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

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Abstract

The catalytic behavior of $CrV_{0.95}P_{0.05}O_4$ has been studied in the selective oxidation of picolines and the oxidation mechanism is discussed. Brönsted acid site was detected on the surface of $CrV_{0.95}P_{0.05}O_4$, and the amount increased by the addition of steam in the reaction mixture, resulting in an enhanced activity for the selective oxidation. Picoline is adsorbed via the N atom coordination to Brönsted acid site, and the substituted methyl group is oxidized by surface oxide ion to produce aldehyde and then acid. Thus, Mars and van Krevelen mechanism is suggested for picoline oxidation based on the DRIFTS analysis. 2- and 4-Picolines were more quickly oxidized than 3-picoline due to the inductive hyperconjugative 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 picoline-2-carbaldehyde as the main product due to the instability of the acid product, i.e., the decarboxylation of picolinic acid took place to form pyridine.

Keywords: $CrV_{0.95}P_{0.05}O_4$; Picolinic acid; Oxidation

1. Introduction

Solid, heterogeneous catalysts have the advantage of ease of recovery and recycling and are readily amenable to continuous processing. Therefore, the vapor-phase oxidation of organic compounds over heterogeneous catalysts is environmentally benign from the viewpoint of “green chemistry”. The literature on the vapor-phase oxidation of organic compounds catalyzed by binary vanadium oxide catalysts is quite numerous [1,2]. The partial oxidation of 3-picoline has received much attention because its oxidation product, nicotinic acid, is a valuable intermediate for pharmaceuticals and food additives. The vapor-phase oxidation of picolines has been performed on a series of vanadium oxide catalysts, such as V_2O_5/TiO_2 [3] and $(VO)_2P_2O_7$ [4].

We have reported that a new series of chromium vanadates, $Cr_{1-x}Al_xVO_4$ [5,6] and $CrV_{1-x}P_xO_4$ [7,8] were effective in the oxidation of 3-picoline to nicotinic acid. Monoclinic $CrVO_4$-I, which belongs to an α-$MnMoO_4$ structure, showed high activity as well as high selectivity to nicotinic acid. The activity was significantly enhanced when $CrVO_4$-I structure was modified either by replacing the Cr with Al or the V with P element, and the latter replacement was more effective than the former. All the V species is isolated as VO_4 tetrahedra in the $CrVO_4$-I structure and considered to work as the active sites via its reduction–oxidation assisted by Cr atoms and especially a small amount of P atoms. We recently reported on the details of 3-picoline oxidation [8] and in situ DRIFTS study [9] of 2-, 3-, and 4-picoline oxidations over $CrV_{0.95}P_{0.05}O_4$. In the present paper, the details of the oxidation of 2- and 4-picolines are discussed in connection with the previous study.

2. Experimental

$CrV_{0.95}P_{0.05}O_4$ catalyst was prepared following the method proposed by Touboul and co-workers [10]. Aqueous solutions of NH_4VO_3, $Cr(NO_3)_3\cdot 9H_2O$ and $NH_4H_2PO_4$ were mixed, and the pH value of the solution was lowered to 0.1–1.0 to form transparent and dark green solution by adding 3 N nitric acid aqueous solution. Then, the pH value

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was raised and adjusted to 4.0 at 323 K by adding 3 N ammonia aqueous solution, and stirred for 4 h, resulting in the formation of yellowish green precipitate. The precipitate was washed with de-ionized water, dried at 373 K overnight, and finally calcined at 823–843 K in air for 6 h.

$CrV_{0.95}P_{0.05}O_4$ catalyst was characterized by X-ray diffraction (XRD), differential thermal analyses (DTA), BET specific surface areas measurements, temperature programmed reduction (TPR) and diffuse reflectance infrared Fourier-transform spectra (DRIFTS) [8,9].

The catalytic tests were conducted in a fixed-bed reactor at atmospheric pressure and at temperatures from 523 to 673 K [7,8]. A U-shaped Pyrex glass tube reactor with 20 cm length by 8 mm ID was used in an electrically heated oven. 0.2 g of the catalyst particles with the sizes of 26–42 mesh were filled at the bottom of the tube diluted with quartz sand. The liquid mixture of picoline and water was passed through a vaporization zone at 473 K, mixed with oxygen and nitrogen as the carrier gas and finally fed in to the reactor. The feed composition of picoline/H_2O was varied from 1/0 to 1/108 (molar ratio) under a constant gas hourly space velocity around 38,000 ml h^{-1} g-cat^{-1}. Molar ratio of picoline/O_2 was fixed at 1/24. Water and organic compounds were condensed after the reactor, and all samples were analyzed by a FID gas chromatograph. The inorganic components (CO, CO_2, O_2 and N_2) were analyzed by an on-line TCD gas chromatograph.

3. Results and discussion

In the previous papers [6–8], we reported that the presence of excess amount of steam enhanced the yield of nicotinic acid in 3-picoline oxidation, where steam converts Lewis acid sites to Brönsted acid sites or creates Brönsted acid sites by the hydrolysis of V–O–Cr bond on the catalyst surface. Activation energy calculated from picoline consumption was also the lowest over the most active catalyst, i.e., $CrV_{0.95}P_{0.05}O_4$. Moreover, $CrV_{0.95}P_{0.05}O_4$ catalyst revealed a weak reduction peak of V around 620 K separately from a main reduction peak above 780 K in the TPR. The reduction–oxidation behavior was reversibly observed with this peak, and the V reduction–oxidation sites might be effective for oxygen activation [8]. Thus, it was concluded that 3-picoline is selectively oxidized to nicotinic acid on the V reduction–oxidation sites assisted by Brönsted acid sites on the catalyst.

3.1. Oxidation of 2- and 4-picolines

The results of 2-picoline oxidation over $CrV_{0.95}P_{0.05}O_4$ catalyst (picoline/O_2 = 1/24 molar ratio) are shown in Fig. 1. The conversion of 2-picoline increased with increasing the reaction temperature as well as the amount of steam. Both conversion of 2-picoline and yield of pyridine-2-carbaldehyde significantly increased with increasing the amount of steam, i.e., 18.6 and 14.5% in the absence of steam, 34.4 and 30.3% at H_2O/2-picoline = 10.8 (molar ratio), and 69.2 and 50.2% at H_2O/2-picoline = 108 at 573 K. Pyridine-2-carbaldehyde, CO_2 and pyridine were produced as the main products in 2-picoline oxidation, but picolinic acid was not obtained even under the presence of excess amount of steam. 2-Picoline conversion significantly increased, while pyridine-2-carbaldehyde selectivity decreased, with increasing the reaction temperature. Carbon dioxide selectivity increased, and interestingly pyridine selectivity also increased, with increasing the reaction temperature even under the presence of excess amount of steam (2-picoline/H_2O = 1/108). These strongly suggest that picolinic acid formed from pyridine-2-carbaldehyde is quickly decarboxylated to pyridine. This is consistent with the result reported by Järås and Lundin [11].

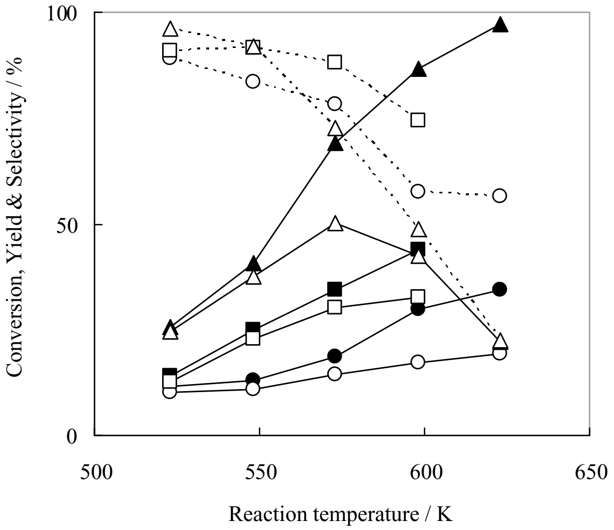

Fig. 1. Oxidation of 2-picoline over $CrV_{0.95}P_{0.05}O_4$. Full symbol and full line: 2-picoline conversion; open symbol and full line: Pyridine-2-carbaldehyde yield; open symbol and dotted line: Pyridine-2-carbaldehyde selectivity. (●, ○) 2-Picoline/H_2O = 1/0; (■, □) 2-picoline/H_2O = 1/10.8; (▲, △) 2-picoline/H_2O = 1/108.

The main products from 4-picoline were pyridine-4-carbaldehyde and isonicotinic acid; pyridine, 4-pyridinemethanol and 4-4′-trimethylenedipyridine were produced as by-products at a high temperature (Fig. 2). The selectivity of isonicotinic acid gradually increased, while that of pyridine-4-carbaldehyde sharply decreased, with increasing the reaction temperature, suggesting that 4-picoline was oxidized to isonicotinic acid via pyridine-4-carbaldehyde. A total yield of both isonicotinic acid and pyridine-4-carbaldehyde was the highest as 93.2% at 598 K. 4-Picoline was more quickly oxidized than 2-picoline, and its conversion was already above 80% at 570 K whether in the presence of steam or not. The selectivity of pyridine-4-carbaldehyde decreased, while that of isonicotinic acid increased, with increasing the steam amount. The highest yield of isonicotinic acid was 84.3% at 4-picoline/H_2O = 1/108. No other by-products were detected except for very small amount of

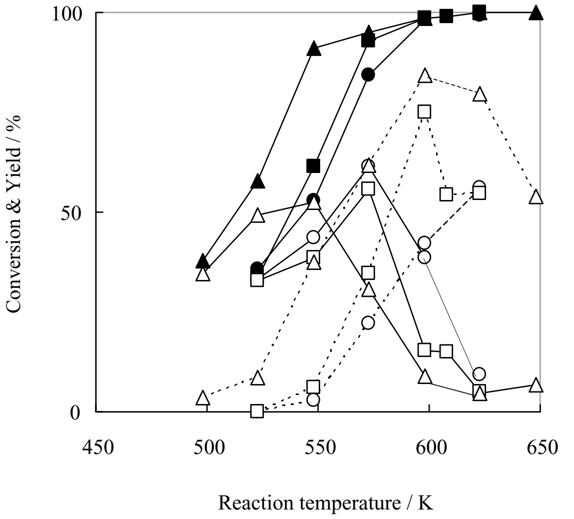

Fig. 2. Oxidation of 4-picoline over $CrV_{0.95}P_{0.05}O_4$. Full symbol and full line: 4-picoline conversion; open symbol and full line: pyridine-4-carbaldehyde yield; open symbol and dotted line: isonicotinic acid yield. (●, ○) 2-Picoline/H_2O = 1/0; (■, □) 2-picoline/H_2O = 1/10.8; (▲, △) 2-picoline/H_2O = 1/108.

pyridine, suggesting that water was very efficient for the selective oxidation of 4-picoline to isonicotinic acid.

3.2. DRIFTS of picoline adsorbed

In order to identify the intermediate species formed on the catalyst surface at high temperature, the temperature dependent DRIFTS of 4-picoline were studied on $CrV_{0.95}P_{0.05}O_4$ in the temperature range between 423 and 673 K (Fig. 3). A band around 1710 cm^{-1} appeared around 430 K and is assigned to C=O vibration corresponding to the characteristic ν(C=O) absorption of free aldehyde [12], suggesting that pyridine-carbaldehyde is produced and physically adsorbed on the surface. Bands between 2860 and 2970 cm^{-1} assigned to the symmetric and asymmetric stretching vibrations of CH_3 group, respectively [13,14], decreased gradually intensities when the temperature was raised from 303 to 573 K. These bands are no longer detected above 573 K, indicating that all hydrogen atoms of CH_3 group have been abstracted. ν(C–H) bands of pyridine ring around 3040–3080 cm^{-1} decreased their intensities with increasing temperature, which may be due to a transformation of adsorbent or a desorption of product.

Assignments of the absorption bands observed with 2- and 4-picolines are shown in Table 1. It was reported that the infrared spectra of carboxylate ion has relatively strong symmetric (ν_s) and strong asymmetric (ν_{as}) COO^- stretching vibrations at 1280–1400 and 1510–1650 cm^{-1}, respectively [15,16]. An intensity of the band around 1415 cm^{-1} prominently increased with increasing the temperature from 523 to 623 K and can be assigned to the symmetrical vibration of the COO^- group [15–17], while the asymmetrical vibration of the carboxylate stretching appeared around 1585 cm^{-1}.

When 2-picoline was adsorbed on $CrV_{0.95}P_{0.05}O_4$, the ring breathing bands (1450–1620 cm^{-1}) were observed at higher frequencies than neat 2-picoline due to the interaction of 2-picoline with the catalyst. The band at 1636 cm^{-1} appeared suggesting a protonation of the ring N atom by the interaction with Brönsted acid sites. Thus, referring to the vibration spectra of neat picoline isomers [11,14] and FTIR spectra of 2-picoline adsorbed on silica [18], 2-picoline is suggested to be adsorbed through N atom on $CrV_{0.95}P_{0.05}O_4$. The characteristic band at 1716 cm^{-1} due

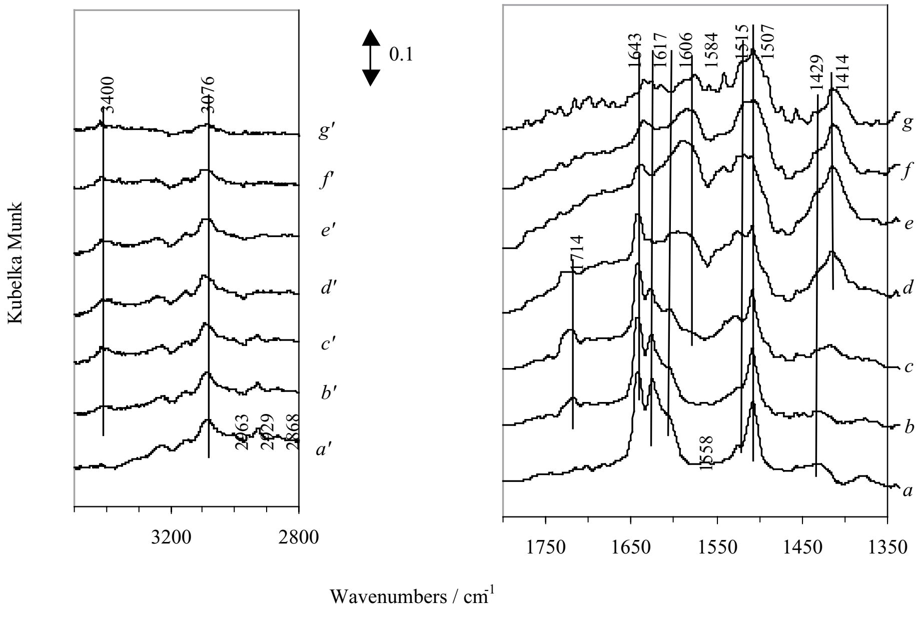

Fig. 3. In situ DRIFTS of 4-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$. Temperature, 303 K (a, a′), 423 K (b, b′), 573 K (c, c′), 523 K (d, d′), 573 K (e, e′), 623 K (f, f′) and 673 K (g, g′).

Table 1
Assignment of IR bands of 2- and 4-picolines adsorbed, followed by the reaction, on $CrV_{0.95}P_{0.05}O_4$ catalyst

2-Picoline (cm^{-1})	4-Picoline (cm^{-1})	Assignment	Characteristic of
3065, 3086	3076	ν(C–H)	Pyridine ring
2856, 2932, 2968	2868, 2929, 2963	ν(C–H)	$-CH_3$ group
1716	1714	ν(C=O)	Physically adsorbed pyridine-carbaldehyde
1670	–	ν(C=O)	Aldehydic adsorbate
1455, 1473, 1489, 1542, 1542, 1571, 1621, 1636[a]	1429, 1507, 1515, 1558, 1606, 1617, 1643[a]	ν(C–C) or ν(C–C, C–N)	Pyridine ring
1594	1584	$\nu_{as}(COO^-)$	Carboxylate (picolinate, nicotinate, isonicotinate)
1417	1414	$\nu_s(COO^-)$	Carboxylate (picolinate, nicotinate, isonicotinate)

[a] Suggested to be originated from Brönsted acid site.

to ν(C=O) of pyridine-2-carbaldehyde was observed above 423 K, and an intensity of the band distinctly increased with temperature. A higher yield of aldehyde was observed in the oxidation of 2-picoline than 3-picoline. Increasing temperature to 523 K caused an appearance of the bands at 1417 and 1594 cm^{-1} assigned to carboxylate species accompanied by a weakening of the bands at 2800–2900 cm^{-1} due to ν(C–H) of methyl group. Even though the intensity of the former bands increased with temperature, indicating that more carboxylate formed, no picolinic acid was found in the products except for pyridine and CO_2 at high temperature. This suggests that picolinate is formed on the catalyst surface, but is easily decarboxylated after it is desorbed from the catalyst surface. This was confirmed by the fact that picolinic acid was rapidly decarboxylated to pyridine even when picolinic acid itself was passed through catalyst bed in the glass tube reactor heated at 573 K. This may be partly due to the fact that the electron withdrawing ability of nitrogen in the pyridine ring remarkably affects the reactivity of carboxyl group at 2-position due to both inductive and resonance effect of the ring nitrogen. In fact, semi-empirical calculation by Spartan shows the lowest electron density of -0.072 at 2-position compared to -0.181 and -0.093 at 3- and 4-position, respectively, of carbon atom of pyridine ring.

In situ DRIFTS of 4-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$ revealed the bands at 1400–1630 cm^{-1} mainly assigned to pyridine ring (C–C and C–N) skeletal stretching modes. The band at 1643 cm^{-1} is ascribed to protonation of the ring N resulting from the interaction with Brönsted acid sites on $CrV_{0.95}P_{0.05}O_4$ in consideration of the same adsorption model as described for 2-picoline adsorption. The characteristic band of aldehyde at 1714 cm^{-1} (C=O) appeared at 423 and disappeared above 523 K. Furthermore, the bands at 1414 and 1584 cm^{-1}, which are characteristic of carboxylate group, grew prominently from 473 to 573 K, and then diminished at higher temperature. This indicates that aldehyde was formed at the first step and then transformed to isonicotinate. The desorption of isonicotinate accounts for the reduction of both intensities of 1414 and 1584 cm^{-1} bands at higher temperature coinciding with the fact that an intensity of pyridine ring C–H stretching vibration at 3076 cm^{-1} decreased relatively.

3.3. Oxidation mechanism

As described above, though there is a large difference in the reactivity and the product selectivity between 2-, 3-, and 4-picolines oxidations over $CrV_{0.95}P_{0.05}O_4$, a good similarity was observed in the adsorption and the oxidation behaviors based on the analysis of in situ DRIFTS. On the basis of experimental results and literature surveys [3,19], a possible Mars and van Krevelen mechanism [20] of surface reactions over the catalyst surface is proposed. In the first step, a protonated picoline forms by the interaction with a Brönsted acid site. Then, a hydrogen atom of the methyl group is abstracted by a lattice oxide (O^{2-}) and interacts with the oxygen atom to form a hydroxyl group. Another active lattice oxide attacks the activated methyl group and forms aldehyde-like intermediate. In order to compensate the loss of the lattice oxide ion, the adsorbed oxygen from gas phase migrates to fill the oxygen vacancy. A part of reaction product, for example, pyridine-carbaldehyde, desorbs from the catalyst surface into gas phase. Part of pyridine-carbaldehyde still remains on the catalyst surface and can be further oxidized to carboxylate at higher temperature. The carboxylate desorbs to form carboxylic acid, and at the same time some pyridine and CO_x formed if the decarboxylation is possible. If the temperature is very high, then deep oxidation will take place appreciably.

References

[1] W.F. Holderlich, Appl. Catal. A 194–195 (2000) 487.
[2] A. Martin, B. Lucke, Catal. Today 57 (2000) 61.
[3] D. Heinz, W.F. Hoelderich, S. Krill, W. Boeck, K. Huthmacher, J. Catal. 192 (2000) 1.
[4] A. Martin, B. Lucke, H.-J. Niclas, A.A. Forster, React. Kinet. Catal. Lett. 43 (1991) 583.
[5] Z. Song, E. Kadowaki, T. Shishido, Y. Wang, K. Takehira, Chem. Lett. (2001) 754.
[6] T. Shishido, Z. Song, E. Kadowaki, Y. Wang, K. Takehira, Appl. Catal. A 239 (2003) 287.
[7] Z. Song, T. Matsushita, T. Shishido, K. Takehira, Chem. Comm. (2002) 1306.
[8] Z. Song, T. Matsushita, T. Shishido, K. Takehira, J. Catal. 218 (2003) 32.
[9] T. Shishido, Z. Song, T. Matsushita, K. Takaki, K. Takehira, Phys. Chem. Chem. Phys. 5 (2003) 2710.

[10] E. Baudrin, S. Denis, F. Orsini, L. Seguin, M. Touboul, J.-M. Tarascon, J. Mater. Chem. 9 (1999) 101.
[11] S. Järås, S.T. Lundin, J. Appl. Chem. Biotechnol. 27 (1977) 499.
[12] S. Besselmann, E. Loffler, M. Muhler, J. Mol. Catal. A 162 (2000) 401.
[13] I.L. Tocon, M.S. Wooley, J.C. Otero, J.I. Marcos, J. Mol. Struct. 470 (1998) 241.
[14] J.F. Arenas, I.L. Tocon, J.C. Otero, J.I. Marcos, J. Mol. Struct. 476 (1999) 139.
[15] R.C. Mehrotra, R. Bohra, Metal Carboxylates, Academic Press, New York, 1983.
[16] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley, New York, 1997.
[17] F. Wang, K.A. Berglund, Ind. Eng. Chem. Res. 39 (2000) 2101.
[18] S.C. Ringwald, J.E. Pemberton, Environ. Sci. Technol. 34 (2000) 259.
[19] A. Andersson, A.S.T. Lundin, J. Catal. 58 (1979) 383.
[20] J.E. Sambeth, M.A. Centeno, A. Paul, L.E. Briand, H.J. Thomas, J.A. Odriozola, J. Mol. Catal. A 161 (2000) 89.