Hydrothermal synthesis of Mo–V–M–O complex metal oxide catalysts active for partial oxidation of ethane

Wataru Ueda,*[b] Ning Fang Chen[a] and Kenzo Oshihara[b]

[a] *Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama, 226-0087 Japan*

[b] *Department of Materials Science and Engineering, Science University of Tokyo in Yamaguchi, 1-1-1 Daigaku-dori, Onoda, Yamaguchi, 765-0884 Japan. E-mail: ueda@ed.yama.sut.ac.jp*

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Mo–V–M–O (M = Al, Fe, Cr and Ti) complex metal oxide catalysts have been prepared by hydrothermal synthesis for the first time and showed activity for the partial oxidation of ethane to ethene and acetic acid.

In the last decade much progress has been made in the selective partial oxidation of light alkanes with molecular oxygen in gas phase.[1] Many types of metal oxides have been used to create catalytically active solid phases for various oxidation processes for promoting both the conversion of alkanes and the selectivity to partial oxidation products.[2] The most well known catalyst is crystalline V–P–O complex oxide for the selective oxidation of *n*-butane to maleic anhydride.[3] Crystalline forms or fine composites of complex metal oxides seem to be necessary for achieving high conversion and selectivity in alkane oxidation. It has already been shown that the Mo–V–O catalyst system, characterized by an X-ray diffraction peak near 4.0 Å (2θ = 22°, CuKα), is active for the oxidative dehydrogenation of ethane.[4,5] We have thus started studies to prepare monophasic materials or uniform fine composites of Mo–V–M–O catalysts by a hydrothermal synthetic method and recently succeeded in synthesizing solid materials which gave the same X-ray diffraction peaks and were catalytically active for the partial oxidation of ethane to ethene and acetic acid. We report here the synthetic method and the catalytic performance.

Since hydrothermal treatments at 175 °C did not give solid materials either from a mixed aqueous solution of $(NH_4)_6Mo_7O_{24}$ and NH_4VO_3 or from a solution of $(NH_4)_6Mo_7O_{24}$ and $VOSO_4$, we tried to add other metal cations for organization of Mo and V. For this purpose, Anderson-type heteropolymolybdates were chosen and metal cations such as Al, Fe, Cr, Bi, Co as heteroatoms in the Anderson structure were found to be effective organization elements. The Anderson-type heteropolymolybdates were prepared according to the reported procedure using $(NH_4)_6Mo_7O_{24}$ and metal sulfate (or alum).[6,7] The phase purity of the crystallized heteropolymolybdate samples was ascertained by XRD analysis. Hydrothermal reaction of the various Anderson-type heteropolymolybdates and $VOSO_4$ in water was carried out at 175 °C for 48 h in a PTFE lined autoclave (50 ml) without mixing. Typically, a sample, such as MoVAlO(621), where the numbers in parentheses show the atomic ratios of each element in the preparation, respectively, was synthesized in the following manner. To an aqueous solution (25 ml) of the prepared crystalline Anderson-type heteropolymolybdates, $(NH_4)_3H_6AlMo_6O_{24}\cdot 7H_2O$ (2.4 mmol) and an aqueous solution (15 ml) of $VOSO_4$ (4.8 mmol) was added dropwise with stirring at 50 °C, giving a brown–black liquid which was then allowed to undergo hydrothermal reaction in the autoclave. All reagents used were of commercially available research grade. After *ca.* 4 h reaction a small amount of black solid became observable on the wall of the autoclave and the mixed solution was black–blue. After 48 h the reaction was almost complete, yielding a substantial amount of solid in the bottom of the autoclave as well as on the wall. The obtained dark purple solid material was separated from the solution which was light green–yellow probably due to remaining V^{5+} in solution. The separated mass was washed with distilled water and dried at 40 °C overnight in air. The yield was 60 wt%. It was ascertained by XPS that the oxidation states of molybdenum and vanadium in the hydrothermally synthesized sample were 6+ and 4+, respectively, and an ICP analysis revealed that the sample contained each metal cation with a composition of $Mo_6V_{2.1}Al_{0.9}O_x$. Samples containing other metal cations (Fe, Cr, Bi or Co) were also synthesized by the same manner.

XRD patterns of the samples are shown in Fig. 1. The patterns are quite characteristic; only two sharp diffraction peaks were observed at 2θ *ca.* 22 and 45° ascribed to (00*l*) reflections and other very broad diffraction peaks appeared at 8, 11 and 27°. Mo–V–O based complex oxides giving these characteristic diffractions at 22 and 45° has already been reported in papers and patents as a key catalyst phase for acrolein oxidation to acrylic acid, ethane oxidation to ethene, and propane ammoxidation to acrylonitrile.[4–10] In these cases, however, the materials were synthesized through complicated reduction–oxidation processes in the preparation liquid and also by high-temperature heating processes, so that the materials thus prepared are multiphasic and of poor crystallinity. In the hydrothermal synthesis presented here for the first time, the preparation is very simple and highly reproducible, and sharp XRD diffraction peaks were observed, implying that the hydrothermally synthesized materials have higher crystallinity. In fact we observed rod-shape uniform crystals (0.1 μm × 0.3 μm × 10 μm on average) by SEM.

As can be seen in Fig. 1, the XRD characteristics are almost independent of the added metal cations but the relative intensities between the sharp and broad peaks are obviously different. It is, therefore, obvious that all the samples are at least

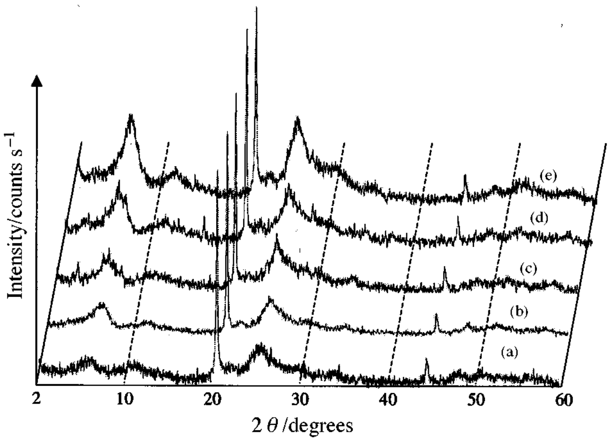

Fig. 1 XRD patterns of the hydrothermally synthesized Mo–V–M–O catalysts. XRD data were collected using a X-ray diffractometer with Cu-Kα radiation: (a) MoVCrO(621), (b) MoVFeO(661), (c) MoVBiO(621), (d) MoVAlO(621), (e) MoVCoO(621).

biphasic; one gives a set of the narrow diffraction lines and the other a set of the broad lines. For the phase giving the set of the narrow diffraction lines, we speculate, on the basis of layer-type structures proposed for Mo–V–O based oxides giving a diffraction peak at $2\theta = 22°$,[9,11] that self-organization takes place between Anderson-type heteropolyanion units and vanadyl cations under the hydrothermal reaction conditions, forming slabs with these being stacked to form a solid with a layer structure in which one crystal direction is ordered giving clear XRD peaks. Obviously we need more experimental results to clarify the structure and such work is being undertaken now.

The hydrothermally synthesized solid materials showed high catalytic activities for C_1–C_4 alkane oxidation, particularly for the production of ethene and acetic acid from direct ethane oxidation as shown in Table 1. Prior to the catalytic ethane oxidation, the catalysts were heat-treated at 410 °C for 2 h in a nitrogen stream. By this treatment the catalysts became active for the reaction but the XRD patterns did not change. When the reaction was conducted using the catalyst containing Al, Fe or Cr at 340 °C under the conditions indicated, ethane was oxidized into ethene and acetic acid quite selectively and the other products were carbon oxides. The Cr-containing catalyst tends to promote more complete oxidation. All the catalysts were highly stable under the reaction conditions, giving constant activity and selectivity. We also tried to incorporate titanium into the Mo–V–Al–O catalyst in order to improve the catalytic performance since the benificial effect of titanium has already been reported in the V–Ti–O system.[12] The catalysts MoVAlTiO were prepared by adding known amounts of $(NH_4)_2Ti(C_2O_4)_2$ into the preparative solution for hydrothermal reaction. As shown in Table 1 we observed a significant increase of the oxidation activity without significant alteration in the product selectivities. Since no additional XRD peaks were observed in the MoVAlTiO catalysts but the peaks of (00l) reflections widened, the activity increase seems to result from the increase of active area of the catalysts. As a consequence, the present result provides a new preparation route to Mo–V–O based complex oxide catalysts.

Table 1 Partial oxidation of ethane over Mo–V–M–O catalysts[a]

	Conversion (%)		Selectivity (%)			
Catalyst	C_2H_6	O_2	C_2H_4	$MeCO_2H$	CO_2	CO
MoVAlO(621)	3.9	13.2	70.4	8.1	7.6	13.9
MoVCrO(621)	4.2	18.4	55.8	10.7	12.4	21.0
MoVFeO(621)	2.6	8.4	71.0	11.2	6.8	11.0
MoVAlTiO(621-0.5)	9.1	36.3	61.5	11.9	9.1	17.5
MoVAlTiO(621-0.7)	14.7	61.3	59.6	11.5	9.9	19.0

[a] *Reaction conditions*: reaction temperature, 340 °C; catalyst weight, 1.0 g; reactant gas feed, atmospheric pressure, total flow rate, 50 ml min^{-1}; feed composition, $C_2H_6:O_2:H_2O:N_2 = 30:10:20:40$ (mol%).

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