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Crystalline $CrV_{0.95}P_{0.05}O_4$ catalyst for vapor-phase oxidation of picolines

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$CrV_{0.95}P_{0.05}O_4$ prepared as a pure crystalline form was found to be highly active for the vapor-phase oxidation of picolines to the corresponding aldehydes and acids in the presence of water.

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. 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 the heterogeneous catalysts is environmentally benign. The vapor phase oxidation of 3-picoline has been performed on a series of vanadium containing catalysts such as V_2O_5/TiO_2,[1–5] V_2O_5/SnO_2,[6] and overviewed recently.[7]

We have reported that $Cr_{0.5}Al_{0.5}VO_4$ was active for the vapor phase oxidation of 3-picoline to nicotinic acid.[8] Monoclinic $CrVO_4$-I, which belongs to the α-$MnMoO_4$ structure, was effective and, moreover, its activity was enhanced by replacing half of Cr atoms by Al. Attfield[9] reported that replacement of V in $CrVO_4$-I with P is also possible, still keeping the α-$MnMoO_4$ structure. Indeed, it is expected that the activity of $CrVO_4$-I can be modified by replacing the V^{5+} by P^{5+} in the VO_4 tetrahedra, considering the ionic radii of 0.40 and 0.35 Å, respectively.[10]

The $CrV_{1-x}P_xO_4$ (x = 0.02–1.0) catalysts were prepared following the method proposed by Touboul *et al.*[11,12] Aqueous solutions of NH_4VO_3, $Cr(NO_3)_3{\cdot}9H_2O$ and $NH_4H_2PO_4$ were mixed to form a homogeneous solution by controlling the pH below 1.0. Then, the pH value was adjusted to 4.0 at 323 K to form the precipitates which were washed, dried at 373 K overnight, and finally calcined at 823–973 K in air for 6 h. The catalytic tests were performed in a fixed-bed reactor at atmospheric pressure between 523 and 673 K. 0.2 g of the catalyst was diluted with quartz sand and filled in the Pyrex glass tube reactor. The molar ratio of picoline/$H_2O/O_2/N_2$ was fixed at 1/108/31/57 at a gas hourly space velocity of 31000 ml h^{-1} g-cat^{-1}. The products were analyzed by a FID and an on-line TCD gas chromatograph.

The calcination temperature of the catalyst was selected based on the results of DTA measurement. A sharp exothermic peak appeared at 811 K with $CrVO_4$ and was assigned to the crystallization of $CrVO_4$-I.[12] The temperature of this exothermic peak increased gradually with increasing x in $CrV_{1-x}P_xO_4$ and finally disappeared for $CrPO_4$ at temperatures below 1200 K. This crystallization to the $CrVO_4$-I phase was clearly confirmed by the results of XRD measurements of the catalysts (Fig. 1). Numbers in the parenthesis at the end of the catalyst symbol shows the calcination temperature. $CrV_{0.95}P_{0.05}O_4$(843) (Fig. 1(d)) showed mainly the patterns of monoclinic $CrVO_4$-I structure,[10] while $CrV_{0.95}P_{0.05}O_4$(623) was totally amorphous (Fig. 1(c)). $CrV_{0.75}P_{0.25}O_4$(843) was amorphous (Fig. 1(f)), but $CrV_{0.75}P_{0.25}O_4$(923) crystallized as $CrVO_4$-I as well as $CrVO_4$-III (Fig. 1(g)) and the crystallinity of the latter increased with increasing calcination temperature (Fig. 1(h)). Numbers I and III refer to the parent $InVO_4$ forms.[13] $CrVO_4$-I can be compared with $InVO_4$-I, while $CrVO_4$-III is isostructural to $InVO_4$-III and belongs to the orthorhombic form of $CrVO_4$. The diffraction lines of the monoclinic $CrVO_4$-I phase were observed exclusively for $CrV_{1-x}P_xO_4$ catalysts with $0 \leqslant x \leqslant 0.05$ and, moreover, the diffraction lines of both (−110) and (−220) in $CrVO_4$-I shifted toward lower d values with increasing x following Vegard's law. These results strongly suggest that P atoms were incorporated in the structure of $CrVO_4$-I probably by replacing the V sites in the VO_4 tetrahedra linking the Cr_4O_{16} clusters.[14] When x was increased to 0.5 in $CrV_{1-x}P_xO_4$, the $CrVO_4$-III phase alone was observed (Fig. 1(i)), even though the diffraction lines were weak and broad. A totally replaced $CrPO_4$ showed only an amorphous phase even after calcination at 973 K (Fig. 1(j)). Different hydrates of $CrPO_4$ are known;[15] their calcination at high temperature allows the anhydrous material to be formed in two types of the polymorphic forms: β-$CrPO_4$ above 1273 K and α-$CrPO_4$ above 1448 K. Thus, amorphous $CrPO_4$ is stable and does not crystallize even at the high temperature of 1173 K. Surface areas of crystallized $CrV_{1-x}P_xO_4$ were between 15 and 25 m^2 g-cat^{-1}, while those of amorphous forms, $CrV_{0.95}P_{0.05}O_4$(623), $CrV_{0.75}P_{0.25}O_4$(843) and $CrPO_4$(973) were 103.6, 52.9 and 6.4 m^2 g-cat^{-1}, respectively.

FT-IR spectra of $CrV_{1-x}P_xO_4$ correlated well with the results of XRD analyses. The $CrV_{1-x}P_xO_4$ catalysts containing P in the range of $0 \leqslant x \leqslant 0.1$ showed absorption bands at 954,

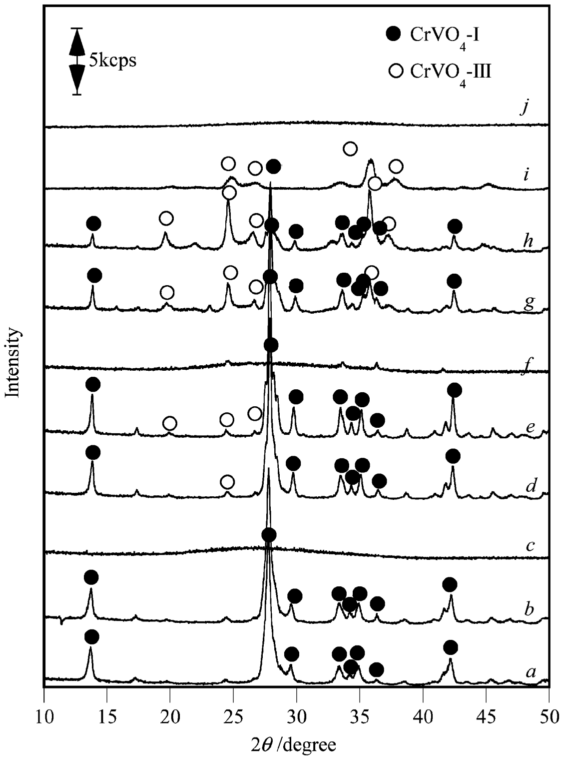

Fig. 1 XRD patterns of the $CrV_{1-x}P_xO_4$ catalysts. (a) $CrVO_4$(823), (b) $CrV_{0.98}P_{0.02}O_4$(843), (c) $CrV_{0.95}P_{0.05}O_4$(623), (d) $CrV_{0.95}P_{0.05}O_4$(843), (e). $CrV_{0.9}P_{0.1}O_4$(843), (f) $CrV_{0.75}P_{0.25}O_4$(843), (g) $CrV_{0.75}P_{0.25}O_4$(923), (h) $CrV_{0.75}P_{0.25}O_4$(973), (i) $CrV_{0.5}P_{0.5}O_4$(973) and (j) $CrPO_4$(973).

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886, 753, 734 and 673 cm^{-1}, probably assigned to V–O–V, V–O–Cr and Cr–O–Cr stretching vibrations of the monoclinic $CrVO_4$-I structure. An increase in the P content resulted in a blue shift of the bands of $CrVO_4$-I, indicating that some V–O bonds are replaced by P–O. $CrV_{0.95}P_{0.05}O_4$(623), $CrV_{0.75}P_{0.25}O_4$(843) and $CrPO_4$(973) showed no absorption bands probably due to the amorphous structures, because of too low calcination temperatures for their crystallization.

In the oxidation of 3-picoline over $CrV_{1-x}P_xO_4$, the main products were nicotinic acid (NA) and pyridine-3-carbaldehyde (3-Ald), as well as CO_2 as a by-product. A small amount of pyridine (Pyr) was formed probably by decarboxylation of nicotinic acid. Mass balance calculated between 3-picoline conversion and the product yields was above 95% in every reaction. $CrV_{0.95}P_{0.05}O_4$(843) showed the highest yields of nicotinic acid and pyridine-3-carbaldehyde, followed by $CrV_{0.98}P_{0.02}O_4$(843), although their surface areas were lower than $CrVO_4$(823). When x exceeded 0.05, the yields gradually decreased with increasing x, and finally $CrPO_4$(973) showed a sudden decline in the activity, resulting in no formation of nicotinic acid. Yields of the products per surface area of $CrV_{0.95}P_{0.05}O_4$ calcined at 623 and 843 K are compared in Fig. 2. $CrV_{0.95}P_{0.05}O_4$(623) showed extremely low values, but $CrV_{0.95}P_{0.05}O_4$(843) showed the highest values among the catalysts tested. The surface area was 103.6 m^2 g-cat^{-1} for $CrV_{0.95}P_{0.05}O_4$(623) and 21.1 m^2 g-cat^{-1} for $CrV_{0.95}P_{0.05}O_4$(843). Nonetheless of such significant discrepancy in the surface area, the effect of crystallization of $CrVO_4$-I structure by calcination was clearly observed. A similar effect of the calcination temperature was observed over $CrV_{0.75}P_{0.25}O_4$. These critical features can be explained by the structure change from amorphous to crystalline as observed by XRD (Fig. 1(c) and (d)). Interestingly, it is concluded that monoclinic $CrVO_4$-I-based structure is essential for the selective oxidation of 3-picoline and its activity is enhanced by the incorporation of P in the V-site in the crystal structure.

Increasing temperature is favorable for the selective oxidation of 3-picoline to nicotinic acid and the optimum temperature was found to be 633 K (Fig. 3). Above 633 K, the reaction temperature could not be controlled probably due to increasing combustion, resulting in decreasing selectivity. The activity of $CrV_{0.95}P_{0.05}O_4$(843) for nicotinic acid production was higher than that of $Cr_{0.5}Al_{0.5}VO_4$ previously reported.[8] The highest yields of nicotinic acid, 78.4%, and pyridine 3-carbaldehyde, 5.4%, at a conversion of 92.6% were found at 633 K. It was reported that V_2O_5/TiO_2 catalyzed the selective 3-picoline oxidation at 520–550 K and afforded nicotinic acid with a selectivity above 90% at a conversion above 90%.[2,3] However only anatase TiO_2 was effective as the support and is possibly transformed to rutile TiO_2, resulting in the deactivation, during the exothermic reaction. On the other hand, $CrV_{0.95}P_{0.05}O_4$(843) is thermally stable and a promising catalyst for the oxidation reaction. $CrV_{0.95}P_{0.05}O_4$(843) showed again the highest activity in the oxidation of both 2- and 4-picolines. 2-Picoline afforded pyridine-2-carbaldehyde with a yield of 50.2% at a conversion of 69.2% and no picolinic acid was formed at 573 K. 4-Picoline afforded pyridine-4-carbaldehyde (yield, 8.9%), isonicolinic acid (yield, 84.3%) at a conversion of 98.7% at 598 K.

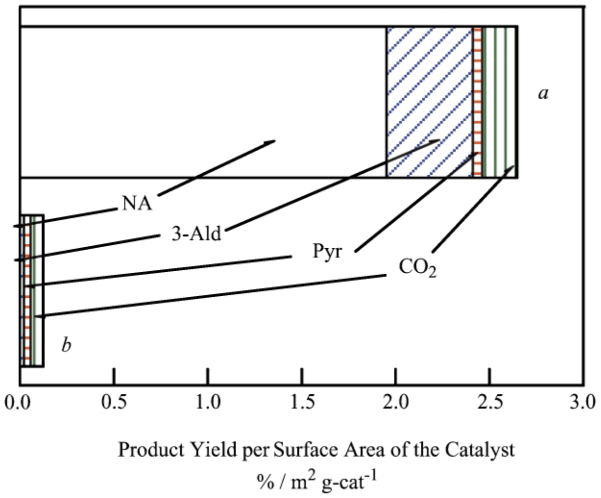

Fig. 2 Oxidation of 3-picoline over the $CrV_{0.95}P_{0.05}O_4$ catalysts. Reaction temperature: 623 K. (a) $CrV_{0.95}P_{0.05}O_4$(843) and (b) $CrV_{0.98}P_{0.02}O_4$(623).

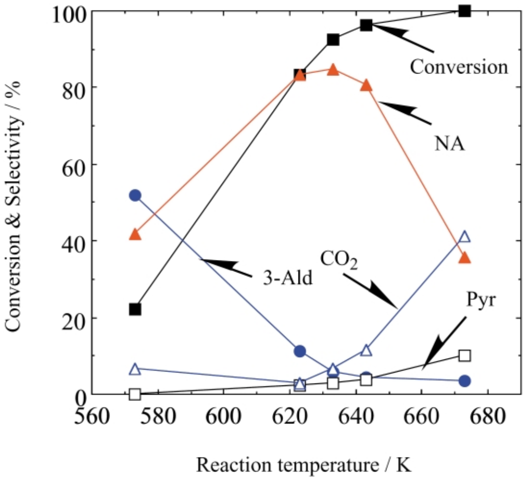

Fig. 3 Oxidation of 3-picoline over $CrV_{0.95}P_{0.05}O_4$(843).

NH_3-TPD showed an increase in the number of acid sites by replacing V with small amount of P in $CrVO_4$-I. The favorable effect of water addition and the results of DRIFTS measurement of pyridine adsorbed on the catalyst[16] in the presence of water suggest that Brønsted acid sites are the active species. Moreover, all the V species are present as VO_4 tetrahedra in the $CrVO_4$-I structure[14] and considered to act as active sites *via* their redox properties. It is concluded that picolines can be selectively oxidized on the $CrV_{0.95}P_{0.05}O_4$ catalyst having Brønsted acid sites assisted by the redox properties. This thermally stable crystalline structure seems to be favorable as the active phase for the oxidation reaction with gaseous oxygen that tends to form hot spots in the catalyst bed.

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