Synthesis of MoVNbTe(Sb)O$_x$ Composite Oxide Catalysts via Reduction of Polyoxometalates in an Aqueous Medium

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Designing and synthesizing the transition-metal composite oxide catalysts from defined constituents whose high performance could be rationalized remains an elusive goal of research for heterogeneous oxidation catalysts.[1] The self-organization of mononuclear oxometalates and polyoxometalates (POMs) used as a pre-designed building block to larger constituents should be a promising strategy by which to synthesize them.[2] While much attention has been paid to hydrothermal synthesis as a technique for creating novel oxide materials by the self-organization of POMs containing molybdenum and vanadium,[3] these POMs are known to be linkable by reduction under mild conditions through intermediates with a highly negative charge.[4] Recently, the reductive linkage of POMs using reducing agents such as hydrazine and hydroxylamine or their salts has been applied to the synthesis of interesting large or giant POM clusters and extended solid-state oxide materials.[5] In addition, to use a reducing agent under mild conditions enables easy access to metastable or low-temperature oxide phases. Goodenough and co-worker[6] successfully prepared single and binary oxides with reduced phases via the reduction of the ammonium salts of transition-metal oxoanions using similar reducing agents followed by heat treatment in an inert atmosphere. We have investigated the preparation of molybdenum- and vanadium-based composite oxide catalysts with metastable phases based on the self-organization of POMs and found that highly active catalysts could be prepared by using reducing agents under mild conditions. In this communication, we wish to report the synthesis of MoVNbTe(Sb)O$_x$ composite oxide catalysts [7] via the reduction of heteropolymolybdate and vanadate in an aqueous medium.

In the synthesis presented here, the highly crystalline composite oxides of a black color could be reproducibly obtained by a very simple procedure including the reduction of POMs under mild conditions, followed by drying of the reduced condensate and calcination under an O$_2$ excluded atmosphere for maintaining the partially reduced state of the systems. With regard to making up the solution mixture, an aqueous solution of NH$_4$VO$_3$ was first mixed with an aqueous solution of Anderson-type heteropolymolybdates[8] that was prepared by using (NH$_4$)$_6$Mo$_7$O$_{24}$ and telluric acid or antimonic acid, followed by the addition of Nb$_2$O$_5$ sol. For reducing agents, hydrazine, hydroxylamine, and their salts were used. The action of these reducing agents was enough to reduce the heteropolymolybdate and vanadate at temperatures below 100 °C.[9] An organic compound such as acetol was also found to be useful although the chemical equation is speculatively given as follows.

$$CH_3C(O)CH_2OH \rightarrow C_2H_2 + 4H^+ + 4e^- + CO_2 \qquad (1)$$
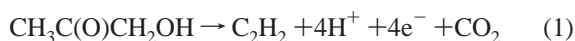
The prepared MoVNbTe(Sb)O$_x$ composite oxides showed high catalytic performance for the propane ammoxidation to acrylonitrile

and the oxidation to acrylic acid, which are promising targets for a commercial process using alkane feedstocks.[1] Table 1 lists the typical catalyst compositions and the optimum amount of the reducing agents giving the highest yield for each of the reactions. The maximum yield of acrylonitrile and acrylic acid with the MoVNbTeO$_x$ system exceeded 50% and 45%, respectively. The catalytic performance of the MoVNbSbO$_x$ system was relatively poor as compared to that of the MoVNbTeO$_x$ system. The other products were mainly CO and CO$_2$, with acetonitrile and hydrogen cyanide for the ammoxidation and acetic acid for the oxidation also produced in small amounts. The preferable oxide compositions concerned with the active phase stated below were almost the same for both reactions. As shown in Table 1, the composite oxides prepared without reduction in an aqueous medium showed poor catalyst performance. The dried samples prior to calcination also showed catalytically negligible activity. It is suggested that the metastable phase formed at an elevated temperature with a specific oxidation state corresponds to the catalytic activity. The performances of the catalysts prepared using hydrazine sulfate were better than those of the catalysts prepared using hydrazine hydrate. This indicates that acidic control of the reduced slurry is effective for obtaining the catalysts with superior performance. It should be noted that the optimum amount of reducing agent was different for the oxide compositions and for the target reactions as illustrated in Table 1, but it was almost the same, regardless of the kind of reducing agent, after taking into account the reducing efficiencies.

According to the recent synthesis of transition-metal oxide clusters and extended solids based on self-organization using POMs building blocks,[5] self-organization in the present synthesis should follow the mechanism that highly negatively charged (nucleophilic) intermediates generated by reduction are connected by electrophilic species. Therefore, it is interesting for the present systems to reveal the process in which large molecular constructions are formed. The XRD patterns of the samples for Mo$_1$V$_{0.25}$Nb$_{0.20}$Te$_{0.17}$O$_x$ after each preparation step are shown in Figure 1. The pattern of the sample obtained by drying the reduced slurry at 170 °C showed that the precursor gel prior to calcination is amorphous with negligible catalytic activity. This indicates that the reduction of the Anderson-type heteropolymolybdate and vanadate under mild conditions does not form any long range-ordered structure in contrast to the case of the hydrothermal synthesis of MoV(Ti)MO$_x$ (M = Al, Fe, Cr, Co, Bi) and MoVNbTe(Sb)O$_x$ catalysts using VOSO$_4$ at 175 °C, in which catalytically active crystalline phases are grown in one direction giving a clear XRD peak near the d-spacing of 4.0 Å (2θ = 22 ° Cu Kα).[10] Here the crystalline phases containing the layered structure characterized by a peak near 4.0 Å were formed during calcination at 550−650 °C under an O$_2$-excluded atmosphere. Molybdenum and vanadium-based composite oxide catalysts with this characteristic diffraction have already been reported as a key

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Table 1. Catalytic Performance of MoVNbTe(Sb)Ox for (Amm)Oxidation of Propane[a]

catalyst composition[b]	amount of reducing agents (mol/mol-Mo)	calcin- ation[c] temp (°C)	reaction temp (°C)	conversion[d] of propane (%)	yield[d] of acrylonitrile or acrylic acid (%)
ammoxidation[e]					
$Mo_1V_{0.30}Nb_{0.12}Te_{0.17}O_x$	0.000	600	427	11.4	4.6
$Mo_1V_{0.30}Nb_{0.12}Te_{0.17}O_x$	0.134[g]	600	428	86.9	51.6
$Mo_1V_{0.30}Nb_{0.12}Te_{0.17}O_x$	0.134[h]	600	427	81.8	48.1
$Mo_1V_{0.30}Nb_{0.12}Te_{0.17}O_x$	0.268[i]	600	426	77.7	45.2
$Mo_1V_{0.30}Nb_{0.12}Te_{0.16}O_x$	0.136[j]	600	429	85.7	53.5
$Mo_1V_{0.25}Nb_{0.20}Te_{0.17}O_x$	0.131[g]	600	424	67.6	41.1
$Mo_1V_{0.30}Nb_{0.07}Sb_{0.17}O_x$	0.068[g]	625	434	81.8	46.4
$Mo_1V_{0.30}Nb_{0.07}Sb_{0.17}O_x$	0.068[h]	625	435	61.2	30.0
oxidation[f]					
$Mo_1V_{0.25}Nb_{0.20}Te_{0.17}O_x$	0.096[j]	600	432	69.2	46.3
$Mo_1V_{0.30}Nb_{0.07}Sb_{0.17}O_x$	0.051[g]	625	427	62.4	34.2

[a] Determined by on-line GC using an internal standard. [b] Determined by energy dispersive XRF. [c] For 2 h in a stream of N_2. [d] Based on feed propane. [e] Catalyst (550 mg), feed gas (500 N mL/h), mol ratio (C_3H_8/NH_3/air = 1/1.2/15). [f] Catalyst (550 mg), feed gas (880 N mL/h), mol ratio (C_3H_8/O_2/N_2/H_2O = 1/3/7/19). [g] Hydrazine sulfate. [h] Hydrazine hydrate. [i] Hydroxylamine sulfate. [j] Acetol (hydroxyacetone).
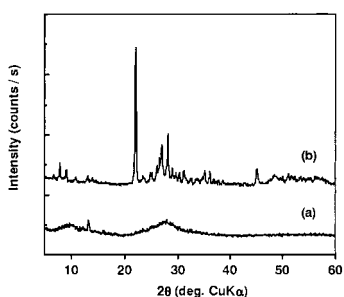
Figure 1. X-ray diffraction patterns of solid samples for $Mo_1V_{0.25}Nb_{0.20}Te_{0.17}O_x$ composite prepared using hydrazine sulfate (0.131 mol/mol-Mo): (a) dried gel prior to calcination, (b) after calcination at 600 °C 2 h in a stream of N_2.
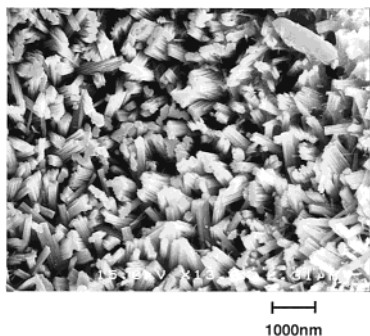
Figure 2. SEM image of $Mo_1V_{0.25}Nb_{0.20}Te_{0.17}O_x$ composite oxide prepared by using hydrazine sulfate (0.131 mol/mol-Mo) and calcined at 600 °C for 2 h in a stream of N_2.

catalyst structure for the selective oxidation not only of alkanes[7,10–12] but also other oxygenates.[13] Ueda et al. speculated that the phase with a layered structure resulted from a directed stacking of slabs due to the self-organization of Anderson-type heteropolymolybdate units.[10a] However, the formation of the layer at the 4.0 Å *d*-spacing was not explained by assembly of the Anderson-type units consisting of only edge-sharing octahedra. The process should contain the covalent linkages of POMs through corner-sharing octahedra and the rearrangement accompanying them.

Although the Mo_5O_{14} structure in which the corner and edge-sharing MoO_6 octahedra are involved, typically exhibits this layered pattern at 4.0 Å *d*-spacing in XRD,[5b,13] the dominant diffraction peaks for the catalytically active MoVNbTe(Sb)O_x were not identified with the Mo_5O_{14} structure as demonstrated in Figure 1. Moreover, as can be seen in the SEM image (Figure 2), the formation of the well-crystallized rod-shape crystallites with a

notched edge was produced during the calcination. Similar types of crystallites were also observed for all the active and selective catalysts with the characteristic XRD patterns. We consider that the superior catalytic performance (including the activation of alkanes) originates from the crystallites with the specific disposition of constituents in addition to the layered structure and that niobium plays an important role in the formation of the crystalline phase. The structural identification of the crystalline phase for MoVNbTe-(Sb)O$_x$ will be reported elsewhere, and the manner of POM linkage relevant to the structure is now under investigation.

The present results provide a new synthesis route to molybdenum- and vanadium-based composite oxide catalysts and also suggest that the self-organization of POMs with the reduction precisely controlled under mild conditions is a potential tool to diversify a new class of oxides including metastable or low-temperature oxide phases. We believe that the exploration and comprehension of the block-construction manner using linkable POMs will lead to the generation of innovative inorganic materials pre-designed with interesting physical, chemical, and structural properties.

Supporting Information Available: Experimental procedures including typical preparation of the catalyst and Figure showing variation in catalytic performance with amount of reducing agent (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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