With this mechanism a number of fundamental facts concerning hydrocarbon synthesis can be satisfactorily explained as follows:

1. The fact, that the lowest temperature at which the hydrocarbon formation begins with the cobalt catalyst is 160°C , is attributed to the fact that at this temperature the concentration of atomic hydrogen on the catalyst reaches just to the sufficient amount.
2. The fact that the reaction temperature of the Fe catalyst is higher than that of Co catalyst is due to the fact that the temperature of Fe carbide formation is higher.
3. As the desorption velocity of H_2O is higher on the Co catalyst, while that of CO_2 is higher on the Fe catalyst, H_2O is formed with Co catalyst and CO_2 with Fe catalyst.
4. Kieselgur has action to increase largely the number of the activation center for both hydrogen adsorption and carbide formation, which is regarded as the cause kieselgur is a effective carrier.
5. Addition of ThO_2 results not only in lowering H_2 adsorption temperature but also in increasing the adsorption amount itself, so that ThO_2 is a very efficient promoter for Co catalyst.
6. Action of K_2CO_3 to increase unsaturation and mean molecular weight of products is explained by the fact that K_2CO_3 depresses adsorption of H_2O and promotes carbide formation.
7. H_3BO_3 reveals the exactly opposite behaviours.

Besides, pursuing the change of Fe catalyst in the course of hydrocarbon

synthesis by X-ray diffraction method, it was found that Fe in the catalyst was gradually converted to iron percarbide, and this result was confirmed also by chemical analysis.

II. Studies on the Synthesis of 2-3-Dimethylbutane

By S. Kodama, K. Tarama, T. Ishibashi and T. Kubota

Synthesis of 2-3-di-methylbutane from C_2H_4 and $i-C_4H_{10}$ with $AlCl_3$ -catalyst was investigated. By the flow method under the pressure 1-10 atm, $40^\circ C$, the mixing ratio of $i-C_4H_{10}/C_2H_4$ 4 and the contact time 30 sec, 134.3cc/(mol C_2H_4) of liquid hydrocarbon containing ca. 50% of 2-3-di-me-butane was obtained. (J. Ind. Chem. Soc. Japan (1946)).

III. Studies on a Systematic Method for Gasoline Analysis

By W. Funasaka

The following method was proposed as adequate for the analysis of olefine rich gasoline and also adequate even for a comparatively small amount.

(1) Olefine content is calculated from iodine value determined by the Cortese B method or the Hanus method, and the value of average molecular weight is determined from the freezing point depression.

(2) Aromatic content is determined by the Kattwinkel's method from the sample whose olefines have been selectively hydrogenated with Pd catalyst.

(3) Naphthene content is calculated from the aniline point depression of hydrogenated aromatic free sample (1% naphthene corresponds to the depression of $0.325^\circ C$).

(4) Paraffine content is calculated as difference.

(5) Iso-Paraffine content may be roughly estimated by the antimony pentachloride method. (J. Fuel. Soc. Japan, 28, 180 (1949)).

IV. Catalytic Cracking of Hydrocarbon Oils

By W. Funasaka

Some hydrocarbons (Cetane, Cetene, Heptane and Heptene fraction of synthetic gasoline) were decomposed on alumina-gel or silica-gel at $450, 500$ and $550^\circ C$ and liquid space velocity 2-3, and the main actions of alumina-gel were found to consist of dehydrogenation and aromatization; on the other hand those of silicagel mainly consist of C-C linkage splitting. (J. Soc. Chem. Ind. Japan, 47, 160 (1947)).

V. Studies on Coal Chemistry

1. Conversion of Low Temperature Tar into Fuel Oil

By W. Funasaka, C. Yokokawa and S. Suga

Separation of tar acids from low temperature tar and its conversion into neutral oil were studied.

(1) Separation of tar acids.

The selective extraction of tar acids was tried with methanol-water mixture. For the middle boiling tar (B. P. 266-300°C, acid content about 40%), the use of 80% methanol at ordinary temperature was found to be most suitable, and refined neutral tar contained 3% acids, while the purity of extracted acids was 89%.

(2) Conversion of tar acids.

Low-temperature tar, tar acids and phenol were destructively hydrogenated under atmospheric hydrogen stream at 450-500°C with various metallic catalysts. Mo or Fe-catalysts were very active, and the oil obtained scarcely contained acids. Action of Fe-catalysts was so vigorous that only 20-30% oil was obtained. FeOOH-keselgur, Fe-Cr-kies., Fe-Ni-kies. and Japanese yellow ochre catalysts were examined, and Japanese yellow ochre was found most adequate.

For example, phenol was reduced into pure benzene (68.4% of theoretical), and middle boiling tar (as mentioned above, average molecular weight 243.2) was converted into fuel oil (B. P. 110-307°C, acid content 8%, average molecular weight 130, 85% yield) at 480°C with Japanese yellow ochre.

Moreover, synthetic phenetol was treated in the same way (on Mo-catalyst), and the mechanism of these reactions was discussed. (J. Soc. Chem. Ind. Japan, **51**, 26 (1948), **52**, 26 (1949)).

2. Caking Property of Coal

By W. Funasaka, C. Yokokawa and S. Suga

Relations between some properties (moisture content, permanganate number and specific surface area) of Japanese coals and their rank or range were investigated; and studying the caking phenomena in the heating process of coal caking property was quantitatively demonstrated.

(1) When the equilibrium moisture content for sixty kinds of coal was determined, the hystereses were observed except anthracite; the width of hysteresis loop varied considerably in accordance with the rank of coals. Both the equilibrium moisture content at 78% humidity and the specific surface area calculated from the amount of iodine adsorption were found to have relations with the rank, and to remain below certain values in the caking coals. The internal area showed the minimum value in the case of the coals of fuel ratio 2.0, and it increased in both low rank and anthracite range coals. Relations between permanganate number and rank of coal were similar to the above-mentioned relations.

(2) Various characteristic temperatures such as temperature of maximum gas evolution rate and softening or swelling temperature, and degrees of softening and swelling were determined by the modified K. B. S apparatus. These characteristic temperatures were seen to rise according to the increase of the rank almost in a linear relation. The maximum in the degree of softening and swelling was found at the coals whose fuel ratio were nearly 1.0. (Bull. Inst. Chem. Res., Kyoto Univ., **24**, 83 (1951)).

3. On the formation of coal

By **W. Funasaka** and **C. Yokokawa**

Cellulose, or other carbohydrates, lignin and other substances, considered to have relations with bituminous substances, were artificially coalified according to the Bergius' method, chiefly in water medium and sometimes in alkaline or acidic medium at $300 \pm 10^\circ\text{C}$ under corresponding pressure (150-160 atm.).

The following facts were observed.

- (1) Cellulose gives a comparatively large amount of bituminous substances, and such cellulose coals which have moderately volatile matter show a caking property.
- (2) Resin, fat and wax scarcely gives artificial coal, and this coal never shows caking phenomena.
- (3) Lignin gives a large amount of humin, and lignin coals have no caking property, too.

Experimental results lead to the conclusion that caking coal must have been formed under such conditions where there remained still comparatively large amounts of decomposition products of cellulose during the huminificating processes and the degree of coalification was suitable. On the other hand, when cellulose was decomposed severely beyond a certain degree sintering or non-caking coal must have been formed. In other words, generally with respect to this subject, the cellulose theory, that not only but also cellulose are important original materials of natural coal, seems in any case to be reasonable. (J. Soc. Chem. Ind. **52**, 47, 49, 95, 96 (1949) Memoirs of the Faculty of Engineering, Kyoto University, **7**, 128 (1950)).

VI. Studies on Hydrocarbon Chemistry

By **H. Shingu**, **M. Kono**, **N. Mutsuda**, **K. Ichikawa** and **Z. Ri**

With a view of obtaining high grade liquid fuels the following hydrocarbon reactions were studied intensively during the period 1940-1945, i.e. (1) polymerization and depolymerization of gaseous olefins and their polymers in the presence of acidic catalysts, especially phosphoric acid catalyst, (2) isomerization of butylenes, butane and saturated liquid hydrocarbons into the branched isomers, and (3) the isoparaffin-olefin alkylation catalyzed by concentrated sulphuric acid. Mechanisms of these reactions were elucidated both on experimental and theoretical bases, which resulted in several patents and new processes e. g. patents in the isomerization of butylenes (Jap. Pat. 176510, 175971, and 167664) and that on the isomerization of n-butane by the sulphuric acid catalyst (Jap. Pat. 173413). Copolymerization and isomerization of butylenes have found their way in industrial application in 1944-5, and other researches were developed into pilot plant investigations, among which alkylation of the low boiling constituents of synthetic petrol "kogasin" with isobutane may be of some value to be referred to here.

VII. Studies on the Theory of Reactivity of Organic Compounds

By **H. Shingu**, **Y. Takegami**, **K. Okamoto** and **H. Matsushita**

Theoretical aspects of synthetic organic chemistry have been studied on the basis of chemical kinetics since 1945. Mechanism of the Friedel-Crafts type reactions

and that of the so-called solvolytic reactions of the carbonium-ion type were elucidated in a quantitative and systematic way. In this connection a general scope of the theory of the reactivity of organic compounds was disclosed with special reference to the ionoid reactions, resulting, for example, in an expansion of the Hammett's rule and in some reexaminations and revisions of the electronic theory of the English school (Bull. of the Inst. for Chem. Research, Kyoto Univ., Vol. 18, 1949). Kinetical studies on the sulphonation and desulphonation of naphthalene and isomerization of the naphthalene monosulphonic acids which revealed new quantitative information for this unit process in organic synthesis may also be referred to here.

VIII. Studies on Macropolymerization of Ethylene

By *S. Kodama, I. Taniguchi and S. Yuasa*

Research in the polymerization of ethylene under high pressures has been in progress since 1944, and six reports have been so far published in the Rev. of Phys. Chem., Japan and the J. Chem. Soc., Japan.

It was found that polymerization of ethylene at 1000-1800 atm. and 250-285°C seemed to be a homogeneous reaction of the second order, the activation energy of which was about 40 Kcals. When a small amount of oxygen, 0.03-0.08%, was added to ethylene, rapid reaction was observed at 150-165°C, and it was attributed to the action of oxygen.

Furthermore, the stepwise depression of the velocity constants was observed as the reaction proceeded at the temperatures higher than 250°C in some cases; it was also attributed to the action of a small amount of oxygen which had been contained in ethylene.

Polymerization of ethylene in the presence of such catalysts as Ni, Co, Cu, AlCl₃, ZnCl₂, H₃PO₄ on kieselgur, acid clay and alumina was studied at 1000-1500 atm. but no catalyst available for polyethylene formation was found.

Copolymerization of ethylene with styrene and isobutylene was carried out at 1000-1600 atm. and 250-270°C. At the addition of a small amount of styrene to ethylene, the rate constants were found to be proportional to the surface area of the added styrene consisting in a liquid state in the reaction vessel and the addition of 6.4-7.2% isobutylene to ethylene made the initiation reaction 5 times faster than that of ethylene only.

Besides the above-mentioned fundamental studies, a pilot plant of 500 g daily production was erected, and oxygen free synthesis was successfully operated.

IX. Studies on Catalysts for Water Gas Shift Reaction

By *S. Kodama, Y. Murata and K. Fukui*

Effects of various promoters on the activities of natural ochre and precipitated iron catalyst for water gas shift reaction were studied.

The simultaneous addition of 10-15% Cr₂O₃ and 5-10% K₂CO₃ to the ochre catalyst was highly effective, and Cr₂O₃, 1-2% K₂CO₃ and 0.2-0.5% Cu were effective as promoters for the iron catalyst.

At the same time, the amount of Fe formed by the reduction of oxide, the accumulation of iron carbide, and that of free carbon on promoted iron oxide catalysts

during the runs were measured by chemical analyses, and the actions of catalysts were discussed. (J. Chem. Soc., Japan (Ind. Chem. Section 52, 41 1949)).

On the other hand, reaction kinetics was studied by a flow method in which reaction temperature and water vapor ratio were varied, and a rate equation

$$-\frac{dP_{\text{CO}}}{dt} = k \frac{P_{\text{CO}}P_{\text{H}_2\text{O}} - KP_{\text{H}_2}P_{\text{CO}}}{P_{\text{CO}_2} + P_{\text{H}_2\text{O}}}$$

was proved satisfactory, where ε is a constant and K the equilibrium constant.

The theoretical derivation of this equation was also attempted.

X. A Study on the Rate of the Thermal Decomposition of Methane

By S. Kodama, K. Tarama and S. Hayakawa

The reaction mechanism of the thermal decomposition of CH_4 was kinetically studied from 1941 to 1949, and the results were presented in three reports for the J. Chem. Soc. Japan (1949-1950).

At first, the rates of the thermal decomposition of pure CH_4 were measured under the conditions of relatively lower pressure 1.5-15 mm.Hg and at the temperature 1079-1198°K. The presence of induction periods was confirmed with reproducible regularity which were followed by CH_4 -decomposition of the first order, and this first order rate constant (k_1) became smaller as the initial pressure of CH_4 (P_0) decreased in such a manner as the linear relation existed between $1/k_1$ and $1/P_0$. The slope of these straight lines varied with the surface/volume ratios (S/V) of the reaction vessels, but the values of the rate constants at high pressure (k_∞) were independent of S/V , and coincided with Kassel's values.

The carbon produced by decomposition of CH_4 or other gaseous hydrocarbons such as C_2H_6 , C_2H_4 and C_2H_2 accelerated the decomposition rate of CH_4 .

By the addition of H_2 or of a small amount of NO , the CH_4 -decomposition was retarded.

In our experimental condition, mean chain length seemed small, and also its value remained nearly unchanged with the variation of the CH_4 -pressure.

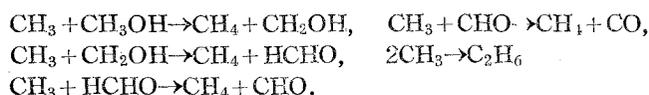
A mechanism of CH_4 -decomposition to explain all the experimental results were proposed, taking into consideration, besides the Kassel's mechanism, the activation and deactivation processes of CH_4 , influence of the vessel surface and carbon, and chain reaction.

XI. Studies on the Reaction of Methyl Radicals With Some Oxygen-Containing Organic Compounds

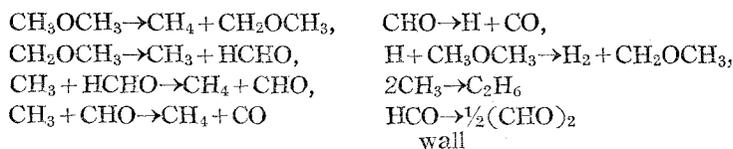
By S. Kodama and Y. Takezaki

The reactions of free methyl radicals with methanol, dimethyl ether, formaldehyde and acetone were studied at 310°C. by a static method using azomethane as a source of methyl radicals. From pressure changes and analyses of reaction products in the course of reactions, the following reaction mechanisms were proposed, and the kinetic equations derived on the basis of these were found to reproduce the observed facts quantitatively.

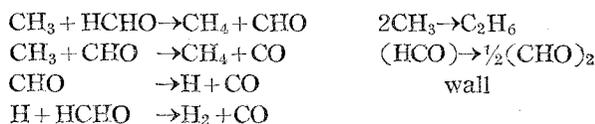
Methanol:



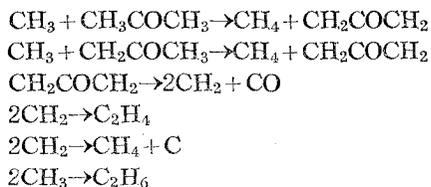
Dimethyl ether:



Formaldehyde:

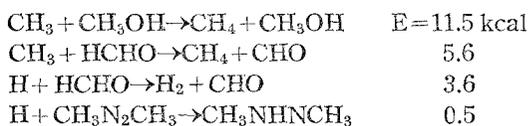


Acetone:



Characteristic differences in these reactions are: (1) in the reactions of methanol and acetone no chain reaction is included, and especially in the latter presence of free methylene is highly probable, and (2) in ether and aldehyde the reaction chains containing H atom are induced and these chain reactions last quite long after the primary supply of CH_3 has ceased.

The following activation energies were found:



These results were presented before the meetings of the Soc. Chem. Japan between 1948-1951.

XII. Theoretical Studies on Temperature Distribution in Self-Heat-Exchanger Type Catalytic Reactors

By S. Kodama and K. Fukui

Studies were made theoretically and systematically from the standpoint of temperature distribution in various types of self-heat-exchanger-type catalytic reactors.

The general differential equation for the temperature distribution was derived under reasonable assumptions and its solutions were obtained for various types of self-heat-exchanger type converters, such as:

- (I). Counter-Current Two-Path Type,
- (II). Con-Current Two-Path Type,
- (III). Counter-Current Three-Path Type,
- (IV). Con-Current Three-Path Type,
- (V). Con-Counter-Current Three-Path Type,
- (VI). Some Four-Path Types.

Each type of such reactors was proved to have its own characteristic temperature distribution through mathematical analyses of the above-mentioned solutions, and thus it became possible to select the most suitable reactor type according to the nature of the related chemical reaction. For example, in the case of SO_3 production by catalytic oxidation of SO_2 , it is recommended to use the Type (I), if uniform temperature distribution is desired, Types (II) and (V) may be recommended. Also in many other cases, such considerations were made, and thus a theoretical foundation for designing reaction chambers was established. The results were reported for the J. Chem. Soc. Ind., Japan in ten papers, 1949-1951.