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Hydrothermal synthesis of microporous W–V–O as an efficient catalyst for ammoxidation of 3-picoline

Yoshinori Goto[a], Ken-ichi Shimizu[a,b], Toru Murayama[a,c], Wataru Ueda[d,*]

[a] Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan
[b] Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan
[c] Research Center for Gold Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan
[d] Kanagawa University, Rokkakubashi 3-27-1, Yokohama 221-8686, Japan

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ABSTRACT

W–V complex metal oxide (W–V–O) was prepared by hydrothermal synthesis method. Characterization by XRD, XPS, ICP-AES, N_2 adsorption, and STEM showed that W–V–O had a layered structure with micropore. W–V–O was tested for the vapor phase ammoxidation of 3-picoline (PIC) to 3-cyanopyridine (CP) and compared with VO_x/WO_3 catalyst prepared by impregnation method and other V-based catalysts which were reported to be efficient for this reaction. W-added vanadium oxides, W–V–O and VO_x/WO_3, showed higher CP selectivity than conventional catalysts such as VO_x/TiO_2. The W–V–O catalyst showed the highest CP selectivity of 99.5% at full PIC conversion. Kinetic studies showed that CP was the primary product and small amount of pyridine and CO_2 were produced from CP. The reaction by W–V–O in low NH_3 concentration condition or without co-feeding of water was also studied to evaluate the catalytic performance of W–V–O in industrially relevant conditions.

1. Introduction

Direct synthesis of nitriles via partial oxidation of hydrocarbons in the presence of ammonia (NH_3), so called ammoxidation, is an industrially important reaction [1,2]. The gas-phase ammoxidation of substituted aromatics/heteroaromatics is currently used in the production of fine chemicals and intermediates [1–18]. Especially, the ammoxidation of 3-methylpyridine (3-picoline) to nicotinonitrile (3-cyanopyridine) has been extensively studied [3–16] due to the commercial importance of 3-cyanopyridine for the industrial production of vitamin B3 (nicotinamide and nicotinic acid) as feed additives [19]. These compounds are also used as a precursor for commercial compounds such as cancer drugs, antibacterial agents, and pesticides [2]. Various metal oxide-based catalysts have been reported to be efficient for the ammoxidation of 3-methylpyridine (PIC) to 3-cyanopyridine (CP) [3–16]. Most of the reported catalysts are vanadium (V)-based catalysts, including VO_x/Nb_2O_5 [3], V_2O_5 [4], $(VO)_2P_2O_7$ [5,6], γ-$VOHPO_4$ [7], VO_x/TiO_2 [8], V–Sb–O [9], V–Cr–O [10], VZrPO [11], VZr(Al)PON [11–13], industrial $VTiSbSiO_x$ catalyst [14], V_2O_5/MgF_2 [15], and V_2O_5/CeF_3 [16]. Mechanistic studies on this reaction and related selective oxidation reaction of picolines [20–22], methylpyradine [23] and toluene [24] suggested bifunctional catalysis as a catalyst design concept, where the VO_x sites catalyze partial oxidation of hydrocarbons to oxygenate intermediate and acid sites originated from co-catalysts, such as PO_x, act as adsorption site of basic substrate (picolines and NH_3). Knowing the fact that oxides of tungsten (W) are well known acidic co-catalysts of V-based catalysts, one hypothesizes that W–V–O oxides can be an attractive candidate of the catalyst for the ammoxidation of picolines. To the best of our knowledge, quite a few efforts have been devoted to the development of W–V binary oxides as an attractive candidate of catalyst for the ammoxidation of picolines.

Our research group has focused on the hydrothermal synthesis of single crystalline Mo–V–O based catalysts [25–27]. Particularly, single phasic orthorhombic Mo_3VO_x, having a microporous and layered structure, is of importance because it catalyzes selective oxidative dehydrogenation of ethane even at around 300 °C [26]. The single phase Mo–V–P catalyst also catalyzeds the ammoxidation of propane [27]. Recently, we extended the hydrothermal synthetic methodology to metal oxides consisted of various group 5 and 6 elements, and prepared a series of metal oxides with similar microporous and layered structure as orthorhombic Mo_3VO_x [28,29]. We hypothesized that W–V–O oxides with similar structure may show redox/acid bifunctional catalysis for ammoxidation

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* Corresponding author.
E-mail address: uedaw@kanagawa-u.ac.jp (W. Ueda).

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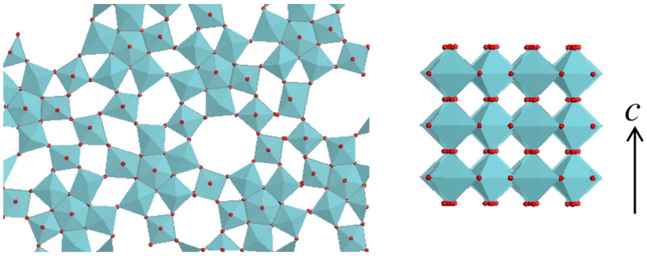

Fig. 1. Polyhedral model of the microporous and layered W–V–O oxide.

Table 1
Surface area and composition of the catalysts.

Catalyst	S.A.[a] ($m^2 g^{-1}$)	Bulk W/V[b]	Surface W/V[c]
V_2O_5	4.8	–	–
VO_x/WO_3	14	62/38	60/40
W–V–O	16	67/33	76/24

[a] Surface area determined by the BET method.
[b] W/V atomic ratio determined by ICP-AES.
[c] W/V atomic ratio determined by XPS.

of 3-picoline. There are no attempts on the development of W–V binary oxides for the ammoxidation of picolines. We report herein the first example of ammoxidation of 3-picoline by hydrothermally prepared W–V–O oxide with microporous and layered structure.

2. Experimental

2.1. Catalyst preparation

Inorganic materials were purchased from Wako Pure Chemical Industries. The complex metal oxide of W and V (W–V–O) was prepared by a hydrothermal synthesis method. An aqueous solution (40 mL) of $(NH_4)_6[H_2W_{12}O_{40}]\cdot nH_2O$ (6.24 mmol), $VOSO_4\cdot nH_2O$ (4.16 mmol) and oxalic acid (0.10 mmol) was introduced into a stainless steel autoclave with a Teflon inner tube (50 mL), followed by filling the inner space of the tube by Teflon thin sheet (50 mm × 1000 mm). The presence of the sheet is important to prepare W–V–O. Then, N_2 was fed into the solution for 10 min to remove residual oxygen. The autoclave placed to rotating machine was installed in an oven. The mixture underwent hydrothermal reaction at 175 °C for 24 h under mechanical rotation (1 rpm). The formed solid was filtered, washed with ion-exchanged water, dried at 80 °C overnight and then heated at 500 °C for 2 h under N_2 flow.

V_2O_5 and WO_3 for catalytic studies were commercially supplied from Wako Pure Chemical Industries. Tungsten oxide-supported vanadia (VO_x/WO_3) was prepared by impregnation method. A suspension of WO_3 (8.01 mmol) in an aqueous solution (50 mL) of NH_4VO_3 (4.91 mmol) was heated to 90 °C for 30 min to evaporate water, followed by drying at 80 °C overnight, and by heating at 500 °C for 2 h under N_2 flow. The bulk and surface compositions and surface area of the W–V–O and VO_x/WO_3 catalysts are listed in Table 1. The composition and surface area of VO_x/WO_3 are close to those of W–V–O.

According to the literature [8], TiO_2-supported vanadia (VO_x/TiO_2) with V loading of 5.9 wt% was prepared by impregnation method. A suspension of anatase TiO_2 (4 g) in aqueous oxalic acid solution (50 mL) of NH_4VO_3 (4.9 mmol) was evaporated at 50 °C, followed by drying at 100 °C, and by heating at 450 °C for 6 h under air.

Mixed oxide of VZrPO was prepared according to the literature [11]. To aqueous solution of $ZrO(NO_3)_2$ (8.6 mmol, 0.02 M), aqueous HNO_3 solution of NH_4VO_3 (17.1 mmol, 0.02 M, pH 3) was added under stirring at 70 °C. After adding the corresponding amount of phosphoric acid (7.7 mmol, 3 M), a gel was formed, which was stirred for 1 h at 70 °C, followed by adding 55 g of citric acid, stirring for 16 h at 70 °C, evaporation to dryness using a rotating evaporator, and by drying at 120 °C for 16 h. After grinding, the resulting brown powder was calcined under flowing air (6 L/h) for 16 h at 500 °C and for another 6 h at 600 °C.

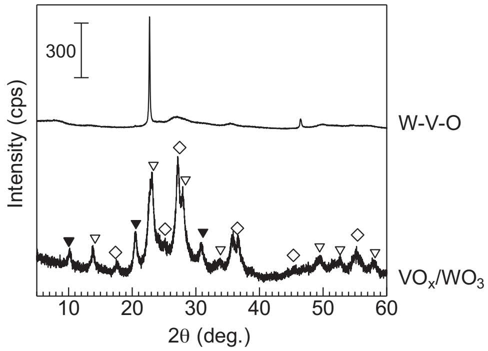

Fig. 2. XRD patterns of W–V–O and VO_x/WO_3: ▽ = WO_3 (PDF#00-033-1387), ▼ = V_2O_5 (PDF#00-040-1297), ◇ = VO_2 (PDF#43-1051).

Mixed oxide of V and Cr (VCrO) was prepared as follows [10]; V_2O_5 (5.28 mmol) and CrO_3 (13.2 mmol) were dissolved in an aqueous oxalic acid solution, followed by drying at 110 °C for 10 h, and by calcination in air at 500 °C for 6 h.

2.2. Catalyst characterization

Nitrogen adsorption experiments at −196 °C were carried out with a BELSORP MAX (BEL Japan Inc.) sorption analyzer. Prior to the measurement, the samples were evacuated at 200 °C for 2 h. Specific surface area of the catalysts was estimated by BET method. Powder X-ray diffraction (XRD) pattern of the catalysts was recorded on RINT2200 (Rigaku) with Cu Kα radiation (tube voltage: 40 kV, tube current: 20 mA). Scanning transmission electron microscopy (STEM) images were obtained with a HD-2000 (Hitachi High-Tech Inc.). Bulk composition of the catalysts was determined by an inductive coupling plasma (ICP-AES) method (ICPE-9000, Shimadzu). Surface composition of the catalysts was estimated by X-ray photoelectron spectroscopy (XPS) measurements using a JEOL JPS-9010MC (MgKα irradiation).

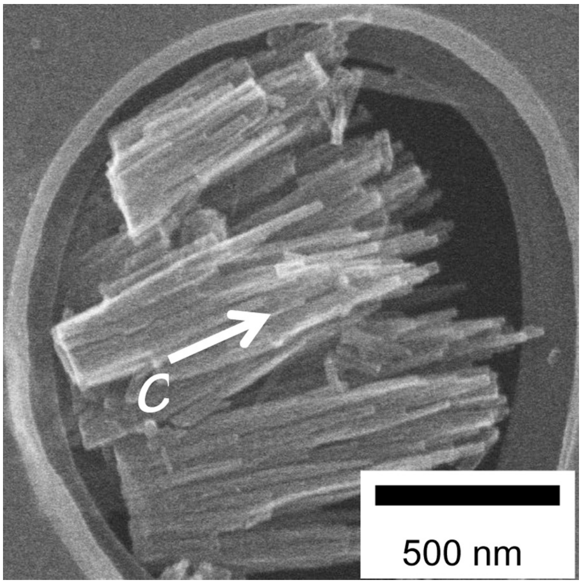

Fig. 3. STEM image of W–V–O.

Table 2
Ammoxidation of 3-picoline.[a]

Catalyst	Cat. wt. (g)	*T* (°C)	Conversion (%)		Selectivity (%)					
			PIC	O_2	CP	NAc	NA	Pyr	CO	CO_2
WO_3	1.00	383	0.0	11.5	0.0	0.0	0.0	0.0	0.0	0.0
VO_x/WO_3	0.38	389	100	47.3	98.0	0.0	0.0	0.7	0.1	1.2
W–V–O	0.75	386	100	51.7	99.5	0.0	0.0	0.2	0.0	0.3
V_2O_5	0.85	381	100	59.8	91.0	0.0	0.7	3.8	0.2	4.3

[a] Conditions: gas composition, $PIC/H_2O/NH_3/O_2/He = 1/8/6/4.4/19.6$.

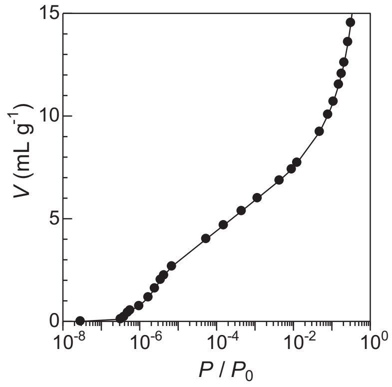

Fig. 4. N_2-adsorption isotherm of W–V–O.

2.3. Catalytic testing

Ammoxidation of 3-picoline was carried out at atmospheric pressure using a fixed-bed flow reactor (Pyrex glass tube) with an inner diameter of 9 mm. Catalyst powders were pressed to pellets, crushed, and sieved. Catalyst pellets (0.25–0.50 mm size), diluted with quartz (0.2–0.4 mm) in a volumetric ratio of 1:6, were set in the reactor. The reaction temperature was measured inside the catalyst bed by a thermocouple. The gas stream ($NH_3/O_2/He$) was fed to the reactor with mass flow controller. The aqueous solution of 11 mol% 3-picoline (PIC) was fed continuously into the gas stream at 150 °C from a syringe pump with a micro-feeder. The volumetric composition of reaction gas was $PIC:H_2O:NH_3:O_2:He = 1:8:4:4.4:19.6$ ($PIC/H_2O/NH_3/O_2/He = 2.7\%/21.6\%/10.8\%/11.9\%/53.0\%$). Total flow rate was 37 mL min^{-1}. CH_4 gas was fed into outlet gas as external standard. The gas phase products (CO and CO_2) in the outlet gas were collected in a gas bag and analyzed by TCD-GC (GL science GC-3200, 6 m SHINCARBON-ST packed column). Organic products, trapped in ethanol at 0 °C, followed by adding n-octane as external standard, were analyzed with FID-GC (Shimadzu GC-14A, 30 m 0.32 mm TC-5 capillary column). Note that carbon balance and oxygen balance for the catalytic results were 100.1 ± 0.6% and 97.5 ± 2.6%, respectively.

3. Result and discussion

3.1. Catalyst characterization

Previously, we have reported a series of studies on the hydrothermal synthesis of metal oxides consisted of group 5 and 6 elements. A group of the synthesized metal oxides have micropore due to heptagonal channel and layered structure as illustrated in Fig. 1, which is characterized by the common structural results as follows: (i) two sharp diffractions around 23° and 46° along with broad diffraction peaks around 8° and 27° observed by XRD, (ii) long rod-shaped crystal morphology, (iii) the presence of micropore. The diffractions around 23° and 46° have been attributed to the (0 0 1) and (0 0 2) planes of the layered structure in *c*-axis direction.

The rod-shaped crystal is due to stacking of the layers along the *c*-axis by sharing the apex oxygen. The microporosity is suggested to be due to the heptagonal channel structure of the a–b plane. The following results of XRD, STEM, N_2 adsorption suggest that the present W–V–O catalyst has the same structural characteristics as the porous and layered structure illustrated in Fig. 1. The XRD pattern of W–V–O (Fig. 2) showed two sharp diffraction lines at 22.7° and 46.5°. The XRD pattern of VO_x/WO_3 showed diffraction lines attributed to VO_2, V_2O_5 and WO_3.

The STEM image of W–V–O (Fig. 3) shows rod shaped crystals. The N_2-adsorption isotherm of W–V–O (Fig. 4) shows N_2 adsorption feature at low relative pressure ($P/P_0 < 10^{-6}$) which is characteristic to microporos materials. The micropore volume estimated by the *t*-plot method is 7.7×10^{-3} mL g^{-1}.

3.2. Catalytic performance

First, four catalysts (WO_3, V_2O_5, VO_x/WO_3, W–V–O) were tested for the ammoxidation of PIC at 383–389 °C. Table 2 lists the conversions of PIC and O_2 and selectivities to cyanopyridine (CP), nicotinamide (NA), nicotinic acid (NAc), pyridine (Pyr), CO, and CO_2. As previously reported [4], V_2O_5 showed good selectivity of CP at high conversion level (99.2%), while WO_3 showed no conversion of CP. This indicates that vanadium is an indispensable element for this catalytic system. The W-added vanadium oxides, VO_x/WO_3 and W–V–O, were tested for the reaction under the conditions of full CP conversion. VO_x/WO_3 and W–V–O show higher CP selectivities than V_2O_5, which indicates that tungsten oxides as co-catalysts increase the CP selectivity of V-based ammoxidation catalysts. Especially, the W–V–O catalyst showed the highest CP selectivity of 99.5%.

The catalytic performances of the V-based catalysts, including a well established VO_x/TiO_2 catalyst for this reaction [8], were further compared under different contact time at 380 °C. From the slope of the curve in the plot of CP conversion versus contact time (Fig. 5), the order of the catalytic activity is as follows: $VO_x/WO_3 > VO_x/TiO_2 > W–V–O \approx V_2O_5$. The selectivities of the main product (CP) and byproducts (Pyr and CO_2) are plotted as a function

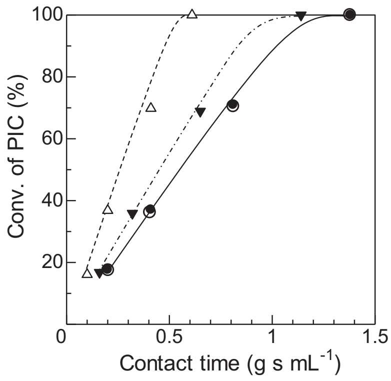

Fig. 5. Effects of contact time on PIC conversion for ammoxidation of PIC over (○)W–V–O, (△) VO_x/WO_3, (●) V_2O_5, and (▼) VO_x/TiO_2. Conditions: catalyst amount = 0.5 g, *T* = 380 °C, gas composition, $PIC/H_2O/NH_3/O_2/He = 1/8/6/4.4/19.6$.

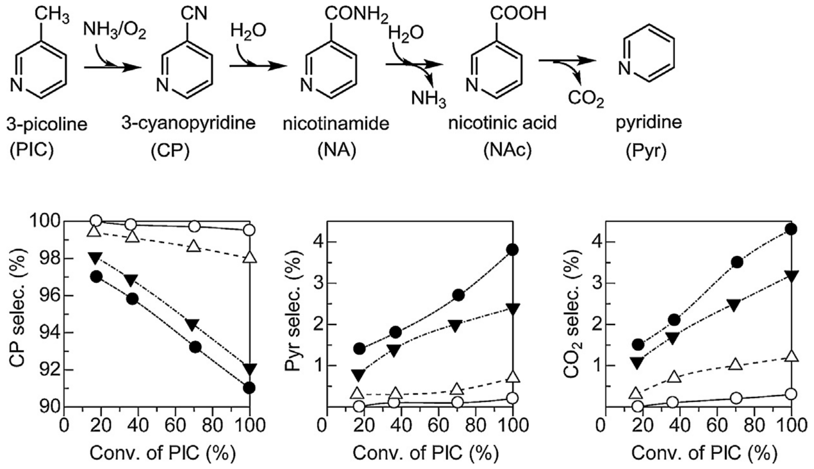

Fig. 6. Selectivity versus PIC conversion for ammoxidation of PIC over (○) W–V–O, (△) VO_x/WO_3, (▼) VO_x/TiO_2 and (●) V_2O_5. Conditions are the same as those in Fig. 5.

of the CP conversion in Fig. 6. A possible pathway of the formation of CP, NA, NAc, Pyr and CO_2 is also included in Fig. 6. Generally, Pyr and CO_2 were the main byproducts. The selectivities to NA, NAc, and CO were quite low (<0.2%) for the W–V–O and VO_x/WO_3 catalysts, while NA was also produced in 0.6–1.4% selectivity for VO_x/TiO_2 and V_2O_5 at high conversion levels. For all the catalysts tested, the CP selectivity decreased with the increase of the conversion, while the selectivities of the byproducts (Pyr and CO_2) increased. This indicates that CP is the product of the ammoxidation of PIC and Pyr and CO_2 are produced from CP probably via consecutive reactions of CP → NA → NAc → Pyr + CO_2 or via direct oxidation of CP to Pyr and CO_2. In the whole range of the conversion level, the W-added vanadium oxides (VO_x/WO_3 and W–V–O) showed higher CP selectivities than V_2O_5 and VO_x/TiO_2. Especially, the W–V–O catalyst showed the highest CP selectivity as well as the lowest selectivities of Pyr and CO_2.

To investigate the formation pathway of the byproduct in Fig. 6, we carried out hydration of CP (CP + H_2O reaction in the absence of O_2) by the W–V–O catalyst under the conditions shown Fig. 7. As shown in Fig. 7A, the conversion of CP increased with the reaction temperature. With increase in the temperature, the selectivity of NA decreased and the selectivities of Pyr and CO_2 the increased. The result indicates that NA, NAc, Pyr and CO_2 are produced by hydration of the nitrile (CP) in the absence of O_2. The result in Fig. 7A is re-plotted in Fig. 7B where the selectivities are plotted as a function of the CP conversion. With increase in the conversion, the selectivity of NA decreased and the selectivities of Pyr and CO_2 the increased. The selectivity of NAc increased up to 14% conversion and then decreased with the conversion. The result suggests that NA, NAc, Pyr and CO_2 are produced from CP via consecutive reactions of CP → NA → NAc → nPyr + CO_2. The hydration of the nitrile (CP) gives the amide (NA), which undergoes further hydration to give the carboxylic acid (NAc) and NH_3. Pyr and CO_2 can be produced by the decomposition of NAc.

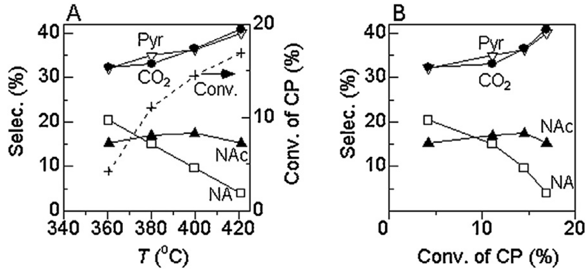

Fig. 7. Hydration of CP on W–V–O (0.5 g): gas composition, $CP/H_2O/He = 1/10/10$, flow rate = 21 mL min^{-1}. (A) Temperature dependence of (+) CP conversion and selectivities of (□) NA, (▲) NAc, (▽) Pyr, (●) CO_2. (B) Selectivities of (□) NA, (▲) NAc, (▽) Pyr, (●) CO_2 versus CP conversion.

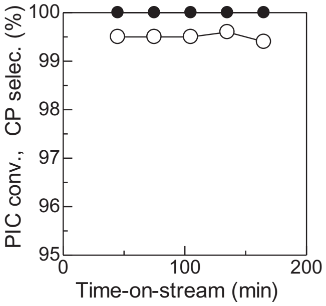

Fig. 8. (●) PIC conversion and (○) CP selectivity as a function of reaction time for ammoxidation of 3-picoline over W–V–O. Conditions: catalyst amount = 0.5 g, T = 380 °C, gas composition, $PIC/H_2O/NH_3/O_2/He = 1/8/6/4.4/19.6$.

Next, we tested the ammoxidation of PIC with some representative catalysts (VCrO [10] and VZrPO [11]) which were reported to be efficient for this reaction in the literature (Table 3). The reactions were carried out under the same conditions (contact time, gas composition) except for the temperatures (365–410 °C). The reaction temperature for each experiment was adopted to achieve nearly full conversion of CP (98.9–100%). The result shows that VO_x/WO_3 and W–V–O exhibit higher CP selectivities than the conventional V-based catalysts, and W–V–O showed the highest CP selectivity and the lowest selectivities of Pyr and CO_2 among the catalysts tested. The above results demonstrate excellent catalytic performances of the W–V–O catalyst for the ammoxidation of PIC to CP. It should be noted that the XRD pattern of the W–V–O did not essentially change after the reaction, suggesting no change in the catalyst structure during the reaction.

From a viewpoint of industrial catalysis, long time durability and the reaction without co-feeding of water or without too much excess of NH_3 are important. The stability versus time-on-stream of the best performing W–V–O catalyst has been investigated and the result is shown in Fig. 8. The data show that the CP selectivity remains essentially constant (99.4–99.6%) during 3 h of the operation at 380 °C. Fig. 9 shows the catalytic performance of W–V–O under different NH_3 concentration. The result shows that the NH_3 partial pressure of around 12%, corresponding to 4.4 equivalent with respect to CP, is enough to give the highest selectivity at full CP conversion. Finally, we studied the effect of co-feeding of water on the catalytic performance of W–V–O. The temperature dependence

Table 3
Comparison of the catalysts for the ammoxidation of 3-picoline.[a]

Catalyst	S.A ($m^2 g^{-1}$)	T (°C)	Conversion (%)		Selectivity (%)					
			PIC	O_2	CP	NAc	NA	Pyr	CO	CO_2
W–V–O	16	407	99.6	49.2	99.4	0.0	0.0	0.2	0.0	0.4
VO_x/WO_3	14	410	100	50.0	95.8	1.6	0.6	1.0	0.0	1.0
VCrO	23	365	98.9	54.3	92.0	1.0	1.1	1.6	0.9	3.3
VZrPO	30	370	99.0	53.7	83.4	2.7	0.8	0.7	0.0	12.3

[a] Conditions: catalyst amount = 0.5 g; gas composition, $PIC/H_2O/NH_3/O_2/He$ = 1/8/6/4.4/19.6.

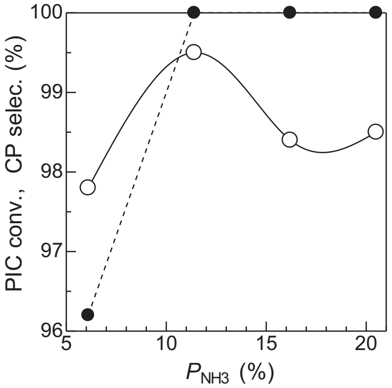

Fig. 9. (●) PIC conversion and (○) CP selectivity as a function of the concentration of NH_3 for ammoxidation of 3-picoline over W–V–O (0.5 g) at 380 °C.

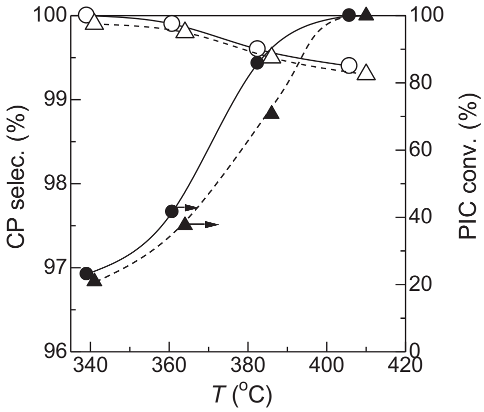

Fig. 10. (●,▲) PIC conversion and (○,△) CP selectivity as a function of temperature with water-dosing (▲,△) in the feed or without the water-dosing (●,○) over W–V–O catalyst. Gas composition, $PIC/H_2O/NH_3/O_2/He$ = 1/8/6/4.4/19.6 or $PIC/NH_3/O_2/He$ = 1/6/4.4/19.6.

of the reaction data with or without co-feeding of 21.6% water vapor is shown in Fig. 10. The result shows that the CP selectivity and PIC conversion without water-dosing are slightly higher than those with water-dosing. These results suggest that the present catalytic system is effective even without the additional water-dosing. Considering the fact that most of the previous catalytic systems for this reaction have been carried out under water-dosing conditions, our system is a rare example of the high yield catalytic system for the reaction without the water-dosing. The above characteristics suggest that the ammoxidation by W–V–O is important from a viewpoint of industrial production of CP from PIC.

4. Conclusion

The microporous and layered W–V metal oxide, W–V–O, was synthesized by hydrothermal method. For the vapor phase ammoxidation of 3-picoline, the W–V–O catalyst gave an exceptionally high 3-cyanopyridine selectivity of 99.5% under full conversion conditions. The selectivity of W–V–O was higher than those of VO_x/WO_3 and other catalysts reported to be efficient for this reaction such as VCrO, VZrPO, and VO_x/TiO_2. The W–V–O catalyst gave high catalytic performance even in the absence of co-feeding of water, demonstrating that the present system can be of importance from a viewpoint of industrial production of 3-cyanopyridine from 3-picoline. Silent finding of this study was that the VO_x/WO_3 catalyst showed higher activity and selectivity for this reaction than previous V-based catalysts.

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