



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

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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, N₂ 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/WO₃ 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/WO₃, showed higher CP selectivity than conventional catalysts such as VO_x/TiO₂. 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 CO₂ were produced from CP. The reaction by W–V–O in low NH₃ concentration condition or without co-feeding of water was also studied to evaluate the catalytic performance of W–V–O in industrially relevant conditions.

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1. Introduction

Direct synthesis of nitriles via partial oxidation of hydrocarbons in the presence of ammonia (NH₃), 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 ammoxidation 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/Nb₂O₅ [3], V₂O₅ [4], (VO)₂P₂O₇ [5,6], γ-VOHPO₄ [7], VO_x/TiO₂ [8], V–Sb–O [9], V–Cr–O [10], VZrPO [11], VZr(Al)PON [11–13], industrial VTiSbSiO_x catalyst [14], V₂O₅/MgF₂ [15], and V₂O₅/CeF₃ [16]. Mechanistic

studies on this reaction and related selective oxidation reaction of picolines [20–22], methylpyridine [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 NH₃). 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 Mo₃VO_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 catalyzes 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 Mo₃VO_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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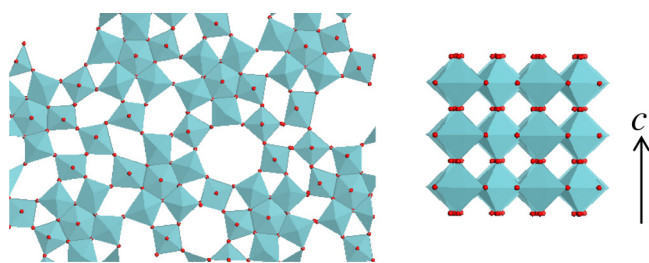


Fig. 1. Polyhedral model of the microporous and layered W–V–O oxide.

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 ₂ O 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 (NH₄)₆[H₂W₁₂O₄₀]·nH₂O (6.24 mmol), VOSO₄·nH₂O (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, N₂ 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 N₂ flow.

V₂O₅ and WO₃ for catalytic studies were commercially supplied from Wako Pure Chemical Industries. Tungsten oxide-supported vanadia (VO_x/WO₃) was prepared by impregnation method. A suspension of WO₃ (8.01 mmol) in an aqueous solution (50 mL) of NH₄VO₃ (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 N₂ flow. The bulk and surface compositions and surface area of the W–V–O and VO_x/WO₃ catalysts are listed in Table 1. The composition and surface area of VO_x/WO₃ are close to those of W–V–O.

According to the literature [8], TiO₂-supported vanadia (VO_x/TiO₂) with V loading of 5.9 wt% was prepared by impregnation method. A suspension of anatase TiO₂ (4 g) in aqueous oxalic acid solution (50 mL) of NH₄VO₃ (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(NO₃)₂ (8.6 mmol, 0.02 M), aqueous HNO₃ solution of NH₄VO₃ (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

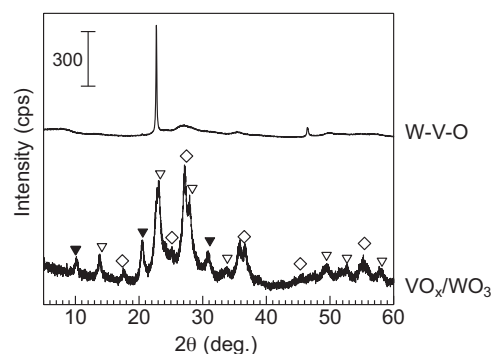


Fig. 2. XRD patterns of W–V–O and VO_x/WO₃: ▽ = WO₃ (PDF#00-033-1387), ▼ = V₂O₅ (PDF#00-040-1297), ◇ = VO₂ (PDF#43-1051).

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.

Mixed oxide of V and Cr (VCrO) was prepared as follows [10]; V₂O₅ (5.28 mmol) and CrO₃ (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).

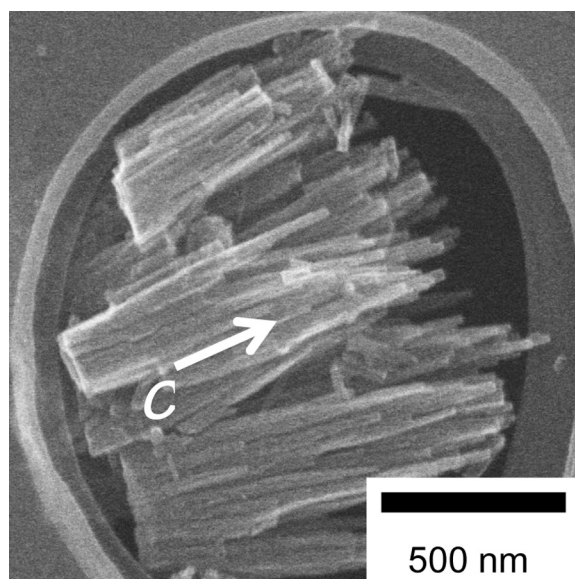


Fig. 3. STEM image of W–V–O.

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