

[Review Paper]

Preparation of Crystalline CrVO_4 Catalyst by Soft Chemistry Technique and Application for Vapor-phase Oxidation of Picolines

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A series of Cr–V mixed oxide catalysts (CrVO_4 , $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ and $\text{CrV}_{1-x}\text{P}_x\text{O}_4$) have been prepared by “soft chemistry” technique. By mixing the aqueous solution of the raw materials and controlling the pH value, chromium vanadates (CrVO_4 -I and III) were prepared as the pure orthovanadate crystalline form. Prepared chromium vanadates were employed in the vapor phase oxidation of 2-, 3-, and 4-picolines in order to investigate the relationship between the catalysis and structure of chromium vanadate. CrVO_4 -I (monoclinic) showed much higher activity than CrVO_4 -III (orthorhombic), suggesting that the bridging oxygen in the V–O–Cr bond is responsible for the catalytic activity. When a part of Cr or V was replaced with Al or P without changing the CrVO_4 -I type structure, the activities were enhanced. The acidity increased by the replacement of Cr with Al and V with P in CrVO_4 -I, resulting in the accelerating desorption of products. A partial replacement of V with P significantly improved activity and this is probably due to the modification of the redox properties of V–O–Cr site in addition to the accelerating desorption of products. An addition of large amount of steam in the reactants improved the yield of desired products. Both Lewis and Brønsted acid sites were detected on the surface of $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$, and the number of the latter increased by the addition of steam. The enhanced activity by the addition of steam is interpreted by the fact that Brønsted acid sites are produced by the hydrolysis of V–O–Cr bond on the surface and activate picoline molecules by withdrawing the electrons of the pyridine ring, and at the same time, enable to accelerate the desorption of the acid products. Even in the absence of gaseous oxygen, the oxygenated products were formed, thus, a Mars and van Krevelen mechanism was suggested.

Keywords

Chromium vanadate catalyst, Soft chemistry, Picoline, Vapor phase oxidation, Brønsted acid site, Mars and van Krevelen mechanism

1. Introduction

Partial oxidation of 2-, 3- and 4-picolines has received much attention because their oxidation products, picolinic acid, nicotinic acid and isonicotinic acid, respectively, are valuable intermediates of vitamins, food additives and pharmaceuticals^{1)–16)}. For example, 2-pyridinecarbaldehyde and picolinic acid are vitamins, feed stocks for synthesis of physiologically active substances, dyes and other synthetic chemicals. Nicotinic acid is an important vitamin of the B-complex and so is its amide. Many drugs¹⁷⁾ based on nicotinic acid have curative effects such as: lowering the level of cholesterol and free fatty acids in the blood, stimulation of the respiratory apparatus, antispasmodic and antirheumatic action *etc.* The isonicotinic acid has been used in the form of its hydrazide, in the treatment of tuberculosis.

Now, 2-, 3-, and 4-pyridinecarbaldehydes and 2-, 3-, and 4-pyridinecarboxylic acids are usually prepared by

oxidizing the corresponding alkylpyridines in the liquid phase. However the use of stoichiometric oxidants known to be toxic and expensive complexes and also the use of environmentally unfriendly organic solvents have been identified to be the major limitations of this method. These limitations of conventional way of picoline oxidation necessitated the development of catalytic methods using clean and atom-efficient oxidants like molecular oxygen without organic solvents. Solid, heterogeneous catalysts have the advantages of ease of recovery and recycling, and are readily amenable to continuous processing. Therefore, the vapor phase oxidation of organic compounds over heterogeneous catalysts with molecular oxygen is environmentally acceptable from the viewpoint of “green chemistry,” and its wide applications are being found in chemical industry by replacing some harmful liquid oxidation processes.

The vapor phase oxidation of 3-picoline has been performed on a series of vanadium containing catalysts such as $\text{V}_2\text{O}_5/\text{TiO}_2$ ^{8),11)–14),19)}, $\text{V}_2\text{O}_5/\text{SnO}_2$ ²⁰⁾, and over-

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viewed²¹⁾ recently. Shishido and co-workers have reported that CrVO_4 prepared by “soft chemistry” technique in the pure crystalline form (CrVO_4 -I, monoclinic) is also active for the vapor phase oxidation of picolines^{22)–26)}. In this article, the characterization of Cr-V mixed oxide catalysts by using XRD, FT-IR, TG-DTA, NH_3 -TPD, Raman, and TPR techniques, and their catalysis in vapor phase oxidations of 2-, 3- and 4-picolines are demonstrated. The correlation between surface structure and catalytic behavior of a series of Cr-V mixed oxide catalysts prepared by “soft chemistry” technique are briefly reviewed.

2. Experimental

2.1. Catalyst Preparation

A series of CrVO_4 , $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ ($x = 0.25, 0.5, 0.75$ and 1.0) and $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ ($x = 0.02$ – 1.00) catalysts were prepared following method proposed by Touboul and co-workers^{27),28)}. Aqueous solutions of NH_4VO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed and the pH value of the solution was lowered below 1.0 to form homogeneous solution by adding 3 M ($1 \text{ M} = 1 \text{ mol} \cdot \text{dm}^{-3}$) nitric acid. Then, the pH value of the solution was adjusted to 4.0 at 323 K to give the precipitate by adding 3 M ammonia aqueous solution. The obtained precipitate was filtered, washed with distilled water, dried at 373 K for overnight, and finally calcined in air for 6 h.

2.2. Vapor Phase Oxidation of 2,3 and 4-Picolines

The catalytic tests were carried out in a fixed-bed reactor at atmospheric pressure. 0.2 g of the catalyst was diluted with 1.0 g of quartz sand and filled in the Pyrex glass tube reactor. The liquid mixture of substrate and water was passed through a vaporization zone at 473 K, mixed with oxygen and nitrogen as the carrier gas and finally fed into the reactor. The line from the vaporizer to the reactor was heated to a temperature above 523 K. Water, the organic products were condensed after the reactor, and all samples were analyzed by a hydrogen-flame ionization detector (FID) gas chromatograph. The inorganic components (CO , CO_2 , O_2 and N_2) were analyzed by an on-line thermal conductive detector (TCD) gas chromatograph. Prior examinations confirmed that the vapor phase consists only of products of total oxidation, *i.e.* CO_2 , CO and HCN , among which HCN was not determined.

2.3. Characterization

The X-ray diffraction (XRD) was carried out on a Mac Science MX18XHF-SRA using $\text{Cu K}\alpha$ radiation. Fourier Transform-Infrared (FT-IR) spectra were recorded on a Nicolet Magna-IR 560 spectrometer. Differential thermal analyses (DTA) were carried out using a Shimadzu DTG-50H at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ from room temperature to 1273 K with $\alpha\text{-Al}_2\text{O}_3$ as a reference. The temperature-programmed desorp-

tion of ammonia (NH_3 -TPD) was performed to scrutinize the acidic properties of the catalysts. Prior to the adsorption with ammonia, the catalyst was pretreated for 1 h in a helium stream at 773 K. Then, ammonia was exposed to the catalyst at 373 K. After adsorption, the gas stream was switched to helium ($50 \text{ mL} \cdot \text{min}^{-1}$) to remove physically adsorbed ammonia from the catalyst surface. The ammonia desorption profile was detected by a Bell Japan TPD-1-AT at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ $50 \text{ mL} \cdot \text{min}^{-1}$ helium flow. The H_2 -TPR profiles were measured to reduction-oxidation property of catalysts. The fresh catalysts were oxidized with O_2 at 573 K for 1 h prior to determination of the TPR profile. The change in the H_2 concentration was monitored by TCD. BET specific surface areas of the catalysts were measured by N_2 adsorption using a Shimadzu Micromeritics Flow Sorb II 2300 in liquid nitrogen at 77 K.

3. Results and Discussion

3.1. CrVO_4 -I and III

3.1.1. Structures of CrVO_4 -I and III

Takehira *et al.* have reported that Cr-V mixed oxide catalysts showed high activity for the liquid phase oxidation of acrolein²⁹⁾ and cyclohexene³⁰⁾ in 1970's. However, in these studies, various mixtures of Cr-V mixed oxide, chromium oxide or vanadium oxide are used as catalyst. Therefore, the relationship between the structures of Cr-V mixed oxides and their catalysis are still not made clear. Recently it has been reported that some metal vanadates were synthesized by “soft chemistry” technique in the pure crystalline form just by controlling the pH of the aqueous solution of the mixture of raw materials^{27),28)}.

Monoclinic ($a = 9.791(6) \text{ \AA}$, $b = 8.848(5) \text{ \AA}$, $c = 6.843(6) \text{ \AA}$ and $\beta = 107.8(1)^\circ$, $1 \text{ \AA} = 10^{-10} \text{ m}$; $D_x = 3.98$ with $Z = 8$; and space group $C2/m$.) CrVO_4 belonging to the $\alpha\text{-MnMoO}_4$ structure of the same as $\beta\text{-CdCrO}_4$ and $\beta\text{-MgCrO}_4$ compounds^{31),32)} was prepared by mild heating of amorphous precursors and was named as CrVO_4 -I (**Fig. 1 (a)**)^{27),28)}. Orthorhombic chromium vanadate (CrVO_4 -III) (**Fig. 1 (b)**) was first characterized by Brandt³³⁾ in 1943. It can be easily prepared by a solid-state reaction between Cr_2O_3 and V_2O_5 at 1023–1073 K^{33),34)}. Recently, it has also been synthesized by heating its amorphous precursors at high temperature²⁷⁾. Numbers I and III refer to the parent InVO_4 forms²⁸⁾. The orthorhombic form of CrVO_4 , CrVO_4 -III, is isostructural to the InVO_4 -III^{27),34),35)}, and the monoclinic form, CrVO_4 -I, is compared with InVO_4 -I compound²⁸⁾.

As for CrVO_4 -I with isostructure to $\alpha\text{-MnMoO}_4$, the Cr and V atoms replace Mn and Mo, respectively, forming CrO_6 octahedra and VO_4 tetrahedra, respectively. The arrangement of these polyhedra is totally different from that of stable CrVO_4 -III form^{33),34)}. In the latter

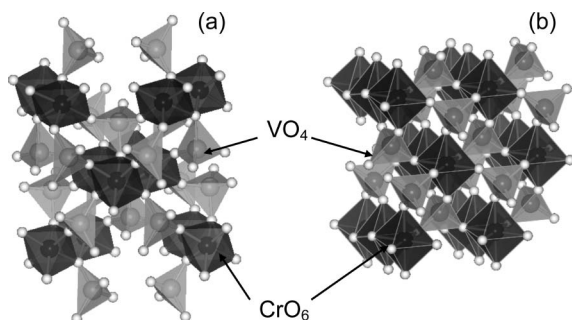


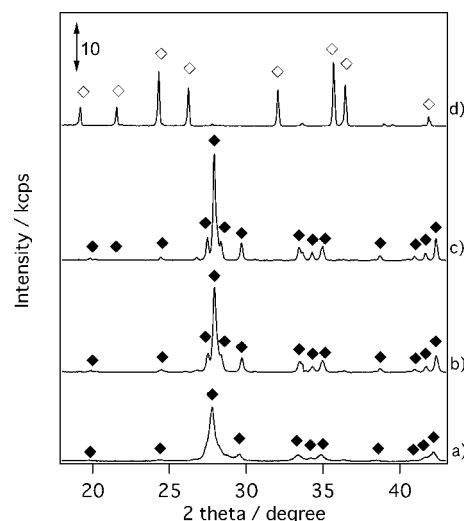
Fig. 1 Crystal Structures of (a) CrVO₄-I and (b) CrVO₄-III

structure, there are, along the (0 0 1) direction, chains of edge-sharing CrO₆ octahedra linked by VO₄ tetrahedra. However, the CrVO₄-I structure does not show any chains but contain some cluster. It consists of an infinite network of Cr₄O₁₆ clusters of four edge-sharing CrO₆ octahedra linked to the other clusters by VO₄ tetrahedra. In CrVO₄-I, each cluster is built from two pairs of two crystallographically independent Cr atoms, which are located within irregular octahedra of oxygen atoms. The mean Cr₁-O and Cr₂-O distances are practically equal (1.98 Å and 1.97 Å, respectively). In the same way, there are two crystallographically independent V atoms, which are located at the center of distorted tetrahedra. The mean V₁-O and V₂-O distances are practically equal to 1.73 Å and 1.72 Å, respectively. In CrVO₄-III, the mean Cr-O and V-O distances (2.012 Å and 1.764 Å, respectively) do not differ greatly from CrVO₄-I. The main difference between the two forms is that CrVO₄-III presents only one type of CrO₆ octahedra and VO₄ tetrahedra against the two types in CrVO₄-I.

3. 1. 2. Effect of the Structure of CrVO₄ on the Activity

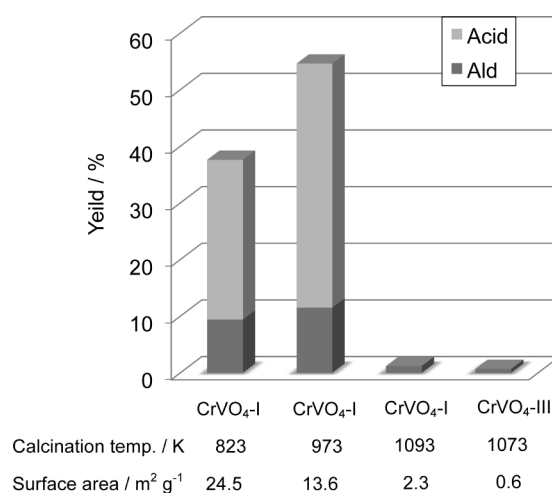
XRD patterns of CrVO₄ catalysts calcined at various temperatures are shown in Fig. 2. The CrVO₄-I monoclinic crystal structure grew by increasing the calcination temperature, but no transition to CrVO₄-III was observed. It is reported that orthorhombic CrVO₄ (CrVO₄-III) was obtained by heating CrVO₄-I at 933 K²⁷⁾. However, CrVO₄-III could not be obtained even when CrVO₄-I was calcined at 1093 K for 6 h. The sample of CrVO₄-III was prepared by the solid phase reaction between V₂O₅ and Cr₂O₃ at 1073 K for 10 h.

Figure 3 shows the results of 3-picoline oxidation over CrVO₄ catalysts calcined at various temperatures. The activity was shown as the yield of nicotinic acid and 3-pyridinecarbaldehyde. Interestingly, the activity of CrVO₄-I for the selective oxidation increased after the calcination at 973 K compared with that at 823 K, none the less the BET surface area of the catalyst decreased (24.5 to 13.6 m²·g⁻¹). Further calcination at 1093 K for 6 h resulted in a decrease in the activity



a) calcined at 823 K, b) calcined at 973 K, c) calcined at 1093 K, d) CrVO₄-III, (◆) CrVO₄-I, (◇) CrVO₄-III.

Fig. 2 XRD Patterns of Catalysts Calcined at Various Temperatures



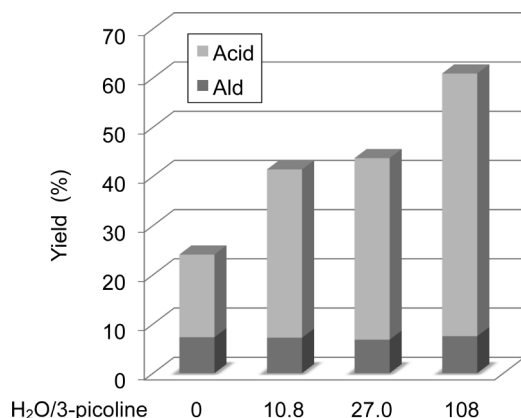
Reaction temperature 633 K, 3-picoline/H₂O/O₂/N₂ = 1/10.8/24/125, GHSV = 38,000 mL·h⁻¹·g-cat⁻¹.

Ald., pyridine-3-carbaldehyde; Acid, nicotinic acid.

Fig. 3 3-Picoline Oxidation over CrVO₄ Catalysts Calcined at Various Temperatures

together with a significant decrease in the surface area (2.3 m²·g⁻¹), but catalyzed the selective oxidation of 3-picoline to pyridine-3-carbaldehyde. CrVO₄-III showed a further low activity. The blank test with quartz sand showed only low conversion with no oxygenated products, but did produce pyridine together with CO₂.

Recent studies on surface vanadium oxide species on oxide supports suggest that the bridging oxygen in the V-O-support bond is responsible for the catalytic activity for hydrocarbon oxidation^{36),37)}. The selective oxida-



Ald., pyridine-3-carbaldehyde; Acid, nicotinic acid. GHSV = 38,000 mL·h⁻¹·g-cat⁻¹.

Fig. 4 Effect of Water on 3-Picoline Oxidation over CrVO₄ Catalyst

tion of 3-picoline to nicotinic acid has recently been investigated on V₂O₅/TiO₂ catalysts^{11)~14)}. The increase of the interface between vanadia and titania phases is the determining factor to improve the activity of catalysts. Monomeric vanadia species with vanadium in tetrahedral coordination were formed and the bridging oxygen in the V–O–Ti bond is suggested to be responsible for the catalytic activity. As mentioned in the previous section, none the less the VO₄ tetrahedra are separated well in both CrVO₄-I and CrVO₄-III, the CrO₆ octahedra are more efficiently separated as the clusters in CrVO₄-I than as the chains in CrVO₄-III. Therefore, it can be thought that the V–O–Cr bond is more efficiently dispersed in CrVO₄-I than in CrVO₄-III. This difference in the structure may affect the catalytic activity of CrVO₄-I phase coupled with the large surface area. The most potential candidates as active sites are the isolated V sites bearing the redox properties assisted by Cr in the CrVO₄-I structure.

3. 1. 3. Effect of Steam on the Activity

The positive effect of steam on the activity and selectivity has been reported in various types of hydrocarbon oxidation^{38)~45)}, e.g., toluene oxidation over V₂O₅/TiO₂ catalyst^{38),39)}. A decline in the activity was observed by the presence of steam in *n*-butane oxidation^{40),41)}, while a contradictory result, i.e., the promotion by steam addition was recently reported in the *n*-butane oxidation on the same (VO)₂P₂O₇ catalyst⁴²⁾. The yields of carboxylic acids were improved in ethane and propene oxidation, though the effect of steam addition is a little complex^{43),44)}. In the oxidation of 3-picoline, an addition of a large amount of steam into the reaction media often accelerates the nicotinic acid formation. **Figure 4** shows the effect of water on the catalytic performance of CrVO₄-I catalyst calcined at 623 K. The conversion and selectivity to nicotinic acid increased with increasing the molar ratio of H₂O to 3-picoline,

whereas the selectivities to CO₂ and pyridine-3-carbaldehyde decreased. When the molar ratio of H₂O to 3-picoline was 108, the selectivity and yield of nicotinic acid were 69.9% and 39.6%, respectively. Pyridine disappeared after increasing the amount of water on CrVO₄-I. Thus, it is concluded that the presence of a sufficient amount of steam enhances the selective oxidation of 3-picoline to nicotinic acid on CrVO₄-I.

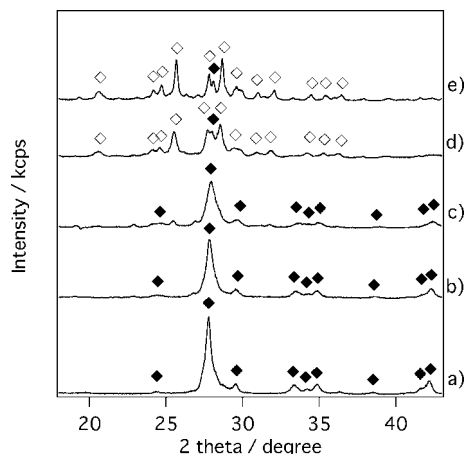
As for the role of steam in hydrocarbons oxidation on V₂O₅/TiO₂ catalyst, some authors considered that the oxidation reaction was promoted because the addition of steam could alter the catalyst surface property and activate the lattice oxygen during the reaction process^{38),42),45)}. The hydrolysis of V–O–V bonds was induced in the presence of steam. Furthermore, the strongly adsorbed intermediates can be hydrolyzed and taken away from the catalyst surface by H₂O so that more active sites are responsible for the reaction³⁸⁾. The contrary results that steam lead to the reduction of activity can be explained that H₂O blocks the active center of catalyst^{40),41)}. Our experimental results confirmed the promotion effect of steam. Addition of steam may cause to form a large amount of OH on the catalyst surface, resulting in increasing Brønsted acidity. The increased Brønsted acid sites promoted the 3-picoline oxidation and facilitated the formation of nicotinic acid.

3. 2. Cr_{1-x}Al_xVO₄ Catalysts

Solid solutions Cr_{1-x}Fe_xVO₄ can be formed over a wide composition range and are thermally stable above 1173 K^{46),47)}. They are isomorphous with α-MnMoO₄, rather than adopting the CrVO₄ and FeVO₄ structure. Ionic radii of high spin and low spin Fe³⁺, and Cr³⁺ are 0.79, 0.69, and 0.76 Å⁴⁸⁾, respectively. The ionic radius of Al³⁺ is 0.68 Å⁴⁸⁾. AlVO₄ and FeVO₄ are isostructural⁴⁹⁾. The samples, Cr_{1-x}Al_xVO₄ (*x* = 0, 0.25, 0.5, 0.75 and 1.0) were prepared and tested for the oxidation of 3-picoline.

3. 2. 1. Structure of Cr_{1-x}Al_xVO₄ Catalysts

The XRD patterns of Cr_{1-x}Al_xVO₄ are shown in **Fig. 5**. As shown in **Fig. 5** a)-c), the patterns of Cr_{1-x}Al_xVO₄ (*x* ≤ 0.5) showed mainly the lines of CrVO₄-I (α-MnMoO₄ structure). The lines due to AlVO₄ were observed in **Fig. 5** c), but the main lines were still assigned to CrVO₄-I. When the Al content increased (*x* > 0.5), the patterns substantially changed to triclinic AlVO₄ structure as seen in **Fig. 5** d). It is likely that the samples with *x* ≤ 0.5 (Cr_{0.5}Al_{0.5}VO₄, Cr_{0.75}Al_{0.25}VO₄, CrVO₄) basically have α-MnMoO₄ structure as the diffraction line-width broadened with increasing the Al content. Vegard's plots of two diffraction lines assignable to (−2 2 0) and (−1 1 0) planes of CrVO₄-I suggested the formation of solid solution Cr_{1-x}Al_xVO₄. It is likely that Al³⁺ replace the site of Cr³⁺ in CrVO₄-I, considering the smaller ionic radius of Al³⁺ (0.68 Å) than Cr³⁺ (0.76 Å)⁴⁸⁾. FT-IR



a) CrVO_4 , b) $\text{Cr}_{0.75}\text{Al}_{0.25}\text{VO}_4$, c) $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$, d) $\text{Cr}_{0.25}\text{Al}_{0.75}\text{VO}_4$, e) AlVO_4 , (◆) $\text{CrVO}_4\text{-I}$, (◇) AlVO_4 .

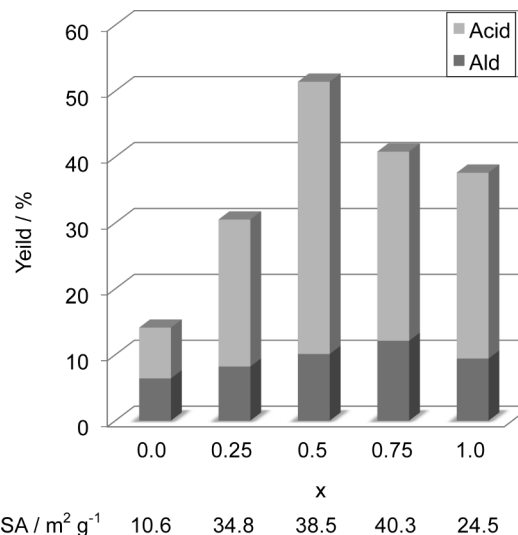
Fig. 5 XRD Patterns of $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ Catalysts

spectra of the $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ catalysts are consistent with the XRD results. $\text{CrVO}_4\text{-I}$ showed strong absorption bands at 960, 875, 744 and 667 cm^{-1} , probably assigned to V-O-V, V-O-Cr and Cr-O-Cr stretching vibrations, respectively^{27),28)}. A shift to higher wavenumber was observed with increasing the Al content, indicating that a part of V-O-Cr bond is replaced by V-O-Al bond. On the other hand, when x was above 0.5, the spectra of $\text{Cr}_{0.25}\text{Al}_{0.75}\text{VO}_4$ changed substantially and became close to that of AlVO_4 , suggesting that AlVO_4 structure predominated in $\text{Cr}_{0.25}\text{Al}_{0.75}\text{VO}_4$.

3. 2. 2. Activity of $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ Catalysts

The results of 3-picoline oxidation on $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ ($x = 0, 0.25, 0.50, 0.75$ and 1.0) in the presence of steam are shown in Fig. 6. AlVO_4 showed a low activity for the selective oxidation to pyridine-3-carbaldehyde and nicotinic acid. The total yield of nicotinic acid and pyridine-3-carbaldehyde increased with increasing the Al content to $x = 0.5$, and then suddenly decreased upon further increasing x . The activity for nicotinic acid production was the highest over the $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ catalyst with the selectivity of 60.4% and the yield of 41.3% of nicotinic acid. In order to discuss the activity based on the reaction kinetics, apparent activation energies were calculated from the rates of 3-picoline consumption over the $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ catalysts. Increasing in the Al content in the range $x \leq 0.5$ resulted in a decrease in the activation energy, and both $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ and $\text{Cr}_{0.75}\text{Al}_{0.25}\text{VO}_4$ showed the low values of about $65\text{ kJ}\cdot\text{mol}^{-1}$, coinciding well with their high activities. Further increase in the Al content caused an increase in the activation energy, and the highest value of $90\text{ kJ}\cdot\text{mol}^{-1}$ was obtained with AlVO_4 .

For better understanding of the results obtained on the $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ catalysts, NH_3 -TPD experiments were carried out on CrVO_4 , $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$, and AlVO_4 . The



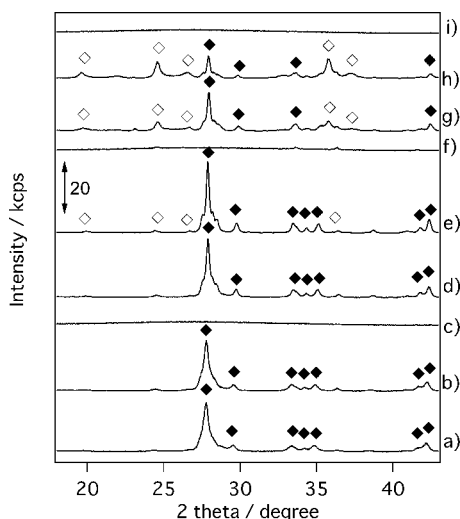
Reaction temperature 633 K, 3-picoline/ $\text{H}_2\text{O}/\text{O}_2/\text{N}_2 = 1/10.8/24/125$, GHSV = $38,000\text{ mL}\cdot\text{h}^{-1}\cdot\text{g-cat}^{-1}$.

Ald., pyridine-3-carbaldehyde; Acid, nicotinic acid.

Fig. 6 3-Picoline Oxidation over $\text{Cr}_{1-x}\text{Al}_x\text{VO}_4$ Catalysts

NH_3 desorption peaks were always observed around 460 K on all the catalysts tested, and the amount of NH_3 desorbed from $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ was larger than the amount of CrVO_4 and AlVO_4 . This result indicates that the number of acid sites increased by the replacement of Cr with Al in the $\text{CrVO}_4\text{-I}$.

The conversion and selectivity to nicotinic acid increased with increasing the molar ratio of H_2O to 3-picoline, whereas the selectivities to CO_2 and pyridine-3-carbaldehyde decreased as well as CrVO_4 . When the molar ratio of H_2O to 3-picoline was 108, the selectivity and yield of nicotinic acid were 73.3% and 58.9%, respectively. A sufficient amount of steam enhanced the selective oxidation of 3-picoline to nicotinic acid on $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ catalyst. The effect of the addition of steam in the catalytic activity was more intensively observed on $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ than on CrVO_4 , *i.e.* the increase in both 3-picoline conversion and total yield of pyridine-3-carbaldehyde and nicotinic acid was more significant on the former than the latter. This strongly suggests that the effective acid site is Brønsted acid. Such a Brønsted acid site can adsorb 3-picoline as a base, and can desorb nicotinic acid. It is thus likely that the increasing Brønsted acid sites on the $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ catalyst results in the acceleration of the oxidation of 3-picoline to nicotinic acid. It was reported that the activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst for the 3-picoline oxidation is partly due to Brønsted acid sites⁵⁰⁾. The oxidation of 3-picoline with O_2 also requires the redox properties due to the V species on the catalyst surface. Thus, 3-picoline can be effectively oxidized with O_2 in the gas-phase to nicotinic acid on the $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ catalyst having Brønsted acid sites in addition to redox proper-



a) CrVO_4 calcined at 823 K, b) $\text{CrV}_{0.98}\text{P}_{0.02}\text{O}_4$ calcined at 843 K, c) $\text{CrV}_{0.95}\text{P}_{0.05}\text{VO}_4$ calcined at 623 K, d) $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 843 K, e) $\text{CrV}_{0.9}\text{P}_{0.1}\text{O}_4$ calcined at 843 K, f) $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 843 K, g) $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 923 K, h) $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 973 K, and i) CrPO_4 , (◆) $\text{CrVO}_4\text{-I}$, (◇) $\text{CrVO}_4\text{-III}$.

Fig. 7 XRD Patterns of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ Catalysts

ties.

3. 3. $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ Catalysts

It was reported by Attfield⁵¹⁾ that a replacement of V in $\text{CrVO}_4\text{-I}$ with P is also possible, resulting in the formation of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ and this compound also belongs to an $\alpha\text{-MnMoO}_4$ structure. Indeed, it will be possible to modify the active V-O-Cr sites by replacing V^{5+} with P^{5+} in the VO_4 tetrahedra, considering their ionic radii of 0.40 Å and 0.35 Å, respectively⁴⁸⁾. In this section, the details of the structure of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ and the effect of replacing V^{5+} with P^{5+} in the VO_4 tetrahedra on both catalytic activities in the vapor-phase oxidation of 3-picoline and the physico-chemical property are described.

3. 3. 1. Structure of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ Catalysts

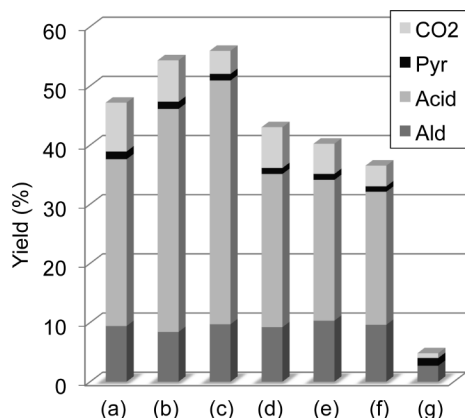
Figure 7 shows the XRD patterns of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ ($x = 0, 0.02, 0.05, 0.1, 0.25, 0.5$, and 1). The diffraction lines of monoclinic $\text{CrVO}_4\text{-I}$ ($\alpha\text{-MnMoO}_4$ structure)^{27),28),34),49)} were distinctly observed for $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ ($0 \leq x \leq 0.25$). The diffraction lines of both $(-1\ 1\ 0)$ and $(-2\ 2\ 0)$ planes shifted toward the lower d values with increasing x following Vegard's law, strongly suggesting that P atoms were incorporated in the structure of $\text{CrVO}_4\text{-I}$ probably by replacing the sites of V in the VO_4 tetrahedra linking the Cr_4O_{16} clusters, taking into account the smaller ionic radius of P^{5+} than V^{5+} ⁴⁸⁾. A sharp exothermic peak was observed at 810 K with CrVO_4 by differential thermal analysis (DTA)²⁵⁾ and was assigned to the crystallization of $\text{CrVO}_4\text{-I}$ by Touboul and Melghit²⁷⁾. In the case of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$, the crystallization to the $\text{CrVO}_4\text{-I}$ structure during calcination was clearly observed and those two typical exam-

ples, *i.e.*, $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ and $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$, are shown in Fig. 7. The $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ was amorphous after the calcination at 623 K (c) and well crystallized to monoclinic $\text{CrVO}_4\text{-I}$ structure after the calcination at 843 K (d). In the case of $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$, the amorphous phase was still observed even after the calcination at 843 K (f), while the crystallized phases of both $\text{CrVO}_4\text{-I}$ and $\text{CrVO}_4\text{-III}$ were detected after the calcination at 923 K (g), and the crystallinity increased with increasing the calcination temperature to 973 K (h). In both samples of $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ and $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$, it was shown that the crystallization of $\text{CrVO}_4\text{-I}$ took place around the temperature of exothermic peak in the DTA curves. When x increased to 0.5 in $\text{CrV}_{1-x}\text{P}_x\text{O}_4$, the $\text{CrVO}_4\text{-III}$ phase alone was observed, even though the diffraction lines were weak and broad. A totally replaced CrPO_4 showed only an amorphous phase even after the calcination at 973 K (i). Different hydrates of CrPO_4 are known⁵²⁾; their calcinations at high temperature allow the anhydrous material to be formed in two types of their polymorphic forms: $\beta\text{-CrPO}_4$ above 1273 K and $\alpha\text{-CrPO}_4$ above 1448 K. Thus, amorphous CrPO_4 is stable and does not crystallize even at high temperature of 1173 K in the DTA curves²⁵⁾.

FT-IR spectra of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ well correlated with the results of XRD analyses. The $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ catalysts containing P in the range of $0 \leq x \leq 0.02$ showed the adsorption bands at 960, 925, 875, 744, and 667 cm^{-1} , probably assigned to V-O-V, V-O-Cr and Cr-O-Cr stretching vibrations of the monoclinic $\text{CrVO}_4\text{-I}$ structure. An increase in the P contents ($0.02 \leq x \leq 0.10$) resulted in a blue shift of the bands of $\text{CrVO}_4\text{-I}$, indicating that a part of V-O-V bond is replaced by V-O-P²⁵⁾. Moreover, new absorption bands appeared between 1000 cm^{-1} and 1200 cm^{-1} probably assigned to some P-O vibrations as observed in the $\alpha\text{-CrPO}_4$ phase. When the P contents increased to $0.25 \leq x \leq 0.5$, the spectra changed substantially and became close to that of $\alpha\text{-CrPO}_4$ ⁵²⁾. $\text{CrV}_{0.98}\text{P}_{0.02}\text{O}_4$ calcined at 923 K, $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 843 K, and CrPO_4 calcined at 973 K showed broad and weak absorption bands probably due to their amorphous structures, because calcination temperatures were too low to crystallize.

3. 3. 2. Activity of $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ Catalysts

Figure 8 shows the yields of nicotinic acid, pyridine-3-carbaldehyde, carbon dioxide and pyridine, in the oxidation of 3-picoline at 623 K. A small amount of pyridine was observed over all the catalysts including CrPO_4 calcined at 973 K and probably formed by decarboxylation of nicotinic acid. $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 843 K showed the highest yields of nicotinic acid and pyridine-3-carbaldehyde, followed by $\text{CrV}_{0.98}\text{P}_{0.02}\text{O}_4$ calcined at 843 K, although their surface areas were smaller than CrVO_4 calcined at 823 K. When x exceeded 0.05, the yields gradually decreased with increasing x , and finally CrPO_4 showed a sudden



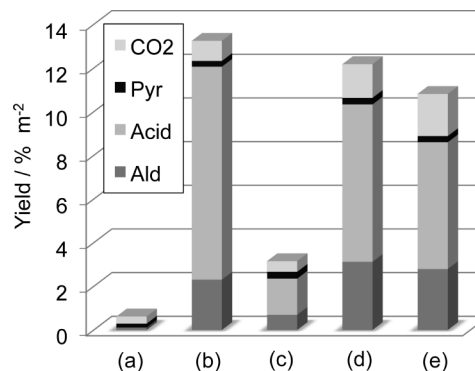
Reaction temperature 633 K, 3-picoline/ $\text{H}_2\text{O}/\text{O}_2/\text{N}_2 = 1/10.8/24/125$, $\text{GHSV} = 38,000 \text{ mL} \cdot \text{h}^{-1} \cdot \text{g-cat}^{-1}$.

(a) CrVO_4 calcined at 823 K, (b) $\text{CrV}_{0.98}\text{P}_{0.02}\text{O}_4$ calcined at 843 K, (c) $\text{CrV}_{0.95}\text{P}_{0.05}\text{VO}_4$ calcined at 623 K, (d) $\text{CrV}_{0.9}\text{P}_{0.1}\text{O}_4$ calcined at 843 K, (e) $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 923 K, (f) $\text{CrV}_{0.5}\text{P}_{0.5}\text{O}_4$ calcined at 973 K, (g) CrPO_4 calcined at 973 K.

Ald., pyridine-3-carbaldehyde; Acid, nicotinic acid; Pyr., pyridine; CO_2 , carbon dioxide.

Fig. 8 Oxidation of 3-Picoline over the $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ Catalysts

decline in the activity, resulting in no formation of nicotinic acid. It is thus suggested that the CrVO_4 -I structure is important for the selective oxidation of 3-picoline and a small amount of phosphorus assists the catalytic activity of CrVO_4 -I. This suggestion was confirmed by the further studies on the effect of the calcination temperature of $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ and $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$. Yields of the products per surface area of the catalysts are shown in Fig. 9 for both $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ and $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at different temperatures. When $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ was calcined at 623 K, the activity was extremely low. By the calcination at 843 K, the activity increased to the highest value among the catalysts tested. Also in the case of $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$, the calcination temperature showed a distinct effect on the activity. The calcination at 843 K afforded a low activity, while those at 923 K and 973 K caused a substantial increase in the activity. These critical features can be explained by the change in the catalyst structure from amorphous to crystalline. As observed in the analytical results of the catalysts by XRD and IR, the amorphous phases of $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 623 K and $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 843 K changed to the crystalline phases of $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 843 K, $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 923 K and $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 973 K by increasing the calcination temperature. The critical temperatures of these phase transitions from amorphous to crystalline are supported by the results of DTA, showing the exothermic peak at 815 K and 968 K due to the crystallization of the monoclinic CrVO_4 -I structure. The temperature of 923 K does not seem high enough, but may be recovered by

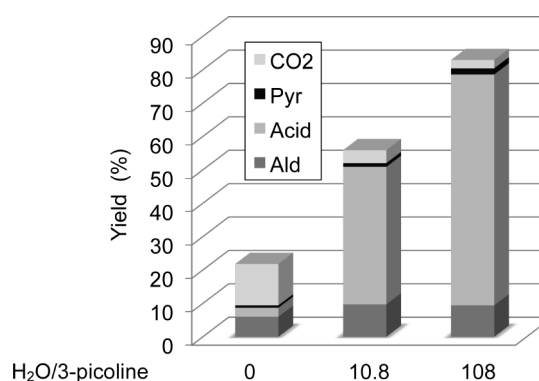


Reaction temperature 633 K, 3-picoline/ $\text{H}_2\text{O}/\text{O}_2/\text{N}_2 = 1/10.8/24/125$, $\text{GHSV} = 38,000 \text{ mL} \cdot \text{h}^{-1} \cdot \text{g-cat}^{-1}$.

(a) $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 623 K, (b) $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 843 K, (c) $\text{CrV}_{0.75}\text{P}_{0.25}\text{VO}_4$ calcined at 843 K, (d) $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 923 K, (e) $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 973 K.

Ald., pyridine-3-carbaldehyde; Acid, nicotinic acid; Pyr., pyridine; CO_2 , carbon dioxide.

Fig. 9 Oxidation of 3-Picoline over the $\text{CrV}_{1-x}\text{P}_x\text{O}_4$ Catalysts—Effect of the Calcination Temperature

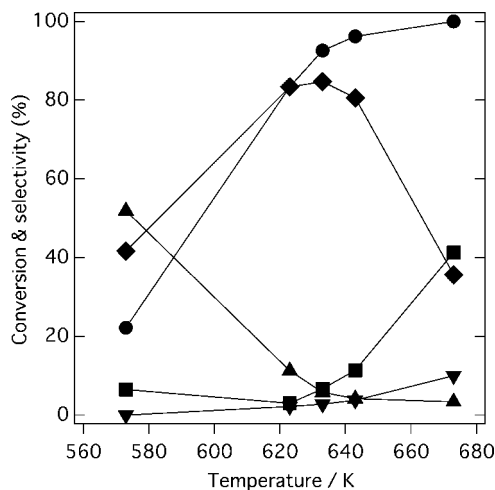


Ald., pyridine-3-carbaldehyde; Acid, nicotinic acid; Pyr., pyridine; CO_2 , carbon dioxide.

Fig. 10 Effect of Water on 3-Picoline Oxidation over $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ Catalyst

calcination for 6 h for assisting the crystallization of the CrVO_4 -I structure in $\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4$ calcined at 923 K. It will be concluded that the monoclinic CrVO_4 -I-based structure is important in the selective oxidation of 3-picoline and the activity is enhanced by the incorporation of phosphorus in the V-site in the structure.

The results of 3-picoline oxidation over $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ calcined at 843 K in the presence of steam are shown in Fig. 10. Both yield and selectivity of nicotinic acid were very low in the absence of steam, while the addition of steam enhanced enormously the selective oxidation of 3-picoline to nicotinic acid. Major product was carbon dioxide from 3-picoline in the absence of water, and in turn substantially changed to nicotinic acid in the presence of water. The rate of 3-picoline consumption was also enhanced by the addition of water, however,



(●) 3-picoline conversion, (▲) pyridine-3-carbaldehyde sel., (▼) Pyr. sel., (■) CO₂ sel., (◆) nicotinic acid sel.

Fig. 11 Effect of Temperature on 3-Picoline Oxidation over CrV_{0.95}P_{0.05}O₄ Catalyst

apparent activation energy was almost constant independent of the amount of water²⁵⁾. This indicates that the rate-determining step does not relate directly to the acid sites enhanced by water addition.

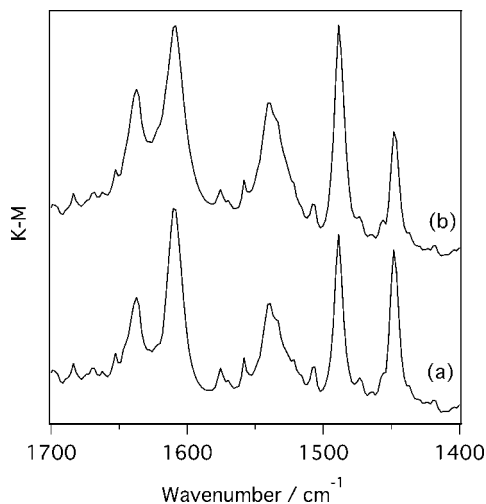
The effect of reaction temperature in the 3-picoline oxidation over CrV_{0.95}P_{0.05}O₄ calcined at 843 K in the presence of an excess amount of water (H₂O/3-picoline = 108) is shown in Fig. 11. Increasing temperature is profitable for the selective oxidation of 3-picoline to nicotinic acid and the optimum temperature was found to be 533 K, giving the highest yields of nicotinic acid (78.4%) and pyridine-3-carbaldehyde (5.4%) at the conversion of 92.6%. However, when the reaction temperature was further increased, the temperature became hard to be controlled, resulting in a drastic decrease in the selectivity to nicotinic acid. The activity of CrV_{0.95}P_{0.05}O₄ calcined at 843 K for nicotinic acid production was far higher than that of Cr_{0.5}Al_{0.5}VO₄^{22),24)}, i.e., the yields of nicotinic acid (58.9%) and pyridine-3-carbaldehyde (10.0%) at the conversion of 80.4%. It was reported that V₂O₅/TiO₂ catalyzed the selective oxidation of 3-picoline at 523–553 K and afforded nicotinic acid with the selectivity above 90% at the conversion above 90%^{11),12)}. However only anatase TiO₂ was effective as the support and is possibly transformed to rutile TiO₂, resulting in deactivation, during the exothermic reaction. On the other hand, CrV_{0.95}P_{0.05}O₄ calcined at 843 K is thermally stable and a promising catalyst for the oxidation reaction.

In the case of 2-picoline oxidation over CrV_{1-x}P_xO₄ ($x = 0.0$ – 1.0) at 598 K, no picolinic acid produced, but both pyridine and CO₂ were observed over all the catalysts including CrPO₄ calcined at 973 K. Both CrV_{0.98}P_{0.02}O₄ calcined at 843 K and CrV_{0.95}P_{0.05}O₄

calcined at 843 K showed the highest yields of pyridine-2-carbaldehyde. When x exceeded 0.05, the yields gradually decreased with increasing x , and finally CrPO₄ calcined at 973 K showed a sudden decline in the activity. It is thus suggested that CrVO₄-I structure is also important for the selective oxidation of 2-picoline and a small amount of phosphorus assists the catalytic activity of CrVO₄-I. In the case of 4-picoline oxidation over CrV_{1-x}P_xO₄ ($x = 0.0$ – 1.0) at 598 K, except for CrPO₄ calcined at 973 K catalyst, 4-picoline conversions exceeded 90% on all the catalysts tested. The CrV_{0.95}P_{0.05}O₄ calcined at 843 K showed the highest yield (75.0%) of isonicotinic acid. Both 2- and 4-picolines were more active and showed higher conversion than 3-picoline probably due to their isomeric molecular structure. Nicotinic acid and isonicotinic acid were obtained from 3- and 4-picolines, respectively. Picolinic acid was not obtained from 2-picoline, since picolinic acid was easily decomposed to pyridine and CO₂.

3.3.3. Acidic Property of CrV_{1-x}P_xO₄ Catalysts

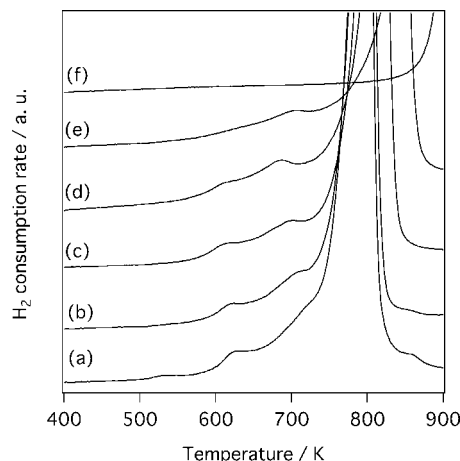
The results of NH₃-TPD showed an increase in the amount of acid sites by the addition of P up to $x = 0.05$ and the decrease with the further increase in the P content. CrVO₄-III as a reference was also tested and compared with the other catalysts of a CrVO₄-I-type crystal structure. A large amount of CrVO₄-III was used considering that the surface area was very small (0.61 m²·g⁻¹). The amount of acid sites estimated from the NH₃-TPD results varied considerably depending on the P content. However, the temperature at the peak top of NH₃-TPD was almost constant with all the catalysts tested including CrVO₄-III, suggesting that the strength of the acid site was not substantially affected by the addition of P. Thus, the acid nature of the catalyst alone cannot explain the kinetics of the oxidation of 3-picoline to nicotinic acid. In the NH₃-TPD, a weak and broad peak of N₂ was observed around 510 K over CrV_{0.95}P_{0.05}O₄ catalysts, but the other catalysts showed no peak of N₂ at any temperature. The temperature of N₂ evolution was somewhat higher than that of NH₃ desorption around 463 K, suggesting that the catalyst was reduced by NH₃. It is likely that the addition of P enhanced the reducibility of V in the catalyst. The results of the pyridine adsorbed diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements are shown in Fig. 12. When pyridine was adsorbed on the pretreated CrV_{0.95}P_{0.05}O₄ calcined at 843 K (a), several absorption bands were observed and can be assigned based on the results reported with vanadyl pyrophosphate⁵³⁾ and VPO/TiO₂⁵⁴⁾ catalysts, as follows. The bands at 1610, 1575, 1489, and 1448 cm⁻¹ are assigned to vibrations of pyridine molecules adsorbed through coordinative interaction with Lewis acid surface sites (L-Py), while the bands at 1637, 1610, 1539, and 1489 cm⁻¹ are assigned to vibra-



(a) Before and (b) after introduction of H₂O.

Fig. 12 DRIFTS of Pyridine Adsorbed on CrV_{0.95}P_{0.05}O₄ Calcined at 843 K

tions of pyridine molecules adsorbed on Brønsted acid sites (B-Py)⁵⁵. Among these bands, the band at 1489 cm⁻¹ contains contributions due to vibration of both pyridinium ions (B-Py) and coordinatively adsorbed pyridine molecules (L-Py). The band at 1610 cm⁻¹ is also probably due to vibration to both 8b of pyridinium ions (B-Py) and 8a of coordinated pyridines (L-Py). These results indicate that both Brønsted and Lewis acid sites are present on the pretreated CrV_{0.95}P_{0.05}O₄ calcined at 843 K surface. Upon exposure of the CrV_{0.95}P_{0.05}O₄ calcined at 843 K sample to water vapor (Fig. 12 (b)), the intensity of the band at 1448 cm⁻¹ (L-Py) decreased significantly, while that of the band at 1539 cm⁻¹ (B-Py) increased. The ratio of intensities of the bands at 1539 cm⁻¹ and 1448 cm⁻¹ (B-Py/L-Py) changed from 0.96 to 2.27 by exposure to water vapor. This result indicates that a part of Lewis acid sites on the surface of CrV_{0.95}P_{0.05}O₄ calcined at 843 K was converted to Brønsted acid sites by the addition of water vapor⁵⁶. Water should also contribute in the hydrolysis of V-O-P bonds resulting in the formation of new Brønsted acid sites. The remarkable increase in the activity in the presence of water can be well explained by this increase in Brønsted acid sites, *i.e.*, Brønsted acid sites contributes rather strongly to the catalytic activity of CrV_{1-x}P_xO₄ than Lewis acid sites as already reported¹¹. It must be also noted that the effect of water is not only in the enhancement of Brønsted acid sites but also in preventing the nonreactive irreversible absorption of 3-picoline as well as in the desorption of nicotinic acid⁵⁶. The higher acidity may enhance the selectivity to nicotinic acid, probably due to a quick desorption of the acid, which will be protected from further deep oxidation.

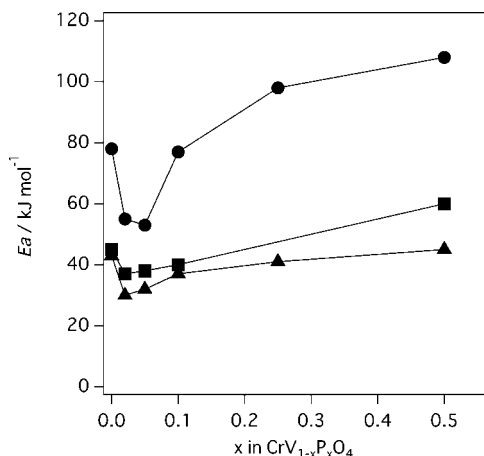


(a) CrVO₄-I calcined at 823 K, (b) CrV_{0.98}P_{0.02}O₄ calcined at 843 K, (c) CrV_{0.95}P_{0.05}O₄ calcined at 843 K, (d) CrV_{0.90}P_{0.10}O₄ calcined at 843 K, (e) CrV_{0.75}P_{0.25}O₄ calcined at 923 K, and (f) CrVO₄-III calcined at 973 K.

Fig. 13 TPR Profiles of the Catalysts

3. 3. 4. Redox Property of CrV_{1-x}P_xO₄ Catalysts

TPR profiles of CrV_{1-x}P_xO₄ catalysts calcined at various temperatures were shown in Fig. 13. The main peak of H₂ consumption was observed at increasing temperatures with increasing P contents. The amount of H₂ consumed decreased with increasing P content, suggesting that V species in the catalyst are reduced. CrPO₄ calcined at 973 K revealed a clearly different curve from the others. CrVO₄-III showed two peaks at 910 K and 1000 K, showing that the V species in CrVO₄-III is more stable than that in CrVO₄-I against the reduction. Interestingly, the active catalysts, *i.e.*, CrVO₄ calcined at 823 K (a), CrV_{0.98}P_{0.02}O₄ calcined at 843 K (b), CrV_{0.95}P_{0.05}O₄ calcined at 843 K (c), CrV_{0.90}P_{0.10}O₄ calcined at 843 K (d), and CrV_{0.75}P_{0.25}O₄ calcined at 923 K (e) gave additional peaks at temperatures lower than the main peak. The first peak appeared around 623 K and the second one around 700 K. The temperature of the first peak almost coincided with the temperature that afforded the highest yield of nicotinic acid, suggesting that catalyst reduction around 623 K is important in the catalytic activity. This temperature varied depending on the P content, and the lowest value, 618 K, was observed with the catalyst giving the highest activity, *i.e.*, CrV_{0.95}P_{0.05}O₄ calcined at 843 K (c). The lowest value of the reduction temperature may well relate to the easy reduction of CrV_{0.95}P_{0.05}O₄ calcined at 843 K proved by the formation of N₂ during the NH₃-TPD. Moreover, the reduction at the first peak was reversibly observed after the reoxidation. After the TPR from room temperature to 623 K, the catalyst was again treated by the TPR, where no reduction peak was observed any more since all active V species have been reduced during the first TPR.



Picoline/H₂O/O₂/N₂ = 1/10.8/24/125. (■) 2-picoline, (●) 3-picoline, (▲) 4-picoline.

Fig. 14 Apparent Activation Energies of the Oxidations of 2-, 3-, and 4-Picolines over CrV_{1-x}P_xO₄ Catalysts

However, when the catalyst was treated by O₂ at 623 K for 1 h, the reduction peak appeared again around 623 K in the TPR. This shows clearly that the reversible reduction-oxidation took place on the V sites around 623 K and contributes to decrease the activation energy on the catalysts containing a small amount of phosphorous (see section 3.3.5.).

3.3.5. Active Sites of CrV_{1-x}P_xO₄ Catalysts

Based on the results of XRD and FT-IR, the change in crystal structure from CrVO₄-I to CrVO₄-III began to appear on CrV_{1-x}P_xO₄ when *x* exceeded 0.1. This structural change was accompanied by the decrease in the activity for the selective oxidation of 3-picoline to nicotinic acid. Moreover, the amorphous phase was not active at all in this selective oxidation. These results strongly suggest that the crystal structure, CrVO₄-I, in the CrV_{1-x}P_xO₄ catalysts played an important role on the catalytic activity.

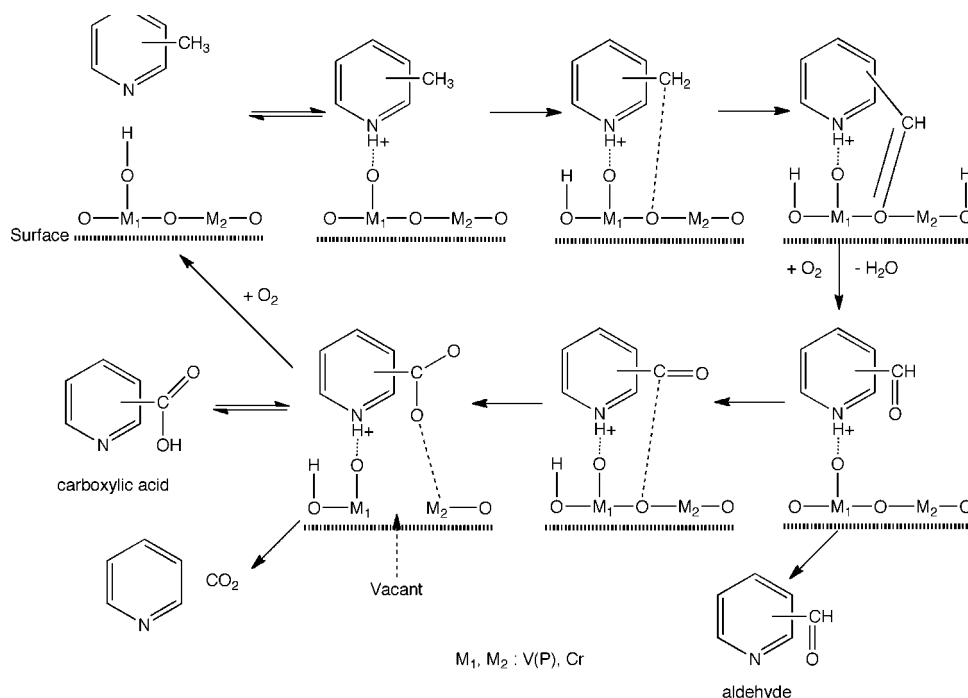
As shown in previous section, the catalytic activity of CrV_{1-x}P_xO₄ may be due to the cooperation between the acid site and the reduction-oxidation property of VO₄²³). This was also suggested in the selective oxidation of 3-picoline over Cr_{1-x}Al_xVO₄ catalysts^{22),24)}. The replacement of V with a small amount of P in CrVO₄-I resulted in an increase in the activity. Activation energies of the CrV_{1-x}P_xO₄ catalyst were calculated from the rate of 2-, 3-, and 4-picolines consumption in the presence of water (molar ratio of H₂O/picolines = 10.8) and are shown in Fig. 14. Evidently the lowest value was observed with CrV_{0.95}P_{0.05}O₄ calcined at 843 K, which coincided well with the order of the activity of CrV_{1-x}P_xO₄ catalysts. Upon increasing the amount of P incorporated in the catalyst, the activation energy was substantially changed, suggesting that the nature of the active site gradually changed with increasing amounts

of P. The replacement of V with a small amount of P was effective for lowering the activation energy, suggesting that the nature of the reduction-oxidation sites is substantially affected by the presence of P.

It is thus concluded that the reduction-oxidation property of V assisted by a small amount of P reveals a definitive role in the rate-determining step of 3-picoline oxidation. Moreover, the V(-P) reduction-oxidation sites are assisted by the efficiently dispersed V-O-Cr bonds in the CrVO₄-I type crystal structure. The rate-determining step may be a H-abstraction from 3-picoline or an oxygen insertion into an active intermediate formed from 3-picoline. Moreover, Brønsted acid sites may be effective for the activation of 3-picoline and/or the desorption of nicotinic acid formed on the catalyst surface. The amount of this acid site was enormously enhanced by the addition of water, and this fact was apparently explained by the conversion of Lewis acid sites to Brønsted acid sites. The role of water should also be given in the hydrolysis of V-O-P bonds resulting in the erection of new Brønsted acid sites. The higher acidity may result particularly in the enhancement of selectivity, probably due to better desorption of the formed acid, which will be protected from further total oxidation. The acid sites are thus important for assisting the selective oxidation of 3-picoline to nicotinic acid on the V sites, while the V sites reveal key role in the selective oxidation 3-picoline by their reduction-oxidation cycles assisted by Cr as well as by a small amount of P.

3.3.6. Mechanism of Picoline Oxidation over CrV_{0.95}P_{0.05}O₄ Catalyst

The catalytic behavior of CrV_{0.95}P_{0.05}O₄ has been investigated in the selective oxidations of 2-, 3- and 4-picolines by *in-situ* DRIFTS, and the model of picoline adsorption and the oxidation mechanism are proposed as shown in Scheme 1. As described in section 3.3.3., both Lewis and Brønsted acid sites were detected on the surface of CrV_{0.95}P_{0.05}O₄, and the number of the latter increased on the addition of steam in the reaction mixture, resulting in enhanced activity for selective oxidations. The enhanced activity due to water addition is interpreted by the fact that Brønsted acid sites are produced by the hydrolysis of V-O-Cr and activate picoline molecules by withdrawing the electrons of the pyridine ring, and at the same time, enable to accelerate the desorption of the acid products from the catalyst surface. Every 2-, 3- and 4-picoline was adsorbed on the catalyst surface via the N atom donating the electrons to the Brønsted acid sites, and the substituted methyl group was oxidized via hydrogen abstraction by surface oxide ion to form the radical intermediate, followed by oxygen insertion to produce the corresponding aldehyde and then acid. Even in the absence of gaseous oxygen, the oxygenated products were formed and observed over the catalyst surface. Thus, a Mars



Scheme 1 Proposed Mechanism of the Oxidation of Picoline over $CrV_{1-x}P_xO_4$ Catalyst

and van Krevelen mechanism was suggested for 2-, 3- and 4-picoline oxidations based on the spectral analysis. Both 2- and 4-picoline were more quickly oxidized than 3-picoline due to the inductive hyper-conjugative effect of nitrogen, resulting in an easy leaving of proton from the methyl group. 4-Picoline produced almost quantitatively isonicotinic acid, while 2-picoline afforded 2-picoline aldehyde as the main product due to the unstability of the acid product, *i.e.*, the decarboxylation of picolinic acid took place to form pyridine.

4. Conclusion

$CrVO_4$ -I (monoclinic) having pure crystalline form was prepared by mixing the aqueous solution of the raw materials and controlling the pH value. $CrVO_4$ -I showed much higher activity than $CrVO_4$ -III (orthorhombic), suggesting that the bridging oxygen in the V–O–Cr bond is responsible for the catalytic activity. When a part of Cr atom or V atom was replaced with Al or P without changing the $CrVO_4$ -I type structure, the activities were enhanced. The acidity increased by the replacement of Cr with Al and V with P in $CrVO_4$ -I, resulting in the accelerating desorption of products. A partial replacement of V with P resulted in a significant increase in the activity probably due to the modification of the redox properties of V–O–Cr site in addition to the accelerating desorption of products. Even in the absence of gaseous oxygen, the oxygenated products were formed, thus, a Mars and van Krevelen mechanism was

suggested.

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要 旨

ソフトケミストリーの手法による結晶性 Cr-V 複合酸化物の調製とピコリン類の気相酸化への適用

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ピコリン類の気相接触酸化に有効な触媒系の探索とその活性サイトの解明を目的として、ソフトケミストリーの手法により各種バナジウム系複合酸化物触媒を調製した。ピコリン類の気相酸化反応には単斜晶の CrVO_4 -I 触媒が高い活性を示した。また、 CrVO_4 -I 構造の Cr の一部分を Al で置換した $\text{Cr}_{0.5}\text{Al}_{0.5}\text{VO}_4$ 、および V の一部分を P で置換した $\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4$ がさらに高い活性を示すことを見出した。さらに、触媒の結晶構造、触媒表

面の性質と触媒活性の関係、Al および P の添加効果、反応系への水蒸気の添加効果および反応機構について検討を行った。Al や P の置換により表面酸量が増加すること、Al および P が置換されたサイトに隣接した格子酸素の反応性が向上することを明らかにした。触媒の表面格子酸素が酸化反応に関与する Mars and van Krevelen 機構により反応が進行していると推定した。