3-Picoline Oxidation over Monoclinic Orthovanadate $Cr_{0.5}Al_{0.5}VO_4$ Catalysts

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Monoclinic orthovanadate $CrVO_4$-I was found to be active for the vapor phase oxidation of 3-picoline to nicotinic acid and was further activated by the solid solution formation with Al at the Cr site.

Nicotinic acid is an important intermediate for pharmaceuticals and food additives and has been produced by the liquid phase oxidation of 3-picoline. Solid, heterogeneous catalysts have the advantages of ease of recovery and recycling and are readily amenable to continuous processing. The selective oxidation of 3-picoline to nicotinic acid has been investigated by using V_2O_5/TiO_2 catalysts.[1,2] Recently it was reported that some metal vanadates have been synthesized in the pure crystalline form just by controlling the pH of the aqueous solution.[3–5] Here, we report a new class of catalyst for the vapor-phase oxidation of 3-picoline to nicotinic acid, i.e., $CrVO_4$-I,[4] which is prepared as the pure crystalline form and shows the high activity when a half of Cr atoms are replaced by Al.

The catalysts were prepared following the method proposed by Touboul et al.[3–5] Aqueous solutions of NH_4VO_3 and $Cr(NO_3)_3{\cdot}9H_2O$ were mixed and the pH value of the solution was lowered below 1.0 to form homogeneous solution by adding 3M nitric acid. Then, the pH value of the solution was adjusted at 4.0 to favor the precipitation process by adding 3M ammonia aqueous solution. The ratio of Cr/V was fixed at 1.0. The precipitates were washed with de-ionized water, dried at 100 °C overnight, and calcined in air at 550 °C for 6 h. Pure orthovanadate $CrVO_4$-I was obtained after the calcination. The other metal (Y, Bi, Fe, Co, Fe and Mn) vanadates were also prepared in a similar way. In the case of $Cr_xAl_{1-x}VO_4$ (x = 0, 0.25, 0.5, 0.75 and 1.0), $Al(NO_3)_3{\cdot}9H_2O$ was used as the third component and treated in a similar way. The samples $Cr_xAl_{1-x}VO_4$ were calcined at 580 °C considering the temperature of crystallization of each phase. As the reference catalyst, $CrVO_4$-III was prepared by solid phase reaction, i.e., by calcining the mixture of V_2O_5 and Cr_2O_3 at 800 °C for 10 h.

The catalytic tests were conducted in a fixed-bed reactor at atmospheric pressure and temperatures from 300 to 360 °C using 0.2 g of the catalyst particles with size of 26–42 mesh. The mixture of 3-picoline/$H_2O/O_2/N_2$ was passed through the reactor at the flow rate of 0.75/8.1/18/100 mL-NTP·min^{-1} and the products were analyzed by gas chromatography. The highest activity for nicotinic acid production was observed for $CrVO_4$-I among the metal vanadates tested. The results of 3-picoline oxidation over several $CrVO_4$ catalysts at 360 °C are shown in Figure 1, together with the surface area of the catalyst. The activity was shown as the yield of nicotinic acid (Acid) or 3-pyridinecarbaldehyde (Aldehyde), or the conversion of 3-picoline per unit surface area of the catalyst. XRD patterns of the catalysts are shown in Figure 2. Crystal structure of $CrVO_4$-I is monoclinic, a = 9.791(6) Å, b = 8.848(5) Å, c = 6.843(6) Å and β = 107.8(1)°; D_x = 3.98 with Z = 8; and space group *C2/m*.[3] It was reported that orthorhombic $CrVO_4$ ($CrVO_4$-III) was obtained by heating $CrVO_4$-I at 660 °C.[4] However, $CrVO_4$-I grew even after the calcination at 700 °C (Figure 2b) and

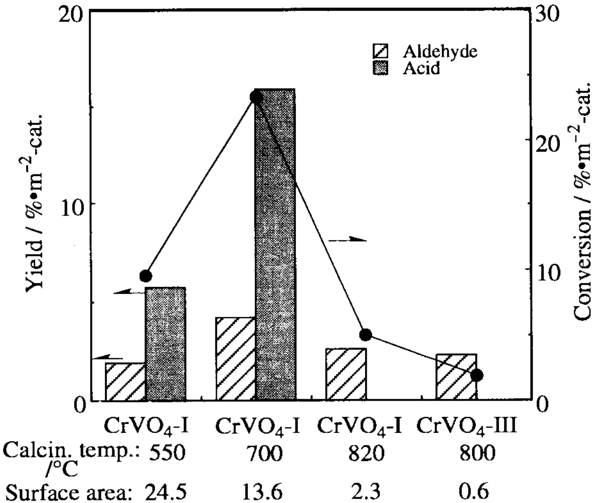

Figure 1. 3-Picoline oxidation over the $CrVO_4$ catalysts.

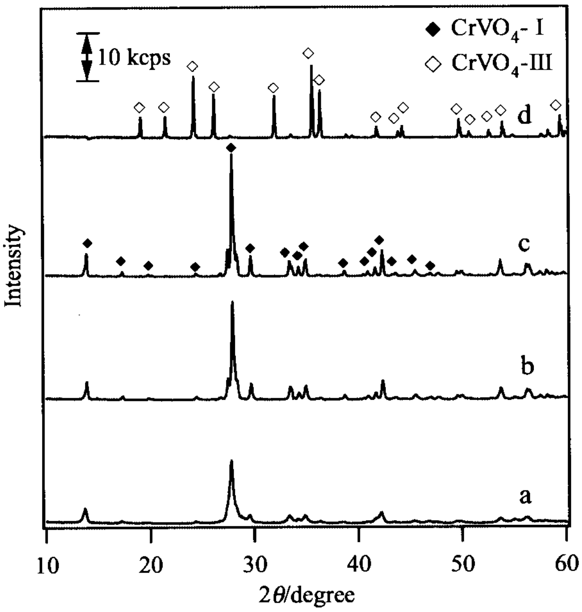

Figure 2. XRD Patterns of the $CrVO_4$ catalysts. **a**: $CrVO_4$-I calcined at 550 °C, **b**: $CrVO_4$-I calcined at 700 °C, **c**: $CrVO_4$-I calcined at 820 °C, **d**: $CrVO_4$-III calcined at 800 °C. Cu Kα radiation.

showed high activity for the selective oxidation, nonetheless the surface area decreased. Further calcination at 820 °C for 6 h resulted in a decrease in both surface area and activity (Figure 2c). $CrVO_4$-III prepared by the solid phase reaction between V_2O_5 and Cr_2O_3 (Figure 2d) showed low surface area as well as low activity for the oxidation of 3-picoline. Thus, it is most likely that $CrVO_4$-I structure with high surface area is active for the oxidation of 3-picoline into nicotinic acid.

The samples of composition $Cr_xAl_{1-x}VO_4$ (x = 0, 0.25, 0.5, 0.75 and 1.0) were prepared and tested for the oxidation of 3-picoline. XRD patterns of $Cr_xAl_{1-x}VO_4$ continuously changed from $CrVO_4$-I (α–$MnMoO_4$ structure) to $AlVO_4$ (triclinic structure, JCPDS 39-276) with increasing the Al content. The samples with $x \geq 0.5$ basically kept α-$MnMoO_4$ structure with broadening the diffraction line-width with increasing x, suggesting that Al^{3+} ion may substitute Cr^{3+} site in $CrVO_4$-I crystal structure. Vegard's plots of the shift in the diffraction lines of $CrVO_4$-I also suggest the formation of solid solution $Cr_xAl_{1-x}VO_4$. It is likely that Al^{3+} replaces the site of Cr^{3+} in $CrVO_4$-I, considering the smaller ionic radius of Al^{3+} (0.68 Å) than Cr^{3+} (0.76 Å).[6] When the content of Al (1–x) exceeded 0.5, the patterns substantially changed to $AlVO_4$ structure and $CrVO_4$-I of α–$MnMoO_4$ type structure was not achieved any more. FT-IR spectra of the samples $Cr_xAl_{1-x}VO_4$ agreed with the XRD results.

The results of the oxidation of 3-picoline over the $Cr_xAl_{1-x}VO_4$ catalysts at 360 °C in the presence of water (H_2O/3-picoline molar ratio: 10.8) are shown in Figure 3. The activity for nicotinic acid production relatively well correlated with the surface area up to a half substitution of Cr with Al. The conversion of 3-picoline and the total yield of nicotinic acid and 3-pyridinecarbaldehyde increased with increasing the Al content up to x = 0.5, and then suddenly decreased upon further increasing the Al content. $AlVO_4$ showed a low activity for the production of nicotinic acid. Apparent activation energies calculated from the rates of 3-picoline consumption over the $Cr_xAl_{1-x}VO_4$ catalysts showed a similar tendency. Both $Cr_{0.5}Al_{0.5}VO_4$ and $Cr_{0.75}Al_{0.25}VO_4$ showed the lowest value well coinciding with their high activities, while an increasing activation energy was observed with increasing the Al content and the highest value was obtained over $AlVO_4$.

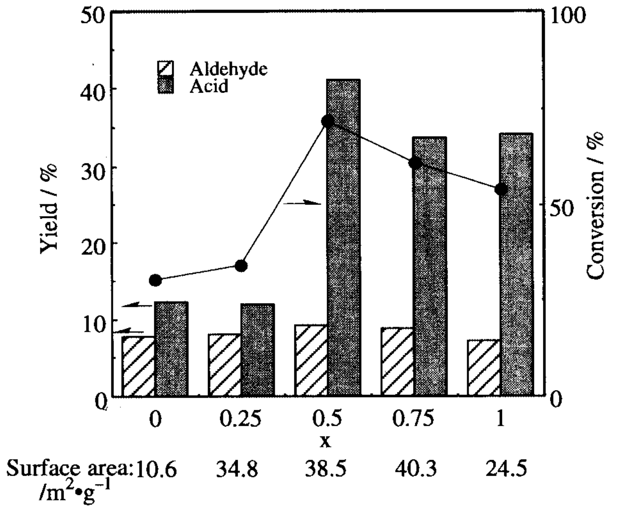

Figure 3. 3-Picoline oxidation over the $Cr_xAl_{1-x}VO_4$ catalysts.

Recent studies on surface vanadium oxide species on oxide supports suggested that the bridging oxygen in the V–O–support bond is responsible for the catalytic activity for hydrocarbon oxidation.[7] It was reported that the increase of the interface between V_2O_5 and TiO_2 phases is the determining factor to improve the catalyst's activity in the selective oxidation of 3-picoline[2] or toluene[8] in the vapor phase. Monomeric vanadia species with vanadium in tetrahedral coordination was formed and the bridging oxygen in the V–O–Ti bond is suggested to be responsible for the catalytic activity during the selective oxidation of toluene.[8] Indeed in the present system, it is likely that V–O–Cr site is responsible for the selective oxidation of 3-picoline. The fact that $CrVO_4$-I has higher activity than $AlVO_4$ suggests that V–O–Cr site is much more important than V–O–Al site.

The structure $CrVO_4$-I belongs to the α-$MnMoO_4$ type. In this vanadate, the Cr and V atoms replace Mn and Mo respectively, in order to form CrO_6 octahedra and VO_4 tetrahedra.[3] The arrangement of these polyhedra is totally different from one in the stable $CrVO_4$-III form [orthorhombic *Cmcm*].[9] In the latter structure, there are, along the [001] direction, chains of edge-sharing CrO_6 octahedra linked by VO_4 tetrahedra. On the other hand, the $CrVO_4$-I structure does not show any chain but contains some clusters as in α-$MnMoO_4$. Indeed, it consists of an infinite network of Cr_4O_{16} clusters of four edge-sharing CrO_6 octahedra linked to the other clusters by VO_4 tetrahedra.[3] Moreover the high activity as well as the high selectivity of the $Cr_{0.5}Al_{0.5}VO_4$ catalyst can be ascribed to its crystal structure based on $CrVO_4$-I. The activity was enhanced by the addition of Al without changing the $CrVO_4$-I type structure, even though the details of the crystal structure are not yet elucidated. Therefore, we conclude that structure of $CrVO_4$-I with high surface area was prepared by the present method and its V–O–Cr sites are active for the selective oxidation of 3-picoline to nicotinic acid. Moreover it was demonstrated that the addition of Al into $CrVO_4$-I caused the effective dispersion of active V–O–Cr sites, resulting in the high activity.

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