Synthesis of Molybdenum and Vanadium-Based Mixed Oxide Catalysts with Metastable Structure: Easy Access to the MoVNbTe(Sb)O_x Catalytically Active Structure Using Reductant and Oxoacid

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The MoVMTe(Sb)O_x (M = Nb, Ta, Ti) mixed oxide systems have drawn much attention as promising catalytic materials for new alkane-based commercial processes since these exhibit a high productivity for propane (amm)oxidation at a moderate reaction temperature around 400 °C.[1−3] Recently, the crystallographic structure of the MoVMTe(Sb)O_x phase relevant to the catalytic activity was proposed as a new molybdenunm oxide family,[3,4] and some studies suggested that this metastable structure is generated from the organization and rearrangement of the polyoxometalate (POM) units.[5,6] However, it was difficult to reliably obtain a high catalytic performance because these catalytic materials had been prepared through the delicate treatment at an elevated temperature in order to adjust the redox state for access to the metastable structure. Recently, we reported the synthesis via reduction of the POM mixture under mild conditions followed by calcination in an O_2-excluded atmosphere as a clue for the simple synthesis of the MoVNbTe(Sb)O_x catalysts and that one of the prime factors for access to the metastable structure catalytically active for propane (amm)oxidation is the precise control of the partially reduced state of the system.[6] Our continuing investigation focusing on the synthetic procedure and conditions revealed that the acidic control of the POM mixture is crucial for the reliable synthesis of the specific structure exhibiting a superior catalyst performance. In this communication, we wish to report the effect of the addition of a strong oxoacid to the POM mixture on the structure and catalytic performance of the resultant material and discuss its role in the generation of the catalytically active structure.

Table 1. Synthetic Parameters and Catalytic Performance of MoVNbTe(Sb)O_x for Ammoxidation of Propane[a]

cat. entry	reductant (mol/mol of Mo)	acid (mol/mol of Mo)	react. temp. (°C)	conv. of C_3H_8 (%)	yield of AN[k] (%)
1[b]	0.134[d]	0.000	427	81.8	48.1
2[b]	0.134[d]	0.134[h]	430	86.6	50.9
3[b]	0.134[e]	0.000	428	86.9	51.6
4[b]	0.280[f]	0.000	433	90.3	47.5
5[b]	0.280[f]	0.134[h]	434	91.1	50.2
6[b]	0.385[f]	0.134[i]	437	93.3	50.2
7[b]	0.136[g]	0.138[h]	432	88.6	54.3
8[c]	0.068[d]	0.000	435	61.2	30.0
9[c]	0.068[d]	0.068[h]	435	80.1	45.9
10[c]	0.068[e]	0.000	434	81.8	46.4
11[c]	0.120[f]	0.000	433	71.3	32.9
12[c]	0.120[f]	0.077[h]	434	82.0	46.0
13[c]	0.135[f]	0.077[i]	435	83.5	45.4
14[c]	0.100[f]	0.100[j]	435	83.2	47.1

[a] Determined by on-line GC using an internal standard. Catalyst (550 mg), feed gas (500 NmL/h), substrate molar ratio (C_3H_8/NH_3/air = 1/1.2/15). [b] $Mo_1V_{0.3}Nb_{0.12}Te_{0.17}O_x$ calcined at 600 °C for 2 h in a stream of N_2. [c] $Mo_1V_{0.3}Nb_{0.07}Sb_{0.17}O_x$ calcined at 625 °C for 2 h in a N_2 stream. [d] $N_2H_4{\cdot}H_2O$. [e] $N_2H_4{\cdot}H_2SO_4$. [f] $(COOH)_2{\cdot}2H_2O$. [g] Acetol. [h] H_2SO_4. [i] HNO_3. [j] $VOSO_4$. [k] Yield of acrylonitrile based on feed propane.

For the synthesis of MoVNbTe(Sb)O_x, NH_4VO_3, niobia sol, and aqueous solution of the Anderson-type heteropolymolybdate prepared in situ from $(NH_4)_6Mo_7O_{24}$ and telluric acid or antimonic acid were mixed in a vessel. To have access to the metastable structures, a definite amount of reductant such as hydrazine, acetol, and oxalic acid was added to the aqueous mixture for adjusting the redox state of the system, although the reducing action of oxalic acid took place during the subsequent heating process. After a rapid evaporation of the aqueous mixture to dryness at 170−200 °C in air, the gel was immediately calcined in an O_2-excluded atmosphere for maintaining the partially reduced state. Thus, the materials were reproducibly made in the form of a black crystalline powder. It was found that the addition of a strong oxoacid such as sulfuric acid to the aqueous mixture prior to the heating process improved the catalytic performance of the material obtained after the calcination. Table 1 illustrates the effect of the acidification on the catalytic performance for propane ammoxidation with the material composition and the optimum amount of oxoacid giving the maximum yield of acrylonitrile.[7] The addition of oxoacid enhanced the activity for the conversion of propane and the selectivity to acrylonitrile. The remarkable improvement of the catalytic performance was observed for the MoVNbSbO_x system prepared from the acidified aqueous mixture, though the achieved catalytic performance was relatively poor as compared to the MoVNbTeO_x system.

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(7) The use of nitric acid was also effective but the optimum amount of reductant deviated from that for the catalysts prepared using sulfuric acid.

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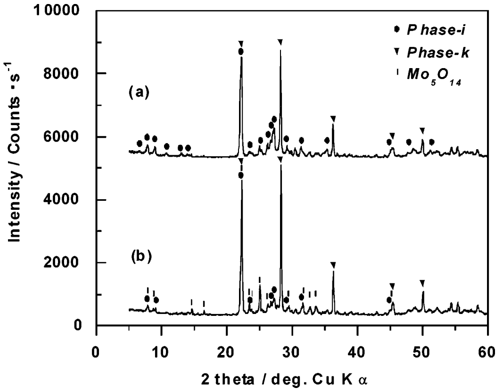

Figure 1. X-ray diffraction patterns of $Mo_1V_{0.30}Nb_{0.07}Sb_{0.17}O_x$ prepared using hydrazine hydrate (0.068 mol/mol of Mo) and calcined at 625 °C for 2 h in a stream of N_2. (a) From the aqueous mixture acidified with H_2SO_4 (0.068 mol/mol of Mo); (b) from the aqueous mixture without acidification.

Using hydrazine sulfate as the reductant produced almost the same effect as the separate addition of hydrazine and sulfuric acid. This suggests that hydrazine sulfate plays the roles in both reducing and acidifying the system. Furthermore, $VOSO_4$ was found to be a useful vanadium source for adjusting the redox state and acidity of the system. After the detailed examination of the $VOSO_4$ content and the simultaneous use of other reductants, $Mo_1V_{0.3}Nb_{0.07}Sb_{0.17}O_x$ prepared using $VOSO_4$ showed the highest yield of acrylonitrile.[8] As a result, the acidification, despite different types of reductants, seemed to be crucial for obtaining a catalyst with superior performance.

A structural difference between the catalyst prepared with and without acidification was apparently demonstrated for the $MoVNbSbO_x$ calcined in an O_2-excluded atmosphere. Figure 1 shows the XRD patterns for the calcined $MoVNbSbO_x$ prepared with and without acidification. The catalyst prepared from the aqueous mixture acidified with H_2SO_4 showed a pattern containing the structure denoted as phase *i* (Figure 2a), which had been recently identified as the catalytically active phase.[4,9] In contrast, the catalyst without the addition of H_2SO_4 showed a pattern of the Mo_5O_{14} structure (Figure 2b) more dominantly. The other significant structure denoted as phase *k*, which is identical to the $Sb_4Mo_{10}O_{31}$ structure (Figure 2c), was observed in both catalysts. The gels dried at 170−200 °C were amorphous for both samples, and the structures appeared above 550 °C during the heating process. Namely, the acidification of the aqueous mixture promoted the formation of the active structure (phase *i*) at an elevated temperature in an inert atmosphere.

While the actual chemistry in an aqueous mixture and the solid-state reaction are still unclear, we infer that one of the roles of the added oxoacid anion is to reoxidize the system limitedly at an elevated temperature during the heating process. Parts (a) and (b) in Figure 3 show the Q-MS profiles of the major *m*/*e* for the gaseous molecules released from the dried gels during the heating process in an inert atmosphere. The heating rate and final temperature were the same as the calcination procedure in the catalyst synthesis. For the dried gel obtained from the aqueous mixture reduced by hydrazine hydrate and acidified with H_2SO_4 (Figure 3a), SO_2 ($m/e = 64$) and the molecule exhibiting $m/e = 28$ were released around 550 °C, and the latter was rapidly terminated just below 600 °C.[10] For the dried gel without the addition of H_2SO_4 (Figure 3b), the release peak of $m/e = 28$ around 550 °C was relatively broad as compared to that for the dried gel with the addition of H_2SO_4. The release peak of $m/e = 28$ around 550 °C was also observed for the dried gels prepared using other reductants such as oxalic acid. Therefore, the peak of $m/e = 28$ appearing around 550 °C is attributed to N_2, which originates from oxidation of the ammonium ions contained in the raw material, $(NH_4)_6Mo_7O_{24}$. It is anticipated that the SO_4^{2-} accelerates the release of NH_4^+ oxidatively and that the lattice oxygen after calcination in an O_2-excluded atmosphere is retained better for the acidified sample due to the sacrifice of SO_4^{2-}. The enriched formation of the active structure for the acidified sample suggests that the active structure, phase *i*, is generated with a slightly higher oxidation state as compared to the Mo_5O_{14} structure. Interestingly, the release termination for the molecules during the heating process was quite consistent with the temperature at which the active structure appeared; that is, it is very likely that the facilitated discharge of NH_4^+ participates in the efficient formation of the active structure. In addition, the high catalyst performance for $MoVNbSbO_x$ was not achieved only by adjusting the amount of reductant without the addition of SO_4^{2-} or NO_3^-. These results prompt the idea that the critical path regulated by the redox state along with the temperature increase exists for access to the catalytically active structure, phase *i*. The added oxoacid would prevent the system from over-reduction by the ammonium ion just below 600 °C and assist the system in

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(8) Example of synthesis of $\mathbf{Mo_1V_{0.3}Nb_{0.07}Sb_{0.17}O_x}$ using $VOSO_4$: NH_4VO_3 (0.94 g, 8.0 mmol) was dissolved in hot water (≈30 mL). It was then added to the POM solution (H_2O, 40 mL) prepared from $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (7.06 g, 40.0 mmol) and Sb_2O_3 (Sb 6.8 mmol) according to the procedure reported in ref 2h; 3.85 g of 10 wt % Nb_2O_5 sol (Taki Chemical Co., Ltd.) was mixed with oxalic acid (2.7 mmol) dissolved in hot water (5 mL). It was then added to this amber solution with vigorous stirring. The resulting mixture was stirred for a few minutes at 50 °C (pH value ≈4.9). $VOSO_4$ (4.0 mmol) dissolved in hot water (30 mL) was then added dropwise, and the slurry was continually stirred for about 20 min at 70 °C. The color of the slurry turned to dark purple and then finally to black. The reduced slurry was then rapidly evaporated to dryness at 200 °C in air, and about 2 g of the dried gel was immediately calcined at 625 °C for 2 h (heating rate 10 °C/min) in a stream of N_2 (100 mL/min) using a quartz tube (i.d. 20 mm ϕ).

(9) The existence of two phases (phases *i* and *k*) has already been suggested in ref 2b as phases M1 and M2. The structure proposed in ref 3a and the $Cs_x(Nb,W)_5O_{14}$ structure (JCPDS 80-0196) suggested in ref 3b as the active phase were slightly different from that proposed in our recent report with Rietveld refinement (ref 4). From ED analysis of the orthorhombic phase, the reflection conditions corresponding to (h00) and (0k0) ($h = 2m$, $k = 2n$) were strongly indicated, which means that the possible space groups of phase *i* are $P2_12_12$, $Pba2$, and $Pbam$. With TEM, XRD simulation, and the elemental analysis of a purified sample, we obtained the plausible space group ($P2_12_12$) and candidates for the coordinates. The ideal structure of phase *i* $(Mo, V)_9Nb_1Sb_1O_{28}$: orthorhombic $P2_12_12$ (No. 18), $a = 26.77$ Å, $b = 21.22$ Å, $c = 4.01$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2277.9$ Å^3, $Z = 4$. As for the Mo_5O_{14} structure (JCPDS 31-1437 or 27-1310), also see Ekström, T.; Tilley, R. J. D. *J. Solid State Chem.* **1976**, *19*, 125. As for the $Sb_4Mo_{10}O_{31}$ structure (JCPDS 33-0104), also see Parmentier, M.; Gleitzer, C.; Tilley, R. J. D. *J. Solid State Chem.* **1980**, *31*, 305.

(10) Sulfur was scarcely observed in the materials after calcination based on the XPS and XRF spectra. It is possible for the $MoVNbTeO_x$ system that part of the telluric acid plays the role similar to those of sulfuric acid and nitric acid. A small amount of sublimed Te metal from the sample was observed during the heating process in an O_2-excluded atmosphere.

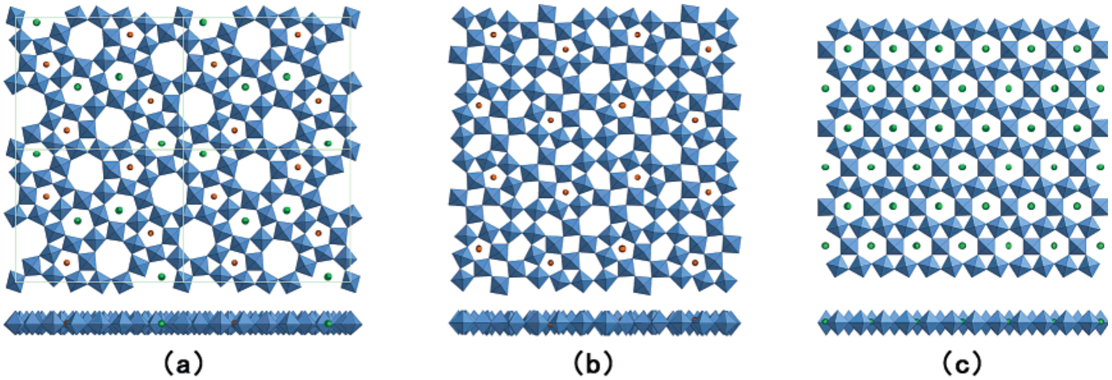

Figure 2. (a) Polyhedral representations of the ideal structure for phase *i*, viewed onto and along [001], showing Sb or Te (green) and Nb (orange). Oxygen atoms on Nb are omitted for clarity. (b) Mo_5O_{14} structure viewed onto and along [001]. (c) $Sb_4Mo_{10}O_{31}$ structure (phase *k*) viewed onto and along [001]. These three structures have a layer with the 4.0 Å *d*-spacing but only phase *i* comprises a unique seven-membered ring of corner-shared octahedras.

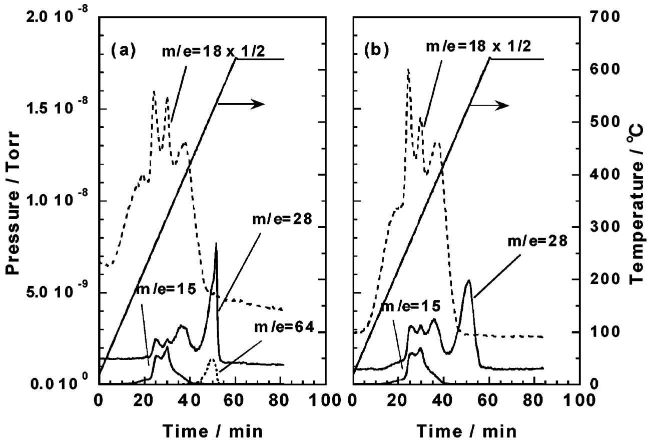

Figure 3. Profiles for selected *m*/*e* of released gaseous molecules from dried gel for $Mo_1V_{0.30}Nb_{0.07}Sb_{0.17}O_x$ during the heating process in a stream of He. (a) From the aqueous mixture reduced by hydrazine hydrate (0.068 mol/mol of Mo) and acidified with H_2SO_4 (0.068 mol/mol of Mo); (b) from the aqueous mixture reduced by hydrazine hydrate (0.068 mol/mol of Mo).

getting into the path for the generation of phase *i* during the heating process.

A detailed investigation about the transition of the redox state during the heating process is now in progress for the straightforward synthesis of the pure phase *i*. Although the presented simple synthesis using a reductant and oxoacid allows a combinatorial approach to diversify Mo and V mixed oxides, the understanding of the POM linkage manner would be strongly desired for the advanced design and synthesis of catalytic materials based on the Mo and V mixed oxides.

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Supporting Information Available: The procedures for the catalytic examination and analysis, figures showing a variation in the catalytic performance with the amount of added oxoacid, and the XRD patterns for the $MoVNbTeO_x$ system (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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