Olefin Oxidation and Ammoxidation Studies over Molybdate, Tungstate, and Vanadate Catalysts Having Point Defects

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Point defects in the form of cation vacancies (ϕ) have been introduced into molybdates, tungstates, and vanadates with the scheelite-type crystal structure according to $A_{1-x}\phi_x MO_4$. Such defect phases have been examined as catalysts for many different reactions, but the primary emphasis has been on olefin oxidation and ammoxidation. The catalytic activity in the system $Pb_{1-3x}Bi_{2x}\phi_x MoO_4$ has been studied for the ammoxidation of propylene to acrylonitrile. When $x = 0$, i.e., $PbMoO_4$, there is essentially no activity. However, good catalytic activity is observed for $x = 0.005$, and the activity thereafter increases with increasing x. Conversions of propylene to acrylonitrile as high as 76% were obtained, and this is significantly higher than obtained for bismuth molybdates. The results were similar in other systems containing bismuth. Some other such systems studied were $Pb_{1-3x}Bi_{2x}\phi_x WO_4$, $Cd_{1-3x}Bi_{2x}\phi_x MoO_4$, $Bi_{1-x}\phi_x V_{1-3x}Mo_{3x}O_4$, and systems of the type $A^{1+}_{.5-3x}Bi_{.5+x}\phi_{2x}MoO_4$ where A^{1+} is Li, Na, or Ag. Defect scheelites of the type $A_{1-x}\phi_x MO_4$ were also studied without bismuth present. In these cases, there was generally a significant increase in activity as defects were introduced, but the activity and selectivity were not as high as in the bismuth containing defect scheelites. Systems with large concentrations of bismuth, but with no intentional defects, also showed very low activity.

INTRODUCTION

Although there has been considerable discussion of defects as active sites for heterogeneous catalysis, little has been reported on systematic studies relating catalytic properties to the type and concentration of defects. The only study of which we are aware is one by Simkovich and Wagner *(1)*

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on the decomposition of tertiary butyl chloride. They found that the rate of dehydrohalogenation over AgCl increased by 1.5 orders of magnitude on doping with $CdCl_2$ to produce point defects, i.e., cation vacancies or anion interstitials.

The catalytic properties of semiconductors have frequently been related to *p* and *n* type doping *(2)*, but in these cases the correlation with electronic properties may be indirect and misleading. The *p* and *n* type dopants may give rise to different types of surface defects which might then be active sites for catalysis. The bulk electronic

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properties may not be of any consequence.

Our purpose was to study the selective oxidation and ammoxidation of olefins as a function of defect concentration (3). Starting with a basically inactive material, point defects were introduced which might become catalytically active sites on the surface. All catalytic compositions studied were completely crystalline oxides with the scheelite-type structure. The ideal formula for the scheelite structure is AMO_4, and cation vacancies were introduced according to $A_{1-x}\phi_xMO_4$ where ϕ represents a vacant A cation site. A detailed report of the synthesis and characterization of these new catalysts is being presented elsewhere (4).

EXPERIMENTAL

Catalyst testing was performed in a fixed bed reactor using ½-in. or ⅜-in. i.d. stainless steel tubing in a U-tube configuration. The catalyst (30 cm³) in the form of ⅛-in. pellets was loaded to equal heights in both sides of the U-tube. The reactors were placed in fluidized sand baths. All runs were made under essentially isothermal conditions. The pressure was 1 atm (0 psig) unless otherwise stated. On-stream analysis of the reactor effluent was by vapor-phase chromatography. Typical feed gas compositions for propylene oxidation or ammoxidation were, respectively: 5% C_3H_6, 10% O_2 and 85% N_2 or 5% NH_3, 4% C_3H_6, 10% O_2 and 81% N_2. Reactor temperatures were in the range 400–500°C with contact times in the range of 2–8 sec. Specific information may be found in figure captions.

All catalyst compositions were prepared by high-temperature calcination, and the details are given elsewhere (4). When a series of phases, e.g., the $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ series, was prepared, all reactants were from the same batches; also, preparative procedures, e.g., calcination temperature and time, were identical. Since the catalysts of this study sintered extensively during their calcination, their surface areas were initially very low. The surface areas were, in fact, too low for us to measure but must have been less than 0.1 m²/g. However, all products were ball milled for 10 hr, and this produced phases with surface areas close

to 1 m²/g. Thus, nearly all the final surface was exposed during the grinding process.

Our initial studies involved the oxidation of propylene over phases of the type $A_{0.5-3x}^+Bi_{0.5+x}\phi_{2x}MoO_4$. We found that conversions to acrolein were significantly higher when SiC was used as a diluent, possibly due to the high thermal conductivity of SiC. Thus, some catalysts were mixed with 50% SiC by weight before testing. However, ammoxidation studies for other catalysts revealed better conversions to acrylonitrile without SiC. Thus, most studies were carried out with no diluent and no support.

RESULTS

$A_{0.5-3x}^+A_{0.5+x}^{3+}\phi_{2x}MO_4$ Systems

The results for the oxidation of propylene over $Na_{0.5-3x}Bi_{0.5+x}\phi_{2x}MoO_4$ compositions are shown in Fig. 1. There are no intentional defects for x equal to zero, i.e., $Na_{.5}Bi_{.5}MoO_4$; and this phase has very low activity. A dramatic increase in activity occurs when 4% of the A cation sites are made vacant, i.e., $x = .02$. The consumption of propylene increases somewhat more as the vacancy content is increased to 8% and again increases slightly when the defect level is raised to 12%. For higher values of x, we are dealing
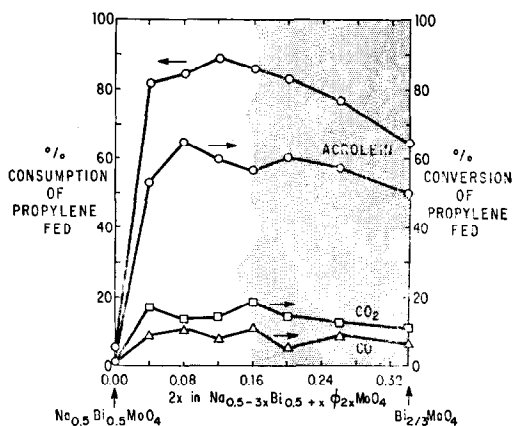

FIG. 1. Propylene consumption and conversion vs $2x$ in the $Na_{0.5-3x}Bi_{0.5+x}\phi_{2x}MoO_4$ system with 50% SiC at 450°C. The feed gas was 5.0% C_3H_6, 10.0% O_2 and 85.0% N_2 with a 4.0 sec contact time. Shaded area is two phase region: $Bi_2(MoO_4)_3$ + $Na_{0.26}Bi_{0.58}\phi_{0.16}MoO_4$.
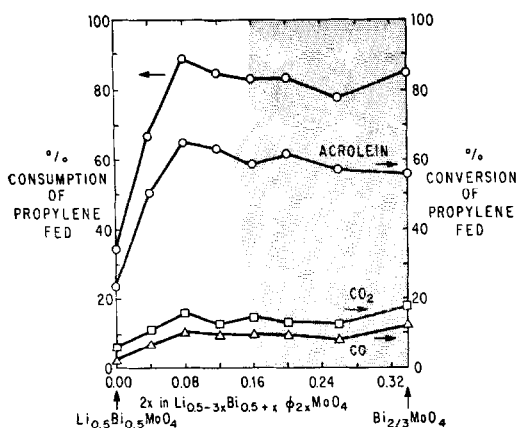
FIG. 2. Propylene consumption and conversion vs $2x$ in the $Li_{0.5-3x}Bi_{0.5+x}\phi_{2x}MoO_4$ system with 50% SiC at 485°C. Feed gas and contact time for Fig. 1 apply. Shaded area is a two phase region: $Bi_2(MoO_4)_3$ + $Li_{0.26}Bi_{0.58}\phi_{0.16}MoO_4$.
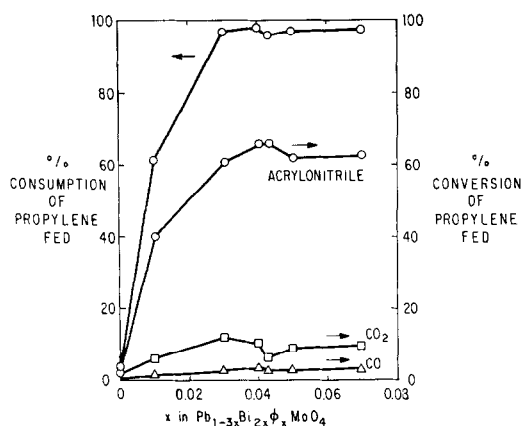

FIG. 3. Propylene consumption and conversion during ammoxidation vs x in the $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ system with 50% SiC diluent. The temperature is 460°C, and the feed is 4% C_3H_6, 4.8% NH_3, 47.7% air, and 43.5% N_2, with a 6.0 sec contact time.

with a two-phase mixture of $Na_{.26}Bi_{.58}\phi_{.16}$-$MoO_4$ and $Bi_{.667}MoO_4$. The selectivity for conversion to acrylonitrile is somewhat better at the 8% defect level than at the 4% or 12% level.

Very similar results were obtained in the $Li_{0.5-3x}Bi_{0.5+x}\phi_{2x}MoO_4$ system (Fig. 2). The $Li_{0.5}Bi_{0.5}MoO_4$ phase, i.e., $x = 0$, appears to be considerably more active than $Na_{0.5}Bi_{0.5}$-MoO_4. However, some defects may have been inadvertently introduced into the nominal $Li_{.5}Bi_{.5}MoO_4$ phase. For example, a phase with a defect level as low as 0.1% might well introduce significant activity, and such levels of defects are difficult to control in this system.

Propylene oxidation was briefly examined over three other $A^+_{0.5-3x}Bi_{0.5+x}\phi_{2x}MO_4$ systems for two compositions each—one composition with defects and one without. In the $Ag_{0.5-3x}Bi_{0.5-x}\phi_{2x}MoO_4$ system with x equal to 0.05, acrolein yields of 65% could be produced with 90% consumption of the propylene. However, when the nondefect phase ($Ag_{0.5}Bi_{0.5}MoO_4$) was tested under the same conditions, only 15% of the propylene was consumed, and the yield of acrolein was only 4%. Phases of the types $Na_{0.5-3x}Y_{0.5+x}\phi_{2x}WO_4$ and $Ag_{0.5-3x}La_{0.5+x}\phi_{2x}MoO_4$ were found to have very low activity with and without defects.

Propylene ammoxidation and 1-butene oxidation were briefly examined over the $Na_{0.32}Bi_{0.56}\phi_{0.12}MoO_4$ catalyst. Yields of 65% acrylonitrile and 67% 1,3-butadiene were obtained, respectively.

$A^{2+}_{1-3x}A_{2x}^{3+}\phi_xMO_4$ Systems

The $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ system was extensively studied for the ammoxidation of propylene. For $x = 0$, i.e., $PbMoO_4$, the activity was very low. However, the consumption of propylene and the yield of acrylonitrile increased rapidly with increasing defect concentration (Fig. 3). The effects of NH_3/C_3H_6 and O_2/C_3H_6 feed ratios on

FIG. 4. NH_3/C_3H_6 ratio vs conversion to acrylonitrile for $Pb_{0.88}Bi_{0.08}\phi_{0.004}MoO_4$ plus 50% SiC. The temperature is 440°C, the feed contains 4.0% C_3H_6 with a O_2/C_3H_6 mole ratio of 2.5, and the contact time is 8.0 sec.
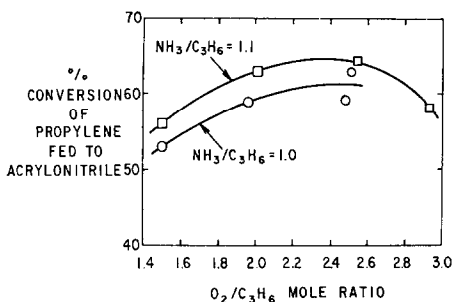
FIG. 5. O_2/C_3H_6 ratio vs conversion to acrylo-nitrile for $Pb_{0.88}Bi_{0.08}Bi_{0.08}\phi_{0.04}MoO_4$ plus 50% SiC. The temperature is 440°C, the feed contains 4.0% C_3H_6, and the contact time is 8.0 sec.

conversion to acrylonitrile are shown in Figs. 4 and 5. The best acrylonitrile yields are obtained with an excess of both NH_3 and O_2 over that stoichiometrically required.

The $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ system was then examined without SiC or any other diluent or support. In contrast to our results in the $A^+_{0.5-3x}Bi_{0.5+x}\phi_{2x}MoO_4$ systems, we found that the conversion to acrylonitrile was in fact improved (Fig. 6). Thus, all subsequent studies were performed on pure single phases—undiluted and unsupported. Figure 6 shows that there is also an increase in ammonia consumption as the defect concentration is initially increased. The effects
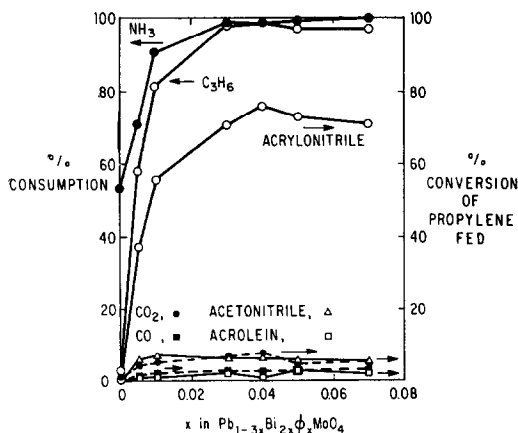

FIG. 6. Propylene and ammonia consumption and conversion vs x in the $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ system without diluent or support. The temperature is 440°C, and the feed is 4.0% C_3H_6, 4.8% NH_3, 47.7% air, and 43.5% N_2, with a 6.0 sec contact time.
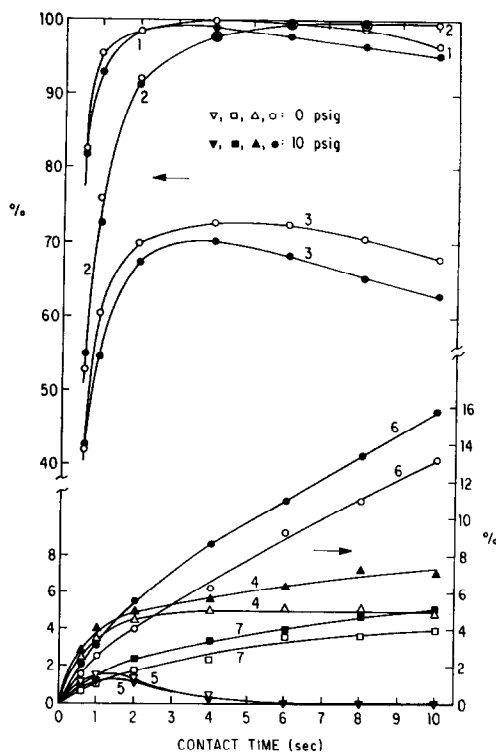

FIG. 7. Propylene and ammonia consumptions and conversions vs contact time for pure $Pb_{0.88}Bi_{0.08}$-$\phi_{0.04}MoO_4$ at 0 psig and 10 psig. The temperature is 450°C, and the feed is 4.0% C_3H_6, 4.8% NH_3, 47.7% air, and 43.5% N_2. Consumption of NH_3 (1) and of C_3H_6 (2). Conversion to acrylonitrile (3), acetonitrile (4), acrolein (5), CO_2 (6), and CO (7).

of increasing the pressure from 0 psig to 10 psig are shown in Fig. 7. Although the consumption of propylene does not change significantly, there is a change in selectivity. The effect of temperature at 10 psig is shown in Fig. 8.

The specific activity for the consumption of propylene during ammoxidation was determined at 450°C for x values of 0.000, 0.005, 0.010, 0.020, 0.030, 0.040, and 0.060. The results are given in Fig. 9. Data for $Bi_2(MoO_4)_3$ are also given for comparison. All data have been normalized to unit surface area. The activity increases steadily with x up to at least 0.060, but the activity has dropped sharply for x equal to 0.333. However, for the phase with x equal to 0.333, the cation vacancies are ordered; therefore they are no longer defects.

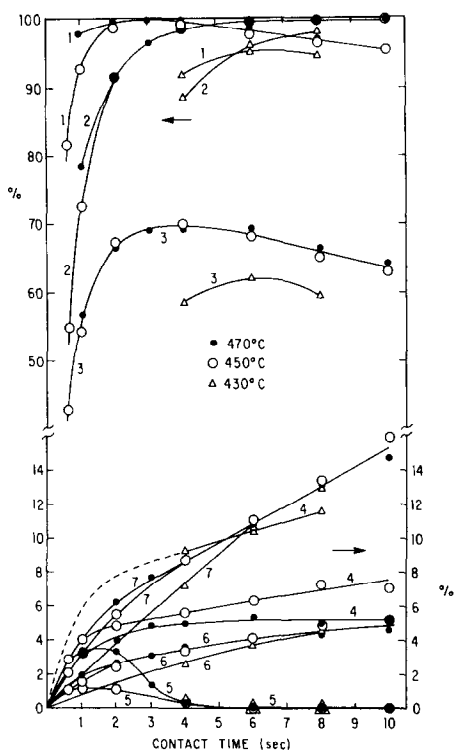Similar results were obtained in the other

FIG. 8. Propylene and ammonia consumptions and conversions vs contact time at 0 psig for pure $Pb_{0.88}Bi_{0.08}\phi_{0.04}MoO_4$. Feed composition and numbers on this figure are the same as for Fig. 7.

FIG. 9. Rate constant for propylene consumption vs defect concentration in the $Pb_{1-3x}Bi_{2x}\phi_x MoO_4$ system. No diluent or support was used, and the feed gas was 5% NH_3, 4% C_3H_6, 10% O_2, and 81% N_2.

were nominally $Pb_{0.92}Ce_{0.04}\phi_{0.04}MoO_4$, and $Pb_{0.88}Ce_{.08}\phi_{0.04}MoO_4$ gave conversions to acrylonitrile of 10% and 13%, respectively.

Other Systems

We have also prepared (4) defect scheelites of the type $Bi_{1-x}\phi_x V_{1-3x}Mo_{3x}O_4$ and $Bi_{1-x}\phi_x$-$V_{1-3x}W_{3x}O_4$. The former, but not the latter, type have also been prepared by Cesari

$A^{2+}_{1-3x}Bi_{2x}\phi_x MO_4$ systems. $PbWO_4$, $CdMoO_4$, and $CaMoO_4$ were all inactive for propylene ammoxidation; however, when defects and bismuth were introduced, good catalytic activity and selectivity were observed. $Cd_{0.87}B_{0.087}\phi_{0.043}MoO_4$, $Ca_{0.7}Bi_{0.2}\phi_{0.1}MoO_4$, and $Pb_{0.82}Bi_{0.12}\phi_{0.06}WO_4$ gave conversions to acrylonitrile of 57%, 52%, and 63%, respectively.

The results were quite different when the phases were free of bismuth. Although $Ca_{0.870}Y_{0.087}\phi_{0.043}MoO_4$ gave a propylene consumption of three times that of $CaMoO_4$ under the same conditions, the activity is still very low compared to the bismuth containing defect scheelites. Furthermore, most of the propylene consumed was converted to CO_2. $Pb_{0.870}La_{0.087}\phi_{0.043}MoO_4$ is definitely a better catalyst than $PbMoO_4$. Still only a 5% conversion of propylene to acrylonitrile was obtained, and again this is very poor compared to the bismuth containing phases. Cerium containing phases which
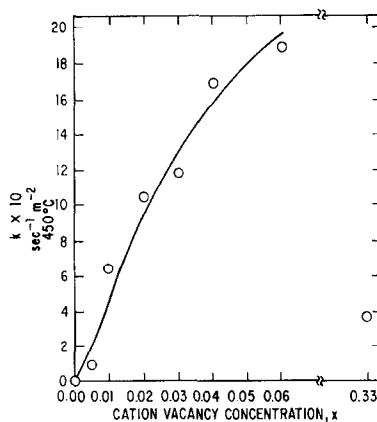
TABLE 1
Complex Phases

Composition	Conversion[a] to acrylonitrile (%)
$Pb_{0.91}Bi_{0.06}\phi_{0.03}Mo_{0.5}W_{0.5}O_4$	73
$Pb_{0.455}Ca_{0.455}Bi_{0.06}\phi_{0.03}MoO_4$	60
$Pb_{0.455}Ca_{0.455}Bi_{0.06}\phi_{0.03}Mo_{0.5}W_{0.5}O_4$	62
$Pb_{0.44}Ca_{0.44}Bi_{0.08}\phi_{0.04}MoO_4$	73
$Pb_{0.44}Sr_{0.44}Bi_{0.08}\phi_{0.04}MoO_4$	67
$Pb_{0.88}Bi_{0.08}\phi_{0.04}Mo_{0.5}W_{0.5}O_4$	76
$Pb_{0.68}Ag_{0.10}Bi_{0.18}\phi_{0.04}MoO_4$	70
$Pb_{0.834}Na_{0.083}Bi_{0.083}MoO_4$	10
$Pb_{0.852}Na_{0.042}Bi_{0.085}\phi_{0.021}MoO_4$	64
$Pb_{0.425}Na_{0.19}Y_{0.24}Bi_{0.08}\phi_{0.065}MoO_4$	50
$Na_{0.38}Y_{0.5}Bi_{0.04}\phi_{0.08}MoO_4$	33
$Pb_{0.5}Bi_{0.5}V_{0.5}Mo_{0.5}O_4$	1.6
$Pb_{0.79}Bi_{0.173}\phi_{0.037}Mo_{0.9}V_{0.1}O_4$	41
$Bi_{0.98}\phi_{0.02}V_{0.47}As_{0.47}Mo_{0.06}O_4$	35

[a] Conditions were 450°C, 4.0 sec time constant, and a feed gas of 4.0% C_3H_6, 4.8% NH_3, 47.7% air and 43.5% N_2.

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et al. (*5*). We find that $BiVO_4$, i.e., $x = 0$, is relatively ineffective as a propylene ammoxidation catalyst to produce acrylonitrile; however, $Bi_{0.97}\phi_{0.03}V_{0.91}Mo_{0.09}O_4$ is a very active catalyst giving conversions to acrylonitrile as high as 71%.

The conversions to acrylonitrile of several more complex phases are presented in Table 1. Good yields are obtained when bismuth and defects are present; otherwise, the yields are low.

DISCUSSION

We have studied many different defect scheelite systems for the oxidation and ammoxidation of propylene. Catalytic activity has consistently increased with increasing defect concentration. This, of course, does not necessarily indicate that such defects are required for selective oxidation over other catalysts. For example, the bismuth molybdate catalysts presumably do not have large concentrations of such defects. However, the defect scheelites are systems where the catalytic properties can be systematically varied by varying the concentrations of bismuth and defects. Such systems should then be of great value for future mechanistic studies. Furthermore, such studies might lead to a rational approach to superior catalysts.

Bismuth must be present in these defect scheelites for high activity and selectivity. Very small amounts, e.g., as in $Pb_{0.985}Bi_{0.010}$-$\phi_{0.005}MoO_4$, have a big effect. However, the bismuth concentration at the surface may be significantly greater than in the bulk. This is in fact, probable for a defect phase. Scheelites with high Bi concentrations but no defects (e.g., $Na_{.5}Bi_{.5}MoO_4$ and $BiVO_4$) are generally not good acrylonitrile catalysts. The active site for catalysis would therefore appear to be a defect in the vicinity of a bismuth cation. From electrostatic considerations, bismuth cations should tend to prefer to be neighbors of a defect. The roles of bismuth and molybdenum in selective oxidation catalysts have been discussed at great length (*6*), and we will not add to that discussion at this time. The possible role of the cation vacancy would be to extract a proton from an olefin to form the well-established allyl intermediate. Such a defect

should offer considerable stabilization to a surface hydroxyl group.

We find that tungstate defect scheelites are nearly as good catalysts as the molybdates. This is in sharp contrast to the bismuth tungstates which are very inferior to the bismuth molybdates as selective oxidation catalysts (*7, 8*). The reason for this contrast may be that bismuth molybdates generally contain tetrahedral molybdenum whereas the bismuth tungstates contain octahedral tungsten. In the scheelites, however, the molybdenum and tungsten are tetrahedrally coordinated by oxygen, and this seems to be favorable for selective oxidation. This would suggest that part of the mechanism for the oxidation or ammoxidation involves an expansion of the Mo or W coordination. Such a coordination change would be easy for tetrahedral Mo or W, but very unlikely for octahedral Mo or W. (Low-temperature Bi_2MoO_6 is an excellent olefin oxidation catalyst where the Mo in the bulk is octahedral but where the surface coordination of Mo might be tetrahedral.)

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