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In situ DRIFTS study of picoline oxidation over $CrV_{0.95}P_{0.05}O_4$ catalyst

T. Shishido, Z. Song, T. Matsushita, K. Takaki and K. Takehira*

Department of Chemsitry and Chemical Engineering, Graduate School of Engineering,
Hiroshima University, 1-4-1 Kagamiyama, Higashi-hiroshima 739-8527, Japan.
E-mail: takehira@hiroshima-u.ac.jp; Fax: +81 824 24 7744; Tel: +81 824 24 7744

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The catalytic behaviour of $CrV_{0.95}P_{0.05}O_4$ 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. Both Lewis and Brønsted acid sites were detected on the surface of $CrV_{0.95}P_{0.05}O_4$, 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 by *in situ* DRIFTS. Thus, a Mars and van Krevelen mechanism was suggested for 2-, 3- and 4-picolines oxidations based on the spectral analysis. Both 2- and 4-picolines 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 isonocotinic 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.

Introduction

In our recent studies on selective oxidation of 3-picoline, a series of chromium vanadates based on $CrVO_4$–I with α-$MnMoO_4$ structure have been found to be a new promising catalyst family, including $Cr_{1-x}Al_xVO_4$[1,2] and $CrV_{1-x}P_xO_4$.[3,4] It was clearly shown that the $CrVO_4$–I based structure was important for the catalytic activity as well as the selectivity to nicotinic acid. Moreover, both activity and selectivity were 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. The addition of water vapor into the reaction mixture substantially promoted the selective oxidation of 3-picoline by erecting Brønsted acid sites on the catalyst surface. It was found that $CrVO_4$–I was originally active and the addition of a small amount of P resulted in a highly enhancement in the catalytic activity.[3,4] NH_3-TPD showed that an increase in the acid site by replacing V with a small amount of P in $CrVO_4$–I. Favorable effect of water addition suggests that Brønsted acid assists the selective oxidation, and this was confirmed by infrared study of pyridine adsorption on the catalysts. The active catalysts, $CrV_{1-x}P_xO_4$ ($0 < x < 0.1$), alone revealed a weak reduction peak of V around 350 °C in the TPR, and the peak temperatures was the lowest over the most active catalyst, *i.e.*, $CrV_{0.95}P_{0.05}O_4$.[4] The reduction-oxidation property was reversibly observed with the peak when the catalyst was treated by H_2 and O_2 atmosphere alternately. Moreover, the activation energy calculated from the 3-picoline consumption was also the lowest over the most active catalyst. All the V species are isolated as VO_4 tetrahedra in the $CrVO_4$–I structure and considered to work as the active sites *via* reduction-oxidation assisted by both chromium and phosphorus atoms. It is concluded that 3-picloine is selectively oxidized on the V sites by reduction–oxidation, further assisted by the Brønsted-acid sites over the crystallized $CrV_{0.95}P_{0.05}O_4$ catalyst, which showed the highest activity, *i.e.*, 3-picoline conversion of 92.6% and nicotinic acid selectivity of 84.7% were obtained at 360 °C.[3,4]

Up to now, only a few papers[5,6] have discussed the reaction mechanism of 3-picoline oxidation, where no detailed datum was shown concerning the reaction intermediates. Oxidation mechanism of toluene has been frequently studied on vanadium based oxide catalyst.[7–9] Although both picoline and toluene have a common six-membered cyclic structure, the nature of nitrogen atom in picoline is quite different from that of the carbon atom in the toluene ring. Considering the electronic configuration, the presence of nitrogen atom makes picoline a much stronger base than toluene, and significantly affects the adsorption behaviors and the reactivity. Furthermore, the electron withdrawing ability of nitrogen in the pyridine ring remarkably affects the reactivity of methyl group, *i.e.* the electrons of methyl groups at the 2- and 4-positions are drawn to pyridine ring due to the inductive and resonance effect of nitrogen, resulting in an easy leaving of proton from the methyl group. On the other hand, the methyl hydrogen of 3-picoline

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is more stable than those of 2- and 4-picolines due to the absence of the resonance effect.[10]

In situ spectroscopic techniques have been widely used in understanding the mechanistic details of chemical reaction at the molecular level. In particular, IR spectroscopy is a well-established method in the characterization of heterogeneous reaction systems under working conditions. Diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) is a powerful tool for the investigation of adsorbed species and active sites, because of its high sensitivity to surface species. The *in situ* DRIFTS technique has been frequently employed in investigating the active sites, the adsorbed species and the intermediates on the catalyst surface under reaction conditions. In the present study, we report the vapor phase oxidation of 2-, 3- and 4-picolines over $CrV_{0.95}P_{0.05}O_4$ by *in situ* DRIFTS. We propose adsorption models and an oxidation mechanism.

Experimental

Preparation of the catalysts

The $CrV_{0.95}P_{0.05}O_4$ catalyst was prepared following the method proposed by Touboul *et al.*, as described previously.[3,4] 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 was raised and adjusted to 4.0 at 50 °C 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 100 °C overnight, and finally calcined at 550–570 °C in air for 6 h.

Characterization of the catalysts

The $CrV_{0.95}P_{0.05}O_4$ catalyst has been characterized by X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FT-IR), differential thermal analyses (DTA), BET specific surface areas measurements, temperature-programmed desorption of ammonia (NH_3-TPD), and temperature programmed reduction (TPR) as reported previously.[4] In this work, diffuse reflectance infrared Fourier-transform spectra (DRIFTS) were recorded with a Nicolet MAGNA-IR 560 spectrometer equipped with an *in situ* diffuse COLLECTOR diffuse reflectance cell. Spectra were obtained from a narrow band MCT detector by 128 scans at 4 cm^{-1} resolution. The catalyst sample powder (*ca.* 40 mg) in an *in situ* diffuse reflectance cell with NaCl windows was pretreated at 500 °C for 1 h in a mixture of dry N_2 (30 ml min^{-1}) and O_2 (4.5 ml min^{-1}), and cooled to 30 °C in N_2 flow. At 30 °C, the spectra was recorded and used as background. Picoline vapor was then introduced in a N_2 (30 ml min^{-1}) flow for 10 min, and shut off. The chamber was purged at 30 °C for 30 min under N_2 atmosphere to remove the gas-phase species and the spectra were recorded until the change was no longer observed in the spectra. Subsequently, the sample was heated up to 150 °C with 10 °C min^{-1} under flowing N_2 (30 ml min^{-1}) and O_2 (4.5 ml min^{-1}), maintained at this temperature for 1–2 s, and cooled to 30 °C. At 30 °C, the spectra were again recorded. Possible transformations of the adsorbed species were recorded in a similar way at a series of increasing temperatures. All gases were delivered to the sample at atmospheric pressure. The flow rate of each gas was controlled by a STEC Model SEC400-MK3 mass flow controller. Circulating water is used to cool the body of the reaction chamber. The temperature was controlled by a thermocouple in direct contact with the sample.

Vapor-phase oxidation of 2-, 3- and 4-picolines over $CrV_{0.95}P_{0.05}O_4$ catalyst

The catalytic tests were conducted in a fixed-bed reactor at atmospheric pressure and at temperatures from 250 to 400 °C, as reported previously.[3,4] A Pyrex glass tube reactor with 20 cm length by 8 mm id was used in an electrically heated oven. The 0.2 g of the catalyst powder was made to pellet and crushed into particles with the sizes of 26–42 mesh; these were filled at the bottom of the tube diluted with quartz sand. The catalyst was activated in an oxygen : nitrogen mixed gas flow (18 : 33 ml min^{-1}) at 540 °C for 1 h and then settled down to the reaction temperature under the O_2 : N_2 mixed gas flow. The liquid mixture of picoline and water was passed through a vaporization zone at 200 °C, mixed with oxygen and nitrogen as the carrier gas and finally fed in to the reactor. The line from the vaporizer to the reactor was heated to a temperature above 250 °C. 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-catalyst)$^{-1}$. 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.

Results and discussion

The catalytic oxidations of 2-, 3-, and 4-picolines

The results of 2-, 3-, and 4-picoline oxidations over $CrV_{0.95}P_{0.05}O_4$ catalyst in the absence of water (picoline : O_2 : N_2 = 0.032 : 0.73 : 4.56 mmol min^{-1}) are shown in Tables 1, 2 and 3. In all cases, the conversions of 2-, 3-, and 4-picolines increased with increasing the reaction temperature. Pyridine-2-carbaldehyde, CO_2 and pyridine were produced as the main products in 2-picoline oxidation, but picolinic acid was not obtained (Table 1). This may be due to the fact that picolinic acid is easily converted to pyridine by the decarboxylation even at a low temperature. This is consistent with the result reported by Järås *et al.*[11] In the oxidation of 3-picoline

Table 1 2-Picoline oxidation over $CrV_{0.95}P_{0.05}O_4$[a]

		Selectivity (%)				Yield (%)	
Temperature/ °C	Conversion (%)	CO_x	2-P. Ald.[b]	P. A.[c]	Pyr.[d]	2-P. Ald.[b]	P. A.[c]
250	11.5	10.9	89.1	0.0	0.0	10.2	0.0
275	13.0	14.6	83.5	0.0	1.6	10.9	0.0
300	18.6	18.1	78.3	0.0	3.0	14.5	0.0
325	29.8	36.7	57.6	0.0	4.8	17.1	0.0
350	34.3	30.9	56.5	0.0	10.5	19.4	0.0

[a] 2-Picoline : O_2 : N_2 = 0.032 : 0.73 : 4.56 mmol min^{-1} = 1: 24 : 152 molar ratio. [b] Pyridine-2-carbaldehyde. [c] Picolinic acid. [d] Pyridine.

Table 2 3-Picoline oxidation over $CrV_{0.95}P_{0.05}O_4$[a]

		Selectivity (%)				Yield (%)	
Temperature/ °C	Conversion (%)	CO_x	3-P. Ald.[b]	N. A.[c]	Pyr.[d]	3-P. Ald.[b]	N. A.[c]
300	6.1	32.6	67.4	0.0	0.0	4.1	0.0
325	8.9	42.4	53.4	0.0	4.2	4.8	0.0
350	21.8	57.1	27.5	12.2	3.1	6.0	2.7
360	31.6	45.2	22.0	29.8	2.9	6.9	9.4
375	37.9	43.9	18.5	32.6	5.0	7.0	12.4

[a] 3-Picoline : O_2 : N_2 = 0.032 : 0.73 : 4.56 mmol min^{-1} = 1 : 24 : 152 molar ratio. [b] Pyridine-3-carbaldehyde. [c] Nicotinic acid. [d] Pyridine.

Table 3 4-Picoline oxidation over $CrV_{0.95}P_{0.05}O_4$[a]

Temperature/ °C	Conversion (%)	Selectivity (%)					Yield (%)	
		CO_x	4-P. Ald[b]	I. A.[c]	Pyr.[d]	Others[e]	4-P. Ald.[b]	I. A.[c]
250	35.8	7.3	92.7	0.0	0.0	0.0	33.2	0.0
275	52.7	12.3	82.4	5.2	0.0	0.0	43.5	2.8
300	84.4	0.8	73.0	26.1	0.0	0.2	61.6	22.0
325	98.1	0.7	39.2	42.9	0.2	15.3	38.5	42.1
350	99.2	10.9	9.4	56.5	0.5	20.0	9.3	56.1

[a] 4-Picoline : O_2 : N_2 = 0.032 : 0.73 : 4.56 mmol min^{-1} = 1 : 24 : 152 molar ratio [b] Pyridine-4-carbaldehyde. [c] Isonicotinic acid. [d] Pyridine. [e] 4-Pyridinemethanol, 4-4′trimethylenedipyridine *etc.*

(Table 2), the selectivity of pyridine-3-carbaldehyde decreased, while the selectivity of nicotinic acid increased with increasing the reaction temperature up to 375 °C, suggesting that 3-picoline was oxidized to nicotinic acid *via* pyridine-3-carbaldehyde. An appearance of pyridine above 325 °C may be due to the decarboxylation of nicotinic acid to form pyridine at the high temperature.[11] The main products from 4-picoline were pyridine-4-carbaldehyde and isonicotinic acid, and pyridine, 4-pyridinemethanol and 4-4′trimethylenedipyridine were produced as by-products at the high temperature (Table 3). The selectivity of both pyridine-4-carbaldehyde and isonicotinic acid strongly depended on the reaction temperature. The selectivity of isonicotinic acid gradually increased, while that of pyridine-4-carbaldehyde sharply decreased with increasing the reaction temperature, also suggesting that 4-picoline was oxidized to isonicotinic acid *via* pyridine-4-carbaldehyde. A total yield of both pyridine-4-carbaldehyde and isonicotinic acid was 83.6%.

In the previous papers,[2–4] we reported that the presence of excess amount of water enhanced the yield of nicotinic acid in 3-picoline oxidation, where water converts Lewis acid sites to Brønsted acid sites or creates Brønsted acid sites by the hydrolysis of V–O–Cr bond on the catalyst surface. Moreover, $CrV_{0.95}P_{0.05}O_4$ catalyst possesses reduction–oxidation sites consisting of V assisted by P, and the V reduction–oxidation sites are effective for oxygen activation. Thus, it was concluded that 3-picoline is selectively oxidized to nicotinic acid on the V reduction-oxidation sites assisted by Brønsted acid sites on the catalyst.

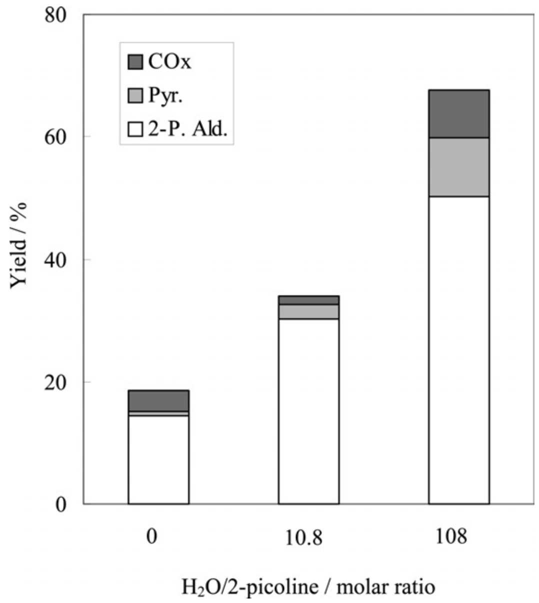


Fig. 1 Effect of water on 2-picoline oxidation over $CrV_{0.95}P_{0.05}O_4$ catalyst. Reaction temperature, 300 °C; 2-P. Ald., Pyridine-2-carbaldehyde; Pyr., Pyridine.

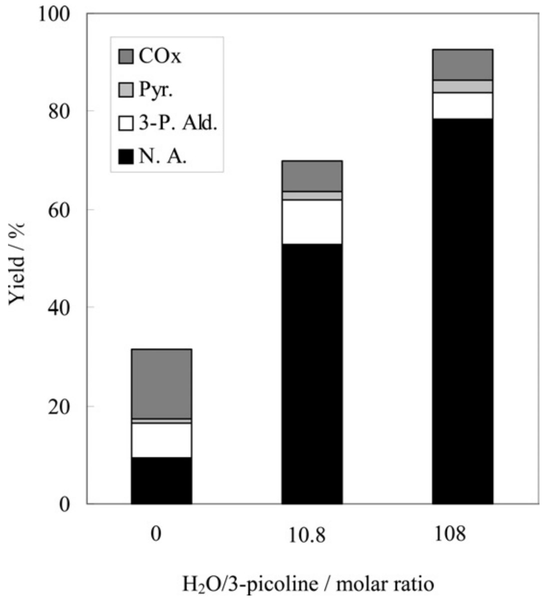


Fig. 2 Effect of water on 3-picoline oxidation over $CrV_{0.95}P_{0.05}O_4$ catalyst. Reaction temperature, 360 °C; N. A., Nicotinic acid; 3-P. Ald., Pyridine-3-carbaldehyde; Pyr., Pyridine.

In the present study, the oxidations of 2- and 4-picolines were carried out over $CrV_{0.95}P_{0.05}O_4$ catalyst in comparison to 3-picoline oxidation. The results of 2-picoline oxidation are shown in Fig. 1. Both conversion of 2-picoline and yield of pyridine-2-carbaldehyde significantly increased with increasing the amount of water, *i.e.*, 18.6 and 14.5% in the absence of water, 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. No picolinic acid was observed, even in the presence of a large amount of water. The results of 3-picoline oxidation are shown in Fig. 2 as a reference. Increasing the amount of water resulted in an increasing yield of nicotinic acid production, as reported in the previous paper.[2–4] The results of 4-picoline oxidation are shown in Fig. 3. 4-Picoline was more quickly oxidized than 2-picoline over $CrV_{0.95}P_{0.05}O_4$ catalyst, and its conversion was always above 80% at 325 °C whether in the presence of water or not. The addition of water remarkably affected the product selectivity. The selectivity of pyridine-4-carbaldehyde decreased, while that of isonicotinic acid

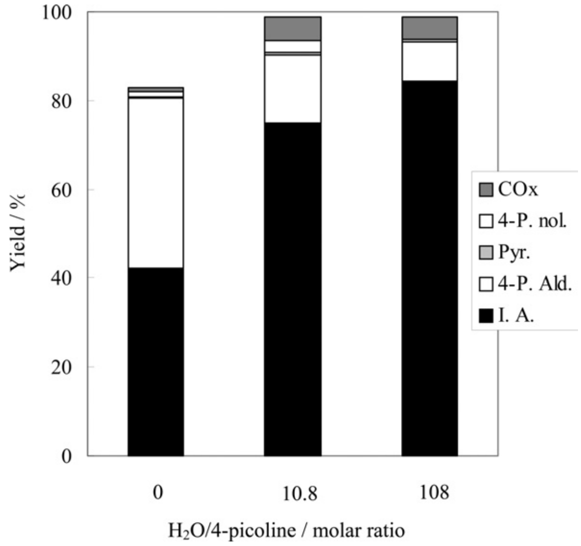


Fig. 3 Effect of water on 4-picoline oxidation over $CrV_{0.95}P_{0.05}O_4$ catalyst. Reaction temperature, 325 °C; I. A., Isonocotinic acid; 4-P. Ald., Pyridine-4-carbaldehyde; Pyr., Pyridine, 4-P.nol, 4-Pyridinemethanol.

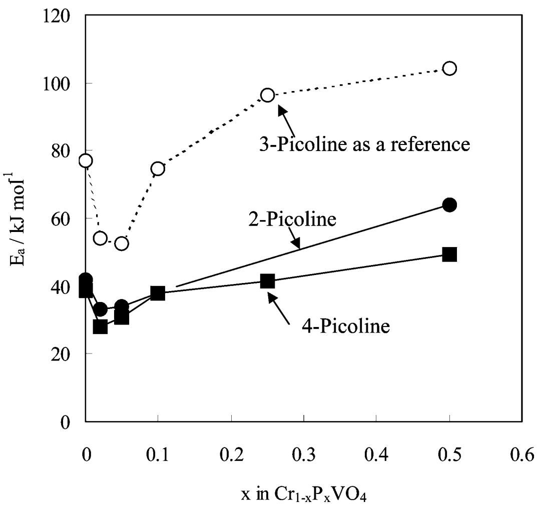


Fig. 4 Apparent activation energy of the oxidation of 2-, 3-, and 4-picolines over $CrV_{0.95}P_{0.05}O_4$ catalyst. Molar ratio of H_2O : picoline, 10.8.

increased with increasing the water amount. This indicates that the presence of water was in favor of the oxidation of pyridine-4-carbaldehyde to isonicotinic acid. The highest yield of isonicotinic acid was 84.3% at 4-picoline : $H_2O = 1 : 108$. In the presence of a large amount of water, no other by-products were detected except for very small amount of pyridine, suggesting that water was very efficient for the selective oxidation of 4-picoline to isonicotinic acid.

Apparent activation energies of the oxidation of 2- and 4-picolines over $CrV_{0.95}P_{0.05}O_4$ catalyst were calculated from the rates of the picolines consumptions at 300–400 °C in the presence of water (molar ratio of H_2O : picoline: 10.8) (Fig. 4). The results obtained with 3-picoline is also shown as a reference. The lower values were obtained with 2- and 4-picolines than that with 3-picoline, among which 4-picoline showed the lowest value. This may be due to the fact that the electron withdrawing ability of nitrogen in the pyridine ring remarkably affects the reactivity of methyl group, *i.e.* the electrons of the methyl group at the 2- and 4-positions are drawn to pyridine ring due to both inductive and resonance effect of nitrogen, resulting in an easy leaving of proton from the methyl group. On the other hand, the methyl hydrogen of 3-picoline is more stable than those of the 2- and 4-picolines due to the lack of resonance effect.[10] A small amount of P addition in $CrVO_4$ catalyst was still effective for the oxidation of both 2- and 4-picolines.

DRIFTS of 3-picoline adsorbed

Fig. 5 shows the FTIR spectra of liquid 3-picoline (*a*), and the DRIFTS of 3-picoline (*b*) and pyridine(*c*) adsorbed on $CrV_{0.95}P_{0.05}O_4$ catalyst at 30 °C. The spectra of both liquid 3-picoline and pyridine adsorbed were recorded as a comparison. The observed IR absorption bands were assigned with reference to the vibration spectra of neat picoline isomers reported[12–14] and are collected in Table 4. The assignments of the absorption bands of 3-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$ were achieved as below. Generally, the bands due to hydroxyl group appear in the 3000–4000 cm^{-1} regions and the bands between 3600–3700 cm^{-1} are assigned to ν(OH) of catalyst surface.[15,16] Thus, two weak negative bands observed around 3620 and 3640 cm^{-1} are assigned to –OH groups on the surface of catalyst. This may be due to the interaction of –OH groups with the adsorbed 3-picoline resulted in the decrease of the intensity that account for the negative bands. The bands at 2884 and 2938 cm^{-1} are due to ν(C–H) of CH_3 groups, symmetric and asymmetric stretching vibrations. The pyridine ring ν(C–H) gives the bands at 3044 and 3078 cm^{-1}.

Besides, another negative band was observed around 2050 cm^{-1}. A similar negative band at 2048 cm^{-1} has been reported with toluene adsorbed on V_2O_5/TiO_2 catalyst, which was assigned to an overtone vibration (2ν(V=O)) of monomeric vanadyl species.[16] It was reported that 3-picoline partially reduced vanadium ions *via* the coordination through nitrogen atom.[17] In fact, the negative band at 2050 cm^{-1} was also observed after the adsorption of pyridine (Fig. 5c) or pyridine-3-carbaldehyde (not shown) in our DRIFTS studies. Here, no V=O exist in the monoclinic crystal structure of $CrV_{0.95}P_{0.05}O_4$,[3,10] and therefore the negative band at 2050 cm^{-1} may be assigned the reduced V–O groups due to the coordination through nitrogen of 3-picoline.

Absorption bands in the region of 1400–1600 cm^{-1} are characteristic aromatic ring vibrations (8a,8b,19a,19b).[12,13] The bands observed at 1425, 1474, 1552, 1583, 1612 and 1634 cm^{-1} are assigned to skeletal stretching modes. These bands appeared at somewhat higher frequencies than those of liquid 3-picoline. This discrepancy can be interpreted by the interaction of 3-picoline with acid sites on the surface of $CrV_{0.95}P_{0.05}O_4$, *i.e.*, a part of electron in the aromatic ring is withdrawn through N atom and is donated to the acid sites. Lewis (coordinatively unsaturated metal atoms) and Brønsted (proton donating OH-groups) acid sites have been observed in the previous study of probing acid sites on the surface of the $CrV_{0.95}P_{0.05}O_4$ catalyst upon pyridine adsorption.[3,10] The presence of Brønsted acid sites was suggested by the characteristic bands of pyridinium surface species (PyH^+) at 1637 cm^{-1} (ν_{8a}).[3,10] Therefore, it is reasonable to assign the band at 1634 cm^{-1} as the 8a stretching vibrations of 3-picoline adsorbed on Brønsted acid sites due to a protonation of the N atom. The other bands of skeletal stretching vibration of 3-picoline also appeared in the region of 1400–1640 cm^{-1}.

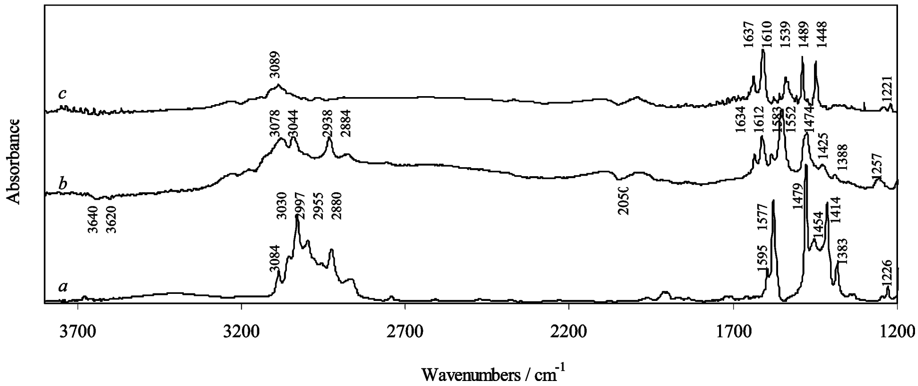
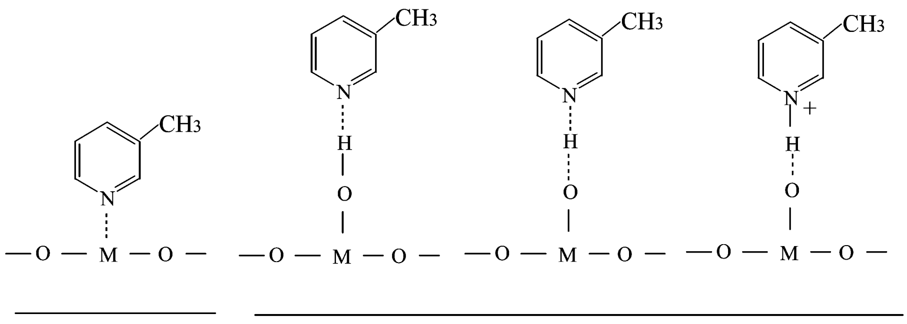


Fig. 5 FTIR spectra of liquid 3-picoline (*a*), DRIFTS of 3-picoline (*b*) and pyridine (*c*) adsorbed on $CrV_{0.95}P_{0.05}O_4$. Temperature, 30 °C.

Table 4 Assignment of IR bands of liquid 3-picoline, and both pyridine and 3-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$ catalyst

Position/cm^{-1}				
Liquid 3-picoline	Adsorbed pyridine	Adsorbed 3-picoline	Assignment	Characteristic of
3030, 3084	3089	3044, 3078	ν(C–H)	Pyridine ring
2880, 2955, 2997	—	2884, 2933	ν(C–H)	–CH_3 group
1414(19b), 1479(19a), 1577(8a), 1595(8b)	1448(19b), 1489(19a), 1539[a](19b), 1575(8b), 1610(8a,8b), 1637[a](8a)	1425, 1474, 1552, 1583, 1612, 1634[a]	ν(C–C) or ν(C–C,C–N)	Pyridine ring
1383, 1454	–	1388	δ(C–H)	–CH_3 group
1226	1221	1257	ν(C–N)	Pyridine ring

[a] Suggested to originate from the Brønsted acid site.



(a) (b)

Scheme 1

As to the 3-picoline adsorption, Andersson *et al.*[17] proposed two adsorption models that occur at different planes of V_2O_5. 3-Picoline could either be adsorbed through nitrogen atom to partially reduced vanadium ions, or through methyl carbon atom to an oxygen species after an abstraction of hydrogen. Based on the present IR results, *i.e.*, the appearance of the bands at somewhat higher frequencies, similar to the case of pyridine adsorbed through N atom, it is considered that the former model is more plausible than the latter. 3-Picoline is adsorbed through N atom and its pyridine ring is oriented perpendicular to the surface. Scheme 1 shows the possible adsorption model of 3-picoline upon both Lewis (*a*) and Brønsted acid sites (*b*).

In situ DRIFTS during 3-picoline oxidation

In order to identify the intermediate species formed on the catalyst surface at high temperature, the temperature dependent IR spectra of 2-, 3- and 4-picolines and pyridine-3-carbaldehyde were studied on $CrV_{0.95}P_{0.05}O_4$ in the temperature range between 150–400 °C.

The DRIFTS of 3-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$ are shown in Fig. 6, recorded at 30 °C (*a*,*a*′), 150 °C (*b*,*b*′), 200 °C (*c*,*c*′), 250 °C (*d*,*d*′), 300 °C (*e*,*e*′), 350 °C (*f*,*f*′) and 400 °C (*g*,*g*′). The observed absorption bands are listed in Table 5 together with those of 2- and 4-picolines. A band at 1718 cm^{-1} observed in Fig. 6, is assigned to C=O vibration corresponding to the characteristic ν (C=O) absorption of free aldehyde around 1710 cm^{-1}.[16,18] This suggests that pyridine-3-carbaldehyde is produced at 150 °C and physically adsorbed on the surface. Both bands at 2884 and 2938 cm^{-1} in Fig. 6 are assigned to ν(C–H) of CH_3 group and decreased gradually intensities when the temperature was raised from 30 to 300 °C. They are typical for the symmetric and asymmetric stretching vibrations of CH_3 group, respectively.[12,13] These bands are no longer detected above 300 °C, indicating that all hydrogen atoms of CH_3 group have been abstracted. ν(C–H) bands of pyridine ring at 3044 and 3078 cm^{-1} decreased their intensities with increasing temperature, which may be due to a transformation of adsorbent or a desorption of product. In addition, the broad band around 3400 cm^{-1} due to ν(OH), is interpreted by a possible formation of water[15,19] or hydrogen bonding to adsorbent.[16,20]

It was reported that the infrared spectra of free carboxlic acids are characterized by the strong absorptions at 1200–1300 and 1700–1750 cm^{-1} associated with the C–O and C=O bonds of the carboxyl group,[21] while the 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.[21,22] Moreover, the absorptions at 1390 and

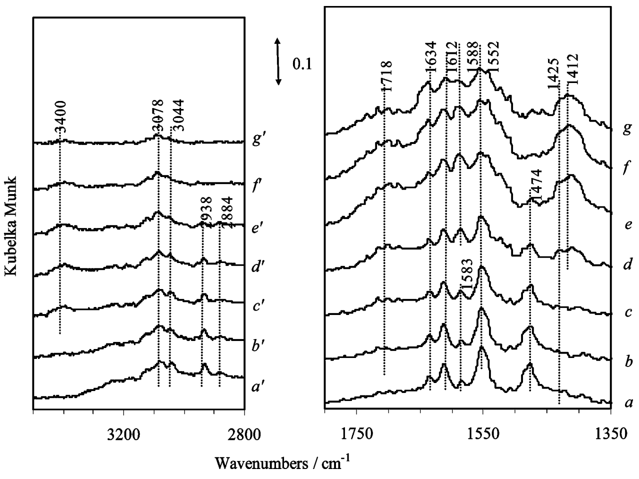


Fig. 6 *In situ* DRIFTS of 3-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$. Temperature, 30 °C(*a*,*a*′), 150 °C (*b*,*b*′), 200 °C (*c*,*c*′), 250 °C (*d*,*d*′), 300 °C (*e*,*e*′), 350 °C (*f*,*f*′), and 400 °C (*g*,*g*′).

Table 5 Assignment of IR bands of 2-, 3- and 4-picolines adsorbed, followed by the reaction, on $CrV_{0.95}P_{0.05}O_4$ catalyst

Position/cm^{-1}				
2-Picoline	3-Picoline	4-Picoline	Assignment	Characteristic of
~3400	~3400	~3400	ν(OH)	H_2O or hydrogen bonding to adsorbent
3065, 3086	3044, 3078	3076	ν(C–H)	Pyridine ring
2856, 2932, 2968	2884, 2933	2868, 2929, 2963	ν(C–H)	$-CH_3$ group
1716	1718	1714	ν(C=O)	Physically adsorbed pyridine–carbaldehyde
1670	—	—	ν(C=O)	Aldehydic adsorbate
1455, 1473, 1489, 1542, 1542, 1571, 1621, 1636[a]	1425, 1474, 1552, 1583, 1612, 1634[a]	1429, 1507, 1515, 1558, 1606, 1617, 1643[a]	ν(C–C) or ν(C–C,C–N)	Pyridine ring
1594	1588	1584	$\nu_{as}(COO^-)$	Carboxylate (picolinate, nicotinate, isonicotinate)
1417	1412	1414	$\nu_s(COO^-)$	Carboxylate (picolinate, nicotinate, isonicotinate)

[a] Suggested to originate from the Brønsted acid site.

1556 cm^{-1} of aqueous nicotinate ion have been assigned to the carboxylate stretching modes.[23] An intensity of the band at 1412 cm^{-1} shown in Fig. 6 (*d–f*), prominently increased with increasing the temperature from 250 to 350 °C. This band can be assigned to the symmetrical vibration of the COO^- group,[21–24] while the asymmetrical vibration of the carboxylate stretching appeared at 1588 cm^{-1}. The assignments of the bands due to carboxylate group were also confirmed by the *in situ* DRIFTS study using pyridine-3-carbaldehyde, in which the same spectra were observed for asymmetric and symmetric COO^- stretching vibration, with increasing the temperature from 30 to 300 °C (Fig. 7). These results suggest that nicotinate was formed and adsorbed on $CrV_{0.95}P_{0.05}O_4$ in both cases of 3-picoline and pyridine-3-carbaldehyde. When the temperature was increased above 350 °C, the intensity of the band at 1412 cm^{-1} turned to decrease. This may be due to the desorption of nicotinate at higher temperature, which can also account for the disapperance of pyridine ring ν(C–H) bands at 3044 and 3078 cm^{-1} at these temperatures. Another reason may be the fact that COO^- groups are transformed to gaseous CO_2, which contributes the band at 2345 cm^{-1} (not shown).

Coordination of carboxylic acids usually takes place through the carboxylate group, and there are three common coordination modes: unidentate, bridging bidentate, and chelating bidentate.[21,25] These can be distinguished in infrared spectra by their bands splitting of carboxylate absorption ($\Delta\nu$). The values of $\Delta\nu$ are generally 350–500 cm^{-1} for unidentate binding, 150–180 cm^{-1} for bridging, and 60–100 cm^{-1} for chelating. In general, there is little change in $\Delta\nu$ between carboxylate ion in solution and the bridging bidentate surface species. As described above, the strong bands at 1412 and 1588 cm^{-1} (Figs. 6 and 7) are assigned to the carboxylate stretching modes of nicotinate adsorbed on $CrV_{0.95}P_{0.05}O_4$. The carboxylate band splitting of the adsorbed species ($\Delta\nu = 1588 - 1412 = 176$ cm^{-1}) is near to that of aqueous nicotinate ion ($1556 - 1390 = 166$ cm^{-1}),[23] suggesting that a bridging bidentate nicotinate species is formed on the catalyst. However, any shift of pyridine ring (C–C and C–N) skeletal stretching vibration was not observed when the nicotinate species formed, suggesting that N atom of pyridine ring is still bound to the catalyst surface. It was reported that salicylic and phthalic acids were adsorbed on metal oxides *via* bidentate interactions, involving coordination through both carboxylate and substituent groups.[26] Therefore, a bridging bidentate surface nicotinate species, coordinated through both N atom of pyridine ring and a C–O bond of the carboxylate group, is the most plausible structure of the intermediate. The $\Delta\nu$ values for the adsorbed species are too low to be normally considered as unidentate carboxylate coordination, but expected to fit for bridging bidentate coordination. Steric considerations are likely to forbid tridentate coordination. Another FT-IR study[27] also reported the value $\Delta\nu$ ($= \nu_{as} - \nu_s$) with various carboxylates; a unidentate structure is responsible when $\Delta\nu$ is clearly larger than 140 cm^{-1}, while a bidentate structure for the smaller $\Delta\nu$ than 140 cm^{-1}. Recent study of the interaction between nicotinic acid and TiO_2 surface immersed in water by ATR-FTIR showed that hydrogen bonding between the protonated pyridinic nitrogen and a vicinal OH surface group.[28] This structure is exactly consistent with the nicotinate adsorbed on the Brønsted acid site as described above. Thus, the adsorption model shown in Scheme 2 (M is the surface metal ion), is proposed for nicotinate on the Lewis acid sites (*a*) and Brønsted acid sites (zwitterionic surface species) (*b*) of metal oxide surface.

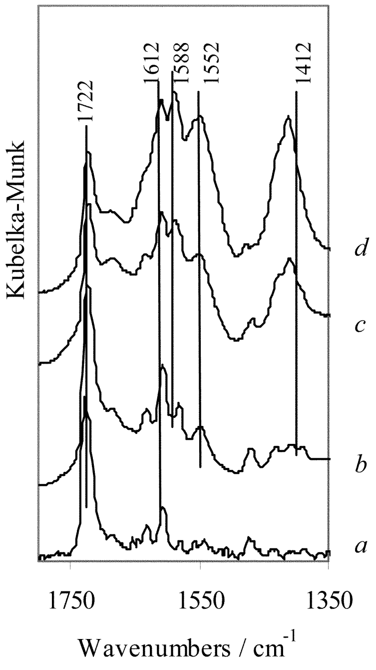
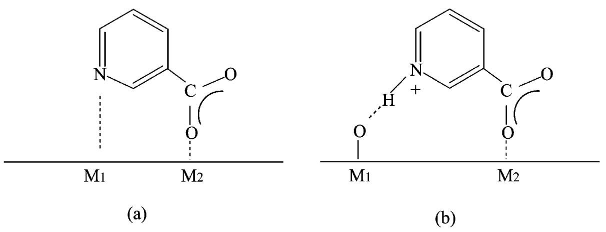


Fig. 7 *In situ* DRIFTS of pyridine-3-carbaldehyde adsorbed on $CrV_{0.95}P_{0.05}O_4$. Temperature, 30 °C (*a*), 150 °C (*b*), 200 °C (*c*), and 300 °C (*d*).

In situ DRIFTS spectra of adsorption and oxidation of 2- and 4-picolines

Fig. 8 shows the *in situ* DRIFTS spectra of 2-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$ catalyst and the observed bands are summarized in Table 5. The spectra (*a*,*a*′) are similar to those reported recently on 2-picoline adsorbed on a hydrated silica surface by Raman and FTIR spectroscopies.[29] The authors suggested that, on hydrated silica, the magnitude of the shift observed for the ring breathing band of adsorbed 2-picoline implies an interaction that is slightly stronger than simple



Scheme 2

hydrogen bonding or an interaction with some Brønsted character; 2-picoline interaction with surface silanols through the N atom is proposed. When 2-picoline was adsorbed on $CrV_{0.95}P_{0.05}O_4$, the ring breathing bands (1455, 1473, 1489, 1542, 1571 and 1621 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 Brønsted acid sites. This may also lead to increase the shift of the ring breathing bands. The presence of Brønsted acid sites over the catalyst has been confirmed by pyridine adsorption.[4] Thus, referring to the vibration spectra of neat picoline isomers[12,13] and FTIR spectra of 2-picoline adsorbed on silica,[29] the model of 2-picoline adsorption over $CrV_{0.95}P_{0.05}O_4$ is suggested to be similar to that of 3-picoline, *i.e.*, adsorbed through the N atom.

The characteristic band at 1716 cm^{-1} due to ν(C=O) of pyridine-2-carbaldehyde was observed above 150 °C in Fig. 8(*b*–*f*) together with the band at 1670 cm^{-1}, and an intensity of the band at 1716 cm^{-1} distinctly increased with temperature. A higher yield of aldehyde was observed in 2-picoline oxidation than in 3-picoline oxidation (Tables 1 and 2). Increasing temperature to 250 °C caused the 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} from the methyl group ν(C–H). A contradiction arose, in that the intensity of the former bands increased with temperature, indicating that more carboxylate formed, but no picolinic acid was found in the products, rather pyridine and CO_2 at higher temperatures in the oxidation of 2-picoline (Table 1). It is likely that the carboxylate is stable on the catalyst surface, but is unstable and easily decarboxylated after it desorbs from the catalyst surface. Based on the carboxylate species bands at 1417 and 1594 cm^{-1}, $\Delta\nu = 1594 - 1417 = 177$ cm^{-1}, thus, a bridging bidentate structure is suggested, again, similar to that of nicotinate.

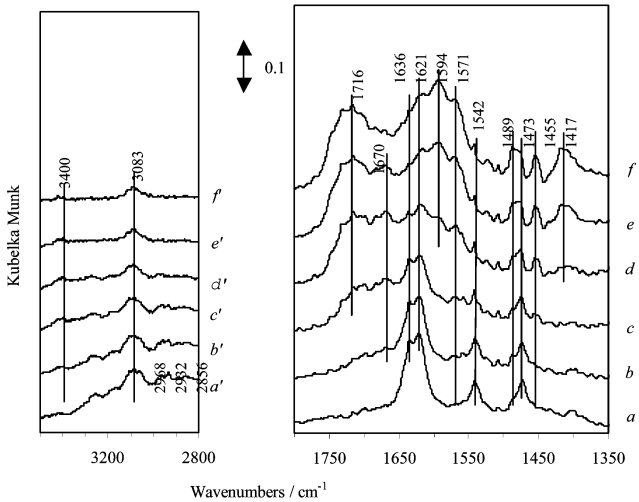


Fig. 8 *In situ* DRIFTS of 2-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$. Temperature, 30 °C (*a,a'*), 150 °C (*b,b'*), 200 °C (*c,c'*), 250 °C (*d,d'*), 300 °C (*e,e'*), and 350 °C (*f,f'*).

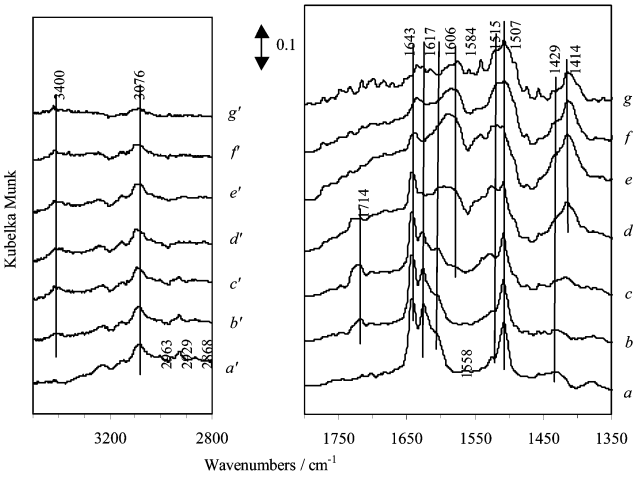


Fig. 9 *In situ* DRIFTS of 4-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$. Temperature, 30 °C (*a,a'*), 150 °C (*b,b'*), 200 °C (*c,c'*), 250 °C (*d,d'*), 300 °C (*e,e'*), 350 °C (*f,f'*) and 400 °C (*g,g'*).

Fig. 9 shows the *in situ* DRIFTS of 4-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$. The strong bands at 1507, 1617 and 1643 cm^{-1} and the weak bands at 1429, 1515, 1558 and 1606 cm^{-1}, shown in Fig. 9(*a*, *a'*), are 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 Brønsted acid sites on $CrV_{0.95}P_{0.05}O_4$ in consideration of the same adsorption model as described for 2 and 3-picoline adsorption. The temperature dependent spectral change is shown in Fig. 9(*b*,*b'*–*g*,*g'*) . The characteristic band of aldehyde expected at 1714 cm^{-1} (C=O) appeared at 150 °C and disappeared above 250 °C. Furthermore, the bands at 1414 and 1584 cm^{-1}, which are characteristic of the carboxylate group, grew prominently from 200 to 300 °C, 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 intensities of both the 1414 and 1584 cm^{-1} bands reducing at higher temperature, coinciding with the relative decrease of the intensity of the pyridine ring C–H stretching vibration at 3076 cm^{-1}.

Mechanism of 2-, 3-, and 4-picoline oxidations

Our previous works[1–4] suggested that the bridging oxygen in the V–O–Cr bond is responsible for the catalytic activity during the oxidation of 3-picoline. A partial replacement of V with P ($CrV_{0.95}P_{0.05}O_4$) resulted in a significant increase in the activity. This may be due to an enhanced oxidizing ability of the V reduction-oxidation sites as observed in an appearance of the reduction peaks in TPR at low temperature.[4] The enhancement in catalytic activity of the V reduction-oxidation sites on $CrV_{0.95}P_{0.05}O_4$ may be assisted not only by the addition of P but also by the Brønsted acidic properties.[4]

The adsorption and oxidation of 3-picoline on $CrV_{0.95}P_{0.05}O_4$ in the absence of gas-phase oxygen have been studied by *in situ* DRIFTS (Fig. 10). The characteristic bands of pyridine ring and methyl group, which are assigned to 3-picoline on $CrV_{0.95}P_{0.05}O_4$, was observed at 100 °C after the purging in N_2 flow (Fig. 10*a*). The characteristic bands of the oxygen-containing species (1412, 1588 and 1718 cm^{-1}) were also observed above 200 °C (Fig. 10*b* and *c*) even under the absence of gas-phase oxygen. This clearly indicates that lattice oxygen of the catalyst involved in the oxidation process. The negative band at 2050 cm^{-1} probably due to the partially reduced V sites was disappeared after oxidation at 400 °C for 20 min (Fig. 10*d*), whereas it was obtained even after the purging in N_2 at 300 °C. It is likely that the reduction-oxidation

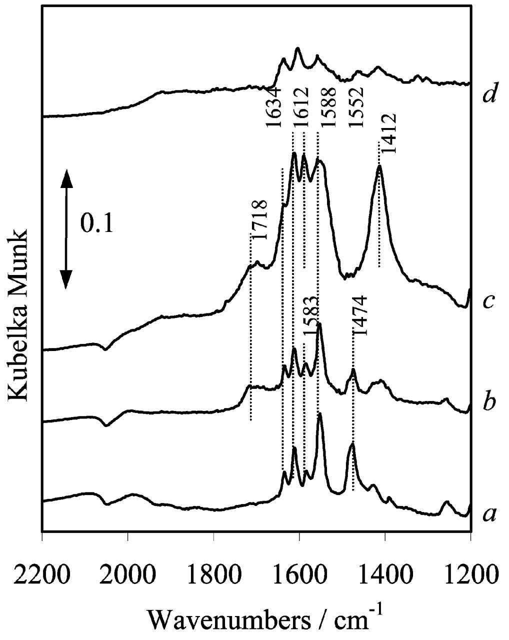


Fig. 10 *In situ* DRIFTS of 3-picoline adsorbed on $CrV_{0.95}P_{0.05}O_4$. In N_2 at 100 °C (*a*), 200 °C (*b*), 300 °C (*c*), and in O_2/N_2 for 20 min at 400 °C (*d*).

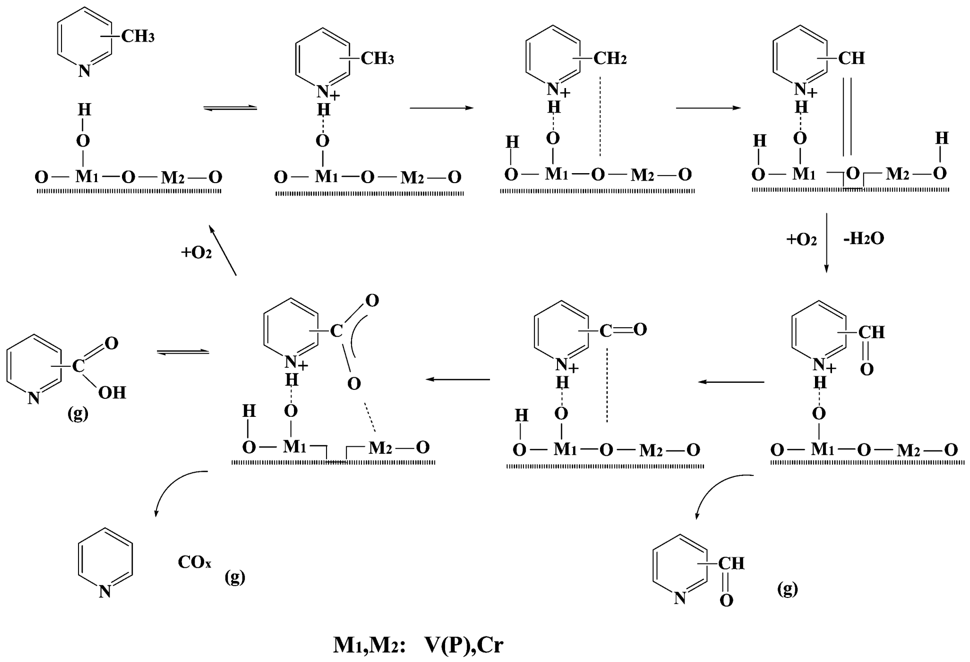
took place on the V sites. *i.e.*, the original intensity of V-O overtone band was almost recovered in the presence of gas-phase oxygen. It is suggested that the oxidation of adsorbed 3-picoline is enhanced due to the replenishment of lattice oxygen by gas-phase oxygen.

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,[5,6] a possible Mars and van Krevelen mechanism[30] of surface reactions over the catalyst surface is proposed (Scheme 3). In the first step, a protonated picoline forms by the interaction with a Brønsted 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 an aldehyde-like intermediate. In order to compensate for the loss of the lattice oxide ion, the oxygen adsorbed from the gas phase migrates to fill the oxygen vacancy. Part of the reaction product, for example pyridine–carbaldehyde, desorbs from the catalyst surface into the 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 form if decarboxylation is possible. If the temperature is very high, then an appreciable amount of deep oxidation will take place.

Water enhancement of the 2-, 3- and 4-picoline oxidations can be explained by the formation of Brønsted acid site (–OH groups). Some Lewis acid sites on the surface of $CrV_{0.95}P_{0.05}O_4$ catalyst could be transformed to Brønsted acid sites in the presence of water.[4] Moreover, some of the water adsorbed on the catalyst surface can dissociatively hydrolyse V–O–Cr bond and produce hydroxyl (–OH) groups as Brønsted acid sites, again. The formation of the surface hydroxyls may also lead to a weakening of V–O bonds or a formation of surface defect, which enables the rate of oxidation reaction to increase.[15,31–33] Furthermore, it is well known that the residence time of an organic species depends on the desorption rate of intermediate products formed on the surface. The ease of desorption of an organic compound depends on acid-base properties of the catalyst surface. A quick desorption of acidic product requires high acidity and low basicity. Herein, the addition of water results in an enhancement of the amount of Brønsted acid sites on the catalyst surface, which accelerates the hydrolysis and desorption of carboxylate from catalyst surface. Consequently, the total oxidation to CO_x can be blocked. Finally, it is concluded that both V reduction–oxidation sites and Brønsted acid sites are collaboratively responsible for the high catalytic activity and the acid selectivity.

Conclusions

The vapor phase oxidations of 2-, 3- and 4-picolines on $CrV_{0.95}P_{0.05}O_4$ catalyst have been studied in connection with



Scheme 3

the results of *in situ* DRIFTS measurement of the adsorbed species. 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 CO_2.

In situ DRIFTS study showed that both Lewis and Brønsted acid sites were present on the surface of $CrV_{0.95}P_{0.05}O_4$, and the adsorptions of 2-, 3- and 4-picolines occurred through the N atom to the acid sites on the catalyst surface. The bridging bidentate adsorption of carboxylate through both N atom and a C–O on the catalyst surface was suggested. Even though there were observed some differences in the reactivity and the product selectivity between 2-, 3- and 4-picoline oxidation over $CrV_{0.95}P_{0.05}O_4$, a good similarity was observed in the adsorption and the oxidation behaviors by *in situ* DRIFTS measurement. Based on these results, a Mars and van Krevelen mechanism of surface reactions over $CrV_{0.95}P_{0.05}O_4$ is proposed.

Addition of water greatly enhanced the activity and the selectivity of the products in 2-, 3- and 4-picolines oxidations. It is interpreted that a large amount of Brønsted acid sites were formed on the catalyst surface in the presence of water, and subsequently enabled the acceleration of the rate of oxidation reaction.

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