Catalysis Today 144 (2009) 358–361

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Selective oxidation of alcohols using novel crystalline Mo-V-O oxide as heterogeneous catalyst in liquid phase with molecular oxygen

Feng Wang [a,b,*], Wataru Ueda [b,*]

[a] CREST, Japan Science and Technology Corporation (CREST-JST), Kawaguchi, Saitama 332-0012, Japan
[b] Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan

ARTICLE INFO

Article history:
Available online 1 April 2009

Keywords:
Mo-V-O crystalline oxide
Alcohol
Oxidation
Heterogeneous catalysis
Oxygen
Reusability

ABSTRACT

Catalytic selective oxidation of benzyl alcohol with molecular oxygen under mild conditions was carried out over novel crystalline Mo-V-O oxide. The present research is focused on investigation of recycling, reusability and stability of the crystalline oxide in the liquid-phase reaction. The Mo-V-O oxide catalyst was used at least four times with comparable activities to that of fresh catalyst. The separation of the catalyst from reaction medium can stop the conversion of benzyl alcohol, and the addition of the catalyst to the reaction medium can trigger the reaction immediately. The catalytic oxidation of 2,3,6-trimethylphenol as a reference reaction suggested that there were no leached active species in the reaction mixture. The results of the ICP–MS analysis, XRD, and SEM characterization confirmed that the structure and composition of the catalyst were stable. Besides, the Mo-V-O oxide can catalyze the oxidation of a series of alcohols with high selectivities for corresponding carbonyl compounds.

1. Introduction

Heterogeneous catalysis is generally considered to be an effective method for the aerobic oxidation [1]. One of its advantages is the facile separation and recovery of catalyst without tedious experimental workup [2], which may lower the production cost. Many mixed oxide solids, such as supported, grafted, tethered and encapsulated catalysts, have been claimed as heterogeneous catalysts in liquid-phase reactions for various applications. However, stability of these catalysts, which is closely related to product separation and endurance, still remains challenging [3]. The leaching of catalytic components is usually caused by stripping off or degradation of active species from catalyst support [4]. In the seminal work contributed by Sheldon [5], he reported that the experiments demonstrating that heterogeneous catalysts can be recovered and recycled without apparent loss of metal content or activity are not definitive proof of heterogeneity, because, for example, when the filtration is conducted at room temperature rather than at the reaction temperature, there is metal adsorption on the solid.

Recently we have described an example using crystalline Mo-V-O oxide catalyst in the selective oxidation of alcohols in liquid phase [6,7]. The crystalline Mo-V-O oxide represents the basic pore structure and phase composition of extensive Mo-V catalysts used in the selective oxidation [8,9]. Structural analysis has shown that the complex mixed-metal oxide is a layered, orthorhombic structure with a slab comprising 6- and 7-member rings of MeO_6 octahedrons and pentagonal $(Me)Me_5O_{27}$ units with a MeO_7 pentagonal bi-pyramidal unit and five edge-sharing MeO_6 octahedrons [10]. However, due to its novelty in liquid-phase reaction, we are cautious to claim the crystalline oxide as heterogeneous catalyst before comprehensively scrutinizing its catalytic behavior.

In this research, we will focus on investigating the heterogeneity of the crystalline Mo-V-O oxide in the catalytic oxidation of benzyl alcohol. Catalyst reusability, hot filtration and triggering test, and the selective oxidation of 2,3,6-trimethylphenol as reference reaction were studied. The catalytic oxidations of other alcohols, such as substituted benzyl alcohols, alkanols and cyclic alcohols, were also tested.

2. Experimental

2.1. Catalyst preparation and characterization

All reagents were analytical grade, purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Distilled water was prepared using Yamato Autostill WG25 (Tokyo, Japan).

The preparation of the Mo-V-O oxide has been reported elsewhere [11]. Typically, $VOSO_4 \cdot nH_2O$ (64.83 wt.%) solution (V concentration 0.10 mol L^{-1}, 120 mL) was added to $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ammonium heptamolybdate tetrahydrate (AHM) solution (Mo concentration 0.42 mol L^{-1}, 120 mL). The above mixture was stirred for 10 min

---

[*] Corresponding authors. Tel.: +81 11 706 9164; fax: +81 11 706 9164.
E-mail addresses: wangfeng@cat.hokudai.ac.jp (F. Wang), ueda@cat.hokudai.ac.jp (W. Ueda).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.12.034

before being transferred to a 300-mL Teflon-lined autoclave. The mixture was deaerated with a flow of nitrogen (50 mL min^{-1}) for 10 min. The autoclave was immediately sealed and placed in a 175 °C oven for 48 h. The dark solid formed on the Teflon liner was filtered out, and dried at 80 °C for 24 h. Ca. 5.2 g solid was obtained. Different batches were very similar in structure and composition. Several batches prepared in separate autoclaves were collected to obtain enough material for this study. The purification of the dried sample was carried out by adding 1.0 g of the dry sample into an oxalic acid solution (0.4 mol L^{-1}, 50 mL). The mixture was thermally treated at 60 °C for 30 min. The solid was filtered out and washed with 500 mL water. The filtrate was dried at 80 °C for 24 h. The yield after purification was 20–30%. The purified sample was pretreated at 400 °C (heating ramp rate 10 °C min^{-1}) in nitrogen (50 mL min^{-1}) for 2 h. The pretreated sample was taken out after the oven temperature decreased below 150 °C. The specific surface area (BET method) of the catalyst in the present research is 10 $\text{m}^2\,\text{g}^{-1}$, which is slightly higher than the reported value of 6.5 $\text{m}^2\,\text{g}^{-1}$ in the previous research [12]. The chemical composition of the catalyst was $\text{Mo}_1\text{V}_{0.33}$ as determined by ICP–AES.

The powder XRD patterns were recorded on a diffractometer (Rigaku, RINT Ultima+) with CuKα radiation (wavelength λ = 1.54056 Å). The concentrations of reactant and product were measured by gas chromatography mass spectrometry (GC–MS) using a flame ionization detector (Shimadzu Classic – 5000, 60 m TC WAX column) operated with a heating program: 100 °C for 10 min, ramp 10 °C min^{-1} to 230 °C (kept for 25 min).

2.2. Catalytic test

Batch reactors were used for catalytic tests. The volume of the reactor was ca. 15 mL. A gas cylinder containing ca. 1 L pure oxygen was connected with the reactor. It was calculated that even if the complete conversion of alcohol to acid was achieved, less than 2% of total oxygen would be consumed. In a typical reaction, the catalyst and magnetic stir bar were initially loaded into the reactor. The oxygen provided by an oxygen cylinder was fed into the reactor through a needle connected with a side-mouth sealed with Teflon septum, through which a mixture of alcohol, toluene, and internal standard was injected. The reactor was placed into a thermally stabilized oil bath. Aliquots were collected at intervals. Catalyst was filtered out using a membrane filter (pore size 0.2 μm). The filtrate was analyzed using GC–MS. ^{1}H NMR was employed to analyze the acid. The ^{1}H NMR analysis of a crude mixture was performed as follows: ca 0.3 mL of reaction mixture was put into a small vial and evaporated under 65 °C in a rotation evaporator under vacuum. About 1 mL of DMSO-d_6 solvent was added before spinning (21–24 °C).

3. Results and discussion

3.1. Reusability and structure stability of the Mo-V-O catalyst

The catalytic oxidation of benzyl alcohol was employed as a model reaction to investigate the catalyst reusability. The selectivity for benzaldehyde was more than 99%. The byproduct of benzoic acid was not detected. The carbon balance was close to 100%. At present, the Mo-V-O catalyst is far less active than the precious metal-based Pd and Ru catalysts [13–15], which usually achieved 100% conversion of benzyl alcohol and 99% selectivity for benzaldehyde. However, the precious metal components may easily leach depending on catalyst preparation method, such as impregnation or grafting. In case of the crystalline Mo-V-O oxide, its structure is highly stable. After reaction, the catalyst was separated by filtration, washed by toluene and pentane, and dried at 80 °C for 14 h. The next reaction was conducted under the same reaction conditions. The catalytic results are given in Table 1. Even in the fourth use, catalytic selectivity was comparable to that of the fresh catalyst. A minor byproduct of benzoic acid was detected. These results suggest that the catalyst can be reused.

Table 1
Reuse of the Mo-V-O catalyst for the selective oxidation of benzyl alcohol[a].

Catalyst	T (°C)	t (h)	Conversion (%)[b]	Selectivity (%)[b]
First use (fresh)	80	24	22	>99
Second use	80	24	21	98
Third use	80	24	20	97
Fourth use	80	24	20	98

[a] Reaction conditions: benzyl alcohol 0.7 mmol, toluene 1.6 mL, catalyst 30 mg, internal standard hexadecane 50 μL, 1 atm O_2. The catalyst was separated from hot reaction mixture by membrane filter (pore size 0.2 μm), washed with toluene, pentane, and dried before next use.

[b] Determined by GC with internal standard.

The structural analysis indicated that the Mo-V-O oxide has a layered, orthorhombic structure and is a rod-like material [10]. The XRD characterization of the catalyst showed that the crystalline structure did not change significantly after reusing (Fig. 1). The SEM images (not shown here) revealed that the morphology of typical rod-like crystal was well kept after reuse.

3.2. Hot separation of catalyst and reaction triggered by catalyst

The catalyst was separated from reaction mixture after the 9 h reaction by hot filtration. The filtration of the catalyst was conducted by quickly purging the reaction mixture through a 0.2 μm Teflon membrane into a fresh reactor, which had been thermally stabilized in the same oil bath with the previous reaction. Prior to use, the second reactor was washed with an EDTA solution (0.1 mol L^{-1}) for 2 h in 80 °C bath to remove metal contamination, and dried at 120 °C. After sampling and filtering, the temperature of the filtrate was ca. 75 °C. The filtrate did not afford further conversion of benzyl alcohol over next 26 h, suggesting that no active species were present in the filtrate. In contrast, a 12% higher conversion of benzyl alcohol was observed in the normal reaction (Fig. 2). A slight increase of conversion from 9% at 9 h reaction to 12% at 35 h may be caused by autocatalysis which could take place under the present reaction conditions [16]. It was shown in our research that in the absence of catalyst, conversion of benzyl alcohol at 80 °C in 24 h was ca. 2%, with benzoic acid, benzyl diether, benzaldehyde and phenol as major products.

The absence of leaching cannot be demonstrated unequivocally from the observed non-catalytic character of the filtrate because the leached species may not be active in the reaction [5]. We made the quantitative analysis of the filtrate by inductively coupled

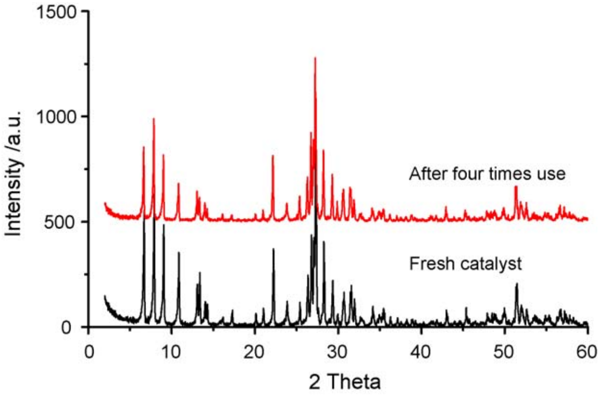


Fig. 1. XRD patterns of fresh and four times used catalyst.

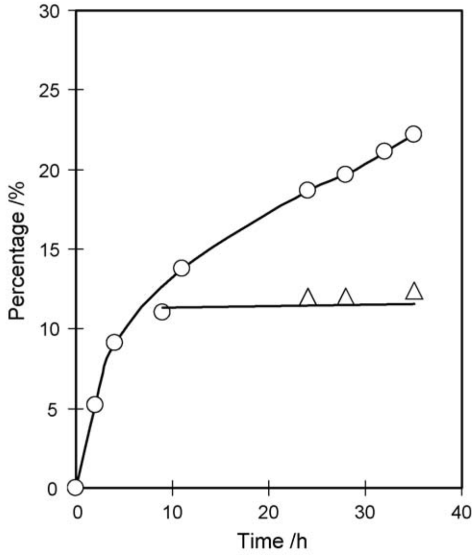


Fig. 2. Evidence of heterogeneous catalysis of Mo-V-O in the oxidation of benzyl alcohol. (○) Continuous reaction; (△) catalyst was removed by hot filtration after 9 h reaction.

plasma mass spectrometry (ICP–MS). It was shown that the concentrations of Mo and V were below their detection limits (detection limit for Mo < 0.5 ppm and V < 1.0 ppm). The results of ICP–MS analysis rule out the possibility of generating homogeneous Mo and V species into solution.

Moreover, the reaction can be triggered by adding the catalyst (Fig. 3). At the moment the catalyst was added into reaction solution, conversion of benzyl alcohol was less than 1%. However, conversion of benzyl alcohol surged up to 27% after the 31 h reaction.

3.3. Catalytic oxidation of 2,3,6-trimethylphenol

We subsequently investigated the oxidation of 2,3,6-trimethylphenol, a bulky molecule. If the reaction takes place homogeneously because of leaching, one can expect the conversion of 2,3,6-trimethylphenol in the presence of leached species [17,18]. Typically, the conversion of 2,3,6-trimethylphenol can be easily recognized by observing the appearance of yellowish brown color of reaction solution due to the formation of quinone. On the other hand, the reaction can take place heterogeneously only on the solid surface of the Mo-V-O catalyst, because the molecule of 2,3,6-trimethylphenol is too bulky to access the pores of the *a*–*b* basal plane [10]. We first conducted a reaction using Mo and V mixture solution (a precursor of Mo-V crystalline structure) and clearly observed the color change of reaction media, suggesting that the homogeneous Mo/V species can catalyze the oxidation of 2,3,6-trimethylphenol. However, we did not observe the color change of reaction mixture when we employed the Mo-V-O catalyst. The reaction mixture was analyzed by GC and no product was detected. We also noted that even if we changed four kinds of solvents, from polar to non-polar ones (Scheme 1), we did not detect any quinone-related product by GC.

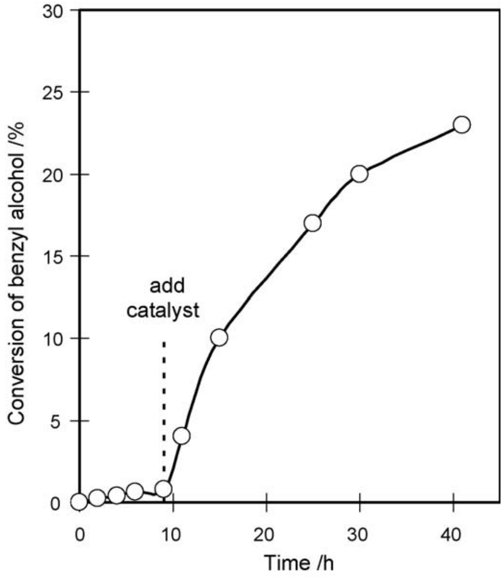
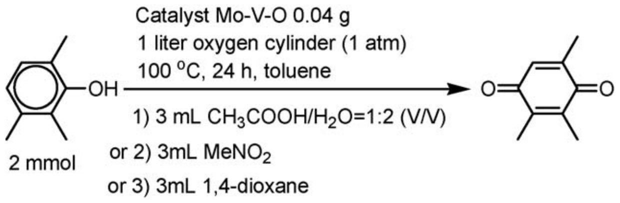


Fig. 3. The conversion of benzyl alcohol triggered by adding catalyst after 9 h reaction.



Scheme 1. Catalytic oxidation of 2,3,6-trimethylphenol over the Mo-V-O catalyst with three different solvent: (1) acetic acid/H_2O; (2) $MeNO_2$; and (3) 1,4-dioxane.

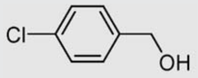
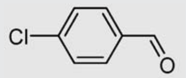
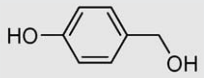
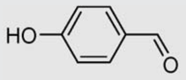
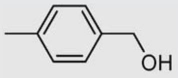
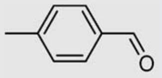
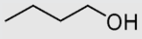
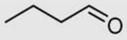
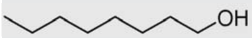
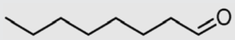
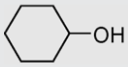
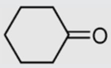
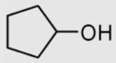
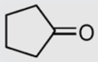
3.4. The understanding of the heterogeneity of the Mo-V-O crystalline oxide

The heterogeneity of the Mo-V-O oxide in this research is understandable since it has a rigid lattice structure, which is different to supported catalysts, where the active species would easily fall off from support to solution. Under mild reaction condition, the lattice oxygen, i.e. O^{2-}, may not join the catalytic cycle. Instead, only the topmost layers of the *a*–*b* basal plane are responsible for catalytic activity. Similar to other reactions [19], the $V^{4+/5+}$ and $Mo^{5+/6+}$ metal centers on the *a*–*b* basal plane may provide active sites for benzyl alcohol. It is possible that substrate is activated on negative oxygen sites located at the peripheral area of channel mouth, forming the surface species of Mo-O(H^+)-V and $PhCH_2O^-\cdots Me^{n+}$ [20]. Such interaction is not strong enough to break the Mo–O–V bonds. There is a possibility that some byproduct, like benzoic acid, may attack the Mo-O-V to form dissociated Mo or V species. We emphasize that such possibility does not exist since the crystal could survive a purification with an oxalic acid solution (0.4 mol L^{-1}, pH 0.9). The purification procedure definitely removes the debris of occluded or loosely connected Mo or V species from the rigid crystal structure.

3.5. Catalytic oxidation of alcohols

The Mo-V-O catalyst also shows good selectivity in some other oxidation reactions. We conducted the oxidation of substituted benzyl alcohol, cyclic alcohols and alkanols. The results are given in Table 2. In all cases, the selectivities for carbonyl compounds were over 90%. The substituent effect was observed over benzyl alcohols. As the substituent was varied from electron-withdrawing (4-chloro benzyl alcohol) to electron-donating (4-methyl benzyl alcohol), the conversion remarkably increased from 18% to 99%. It was noted that 4-hydroxy benzyl alcohol was not oxidized over supported polyoxometalate catalysts, which mainly contained Mo and V species [3]. However, the same oxidation using the crystalline Mo-V-O oxide as catalyst afforded the conversion of 83%. The catalytic oxidation of alkanols offered aldehydes as major products. It is likely that the length of alkane greatly influenced the conversion, since 1-butanol (C4) gave the conversion of 33% and 1-octanol (C8) 1%. The

Table 2
Catalytic performances of crystalline Mo-V-O oxide in the oxidation of alcohols by molecular oxygen.

Substrate	Product	Conversion (%)	Selectivity (%)
		18	>99
		83	>99
		>99	>99
		33	96
		1	91
		11	94
		37	94

Reaction conditions: substrate 0.7 mmol, toluene 1.6 mL, catalyst 0.03 g, 80 °C, 24 h, 1 L oxygen cylinder (1 atm). The conversion of alcohol and selectivity of carbonyl compound were determined by GC with hexadecane as internal standard. The byproducts were analyzed by mass spectrometer.

oxidation of cyclohexanol and cyclopentanol mainly produced cyclic ketones with selectivities over 94%. The byproducts were olefins, suggesting that the dehydrogenation reaction took place. A detailed study on the application of the Mo-V-O catalyst and reaction mechanism is in progress. The future work may be focused on exposing more active facets of the *a*–*b* basal plane by controlling the anisotropic growth of building blocks of the crystal.

4. Conclusion

We have demonstrated that the Mo-V-O crystalline oxide is a heterogeneous catalyst in the oxidation of benzyl alcohol in liquid phase. The catalyst reusability, ICP–MS analysis, XRD and SEM characterization, catalyst separation and triggering test, and catalytic oxidation of 2,3,6-trimethylphenol support this conclusion. It was shown that the Mo-V-O crystalline oxide could catalyze the oxidation of a series of alcohols, with carbonyl compounds as the major products.

Acknowledgement

F. Wang would like to gratefully acknowledge the financial support of CREST–JST (Japan Science and Technology Corporation).

References

[1] G. Centi, F. Cavani, F. Trifiro, Selective Oxidation by Heterogeneous Catalysis (Fundamental and Applied Catalysis), Plenum Pub Corp., New York, 2000.
[2] Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Chem. Rev. 105 (2005) 1603.
[3] R. Neumann, M. Levin, J. Org. Chem. 56 (1991) 5707.
[4] Q.H. Fan, Y.M. Li, A.S.C. Chan, Chem. Rev. 102 (2002) 3385.
[5] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.
[6] F. Wang, W. Ueda, Chem. Lett. 37 (2008) 184.
[7] F. Wang, W. Ueda, Top. Catal. 50 (2008) 90.
[8] R.K. Grasselli, D.J. Buttrey, P. DeSanto, J.D. Burrington, C.G. Lugmair, A.F. Volpe, T. Weingand, Catal. Today 91–92 (2004) 251.
[9] R.K. Grasselli, Catal. Today 99 (2005) 23.
[10] M. Sadakane, N. Watanabe, T. Katou, Y. Nodasaka, W. Ueda, Angew. Chem. Int. Ed. 46 (2007) 1493.
[11] W. Ueda, D. Vitry, T. Katou, Catal. Today 99 (2005) 43.
[12] N. Watanabe, W. Ueda, Ind. Eng. Chem. Res. 45 (2006) 607.
[13] Z. Hou, N. Theyssen, A. Brinkmann, W. Leitner, Angew. Chem. Int. Ed. 44 (2005) 1346.
[14] B. Karimi, S. Abedi, J.H. Clark, V. Budarin, Angew. Chem. Int. Ed. 45 (2006) 4776.
[15] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 122 (2000) 7144.
[16] F. Wang, W. Ueda, Appl. Catal. A 346 (2008) 155.
[17] W. Adam, W.A. Herrmann, J. Lin, C.R. Saha-Moeller, J. Org. Chem. 59 (1994) 8281.
[18] S. Fujibayashi, K. Nakayama, Y. Nishiyama, Y. Ishii, Chem. Lett. (1994) 1345.
[19] P. DeSanto, D.J. Buttrey, R.K. Grasselli, W.D. Pyrz, C.G. Lugmair, A.F. Volpe, T. Vogt, B.H. Toby, Top. Catal. 38 (2006) 31.
[20] N. Watanabe, PhD Thesis, Hokkaido University, 2006.