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Structure dependency of Mo-V-O-based complex oxide catalysts in the oxidations of hydrocarbons

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Abstract

Vapor-phase oxidations of ethane, propane, and acrolein were carried out over crystalline (orthorhombic) and amorphous Mo-V-O catalysts. The Mo-V-O crystalline catalyst was prepared by hydrothermal synthesis for the first time in a new orthorhombic structure. The orthorhombic Mo-V-O catalyst showed extremely high activity for the reactions compared to the amorphous one. Te in the orthorhombic Mo-V-O catalyst increased the selectivity to acrylic acid from propane dramatically.

Keywords: Mo-V-O catalysts; Vapor-phase oxidation; Light alkanes

1. Introduction

Mo–V–Te(Sb)–M–O complex metal oxides have attracted increasing interest because of their catalytic activity for selective oxidation of light alkanes [1–4]. These materials have been reported to assume a layered (orthorhombic) structure with a slab consisting in 5-, 6-, 7-membered rings of octahedra [5]. Mo–V–Te–Nb–O mixed metal oxide has the structure and shows excellent catalytic performance in the ammoxidation and oxidation of propane to acrylonitrile and acrylic acid [1,6]. We have reported that Mo–V–Te(Sb)–O with the same structure could be prepared hydrothermally and gave high selectivity to acrylic acid in the oxidation of propane [2,7–9].

Recently we succeeded in the preparation of a binary Mo-V-O metal oxide in the same orthorhombic structure by hydrothermal method and found that the catalyst showed extremely high activity for the oxidation of propane [10]. We were also able to synthesize amorphous type Mo-V-O with a similar chemical composition. Here we compare the catalytic activity of the structural Mo-V-O (orthorhombic) and the amorphous Mo-V-O in the oxidations of ethane, propane, and acrolein and discuss structure dependency of Mo-V-O-based catalysts.

2. Experimental

2.1. Catalyst preparation

8.82 g of $(NH_4)_6Mo_7O_{24}$ was dissolved in 120 ml of distilled water. Separately, an aqueous solution of vanadium was prepared by dissolving 3.28 g of hydrated $VOSO_4$ in 120 ml of distilled water. The two solutions were mixed at 20 °C and stirred for 10 min before being introduced into a stainless steel autoclave (300 ml Teflon inner tube). The concentration of Mo was $0.2\,mol\,l^{-1}$. Hydrothermal reaction of the liquid (mole ratio: $Mo/V = 1/0.25$) was carried out at 175 °C for 20 h. The obtained gray solid was separated from the solution, washed with distilled water, and dried at 80 °C overnight. The crystalline material was abbreviated as MoV-orth. In the same way, a material in amorphous state (MoV-amor) was obtained with the high Mo concentration ($0.6\,mol\,l^{-1}$) with the same Mo/V ratio. Te-containing catalyst $Mo_6V_3Te_1O_x$ (abbreviated as MoVTe) was also prepared according to our report [8,9].

The Mo-V-O catalysts (MoV-orth and MoV-amor) were heat-treated in N_2 stream ($50\,ml\,min^{-1}$) at 500 °C (MoV-orth-1 and MoV-amor-1) or 600 °C (MoV-orth-2 and MoV-amor-2) for 2 h. The Mo–V–Te–O catalyst was calcined in air at 280 °C before N_2 calcination at 600 °C for 2 h (MoVTe-orth-1) [9]. The heat-treatment conditions for all the catalysts were listed in Table 1 along with some characterization data. The catalysts were characterized

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Table 1
Surface area and bulk composition of Mo–V–(Te)–O catalysts

Catalysts	Pretreatment	S_{BET} ($m^2 g^{-1}$)	Bulk composition[a] (Mo/V/Te)
MoV-orth-1	N_2, 500 °C	6.1	1/0.34/0
MoV-orth-2	N_2, 600 °C	9.3	–
MoV-amor-1	N_2, 500 °C	10.3	1/0.29/0
MoV-amor-2	N_2, 600 °C	7.6	–
MoVTe-orth-1	Air, 280 °C + N_2, 600 °C	5.8	1/0.44/0.1

[a] Bulk composition was determined by ICP analysis.

by the following analytical techniques: BET, XRD, and ICP.

2.2. Catalytic test

Catalytic oxidation in gas-phase was carried out at an atmospheric pressure in a conventional flow system with a fixed bed Pyrex tubular reactor. The feed compositions, the total flow rates of the mixed reactant gases, and the amount of the catalysts used were shown in the footnote of Tables 2 and 3. The reactants and products were analyzed with three on-line gas chromatographs with columns, Molecular Sieve 13X, Gaskuropack 54, and Porapak Q. Carbon balance was always more than 95% but selectivity were calculated on the basis of product sum.

3. Results and discussion

3.1. Characterization of Mo-V-O catalysts

Fig. 1 shows the XRD patterns of hydrothermally synthesized Mo–V–(Te)–O catalysts. The crystalline Mo-V-O catalyst without the heat-treatment (MoV-orth-fresh) showed three characteristic diffraction peaks (6.6°, 7.9°, and 9.0°) at angle region lower than 10° and sharp peaks at $2\theta = 22°$ and 45° (Fig. 1(a)). ICP analysis revealed that the MoV-orth sample had a composition of $Mo_1V_{0.34}O_x$ (Table 1). No other elements were detected besides Mo and V. Phase purity was also ascertained by SEM analysis (data not shown) in which prism-shaped crystalline were observed as a major particle. The XRD pattern was exactly the same as that previously reported in the study of Mo–V–Te–Nb–O catalysts

Table 2
Propane oxidation over Mo-V-O based catalysts[a]

Catalysts	Reaction temperature (°C)	C_3H_8 conversion (%)	Selectivity[b] (%)					
			AA	PEN	AcA	Ace	CO_2	CO
MoV-orth-1	350	24.0	5.7	6.8	19.0	0.4	29.1	39.0
MoV-orth-2	346	10.8	6.4	19.9	24.9	1.1	19.1	28.6
MoV-amor-1	349	12.4	3.2	14.7	29.5	0.9	18.8	32.9
MoV-amor-2	343	5.9	1.1	30.8	23.9	1.2	15.0	28.0
MoVTe-orth-1	354	25.6	49.3	10.4	15.1	2.7	10.2	12.3

[a] Reaction conditions: 0.5 g catalyst, flow rate 20 ml min^{-1}, composition $C_3H_8/O_2/H_2O/N_2 = 6.5/10.0/45.0/38.5$.
[b] AA: acrylic acid, PEN: propene, AcA: acetic acid, Ace: acetone.

Table 3
Oxidations of ethane[a], propane[b], and acrolein[c] over Mo-V-O catalysts

Catalysts	Reactant	Reaction temperature (°C)	Conversion of reactant (%)	Selectivity (%)					
				AA	Ethyl	PEN	AcA	Ace	CO_x
MoV-amor-1	Ethane	345	3.4	–	63.3	–	4.9	–	31.5
MoV-orth-1	Ethane	340	9.0	–	67.4	–	2.8	–	29.8
MoV-amor-1	Propane	349	12.4	3.2	–	14.7	29.5	0.9	51.7
MoV-orth-1	Propane	350	24.0	5.7	–	6.8	19.0	0.4	68.1
MoV-amor-1	Acrolein	230	91.4	93.1	–	–	1.9	–	3.3
MoV-orth-1	Acrolein	230	96.4	94.2	–	–	1.6	–	2.9

AA: acrcylic acid, PEN: propene, AcA: acetic acid, Ace: acetone, Ethyl: ethylene.
[a] Reaction conditions: 0.5 g catalyst, flow rate 50 ml min^{-1}, composition $C_2H_6/O_2/H_2O/N_2 = 30.0/10.0/20.0/40.0$.
[b] Reaction conditions: 0.5 g catalyst, flow rate 20 ml min^{-1}, composition $C_3H_8/O_2/H_2O/N_2 = 6.5/10.0/45.0/38.5$.
[c] Reaction conditions: 0.45 g catalyst (Si–C: 0.05 g), flow rate 100 ml min^{-1}, composition $C_3H_4O/O_2/H_2O/N_2 = 5.0/7.9/27.8/70.4$.

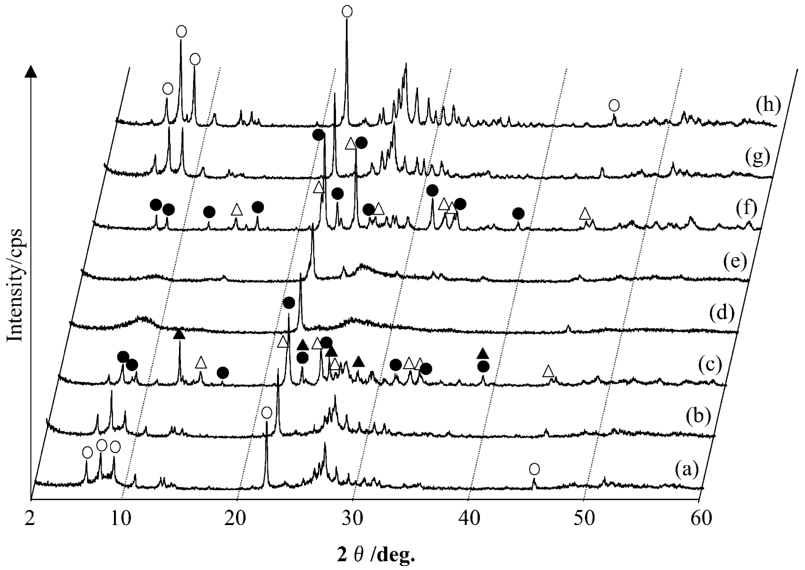

Fig. 1. XRD patterns (Cu Kα) of the Mo–V–(Te)–O catalysts: (a) MoV-orth-fresh, (b) MoV-orth-1, (c) MoV-orth-2, (d) MoV-amor-fresh, (e) MoV-amor-1, (f) MoV-amor-2, (g) MoVTe-orth-fresh, (h) MoVTe-orth-1. (○) orthorhombic Mo-V-O or Mo–V–Te–O phase; (●) $(V_{0.07}Mo_{0.93})_5O_{14}$; (△) $V_{0.95}Mo_{0.97}O_5$; (▲) MoO_3.

system [11] as well as Mo–V–Te(Sb)–O system [2,7–9,12]. The XRD pattern was nicely simulated by using orthorhombic structure with lattice parameter ($a = 21.10$ Å, $b = 26.57$ Å, $c = 4.006$ Å) with Rietveld method. It is reported that there are many structural variants in Mo-V-O system [13] and it can be recognized that the present structural material is a new variant. Additionally, it should be pointed out that Te is no longer necessary element for the formation of the orthorhombic structure in Mo-V-O system, although it has been thought that the structure formation needs Te.

When the preparation solution contained high Mo concentration ($0.6\,\mathrm{mol\,l^{-1}}$) with the same Mo/V ratio as for MoV-orth, we obtained a black-colored solid with one broad diffraction peak at the low angle region instead of the characteristic three peaks (Fig. 1(d)), although the same diffraction peaks at 22° and 45° were observed. Its bulk composition was determined to be $Mo_1V_{0.29}O_x$ (Table 1) which was interestingly quite similar to that of MoV-orth. Based on the observed broad XRD pattern and elemental analysis, we speculate a disordered structure, in which the slabs stack together into c-direction giving a 22° peak while the plane of the slab has a disordered arrangement of Mo and V giving the broad peak at the low angle region. The main structural difference between MoV-orth and MoV-amor is, therefore, whether the slab plane is ordered or not.

After heat-treatment at 500 °C in N_2, the XRD pattern of MoV-orth-1 was scarcely changed (Fig. 1(b)). When the temperature was increased up to 600 °C (Fig. 1(c)), the other phases, such as MoO_3 [JCPDS 76-1003], $V_{0.95}Mo_{0.97}O_5$ [JCPDS 77-0649], and $(V_{0.07}Mo_{0.93})_5O_{14}$ [JCPDS 31-1437] appeared besides the orthorhombic phase. On the other hand, MoV-amor transformed to $V_{0.95}Mo_{0.97}O_5$ phase [JCPDS 77-0649] partially even at 500 °C (Fig. 1(e)). Up to 600 °C, MoV-amor was completely decomposed to $V_{0.95}Mo_{0.97}O_5$ with the additional phase of $(V_{0.07}Mo_{0.93})_5O_{14}$ [JCPDS 31-1437] (Fig. 1(f)). The orthorhombic structure appears to have higher thermal stability than the disordered Mo-V-O. The orthorhombic structure of Mo–V–Te–O was perfectly maintained even after the heat-treatment at 600 °C (Fig. 1(h)). Clearly, the thermal stability of Mo-V-O can be enhanced by the introduction of the third element (Te) into the hexagonal channels of the orthorhombic Mo-V-O catalyst.

3.2. *Propane oxidation over Mo-V-O-based oxide catalysts*

Catalytic activities of all Mo–V–(Te)–O catalysts for propane oxidation are summarized in Table 2. All catalysts showed activities for propane oxidation and gave the products such as acrylic acid, propene, acetic acid, acetone, and CO_x. Prominently, the orthorhombic Mo-V-O catalyst, such a simple catalyst, showed high oxidation activity at relatively low reaction temperature compared to those for V-based propane oxidative dehydrogenation catalysts which normally need more than 400 °C [14]. The oxygenated product selectivity was, however, quite low as listed in Table 2.

The propane conversion over MoV-orth-1 was found to be twice of that of MoV-amor-1, despite the surface area of MoV-orth-1 ($6.1\,\mathrm{m^2\,g^{-1}}$) was smaller than that of MoV-amor-1 ($10.3\,\mathrm{m^2\,g^{-1}}$). It is obvious that the disordered structure brings about poor catalytic activity. This point will discuss in detail later. The data in Table 2 also makes it clear that the material with $(V_{0.07}Mo_{0.93})_5O_{14}$ type structure is much less active for the propane oxidation; the catalysts containing $(V_{0.07}Mo_{0.93})_5O_{14}$ phase as main (MoV-orth-2 and MoV-amor-2, both of which were obtained by the heat-treatment at 600 °C), showed the propane conversions less than half of that of the corresponding MoV-orth-1 and

MoV-amor-1, despite the surface area was in the opposite order (Table 1). It is known that the $(V_{0.07}Mo_{0.93}O)_5O_{14}$ phase belongs to Mo_5O_{14} structure, in which 5-membered rings of octahedra (pentagonal channel) are formed [13]. The orthorhombic Mo-V-O is also constructed with the same pentagonal unit. As a consequence, the intrinsic oxidation activity of the orthorhombic Mo-V-O catalyst cannot attribute to the pentagonal channel but should be to the other structural unit containing vanadium like the 6- or 7-membered rings.

The propane conversion over the orthorhombic Mo-V-O catalyst (24.0%) was almost the same as that over the Mo–V–Te–O catalyst (25.6%). As for the selectivity to acrylic acid, MoV-orth-1 (5.7%) was, however, very low in comparison with MoVTe-orth-1 (49.3%). Since there is no practical difference in the orthorhombic structure in both catalysts, the catalytic results strongly imply that Te does not directly relate to and disturb the intrinsic activity of the catalyst for the propane oxidation. In other words, Mo and V construct active sites for the oxidative conversion of propane. Te mainly involves the generation of the acrylic acid selectivity. One of the roles of Te is presumably that the strength of surface acid site is modified from strong for deep oxidation to moderate for the formation of acrylic acid. Moreover, in the case of Mo–V–Te–O catalyst, the air calcination before the N_2 calcination was needed in order to achieve high selectivity to acrylic acid, while in the case of the orthorhombic Mo-V-O catalyst the air calcination hardly influenced the catalytic performance. Thus, it can be concluded that the air calcination affects on the state of Te exclusively. It seems that a particular oxidation state of Te in the structure involves in the course of selective oxidative conversion of intermediate on the surface.

3.3. *Activity comparison between orthorhombic catalyst and disordered one*

As described above, the orthorhombic Mo-V-O catalyst was active for propane oxidation more than the disordered Mo-V-O catalyst. To elucidate the structural effect more, the oxidations of ethane and acrolein were carried out over the Mo-V-O catalysts (MoV-orth-1 and MoV-amor-1). The results were summarized in Table 3. In the case of ethane oxidation, the conversion over MoV-orth-1 (9.0%) was about three times higher than that over MoV-amor-1 (3.4%). The influence of the orthorhombic structure appeared more clearly in ethane oxidation than in propane oxidation. This seems to be simply because of the lower reactivity of ethane than propane. In the case of acrolein oxidation, both catalysts worked at the surprisingly low reaction temperature (230 °C) and exhibited high acrylic acid yields. Superiority of the orthorhombic catalyst to the disordered one was, therefore, not so prominent in this case.

The higher activity of the ordered orthorhombic Mo-V-O catalyst than that of the disordered one is now clear. This can be explained by the formation of distorted octahedra of Mo and V in the 6- or 7-membered rings, since the distorted octahedra may not be formed in the disordered structure but can be inevitably formed in the orthorhombic structure for constructing the multi-channel system. The distorted octahedra site might be able to provide active oxygen species or active sites easily, so that the high oxidation activity can be generated.

The product selectivity in all three reactions, on the other hand, was almost independent of whether the catalyst is structural or disordered. This could be explained by assuming that product selectivity is mainly determined by the stability of the products against further oxidation. Ethene and acrylic acid are stable compounds compared to propene that can be easily oxidized, so that ethene and acrylic acid could be main products in the oxidations of ethane and acrolein, respectively, while CO_x was main products in propane oxidation over the Mo-V-O catalysts. Te can obviously promote the selective reaction pathway to convert propene to acrylic acid.

4. Conclusion

We succeeded in synthesizing a new orthorhombic Mo-V-O catalyst by hydrothermal method. On the basis of the catalytic results on alkane and acrolein oxidations over the orthorhombic Mo-V-O catalyst and the disordered Mo-V-O catalyst, it was concluded that the catalytic oxidation activity comes from Mo and V oxides and these elements have to be organized in an ordered structure with the formation of distorted octahedra. The selectivity was, on the other hand, almost independent of the catalyst structure but the selectivity to acrylic acid in propane oxidation was greatly improved by the addition of Te without changing the orthorhombic structure.

References

[1] T. Ushikubo, H. Nakamura, Y. Koyasu, S. Wajiki, US Patent 5,380,933 (1995).
[2] W. Ueda, K. Oshihara, D. Vitry, T. Hisano, Y. Kayashima, Catal. Surv. Jpn. 6 (2002) 33.
[3] M. Lin, T. Desai, F. Kaiser, P. Klugherz, Catal. Today 61 (2000) 223.
[4] L. Luo, J.A. Labinger, M.E. Davis, J. Catal. 200 (2001) 222.
[5] H. Watanabe, Y. Koyasu, Proceedings of the Fourth WCOC, vol. 16, Potsdam, 2001 (recent report).
[6] H. Tsuji, Y. Koyasu, J. Am. Chem. Soc. 124 (2002) 5608.
[7] W. Ueda, K. Oshihara, Appl. Catal. A 200 (2000) 135.
[8] D. Vitry, Y. Morikawa, J.L. Dubois, W. Ueda, Top. Catal. 23 (2003) 47.
[9] K. Oshihara, T. Hisano, W. Ueda, Top. Catal. 15 (2001) 153.
[10] T. Katou, D. Vitry, W. Ueda, Chem. Lett. 32 (2003) 1028.
[11] D. Vitry, Y. Morikawa, J.L. Dubois, W. Ueda, Appl. Catal. A 251 (2003) 411.
[12] J.M.M. Millet, M. Baca, A. Pigamo, D. Vitry, W. Ueda, Appl. Catal. A 244 (2003) 359.
[13] T. Ekström, M. Nygren, Acta Chem. Scand. 26 (1972) 1827.
[14] E.A. Mamedov, V. Cortés Corberán, Appl. Catal. A 127 (1995) 1.