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. 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 drugs 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 hydrazone, 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 V2O5/TiO2, V2O5/SnO2, and over...
viewed \textsuperscript{21} 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 \textsuperscript{22}~\textsuperscript{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$_x$, Cr$_{1-x}$Al$_x$VO$_4$ ($x = 0.25, 0.5, 0.75$ and $1.0$) and CrV$_{1-x}$P$_x$O$_4$ ($x = 0.02-1.00$) catalysts were prepared following method proposed by Touboul and co-workers \textsuperscript{27,28}. Aqueous solutions of NH$_4$VO$_3$, Cr(NO$_3$)$_3$·$9$H$_2$O, Al(NO$_3$)$_3$·$9$H$_2$O and NH$_4$H$_2$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 M = 1 mol·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 CO$_2$, CO and HCN, as a reference.

2.3. Characterization

The X-ray diffraction (XRD) was carried out on a Mac Science MX18XHF-SRA using 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 K·min$^{-1}$ from room temperature to 1273 K with $\alpha$-Al$_2$O$_3$ as a reference. The temperature-programmed desorption 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 mL·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 K·min$^{-1}$ to 50 mL·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 \textit{et al}. have reported that Cr-V mixed oxide catalysts showed high activity for the liquid phase oxidation of acrolein \textsuperscript{29} and cyclohexene \textsuperscript{30} 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 \textsuperscript{27,28}.

Monoclinic ($a = 9.791(6)$ Å, $b = 8.848(5)$ Å, $c = 6.843(6)$ Å and $\beta = 107.8(1)$ Å, $1$ Å $= 10^{-10}$ m; $D_\text{c}$ = 3.98 with $Z = 8$; and space group $C2/m$) CrVO$_4$ belonging to the $\alpha$-MnMoO$_4$ structure of the same as $\beta$-CdCrO$_4$ and $\beta$-MgCrO$_4$ compounds \textsuperscript{31,32} was prepared by mild heating of amorphous precursors and was named as CrV$_x$O$_{4-x}$ (Fig. 1 (a)) \textsuperscript{27,28}. Orthorhombic chromium vanadate (CrV$_x$O$_{4-x}$III) (Fig. 1 (b)) was first characterized by Brandt \textsuperscript{33} in 1943. It can be easily prepared by a solid-state reaction between Cr$_2$O$_3$ and V$_2$O$_5$ at 1023-1073 K\textsuperscript{33,34}. Recently, it has also been synthesized by heating its amorphous precursors at high temperature\textsuperscript{27}. Numbers I and III refer to the parent InVO$_4$ forms\textsuperscript{38}. The orthorhombic form of CrVO$_x$, CrV$_x$O$_{4-x}$-III is, isostuctural to the InVO$_4$-III\textsuperscript{37,38,39}, and the monoclinic form, CrV$_x$O$_{4-x}$-I, is compared with InVO$_4$-I compound\textsuperscript{28}.

As for CrV$_x$O$_2$-I with isostructure to $\alpha$-MnMoO$_4$, the Cr and V atoms replace Mn and Mo, respectively, forming Cr$_6$ octahedra and VO$_4$ tetrahedra, respectively. The arrangement of these polyhedra is totally different from that of stable CrV$_x$O$_{4-x}$III forms\textsuperscript{33,34}. In the latter
structure, there are, along the (0 0 1) direction, chains of edge-sharing CrO$_6$ octahedra linked by VO$_4$ tetrahedra. However, the CrVO$_4$-I structure does not show any chains but contain some cluster. It consists of an infinite network of Cr$_4$O$_{16}$ clusters of four edge-sharing CrO$_6$ octahedra linked to the other clusters by VO$_4$ tetrahedra. In CrVO$_4$-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 Cr$_1$-O and Cr$_2$-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 V$_1$-O and V$_2$-O distances are practically equal to 1.73 Å and 1.72 Å, respectively. In CrVO$_4$-III, the mean Cr-O and V-O distances (2.012 Å and 1.764 Å, respectively) do not differ greatly from CrVO$_4$-I. The main difference between the two forms is that CrVO$_4$-III presents only one type of CrO$_6$ octahedra and VO$_4$ tetrahedra against the two types in CrVO$_4$-I.

3.1.2 Effect of the Structure of CrVO$_4$ on the Activity

XRD patterns of CrVO$_4$ catalysts calcined at various temperatures are shown in Fig. 2. The CrVO$_4$-I monoclinic crystal structure grew by increasing the calcination temperature, but no transition to CrVO$_4$-III was observed. It is reported that orthorhombic CrVO$_4$ (CrVO$_4$-III) was obtained by heating CrVO$_4$-I at 933 K$^{27}$. However, CrVO$_4$-III could not be obtained even when CrVO$_4$-I was calcined at 1093 K for 6 h. The sample of CrVO$_4$-III was prepared by the solid phase reaction between V$_2$O$_5$ and Cr$_2$O$_3$ at 1073 K for 10 h.

Figure 3 shows the results of 3-picoline oxidation over CrVO$_4$ catalysts calcined at various temperatures. The activity was shown as the yield of nicotinic acid and 3-pyridinecarbaldehyde. Interestingly, the activity of CrVO$_4$-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 m$^2$ g$^{-1}$). Further calcination at 1093 K for 6 h resulted in a decrease in the activity together with a significant decrease in the surface area (2.3 m$^2$ g$^{-1}$), but catalyzed the selective oxidation of 3-picoline to pyridine-3-carbaldehyde. CrVO$_4$-III showed a further low activity. The blank test with quartz sand showed only low conversion with no oxygenated products, but catalyzed the selective oxidation of 3-picoline to pyridine-3-carbaldehyde.

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$^{16,37}$. The selective oxida-
Steam addition was recently reported in the investigation on V2O5/TiO2 catalysts. The performance of CrVO4-I catalyst calcined at 623 K. The oxidation on the same (VO)2P2O7 catalyst. The oxidation of 3-picoline, the isolated V sites bearing the redox properties assisted by the presence of steam in the reaction 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, e.g., toluene oxidation over V2O5/TiO2 catalysts. A decline in the activity was observed by the presence of steam in n-butane oxidation, while a contradictory result, i.e., the promotion by steam addition was recently reported in the n-butane oxidation on the same (VO)2P2O7 catalyst. The yields of carboxylic acids were improved in ethane and propane oxidation, though the effect of steam addition is a little complex. 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. 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 reaction.

3.2. Cr1-xAlxVO4 Catalysts

Solid solutions Cr1-xFe3xVO4 can be formed over a wide composition range and are thermally stable above 1173 K. 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 Å, respectively. The ionic radius of Al3+ is 0.68 Å. AlVO4 and FeVO4 are isostructural. The samples, Cr1-xAlxVO4 (x = 0, 0.25, 0.5, 0.75 and 1.0) were prepared and tested for the oxidation of 3-picoline.
spectra of the Cr\(_{1-x}\)Al\(_x\)VO\(_4\) catalysts are consistent with the XRD results. CrVO\(_4\)-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 Cr\(_{0.25}\)Al\(_{0.75}\)VO\(_4\) changed substantially and became close to that of AlVO\(_4\), suggesting that AlVO\(_4\) structure predominated in Cr\(_{0.25}\)Al\(_{0.75}\)VO\(_4\).

### 3.2.2 Activity of Cr\(_{1-x}\)Al\(_x\)VO\(_4\) Catalysts

The results of 3-picoline oxidation on Cr\(_{1-x}\)Al\(_x\)VO\(_4\) (\(x = 0, 0.25, 0.5, 0.75\) 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 Cr\(_{0.5}\)Al\(_{0.5}\)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 Cr\(_{1-x}\)Al\(_x\)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 Cr\(_{0.5}\)Al\(_{0.5}\)VO\(_4\) and Cr\(_{0.75}\)Al\(_{0.25}\)VO\(_4\) showed the low values of about 65 kJ 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 kJ mol\(^{-1}\) was obtained with AlVO\(_4\).

For better understanding of the results obtained on the Cr\(_{1-x}\)Al\(_x\)VO\(_4\) catalysts, NH\(_3\)-TPD experiments were carried out on CrVO\(_4\), Cr\(_{0.5}\)Al\(_{0.5}\)VO\(_4\), and AlVO\(_4\). The conversion and selectivity to nicotinic acid increased with increasing the molar ratio of H\(_2\)O 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\(_2\)O 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 Cr\(_{0.5}\)Al\(_{0.5}\)VO\(_4\) catalyst. The effect of the addition of steam in the catalytic activity was more intensively observed on Cr\(_{0.5}\)Al\(_{0.5}\)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 Cr\(_{0.5}\)Al\(_{0.5}\)VO\(_4\) catalyst results in the acceleration of the oxidation of 3-picoline to nicotinic acid. It was reported that the activity of V\(_2\)O\(_5\)/TiO\(_2\) catalyst for the 3-picoline oxidation is partly due to Brønsted acid sites\(^{30}\). 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 Cr\(_{0.5}\)Al\(_{0.5}\)VO\(_4\) catalyst having Brønsted acid sites in addition to redox proper-
3.3.1. Structure of CrV1

The structure of CrV1 described.

VO4 tetrahedra linking the Cr4O16 clusters, taking into account the smaller ionic radii of P5-

Indeed, it will be possible to modify the active V-O-Cr sites by replacing V5+

A totally replaced CrPO4 showed only an amorphous phase even after the calcination at 973 K (i). Different hydrates of CrPO4 are known52); their calcinations at high temperature allow the anhydrous material to be formed in two types of their polymorphic forms: β-CrPO4 above 1273 K and α-CrPO4 above 1448 K. Thus, amorphous CrPO4 is stable and does not crystallize even at high temperature of 1173 K in the DTA curves23).

FT-IR spectra of CrV1-xP2O4 Catalysts well correlated with the results of XRD analyses. The CrV1-xP2O4 catalysts containing P in the range of 0 ≤ x ≤ 0.02 showed the adsorption bands at 960, 925, 744, and 667 cm⁻¹, probably assigned to V-O-V, V-O-Cr and Cr-O-Cr stretching vibrations of the monoclinic CrVO4-I structure. An increase in the P contents (0.02 ≤ x ≤ 0.10) resulted in a blue shift of the bands of CrVO4-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 α-CrPO4 phase. When the P contents increased to 0.25 ≤ x ≤ 0.5, the spectra changed substantially and became close to that of α-CrPO422). CrV0.98P0.02O4 calcined at 923 K, CrV0.75P0.25O4 calcined at 843 K, and CrPO4 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 CrV1-xP2O4 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 CrPO4 calcined at 973 K and probably formed by decarboxylation of nicotinic acid. CrV0.98P0.02O4 calcined at 843 K showed the highest yields of nicotinic acid and pyridine-3-carbaldehyde, followed by CrV0.98P0.02O4 calcined at 83 K, although their surface areas were smaller than CrVO4 calcined at 823 K. When x exceeded 0.05, the yields gradually decreased with increasing x, and finally CrPO4 showed a sudden
decline in the activity, resulting in no formation of nicotinic acid. It is thus suggested that the CrVO4-I structure is important for the selective oxidation of 3-picoline and a small amount of phosphorus assists the catalytic activity of CrVO4-I. This suggestion was confirmed by the further studies on the effect of the calcination temperature of CrV0.95P0.05O4 and CrV0.75P0.25O4. Yields of the products per surface area of the catalysts are shown in Fig. 9 for both CrV0.95P0.05O4 and CrV0.75P0.25O4 calcined at different temperatures. When CrV0.95P0.05O4 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 CrV0.75P0.25O4, 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 CrV0.95P0.05O4 calcined at 623 K and CrV0.75P0.25O4 calcined at 843 K changed to the crystalline phases of CrV0.95P0.05O4 calcined at 843 K, CrV0.75P0.25O4 calcined at 923 K and CrV0.75P0.25O4 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 CrVO4-I structure. The temperature of 923 K does not seems high enough, but may be recovered by calcination for 6 h for assisting the crystallization of the CrVO4-I structure in CrV0.75P0.25O4 calcined at 923 K. It will be concluded that the monoclinic CrVO4-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 CrV0.95P0.05O4 catalyst 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,
apparent activation energy was almost constant independent of the amount of water. 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 CrV0.95P0.05O4 calcined at 843 K in the presence of an excess amount of water 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 CrV0.95P0.05O4 calcined at 843 K for nicotinic acid production was far higher than that of Cr0.5Al0.5VO4 (21,24) and CrVO4-III (25), 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 to 523-553 K and afforded nicotinic acid with the selectivity above 90% at the conversion above 90% (13,12). However, only anatase TiO2 was reported that V2O5/TiO2 catalyzed the selective oxidation of 3-picoline to nicotinic acid with the selectivity above 90% (11,12). However only anatase TiO2 was profitable for the selective oxidation of 3-picoline to nicotinic acid with the selectivity above 90%.

CrV0.95P0.05O4 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 3-picoline and a small amount of phosphorus assists the catalytic activity of CrVO4-I. In the case of 4-picoline oxidation over CrV1-xP0.05O4 (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 CrV0.95P0.05O4 calcined at 843 K showed the highest yield (75.0%) of isonicotinic acid. Both 2- and 4-picelines 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-picelines, respectively. Picolinic acid was not obtained from 2-picoline, since picolinic acid was easily decomposed to pyridine and CO2.

### Acidic Property of CrV1-xP0.05O4 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-I as a reference was also tested and compared with the other catalysts of a CrVO4-I type crystal structure. A large amount of CrVO4-I 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-I, 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 CrV0.95P0.05O4 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 CrV1-xP0.05O4 calcined at 843 K (a), several absorption bands were observed and can be assigned based on the results reported with vanadyl pyrophosphate (51) and VPO/TiO2 catalysts, as follows. The bands at 1610, 1575, 1489, and 1484 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 vibration...
tions of pyridine molecules adsorbed on Brønsted acid sites \((B_{\text{Py}})\)\(^{55}\). Among these bands, the band at 1489 \text{cm}^{-1} contains contributions due to vibration of both pyridinium ions \((B_{\text{Py}})\) and coordinatively adsorbed pyridine molecules \((L_{\text{Py}})\). The band at 1610 \text{cm}^{-1} is also probably due to vibration to both \(8b\) of pyridinium ions \((B_{\text{Py}})\) and \(8a\) of coordinated pyridines \((L_{\text{Py}})\). These results indicate that both Brønsted and Lewis acid sites are present on the pretreated \(\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4\) calcined at 843 K surface. Upon exposure of the \(\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4\) calcined at 843 K sample to water vapor (Fig. 12(b)), the intensity of the band at 1448 \text{cm}^{-1} (\(L_{\text{Py}})\) decreased significantly, while that of the band at 1539 \text{cm}^{-1} (\(B_{\text{Py}})\) increased. The ratio of intensities of the bands at 1539 \text{cm}^{-1} and 1448 \text{cm}^{-1} \((B_{\text{Py}}/L_{\text{Py}})\) 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 \(\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4\) calcined at 843 K was converted to Brønsted acid sites by the addition of water vapor\(^{56}\). 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 \(\text{CrV}_{1-x}\text{P}_x\text{O}_4\) than Lewis acid sites as already reported\(^{11}\). 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 acid\(^{56}\). 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.

3.3.4. Redox Property of \(\text{CrV}_{1-x}\text{P}_x\text{O}_4\) Catalysts

TPR profiles of \(\text{CrV}_{1-x}\text{P}_x\text{O}_4\) catalysts calcined at various temperatures were shown in Fig. 13. The main peak of \(H_2\) consumption was observed at increasing temperatures with increasing \(P\) contents. The amount of \(H_2\) consumed decreased with increasing \(P\) content, suggesting that \(V\) species in the catalyst are reduced. \(\text{CrPO}_4\) calcined at 973 K revealed a clearly different curve from the others. \(\text{CrVO}_4\) showed two peaks at 910 K and 1000 K, showing that the \(V\) species in \(\text{CrVO}_4\)-III is more stable than that in \(\text{CrVO}_4\)-I against the reduction. Interestingly, the active catalysts, i.e., \(\text{CrVO}_4\) calcined at 823 K (a), \(\text{CrV}_{0.98}\text{P}_{0.02}\text{O}_4\) calcined at 843 K (b), \(\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4\) calcined at 843 K (c), \(\text{CrV}_{0.90}\text{P}_{0.10}\text{O}_4\) calcined at 843 K (d), and \(\text{CrV}_{0.75}\text{P}_{0.25}\text{O}_4\) 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., \(\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4\) calcined at 843 K. The lowest value of the reduction temperature may well relate to the easy reduction of \(\text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4\) calcined at 843 K proved by the formation of \(N_2\) during the \(\text{NH}_3\)-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.
However, when the catalyst was treated by \( \text{O}_2 \) 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 \( \text{CrV}_{1-x}\text{P}_x\text{O}_4 \) Catalysts

Based on the results of XRD and FT-IR, the change in crystal structure from \( \text{CrVO}_4\text{-I} \) to \( \text{CrVO}_4\text{-III} \) began to appear on \( \text{CrV}_{1-x}\text{P}_x\text{O}_4 \) 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, \( \text{CrVO}_4\text{-I} \), in the \( \text{CrV}_{1-x}\text{P}_x\text{O}_4 \) catalysts played an important role in the catalytic activity.

As shown in previous section, the catalytic activity of \( \text{CrV}_{1-x}\text{P}_x\text{O}_4 \) may be due to the cooperation between the acid site and the reduction-oxidation property of \( \text{VO}_2^{2+} \). This was also suggested in the selective oxidation of 3-picoline over \( \text{Cr}_{1-x}\text{Al}_x\text{VO}_4 \) catalysts\(^{22,24} \). The replacement of V with a small amount of P in \( \text{CrVO}_4\text{-I} \) resulted in an increase in the activity. Activation energies of the \( \text{CrV}_{1-x}\text{P}_x\text{O}_4 \) catalyst were calculated from the rate of 2-, 3-, and 4-picoline consumption in the presence of water (molar ratio of \( \text{H}_2\text{O}/\text{picolines} = 10.8 \)) and are shown in Fig. 14. Evidently the lowest value was observed with \( \text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4 \) calcined at 843 K, which coincided well with the order of the activity of \( \text{CrV}_{1-x}\text{P}_x\text{O}_4 \) 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 \( \text{CrVO}_4\text{-I} \) 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 \( \text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4 \) Catalyst

The catalytic behavior of \( \text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4 \) has been investigated in the selective oxidations of 2-, 3- and 4-picoline 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 \( \text{CrV}_{0.95}\text{P}_{0.05}\text{O}_4 \), 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
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

CrVO₄-I (monoclinic) having pure crystalline form was prepared by mixing the aqueous solution of the raw materials and controlling the pH value. CrVO₄-I showed much higher activity than CrVO₄-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 CrVO₄-I type structure, the activities were enhanced. The acidity increased by the replacement of Cr with Al and V with P in CrVO₄-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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References

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パラ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独品の CrVO₄-I 触媒が高い活性を示した。また、CrVO₄-I 製造の Cr の一部を Al で置換した Cr₆Al₉V₀₈ および V の一部を P で置換した CrVO₄-P₆O₆ 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、A1 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 および 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鍵となる格子酸素の活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 構機構による反応が進行していると推定した。

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