NH$_3$-efficient ammoxidation of toluene by hydrothermally synthesized layered tungsten-vanadium complex metal oxides

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Abstract

Hydrothermally synthesized W–V–O layered metal oxides (W–V–O) are studied for the vapor phase ammoxidation of toluene to benzonitrile (PhCN). Under similar conversion levels at 400 °C, W–V–O shows higher selectivity (based on toluene) to PhCN and lower selectivity to COx than conventional V-based catalysts (V$_2$O$_5$ and VO$_x$/TiO$_2$). Under the conditions of high contact time, W-V-O shows 99.7% conversion of toluene and 93.5% selectivity to PhCN. Another important feature of W–V–O is high NH$_3$-utilization efficiency in ammoxidation, which originates from the lower activity of W–V–O for NH$_3$ oxidation than that of V$_2$O$_5$. In situ infrared (IR) study shows that toluene is oxidized by the surface oxygen species of W$_83$V$_{17}$ to yield benzaldehyde which undergoes the reaction with adsorbed NH$_3$ to give benzonitrile. Model reaction studies with W–V–O suggest that the rate of NH$_3$ conversion to PhCN in the benzaldehyde+NH$_3$+O$_2$ reaction is 3 times higher than the rate of NH$_3$ oxidation to N$_2$ in the NH$_3$+O$_2$ reaction. It is shown that the high NH$_3$-efficiency of W-V-O is caused by the preferential reaction of NH$_3$ in PhCHO+NH$_3$+O$_2$ over NH$_3$+O$_2$ reaction.

1. Introduction

Ammoxidation of methyl-substituted aromatics such as toluene, xylene and methylpyridine to their corresponding nitriles is an industrially important reaction, and numerous reports have been dealt with this reaction [1-4]. The vapor phase ammoxidation of toluene to benzonitrile has been extensively studied as a model reaction [5-16]. Various metal oxide-based catalysts, including vanadium (V)-based catalysts (V$_2$O$_5$ [5], VO$_x$/TiO$_2$ [6,7], VO$_x$/ZrO$_2$ [8], V$_2$O$_5$/Nb$_2$O$_5$/TiO$_2$ [9], (VO)$_2$P$_2$O$_7$ [10-13]) and other catalysts (MoO$_x$/Nb$_2$O$_5$ [13], MoO$_x$/ZrO$_2$ [14]) have been studied.
shows ammoxidation prepared report herein W effective co elements hydrothermal synthetic methodology to metal oxide structure ethane at oxidation catalysts that of so-called “M1 phase” microporous and layered structure, based catalysts [21] redox site sites) design benzaldehyde concept ammoxidation of utilization in ammoxidation benzonitrile based on toluene. In addition to the ammoxidation of toluene has been discussed in terms of the selectivity or yield of benzonitrile based on toluene. In order to establish a sustainable ammoxidation process, NH3 consumption during the reaction should also be minimized. However, quite a few reports have discussed the benzonitrile selectivity based on the NH3 consumed, or in other words, the efficiency of NH3 utilization in ammoxidation of benzonitrile. Mechanistic studies on vanadium oxides-catalyzed ammoxidation of toluene [6,7,11-13] suggested bifunctional catalysis as a catalyst design concept. It is proposed that the VOx sites catalyze partial oxidation of toluene to benzaldehyde-like intermediate and acid sites act as adsorption site of NH3 [3,11-13]. If one designed a V-based mixed oxide catalyst having NH3 adsorption sites (such as acidic WOx sites) in close proximity to the redox sites (VOx), the aldehyde intermediate formed on the redox site would have react preferentially with NH3 on the acid site, resulting in high efficiency of NH3 utilization in the ammoxidation reaction.

Our research group has focused on the hydrothermal synthesis of single crystalline Mo-V-O based catalysts [17-19]. Particularly, single phasic orthorhombic Mo3V0x, having a microporous and layered structure, is of importance because its structure is basically the same as that of so-called “M1 phase” which is well known as active phase in the industrial selective oxidation catalysts [18]. We have found that the Mo-V-O catalysts, as a structurally well-defined catalytic phase for “M1 phase”, catalyzed the selective oxidative dehydrogenation of ethane at low temperature (300 °C) [18]. The single phase Mo-V-P catalyst with similar structure also catalyzed the ammoxidation of propane [19]. Recently, we have extended the hydrothermal synthetic methodology to metal oxides consisted of various group 5 and 6 elements [20-23], and prepared a series of binary metal oxides (such as W-Ta-O [20,23], W-Nb-O [21] and W-V-O complex oxides [22]) with similar microporous and layered structure as the orthorhombic Mo3V0x [18]. Considering the fact that WOx is an well known acidic co-catalyst of V-based catalysts [24-27], we have hypothesized that the W-V-O oxides act as effective catalysts for the ammoxidation. In this regard, we have recently reported the W-V-O-catalyzed highly selective ammoxidation of 3-picoline to 3-cyanopyridine [22]. We report herein a highly selective gas-phase ammoxidation of toluene by the hydrothermally prepared W-V-O layered oxides. The catalysts show high efficiency of NH3 utilization in ammoxidation as well as high selectivity of benzonitrile based on toluene. In situ IR study shows that the reaction of benzaldehyde with NH3 is a main pathway to benzonitrile on this
catalytic system. Model reaction studies are also conducted to discuss the reason why the W-V-O catalyst shows high efficiency of NH₃ utilization.

2. Experimental

2.1. Catalyst preparation

Inorganic materials were purchased from Wako Pure Chemical Industries. According to our previous report [22], the complex metal oxide of W and V (W-V-O) with W/V molar ratio of 83/17, named W83V17, was prepared by a hydrothermal synthesis method as follows. An aqueous solution (40 mL) of (NH₄)₆[H₂W₁₂O₄₀]·nH₂O (10.4 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). Then, N₂ (20 mL min⁻¹) was fed into the solution for 10 min to remove residual oxygen. The autoclave attached to a rotating machine was installed in an oven, and the mixture underwent hydrothermal reaction at 175 °C for 24 h under mechanical rotation (1 rpm). The solid formed was filtered, washed with ion-exchanged water (1 L), dried at 80 °C overnight and then heated at 400 °C for 2 h under N₂ flow. W64V36 with W/V molar ratio of 64/36 was prepared according to the method in our previous study [22.]

Bulk composition of the catalysts (Table 1) was determined by an inductively coupled plasma (ICP-AES) method (ICPE-9000, Shimadzu). Na⁺-exchanged W83V17 (designated as Na-W83V17) was prepared by mixing W-V-O (2.0 g) with 100 mL of aqueous solution of Na₂SO₄ (19.1 mmol) for 5 h at room temperature, followed by centrifuging and washing with ion-exchanged water four times, drying at 80 °C overnight and by heating at 400 °C for 2 h under N₂ flow. The Na content in Na-W83V17 (0.74 mmol g⁻¹) was determined by ICP-AES analysis. WO₃-supported vanadia (VOₓ/WO₃) with W/V molar ratio of 85/15 was prepared by impregnation method; a suspension of WO₃ (20.0 mmol) in an aqueous solution of NH₄VO₃ (3.5 mmol) was evaporated at 90 °C for 30 min to evaporate water, followed by drying at 80 °C overnight, and by heating at 400 °C for 2 h under N₂ flow. The bulk compositions and surface area of the W-V-O and VOₓ/WO₃ catalysts are listed in Table 1. V₂O₅ and WO₃ for catalytic studies were commercially supplied from Wako Pure Chemical Industries. Vanadia loaded TiO₂ with V loading of 5.9 wt%, named VOₓ/TiO₂, was prepared by impregnation method [22]; a suspension of anatase TiO₂ (4 g, Wako Pure Chemical Industries) 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.

2.2. Catalyst characterization

The BET surface areas of the catalysts were determined by N₂ adsorption at -196 °C using BELCAT (MicrotracBEL). Prior to the measurement, the samples were heated under He flow at
400 °C for 1 h. Powder X-ray diffraction (XRD) pattern of the catalysts were recorded on a Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation. Scanning electron microscope (SEM) images were taken using a JEOL JSM-7400F field emission scanning electron microscope.

The pyridine-adsorption infrared (IR) spectra were measured at 100 °C by a JASCO FT/IR-4200 spectrometer equipped with an MCT detector. The IR disc (38±1 mg, φ = 2 cm) of a catalyst in the flow-type IR cell. (CaF₂ windows), connected to a flow system, was first dehydrated under He flow (30 cm³ min⁻¹) at 500 °C for 0.5 h, followed by cooling to the measurement temperature under He. For the adsorption of organic compounds, 0.3 mmol g⁻¹ of liquid pyridine, toluene, benzaldehyde or benzonitrile was injected to the He flow preheated at 200 °C, and the vaporized organic compound was fed to the IR cell. For the adsorption of NH₃, NH₃(2%)/He (50 cm³ min⁻¹) was fed to the sample. Then, the IR disk was purged with He for 600 s, and IR measurement was carried out. Spectra were measured accumulating 15 scans at a resolution of 4 cm⁻¹. A reference spectrum of the catalyst wafer in He taken at the measurement temperature was subtracted from each spectrum.

2.3. Catalytic reactions

Vapor phase ammoxidation of toluene 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. To maintain a constant reaction temperature, the catalyst pellets (0.25-0.50 mm size; typically 1.5 g (1.1 cm³) of W83V17) were diluted with quartz (0.2-0.4 mm size; 1.5 cm³) to fill the reactor (2.6 cm³). Use of the same volume (2.6 cm³) of the pellets with the same size range will result in the same pressure drop for different catalyst loadings. The reaction temperature was measured inside the catalyst bed by a thermocouple, whose tip was inside the upper side of the catalyst bed. The gas stream (NH₃/O₂/He) was fed to the reactor with mass flow controllers. Toluene was fed continuously into the gas stream at 150 °C from a syringe pump with a micro-feeder. The reactor was fed with toluene/NH₃/O₂/He mixture in the molar ratio of 1/10/4/34 with total flow rate (F) of 49 mL min⁻¹. Under the low NH₃ concentration conditions in Fig. 7, the molar ratio of toluene/NH₃/O₂/He was 1/5/4/39 (F = 49 mL min⁻¹). CH₄ was fed into outlet gas as external standard for GC-TCD analysis.

As a model reaction (Fig. 9), benzaldehyde+NH₃+O₂ reaction by 0.1 g of the catalyst, diluted with the quartz pellets (2.5 cm³), was carried out with the same reactor which was fed with benzaldehyde/NH₃/O₂/He mixture in the molar ratio of 1/10/4/34 (F = 49 mL min⁻¹). A model reaction (Fig. 9) of NH₃+O₂ by 0.1 g of the catalyst was carried out using NH₃/O₂/He mixture in the molar ratio of 10/4/35 (F = 49 mL min⁻¹).

The gas phase products (CO, CO₂ and N₂) in the outlet gas were analyzed by GC-TCD (GL
Science GC-3200, 6 m SHINCARBON-ST packed column). Organic products, trapped in ethanol at 0 °C, followed by adding n-octane as an external standard, were analyzed with GC-FID (Shimadzu GC-14B with TC-5 capillary column). The carbon balance values for all the catalytic results were in a range of 95.9-101.6%.

For the ammoxidation of toluene in the present system, the nitrogen containing products were N\textsubscript{2} and benzonitrile (PhCN) with very small amount of benzamide (amide). GC-TCD analysis showed no formation of N\textsubscript{2}O. Thus, the efficiency of NH\textsubscript{3} utilization in ammoxidation (\(\eta_{\text{NH3}}\)) is defined as

\[ \eta_{\text{NH3}} = \frac{y_{\text{PhCN}}}{y_{\text{PhCN}} + y_{\text{amide}} + y_{\text{N2N}}}, \]

where \(y_{\text{PhCN}}\), \(y_{\text{amide}}\) and \(y_{\text{N2N}}\) are the molar amounts of nitrogen containing products, and \(n_{\text{PhCN}}\), \(n_{\text{amide}}\) and \(n_{\text{N2N}}\) are the number of nitrogen atoms in each product.

3. Result and discussion

3.1. Catalyst characterization

In our recent report [22], we synthesized a W-V-O catalyst with W/V ratio of 67/33 and studied its structure by various characterization methods: XRD, scanning transmission electron microscopy (STEM) and N\textsubscript{2}-adsorption isotherm. Briefly, the results showed three structural features: (i) layered-type structure along c-axis direction characterized by diffraction peaks at 2\(\theta\) = 23° and 46° (XRD), (ii) long rod-shaped crystal morphology due to stacking of the layers along the c-axis by sharing the apex oxygen (STEM), (iii) the presence of micropore (N\textsubscript{2}-adsorption). Considering the structural model that we have proposed for the similar binary metal oxides consisted of group 5 and 6 elements [17-23], the structural model of W-V-O is proposed in Fig. 1. In this paper, W-V-O catalysts with different compositions (W64V36 and W83V17) were prepared. As shown in Fig. 1, their XRD patterns have essentially the same feature: two sharp diffraction peaks around 23° and 46° assignable to the (0 0 1) and (0 0 2) planes of the layered structure along c-axis direction. The XRD pattern of Na-W83V17 also has the same diffraction peaks at 23° and 46°. Although the intensities of Na-W83V17 are lower than those of W83V17, the XRD results indicate that the Na\textsuperscript{+}-exchanged W83V17 (Na-W83V17) has basically the same crystal structure as W83V17. The SEM image of W83V17 (Fig. 2) showed the rod-shaped crystal probably due to stacking of the layers along the c-axis. Before calcination of the hydrothermally prepared binary metal oxides NH\textsubscript{4}\textsuperscript{+} is located in the 6 and 7-membered ring pores, and thermal desorption of NH\textsubscript{3} from the precursor results in the formation of Brønsted acid sites in the pores [18]. The proton is exchangeable to various cations in aqueous solution [18].

Fig. 3 shows IR spectra (the ring-stretching region) of pyridine adsorbed on W83V17 and Na-W83V17. The spectrum for W83V17 shows the adsorption band at 1536 cm\(^{-1}\) due to
pyridinium ion (PyH+) produced by the reaction of pyridine with Brønsted acid sites and the adsorption band at 1447 cm\(^{-1}\) due to coordinatively bound pyridine on Lewis acid sites [28]. The results indicate that the surface of W83V17 has both Brønsted and Lewis acid sites. Note that the weight of the catalyst disc for the IR experiment was the same for different catalysts, so the differences in the peak area at 1536 cm\(^{-1}\) and at 1447 cm\(^{-1}\) between samples corresponds to the difference in the amount of Brønsted and Lewis acid sites. The spectrum for Na-W83V17 shows lower intensities of these bands, which indicates that the H\(^+\)/Na\(^+\) cation exchange results in decrease in the number of Brønsted and Lewis acid sites of W83V17. It should be noted that the results of XRD show that the crystal structures of Na-W83V17 and W83V17 are similar to each other, and the surface area (Table 1) of Na-W83V17 (38.5 m\(^2\) g\(^{-1}\)) is close to that of W83V17 (41.9 m\(^2\) g\(^{-1}\)). These results indicate that the structure of W83V17 is essentially very close to that of Na-W83V17 except for acidity; W83V17 has larger amount of Brønsted and Lewis acid sites than Na-W83V17. The result also shows that W83V17 has larger amount of Bronsted and Lewis acid sites than V\(_2\)O\(_5\).

3.2. Catalytic performance

Fig. 4 shows the effects of contact time on the properties of ammonoxidation by W83V17 at 400 °C. Experiments were carried out by changing the catalyst weight (0.15, 0.75, 1.9, 1.5, 2.0 g) with the same inlet gas flow rate. The conversion of toluene increased with the contact time. The increase in the conversion resulted in slight decrease in the selectivity to benzonitrile (S\(_{\text{PhCN}}\)) and slight increase in the COx selectivity (S\(_{\text{COx}}\)). The selectivities to benzamide (S\(_{\text{amide}}\)) were below 0.9%. Hence, NH\(_3\) can be consumed by two of the competitive reactions: (1) ammonoxidation with toluene to produce benzonitrile and (2) NH\(_3\) oxidation to N\(_2\). Interestingly, the increase in the contact time resulted in the increase in the NH\(_3\)-efficiency (\(\eta_{\text{NH3}}\)). This indicates a preferential promotion of the ammonoxidation by W83V17 over the non-selective NH\(_3\) oxidation.

We tested various V-based catalysts (1.5 g of W83V17, W64V36, Na-W83V17, VO\(_x\)/WO\(_3\) and WO\(_3\) and 0.5 g of V\(_2\)O\(_5\)) for the ammonoxidation of toluene. To compare the selectivities of V\(_2\)O\(_5\) and W-V complex oxide catalysts under the similar conversion levels, the catalyst amount of V\(_2\)O\(_5\) was decreased. For representative catalysts, the effects of temperature on the toluene conversion, selectivity to various products and NH\(_3\)-efficiency are plotted in Fig. 5. Under the similar conversion levels, W83V17 showed higher selectivity to benzonitrile (S\(_{\text{PhCN}}\)) than the conventional V-based catalysts (V\(_2\)O\(_5\) and VO\(_x\)/TiO\(_2\)). V\(_2\)O\(_5\) and VO\(_x\)/TiO\(_2\) showed higher selectivity to COx than W83V17.

Table 2 compares the conversions of toluene and selectivities to benzonitrile (S\(_{\text{PhCN}}\)), benzamide (S\(_{\text{amide}}\)), benzoic acid (S\(_{\text{acid}}\)), benzene (S\(_{\text{Br}}\)) and COx (S\(_{\text{COx}}\)) at 400 °C. A conventional
catalyst, V$_2$O$_5$, showed 71.2% selectivity to benzonitrile at a conversion level of 87.2%. WO$_3$ showed only 9.2% conversion of toluene. This indicates that vanadium is an indispensable element for this catalytic system. W83V17, W64V36 and VO$_x$/WO$_3$ show higher selectivities to benzonitrile than V$_2$O$_5$. This indicates that tungsten oxides as co-catalysts increase the selectivity to benzonitrile. The hydrothermally prepared catalysts (W83V17 and W64V36) showed higher selectivity to benzonitrile than VO$_x$/WO$_3$. Na-W83V17 showed low conversion (12.6%) than W83V17 (85.1%). Combined with the IR results in Fig. 3, we can conclude that Brønsted and/or Lewis acid sites of W83V17 significantly improve the ammoxidation activity in the present system.

Another remarkable feature of the hydrothermally prepared W-V-O catalysts (W83V17, W64V36) is highly efficient utilization of NH$_3$ in ammoxidation. The results in Fig. 5 and Table 2 demonstrated that W83V17 showed high NH$_3$-efficiency ($\eta_{\text{NH}_3}$) than other V-based catalysts. As shown in Table 2, the order of the NH$_3$-efficiency ($\eta_{\text{NH}_3}$) of V-based catalysts is as follows: W83V17 (56.9%) > W64V36 (44.8%) > VO$_x$/TiO$_2$ (42.2%) > VO$_x$/WO$_3$ (36.4%) > V$_2$O$_5$ (34.9%). The result indicates that the W-V-O catalysts (W83V17, W64V36) preferentially promote the ammoxidation over the non-selective NH$_3$ oxidation, while the classical and conventional V-based catalysts show moderate activity for the oxidation of NH$_3$ to N$_2$. The catalytic results in Table 2 are converted to the rate of benzonitrile formation per surface area of the catalysts listed in Table 1. The reaction rates for W-V-O catalysts (W83V17, W64V36) are lower than that of V$_2$O$_5$. It is obvious that the main advantages of the W-V-O catalysts are high selectivity to benzonitrile (low selectivity to COx) and highly efficient utilization of NH$_3$.

Most of the previous reports on ammoxidation of toluene adopted excess NH$_3$ feed conditions. The reaction with lower level of NH$_3$ feed will lead to more sustainable and economical production of benzonitrile. Fig. 6 shows the results for the W83V17-catalyzed ammoxidation with different the amount of NH$_3$ (2, 5, 10 and 15 equiv. with respect to toluene). The selectivity to benzonitrile decreased with decreasing NH$_3$ concentration, but NH$_3$-efficiency ($\eta_{\text{NH}_3}$) increased with decreasing NH$_3$ concentration. At the NH$_3$ molar ratio of 2 equiv. (NH$_3$/toluene = 2/1), the NH$_3$-efficiency was 73.9% and the yield of benzonitrile was 70.2%. This indicates that the present system can produce benzonitrile with high NH$_3$-efficiency and high yield under low NH$_3$ feed conditions. However, it is important to note that the ammonia levels required for achieving good benzonitrile yields are still several times above that required for the stoichiometric reaction. Further studies are necessary to address this issue.

Fig. 7 shows the catalytic results by 1.5 g of W83V17 and 0.5 g of V$_2$O$_5$ for the ammoxidation of toluene with lower NH$_3$ molar ratio (5 equiv.) than the standard conditions in Fig. 5 (10 equiv.). The general trends were basically similar to those for the standard conditions in Fig. 5, but the difference between W83V17 and V$_2$O$_5$ were more significant in Fig. 7. At 440
°C, where the toluene conversion reached 100% for both catalysts, $V_2O_5$ showed 52.1% selectivity to benzonitrile and 29.6% of NH$_3$-efficiency, while W83V17 showed 84.9% selectivity to benzonitrile and 80.5% of NH$_3$-efficiency. The results clearly demonstrate that W83V17 shows high efficiency of NH$_3$ utilization in ammonoxidation as well as high selectivity to benzonitrile based on toluene. For the reaction with W83V17 at 420 °C, the yield of benzonitrile is 85.2 %, corresponding to the benzonitrile productivity of 129 g L$^{-1}$ cat h$^{-1}$. The yield and the productivity of this system are not high compared with the yields (67-92%) and the productivities (52-342 g L$^{-1}$ cat h$^{-1}$) of the benchmark V-based catalysts in the patents for ammonoxidation of toluene [1].

Fig. 8 shows the stability versus time-on-stream of W83V17-catalyzed ammonoxidation of toluene under the standard conditions at 400 °C. The toluene conversion slightly decreased from 98.6% to 95.1% during the 45 h of the continuous reaction. Then, the catalyst was heated at 500 °C for 1 h under He flow. The heat-treatment increased the toluene conversion to 97.6%, and the catalytic system showed high conversions (> 95.9%) for the next 30 h. The benzonitrile selectivity (90.2-90.4%) and NH$_3$-efficiency (50.9-53.1%) were nearly constant throughout the experiment. We also studied the effects of co-feeding of water on the catalytic performance of W83V17. As compared in Table 2, co-feeding of water vapor did not essentially change the toluene conversion, the selectivity to benzonitrile and NH$_3$-efficiency ($\eta_{NH_3}$). These results suggest that the present catalytic system is tolerant to water vapor.

3.3. Mechanistic and in situ IR studies

Previous studies [3, 11] on the mechanism of ammonoxidation of toluene by V-based catalyst suggest that benzonitrile is produced via a benzaldehyde intermediate, which then reacts with NH$_3$ on the surface to yield benzylimine surface species. Finally, the benzylimine intermediate undergoes oxidative dehydrogenation to give benzonitrile [3,11]. We carried out a model reaction of benzaldehyde+NH$_3$+O$_2$ by W83V17 and V$_2$O$_5$ catalysts. The results in Fig. 9 (left) were consistent with the proposed mechanism in the literature [3, 11]; the formation rates of benzonitrile by ammonoxidation of benzaldehyde were more than 6 times higher than those by ammonoxidation of toluene (right) for both catalysts. This suggests that the ammonoxidation of toluene by W83V17 is also driven by the proposed mechanism in the literature [3, 11], eqn. (1), including the partial oxidation of toluene to benzaldehyde as a rate-limiting step.

\[
\text{CH}_3\text{NH}_3\text{CCH}_2\text{O} + \text{O}_2 \rightarrow \text{NH}_3\text{OCH}_2\text{O} \rightarrow \text{NH}_3\text{C}==\text{N} \tag{1}
\]
To verify the hypothetical mechanism, we studied formation and reaction of intermediates on the W83V17 catalyst using in situ IR spectroscopy. First, adsorption of toluene and benzaldehyde was studied in order to identify the adsorbed species that could arise on the surface of W83V17 during the ammoxidation of toluene. Gaseous toluene or benzaldehyde (0.3 mmol g\textsubscript{cat}\textsuperscript{-1}) was introduced to the flow-type in situ IR cell at various temperatures under He flow, followed by purging with He flow for 600 s to obtain the IR spectra in Fig. 10. The spectrum of toluene adsorbed on W83V17 at ambient temperature showed two ring vibration bands of aromatics (1498 and 1588 cm\textsuperscript{-1}) [29] but no band due to C=O or C-O stretching modes, indicating that toluene was not oxidized by the surface oxygen of W83V17 but physically adsorbed on the surface at ambient temperature. At higher temperature (200 °C), a weak band at 1705 cm\textsuperscript{-1} assignable to C=O stretching modes (ν\textsubscript{C=O}) of benzaldehyde [11] and ring vibration bands of aromatics (1498 and 1588 cm\textsuperscript{-1}) were observed. The ν\textsubscript{C=O} band at 1705 cm\textsuperscript{-1} was also observed for benzaldehyde adsorbed on W83V17 at ambient temperature. These results indicate that benzaldehyde is oxidized by surface oxygen species of W83V17 to yield benzaldehyde even at lower temperature (200 °C) than the reaction temperature (400 °C) of the catalytic ammoxidation in this study. In the spectrum of benzonitrile on W83V17, a band at 2262 cm\textsuperscript{-1} due to C≡N stretching modes (ν\textsubscript{C≡N}) of adsorbed benzonitrile was observed.

As shown in Fig. 11, the adsorption of NH\textsubscript{3} at 330 °C resulted in the formation of IR bands due to protonated ammonia (NH\textsubscript{4}\textsuperscript{+}) on Brønsted acid sites at 1410 cm\textsuperscript{-1} [28] and coordinated ammonia on Lewis acid sites at 1256 cm\textsuperscript{-1} [28]. Then, we studied the reaction of the adsorbed NH\textsubscript{3} species with toluene at 330 °C under He flow. Soon after the introduction of gaseous toluene (0.3 mmol g\textsubscript{cat}\textsuperscript{-1}) to the NH\textsubscript{3}+preadsorbed W83V17, the band at 2250 cm\textsuperscript{-1} due to ν\textsubscript{CN} of benzonitrile was observed, and the intensity of the ν\textsubscript{CN} band increased with time. The introduction of toluene decreased the intensities of the bands of NH\textsubscript{4}+ (1410 cm\textsuperscript{-1}) and coordinated NH\textsubscript{3} (1256 cm\textsuperscript{-1}). These results indicate that benzonitrile is produced by the reaction of adsorbed NH\textsubscript{3} and toluene with oxygen atoms on the surface of W83V17 at 330 °C.

The same NH\textsubscript{3} adsorption experiment for V\textsubscript{2}O\textsubscript{5} (Fig. 11B) shows that the amount of adsorbed NH\textsubscript{3} on V\textsubscript{2}O\textsubscript{5} is negligible at 330 °C. Comparison of the results for W83V17 and V\textsubscript{2}O\textsubscript{5} indicates that the acid sites originate from W in W83V17 act as adsorption sites of NH\textsubscript{3} during the ammoxidation reaction. The same experiment for VO\textsubscript{x}/WO\textsubscript{3} shows that it shows adsorbed NH\textsubscript{3} mostly on Brønsted acid sites probably on the surface of WO\textsubscript{3}. However, the introduction of toluene to the adsorbed NH\textsubscript{3} on VO\textsubscript{x}/WO\textsubscript{3} did not result in the formation of adsorbed PhCN. Considering the structural difference between the W83V17 (mixed oxide) and VO\textsubscript{x}/WO\textsubscript{3} (VO\textsubscript{x} islands supported on WO\textsubscript{3}), one could conclude that proximity between W (acid) sites and V (redox) sites is important for the surface reaction between the adsorbed NH\textsubscript{3}, toluene and a reactive oxygen atom on the surface to give PhCN.
Fig. 12 shows the reaction of toluene-derived surface species with NH$_3$ monitored by in situ IR at 200 °C. After the observation of the benzaldehyde (1705 cm$^{-1}$) on W83V17, the flowing gas was switched from He to 2% NH$_3$/He and the IR spectra were observed as a function of the time of NH$_3$ flowing at 200 °C. The ν$_{CN}$ band of adsorbed benzonitrile species (2256 and 2232 cm$^{-1}$) appeared, and the intensity of the ν$_{CN}$ band increased with time. Summarizing the IR results in Figs. 10-12, the following pathway is proposed; toluene is oxidized by the surface oxygen species of W83V17 to yield benzaldehyde which undergoes the reaction with adsorbed NH$_3$ to give benzonitrile possibly via benzylimine. This pathway is consistent with that proposed in the literature [3, 11] shown in eqn. (1).

Fig. 9 compares the reaction rates for benzaldehyde+NH$_3$+O$_2$ (left), NH$_3$+O$_2$ (center) and toluene+NH$_3$+O$_2$ (right) reactions by W83V17 and V$_2$O$_5$. From the results in Fig. 9 and the pathway in eqn. (1), the origin of the higher NH$_3$-efficiency (η$_{NH3}$) of W83V17 than that of V$_2$O$_5$, the rate of NH$_3$ conversion to PhCN in the benzaldehyde+NH$_3$+O$_2$ reaction is 1.5 times higher than the rate of NH$_3$ oxidation to N$_2$ in the NH$_3$+O$_2$ reaction. For W83V17, the rate of NH$_3$ conversion to PhCN is 3 times higher than the rate of NH$_3$ oxidation to N$_2$. These results indicate that, especially on W83V17, NH$_3$ consumption in the condensation of benzaldehyde with NH$_3$ is faster than NH$_3$ consumption in NH$_3$ oxidation to N$_2$. Comparison of Fig. 9 (left) and Fig. 9 (center) shows that, for both catalysts, the presence of benzaldehyde in the feed decreases the rate of the unselective oxidation of NH$_3$ to N$_2$. This indicates that ammoxidation of benzaldehyde competes with NH$_3$ oxidation to N$_2$ during ammoxidation of toluene. W83V17 showed lower rate of NH$_3$ oxidation in the NH$_3$+O$_2$ reaction than V$_2$O$_5$ (Fig. 6, center). From these results, we could conclude that the high NH$_3$-efficiency of W-V-O for ammoxidation of toluene is caused by the preferential reaction of NH$_3$ in the ammoxidation of benzaldehyde over NH$_3$ oxidation to N$_2$ as illustrated in eqn. (2).

\[
\begin{align*}
\text{NH}_3 & \quad \text{PhCHO} + \text{O}_2 \quad \text{PhCN} \\
\text{O}_2 & \quad \text{N}_2
\end{align*}
\]

On the surface of the W-V-O complex oxide, a VO$_6$ octahedron as a redox site is adjacent to WO$_6$ octahedra as NH$_3$ adsorption sites. The benzaldehyde adspecies, once formed by the oxidation of toluene by the VO$_6$ site, can react preferentially with NH$_3$ adspecies on the neighboring WO$_6$ sites, which can result in high efficiency of NH$_3$ utilization in the present catalytic system.

4. Conclusion
The layered-type W-V-O metal oxides (W-V-O), synthesized by hydrothermal method, selectively catalyzed the gas-phase ammoxidation of toluene to benzonitrile. Under similar conversion levels, W-V-O showed higher selectivity to benzonitrile and lower selectivity to COx than conventional V-based catalysts (V2O5 and VOx/TiO2). Additionally, W-V-O was less active for the undesired oxidation of NH3 to N2, resulting in the high NH3-utilization efficiency in ammoxidation than the conventional V-based catalysts. W-V-O showed high durability and high tolerance to co-fed water vapor, demonstrating promising catalytic properties of the present system. Model reaction studies suggested that the high NH3-efficiency of W-V-O was caused by the preferential reaction of NH3 in PhCHO+NH3+O2 over undesired NH3+O2 reaction.

References
Table 1: Surface area, composition and reaction rates of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S (^a) (m(^2)g(^{-1}))</th>
<th>W/V (^b)</th>
<th>V (^c) (mmol h(^{-1}) g(^{-1}))</th>
<th>V (^d) (mmol h(^{-1}) m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>W64V36</td>
<td>27.7</td>
<td>64/36</td>
<td>1.51</td>
<td>0.055</td>
</tr>
<tr>
<td>W83V17</td>
<td>41.9</td>
<td>83/17</td>
<td>1.40</td>
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<tr>
<td>Na-W83V17</td>
<td>38.5</td>
<td>83/17</td>
<td>1.29</td>
<td>0.005</td>
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<tr>
<td>VOx/WO(_3)</td>
<td>14.2</td>
<td>85/15</td>
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<tr>
<td>V(_2)O(_5)</td>
<td>4.8</td>
<td>-</td>
<td>3.03</td>
<td>0.631</td>
</tr>
<tr>
<td>WO(_3)</td>
<td>16.8</td>
<td>-</td>
<td>0.09</td>
<td>0.003</td>
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</tbody>
</table>

\(^a\) BET surface area determined by N\(_2\) adsorption

\(^b\) Composition determined by ICP-AES

\(^c\) Rate of BN formation per weight of the catalysts.

\(^d\) Rate of BN formation per surface area of the catalysts.

Table 2: Catalytic results at 400 °C under the conditions in Fig. 5.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cat. wt. (g)</th>
<th>Conv. (%)</th>
<th>S(_{\text{PhCN}}) (%)</th>
<th>S(_{\text{amide}}) (%)</th>
<th>S(_{\text{acid}}) (%)</th>
<th>S(_{\text{Bz}}) (%)</th>
<th>S(_{\text{COx}}) (%)</th>
<th>η(_{\text{NH}_3}) (%)</th>
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<td>W83V17</td>
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<td>85.1</td>
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<td>0</td>
<td>5.5</td>
<td>56.9</td>
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<tr>
<td>W83V17(^a)</td>
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<td>93.4</td>
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<td>0</td>
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<td>56.0</td>
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<td>0.9</td>
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<tr>
<td>W64V36</td>
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<td>99.9</td>
<td>93.0</td>
<td>0.3</td>
<td>0.1</td>
<td>6.6</td>
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<tr>
<td>VOx/WO(_3)</td>
<td>1.5</td>
<td>83.9</td>
<td>82.5</td>
<td>2.1</td>
<td>0</td>
<td>0</td>
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<td>36.4</td>
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<tr>
<td>VOx/TiO(_2)</td>
<td>1.0</td>
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<td>0.8</td>
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<tr>
<td>V(_2)O(_5)</td>
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<td>87.2</td>
<td>71.2</td>
<td>1.3</td>
<td>1.9</td>
<td>1.8</td>
<td>23.8</td>
<td>34.9</td>
</tr>
<tr>
<td>WO(_3)</td>
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<td>9.2</td>
<td>57.2</td>
<td>42.1</td>
<td>0</td>
<td>0.7</td>
<td>8.1</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Water vapor was co-fed to the catalyst: toluene/NH\(_3\)/O\(_2\)/H\(_2\)O/He=1/10/4/10/24 (F = 49 mL min\(^{-1}\)).
Fig. 1. XRD patterns (left) and polyhedral model (right) of microporous and layered W-V-O oxides. The top layer of the model is highlighted in yellow.

Fig. 2. SEM image of W83V17.
Fig. 3. IR spectra of pyridine adsorbed on the catalyst disc (38±1 mg) at 100 °C

Fig. 4. Ammoxidation of toluene by W83V17 at different contact times (400 °C): conversion of toluene (+), selectivities of benzonitrile (○), benzamide (◇) and COx (●) and NH3-efficiency, η_{NH3}, (□): toluene/NH3/O2/He=1/10/4/34.
Fig. 5. Temperature dependence of the conversion of toluene (+), selectivities of benzonitrile (O), benzamide (△) and COx (●) and NH3-efficiency, ηNH3, (□) for ammoxidation of toluene by 1.5 g of W83V17: toluene/NH3/O2/He=1/10/4/34.
Fig. 6. Effect of the amount to NH₃, with respect to toluene on the conversion of toluene (+), selectivities of benzonitrile (○), benzamide (◇) and COₓ (-) and NH₃-efficiency, ηNH₃, (△) for ammonoxidation of toluene by 2 g of W83V17 at 400 °C: toluene/NH₃/O₂/He=1:10:4:34.

Fig. 7. Ammonoxidation of toluene by 1.5 g of W83V17 and 0.5 g V₂O₅ in the low NH₃ concentration conditions (toluene/NH₃/O₂/He=1:5:4:34); conversion of toluene (+), selectivities of benzonitrile (○), benzamide (◇) and COₓ (-) and NH₃-efficiency, ηNH₃, (△).
Fig. 8. Time course of ammoxidation of toluene by 1.5 g of W83V17 at 400 °C: conversion of toluene (+), selectivities of benzonitrile (○), benzamide (◇) and COₓ (●) and NHₓ-efficiency, \( \eta \text{NH}_3 \) (□), toluene/NH₃/O₂/He=1/10/4/34. After 45 h of the reaction, the catalyst was heated at 500 °C for 1 h under He flow, followed by re-starting the ammoxidation reaction.
Fig. 9. Formation rates of PhCN, COx and N\textsubscript{2} for ammoxidation of benzaldehyde (left), oxidation of ammonia (center), and ammoxidation of toluene (right) by W83V17 (top) and V\textsubscript{2}O\textsubscript{5} (bottom) at 400 °C.

Fig. 10. IR spectra of adsorbed species on W83V17 at various temperatures.
**Fig. 11.** IR spectra of adsorbed species on various catalyst discs (38±1 mg) during the reaction of adsorbed NH$_3$ species with toluene-derived species at 330 °C.

**Fig. 12.** IR spectra of adsorbed species on W83V17 during the reaction of toluene-derived surface species under flowing 2% NH$_3$/He at 200 °C.
Figure Captions

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**Fig. 7.** Ammoxidation of toluene by 1.5 g of W83V17 and 0.5 g V2O5 in the low NH3 concentration conditions (toluene/NH3/O2/He=1/5/4/39): conversion of toluene (+), selectivities of benzonitrile (○), benzamide (◇) and COx (●) and NH3-efficiency, η_NH3 (□).

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