Layered W-V oxides with M1 phase-like local structure for ammoxidation and selective oxidation of toluene

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Abstract: A layered W-V oxide with "M1 phase"-like local structure shows high yields (80-99%) for oxidation of toluene to benzoic acid, ammoxidation of 3-picoline and toluene. Atomic-level structure (HAADF-STEM) and surface reaction mechanism are shown to discuss a catalyst design concept.

Keywords: Selective oxidation, Vanadium oxides, Active site structure.

1. Introduction

Ammoxidation of toluene and methylpyridine to nitriles is a commercial process. V-based catalysts have been reported, but the yields of the nitriles are still below 90%. Mechanistic studies suggested bifunctional mechanism, in which VO_x sites catalyze partial oxidation of toluene to an aldehyde-like intermediate and acid sites act as adsorption site of NH_3. If one could design a V-based mixed oxide catalyst having NH_3 adsorption sites (such as acidic WOx sites) near the redox sites (VOx), the aldehyde intermediate formed on the redox site would have react preferentially with NH_3 on the acid site, resulting in high efficiency for the ammoxidation. Gas-phase selective catalytic oxidation of toluene to benzoic acid by O_2 is of great economical and industrial importance, but it is not commercial process. V-based oxides were reported, but the yields of benzoic acid reported is far from a commercial level. Most of the previous V-based catalysts for the above reactions do not have atomic-level ordering of the active sites. Our group has focused on the hydrothermal synthesis of single phasic V-based mixed oxides with atomic-level ordering. For example, we reported orthorhombic Mo_3VOx for selective oxidation reactions has the same structure as that of "M1 phase" (active phase in the industrial selective oxidation catalyst, MoVTeNb oxide). Considering that WOx acts as acidic co-catalyst for V-catalysts, W-V oxides with "M1 phase"-like structure can act as effective catalysts for selective oxidation, through such materials have not reported in the literature. In this presentation, we show the first example of the W-V oxide with "M1 phase"-like local structure, which is highly effective for ammoxidation of toluene[1] and 3-picoline[2] and oxidation of toluene to benzoic acid.

2. Experimental (or Theoretical)

W–V complex metal oxide with W/V ratio of 83/17 (W83V17) was prepared by hydrothermal synthesis method. Catalytic tests were carried out at atmospheric pressure using a fixed-bed flow reactor.

3. Results and discussion

Characterization of W83V17 by XRD, scanning transmission electron microscopy (STEM) and N_2-adsorption isotherm (Fig. 1) showed three structural features: (i) layered-type structure characterized by diffraction peaks at $2\theta = 23°$ and $46°$ due to the (0 0 1) and (0 0 2) planes of the layered structure along c-axis direction, (ii) long rod-shaped crystal morphology due to stacking of the layers along the c-axis by sharing the apex oxygen (SEM), (iii) the presence of micropore (N_2-adsorption). Calcination of the hydrothermally prepared precursor results in thermal desorption of NH_3 (NH_4^+ in the 7-membered ring pores), leading to the formation of Brønsted acid sites in the pores. The proton is exchangeable to Na^+ in aqueous solution. The XRD pattern of Na^+-exchanged W83V17 (Na-W83V17) has lines at the same positions (23° and 46°), which indicates that the Na-W83V17 has basically the same crystal structure as W83V17. Atomic resolution HAADF-STEM observation and its intensity analysis shows the ordered *a*-*b* plane structure which is composed of W_6O_{21} pentagonal units which are linked with MO_6 (M= V or W) octahedra forming hexagonal and heptagonal channel. The outermost layer of the heptagonal channel consists of VO_6 adjacent to WO_6. Crystallites of orthorhombic phase ("M1 phase") are also observed (Fig. 1).

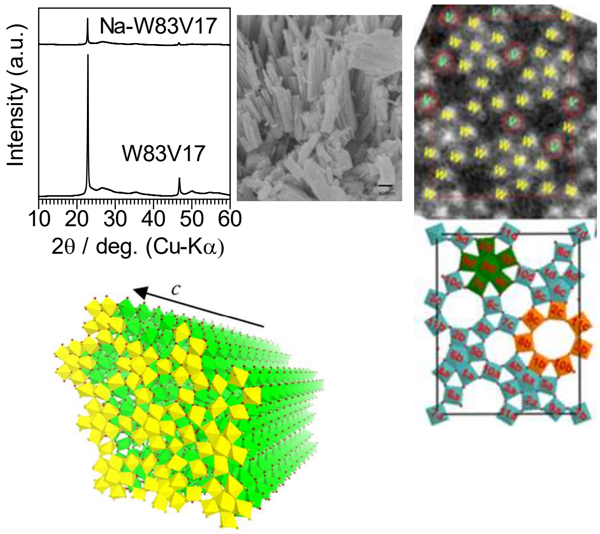
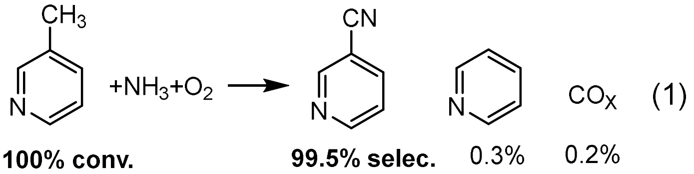
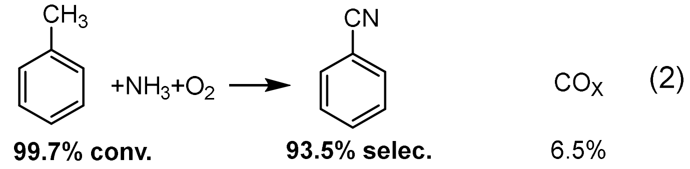


Figure 1. XRD patterns, SEM and HAADF-STEM images, and polyhedral models of microporous and layered W-V oxide (W83V17). The top layer of the model is highlighted in yellow.



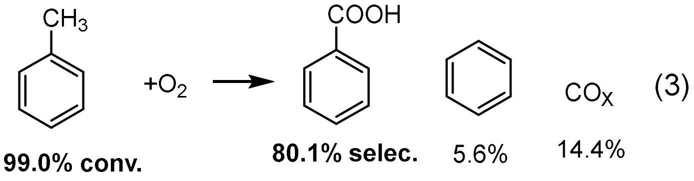
(1)

picoline/NH_3/O_2/H_2O/He = 1/6/4.4/8/19.6, 385°C, W/F=1.2 g s mL^{-1}.



(2)

toluene/NH_3/O_2/He = 1/10/4/34, 400°C, W/F=2.45 g s mL^{-1}.



(3)

toluene/O_2/H_2O/He = 1/4.5/26/8, 450°C, W/F=2.3 g s mL^{-1}.

W83V17 shows higher yields (79-99%) than the previously reported catalysts for the ammoxidation of 3-picoline to 3-cyanopyridine (eqn. 1), ammoxidation of toluene to benzonitrile (eqn. 2), and the selective oxidation of toluene to benzoic acid (eqn. 3). A W-V oxide with hexagonal phase showed lower activity than W83V17, indicating that the heptagonal channel is responsible for the higher activity of W83V17. Na-W83V17 showed significantly lower activity than W83V17, indicating that acid sites play a significant role in the catalysis. Combined with the mechanistic results of in situ IR, we propose a catalyst design concept based on cooperation between redox sites (VO_6) and adjacent WO_X-based acid site at the heptagonal channel on the *a*-*b* plane.

4. Conclusions

The layered and microporous W-V metal oxide having "M1 phase"-like local structure showed high yields for (1) ammoxidation of 3-picoline, (2) ammoxidation of toluene, (3) selective oxidation of toluene to benzoic acid. The result demonstrates the importance of molecularly ordered structure of W-V mixed oxide catalysts for the selective oxidation.

References

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