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Selective Oxidation of Aromatic Compounds Catalyzed by Hydrothermally Synthesized Layered Tungsten-Vanadium Complex Metal Oxides

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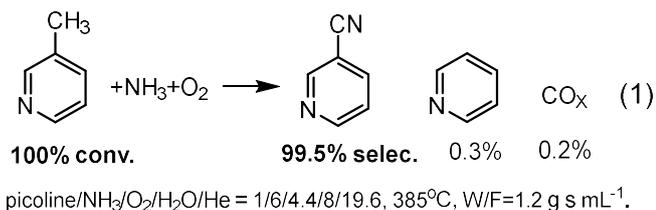
1. Introduction

Our research group has focused on the hydrothermal synthesis of single crystalline Mo-V-O based catalysts. Particularly, single phasic orthorhombic Mo_3VO_x , and trigonal 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. The structure is the orthorhombic Mo_3VO_x is basically the same as that of so called “M1 phase” which is well known as active phase in the industrial selective oxidation catalysts. Recently, the study was extended to the hydrothermal synthesis of 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 [58-61]. Considering the fact that WO_x is an well-known acidic co-catalyst of V-based catalysts, W-V-O oxides with “M1 phase”-like structure can act as effective catalysts for selective oxidation of hydrocarbons. However, there are no reports on the preparation and structure of W-V-O oxides with “M1 phase”-like structure. On these backgrounds, the author hypothesized that that the W-V-O oxides, having a similar structure to that of “M1 phase”, can act as effective catalysts for the selective oxidation of hydrocarbons such as oxidation of toluene and ammoxidation of aromatics. This thesis focuses on the the selective oxidation of toluene and ammoxidation of aromatics by newly synthesized W-V-O oxides, having a similar structure to that of “M1 phase”. The outline of the thesis is as follows.

In the Chapter 2, the author shows hydrothermal synthesis of the W-V-O layered metal oxides (W-V-O). Characterization by XRD, XPS, ICP-AES, N_2 adsorption, and STEM shows that W-V-O has a rod-shaped layered structure due to stacking of the layers along the *c*-axis by sharing the apex oxygen. W-V-O has microporosity due to the heptagonal channel structure of the *a*-*b* plane. These results show that W-V-O has a “M1 phase”-like structure. The catalytic study for the vapor phase ammoxidation of 3-picoline (PIC) to 3-cyanopyridine (CP) demonstrates that W-V-O shows higher selectivity to CP than a VO_x/WO_3 catalyst, prepared by impregnation method, and other V-based catalysts which have been reported to be efficient for this reaction. A detailed study on the catalytic properties of the W-V-O catalyst is also performed to show the advantages and scope of this type of catalysts. In the Chapter 3, the author shows that the W-V-O catalyst is effective for the vapor phase ammoxidation of toluene to benzonitrile (PhCN). W-V-O shows higher selectivity (based on toluene) to PhCN as well as high NH_3 -utilization efficiency than conventional V-based catalysts. In situ infrared (IR) and model reaction studies shows the origin of the high selectivity and high NH_3 -efficiency of W-V-O. Chapter 4 is intended to investigate the molecular structure of the W-V-O catalyst and its properties for selective oxidation of ethane to ethane and selective oxidation of toluene to benzoic acid. The local structure of the active species on the *a*-*b* plane of W-V-O was determined by HAADF-STEM. W-V-O showed higher yield of ethane than VO_x/WO_3 catalyst for selective oxidation of ethane to ethane. For selective oxidation of toluene to benzoic acid, W-V-O showed higher yield than conventional V-based catalysts. Chapter 6 includes the conclusion and scope.

2. Chapter 2¹

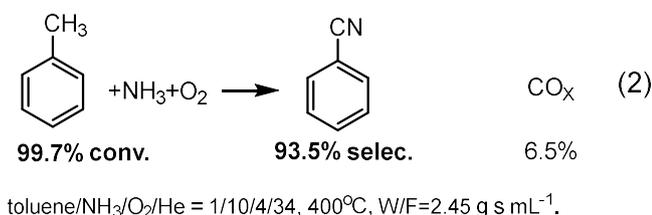
In this chapter, hydrothermal synthesis of microporous W-V-O and its use for ammoxidation of 3-picoline is described. W-V complex metal oxide (W-V-O) was prepared by hydrothermal



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 (eqn. 1). 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.

3. Chapter 3²

In this chapter, 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 CO_x than conventional V-based catalysts (V₂O₅ and VO_x/TiO₂). Under the conditions of high contact time, W-V-O shows 99.7% conversion of toluene and 93.5% selectivity to PhCN (eqn. 2). Another important feature of W-V-O is high NH₃-utilization efficiency in ammoxidation, which originates from the lower activity of W-V-O for NH₃ oxidation than that of V₂O₅. In situ infrared (IR) study shows that toluene is oxidized by the surface oxygen species of W83V17 to yield benzaldehyde which undergoes the reaction with adsorbed NH₃ to give benzonitrile. Model reaction studies with W-V-O suggest that the rate of NH₃ conversion to PhCN in the benzaldehyde+NH₃+O₂ reaction is 3 times higher than the rate of NH₃ oxidation to N₂ in the NH₃+O₂ reaction. It is shown that the high NH₃-efficiency of W-V-O is caused by the preferential reaction of NH₃ in PhCHO+NH₃+O₂ over NH₃+O₂ reaction.

4. Chapter 4

Selective catalytic oxidation of toluene to benzoic acid by molecular oxygen (O₂) is of great economical and industrial importance. Currently, the commercial production of benzoic acid is achieved by the liquid-phase oxidation of toluene in a solution of toluene, cobalt acetate and bromide promoter in acetic acid at 250 °C under pressured O₂. Although complete conversion is achieved, the use of acidic solvents and bromide promoter results in serious problems such as difficulties in purification of the products, co-production of toxic wastes, and equipment corrosion. From environmental and economical points of view, gas-phase selective oxidation of toluene to benzoic acid by is preferable. Various catalysts, mostly V-based oxides, were reported for the vapor phase oxidation of toluene, but the yields of benzoic acid reported so far (mostly below 30%) is far from a commercial production level. Considering that to the most of the previous V-based catalysts for this reaction do not have atomic-level ordering of the active sites, our research group has focused on the hydrothermal synthesis of single phasic V-based mixed oxides with atomic-level ordering. For example, we reported orthorhombic Mo₃VO_x as a highly active and

selective catalyst for selective oxidation reactions. Its structure is basically the same as that of so called “M1 phase” (active phase in the industrial selective oxidation catalyst, MoVTeNb oxide). Considering the fact that WO_x is an well-known acidic co-catalyst for V-based catalysts, W-V oxides with “M1 phase”-like structure can act as effective catalysts for selective oxidation of hydrocarbons, 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 shows higher yields for oxidation of toluene to benzoic acid than previously reported catalysts.

I synthesized a W-V mixed oxide with W/V ratio of 83/17 (W83V17). The 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 $2\theta = 23^\circ$ 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 ($M = \text{V}$ 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).

W83V17 shows higher yields (79-99%) than the previously reported catalysts for 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 plays 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.

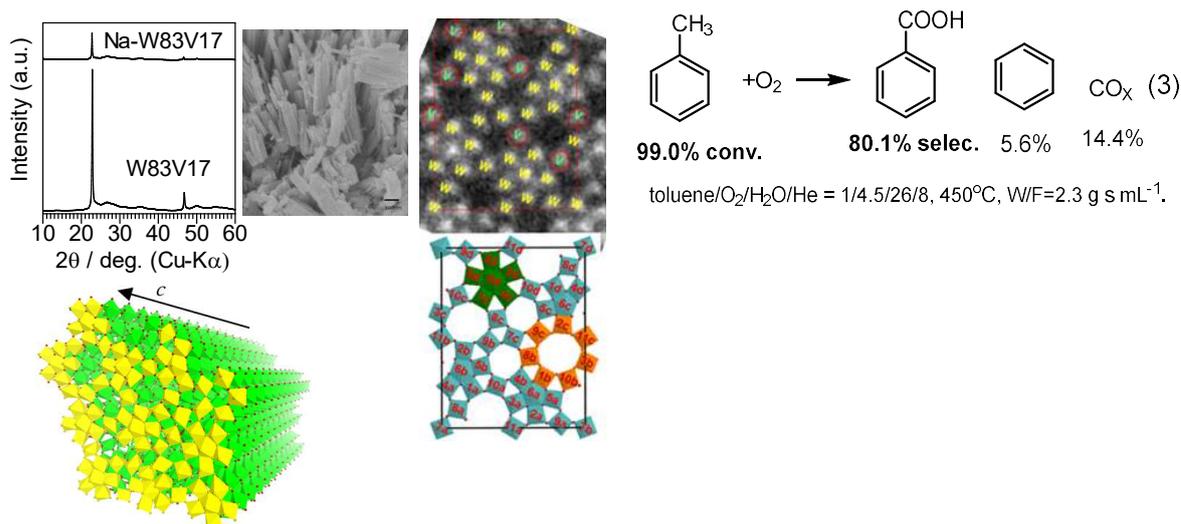


Fig. 1. XRD patterns, SEM and HAADF-STEM images, and polyhedral models of microporous and layered W-V oxide (W83V17). The top layer of the model is highlighted in yellow.

5. General conclusion

In the General introduction (Chapter 1), the author showed critical review of the literature. Based to the review, the author hypothesized that one of the promising strategy for developing V-based selective oxidation catalysts is to prepare a well-defined W-V-O catalysts having a “M1 phase”-like structure, which has not reported in the literature. In this thesis, the author succeeded in the preparation of the W-V-O catalysts, for the first time, and showed that the W-V-O catalysts were generally effective for four types of selective oxidation reactions.

In Chapter 2, the layered W-V metal oxide, W-V-O, synthesized by hydrothermal method was found to show an exceptionally high 3-cyanopyridine selectivity of 99.5% for the vapor phase ammoxidation of 3-picoline under full conversion conditions. The selectivity of W-V-O was higher than those of conventional V-based catalysts reported to be efficient for this reaction. 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.

In Chapter 3, the W-V-O was found to catalyze the vapor phase ammoxidation of toluene to benzonitrile. Under similar conversion levels, W-V-O showed higher selectivity to benzonitrile and lower selectivity to CO_x than conventional V-based catalysts (V₂O₅ and VO_x/TiO₂). 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.

In Chapter 4, the molecular structure of the W-V-O catalyst was investigated. This chapter also demonstrates the catalytic properties of W-V-O for selective oxidation of ethane to ethane and selective oxidation of toluene to benzoic acid. The local structure of the active species on the a-b plane of W-V-O was determined by HAADF-STEM. W-V-O showed higher yield of ethane than VO_x/WO₃ catalyst for selective oxidation of ethane to ethane. For selective oxidation of toluene to benzoic acid, W-V-O showed higher yield than conventional V-based catalysts.

From the summary of each chapter mentioned above, the following conclusions can be drawn:

1. This thesis showed the first example of the layered and microporous W-V metal oxide having a similar structure to that of “M1 phase”
2. The W-V-O catalysts showed high selectivity to the desired products for four types of selective oxidation reactions: (1) ammoxidation of 3-picoline, (2) ammoxidation of toluene, (3) selective oxidation of ethane to ethane, and (4) selective oxidation of toluene to benzoic acid.
3. These conclusions suggest that we can rationally design the V-based catalysts by molecular level design of the V-based complex oxide catalysts.

References

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