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## Scheelite: A Versatile Structural Template for Selective Alkene Oxidation Catalysts

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The scheelite ( $\text{CaWO}_4$ ) structure type serves as the framework for a wide variety of metal oxide catalysts used for the selective oxidation and ammoxidation of alkenes. Among the industrially important processes where these catalysts find application are propylene oxidation to acrolein, propylene ammoxidation to acrylonitrile and butene oxidative dehydrogenation to butadiene. This review examines the body of work used to understand the structure-function relationship of bismuth molybdate scheelite catalysts in selective ammoxidation of propylene to acrylonitrile including the work on the unique bismuth-cerium molybdate solid solution series of selective ammoxidation catalysts.

## 1. Introduction: scheelite structures

A scheelite-structured oxide catalyst, bismuth molybdate, was the basis for the first catalyst discovered and commercialized for selective alkene (amm)oxidation. Acrylonitrile is produced by the so-called SOHIO Process which is the heterogeneously catalyzed reaction of propylene, ammonia and air in a fluid-bed reactor using bismuth molybdate as the catalyst.<sup>1</sup> The process was discovered, patented<sup>2</sup> and commercialized in the first plant in Lima Ohio in 1960. Some of the early fundamental studies of scheelite-structured mixed-metal oxide as selective oxidation catalysts were based on solid solution series of model compounds. This initial work was reviewed by Sleight in the 1970s.<sup>3,4</sup> Since then further studies<sup>5,6</sup> of the structure-function relationship of these materials has yielded new fundamental insights into the solid state structural characteristics and mechanistic aspects that make this class of oxides ubiquitous as selective oxidation catalysts.

The discovery of the bismuth molybdate catalyst and its application in both propylene ammoxidation to acrylonitrile and then oxidation to acrolein initiated an entirely new field for technology development and catalyst design.<sup>7</sup> Multiple generations of catalysts were created and commercialized in the ensuing years. Albeit bismuth molybdate exists in three structural phases, it is the  $\alpha$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  phase that is shown to be the most effective in terms of activity and product yield.<sup>8-10</sup> And so invariably, each generation of bismuth molybdate-based selective (amm)oxidation catalyst had one critical feature in common - the active component responsible for the activation and transformation of propylene to acrolein or acrylonitrile (in the presence of ammonia) was the  $\alpha$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  phase whose structure is derived from that of the mineral scheelite  $\text{CaWO}_4$ .

Although the surface structure and composition of any metal oxide catalyst may differ from that of the bulk, for the purposes of catalyst design and development of better catalysts, the premise is valid that the nature of the surface, and thus the catalytically active site, is materially influenced by the structure and composition of the underlying phase from which it is derived. Thus characterization of the bulk structure of metal oxide catalysts has proven over time to be core to any successful effort to both understand and design improved catalysts for commercial use.

The ideal scheelite structure<sup>11,12</sup> has a tetragonal unit cell with space group  $I4_1/a$  (Figure 1). The general formula is  $\text{ABO}_4$ , where  $\text{A}^{2+}$  is a large cation which is 8-coordinated by oxygen, and  $\text{B}^{6+}$  is a small cation which is tetrahedrally coordinated by oxygen. There are 4 such formula units in the unit cell. Typical divalent A cations that form the ideal scheelite structure include calcium and lead while the hexavalent B cations are molybdenum and tungsten. The incorporation of a trivalent cation into the divalent cation site of normal scheelite (empirical formula  $\text{ABO}_4$ , based on  $\text{CaWO}_4$ ) produces a defect structure containing cation vacancies in order to maintain electro-neutrality.<sup>13-15</sup> The trivalent scheelite crystallizes in a superstructure featuring several (typically 3 or 9) primitive scheelite unit cells arranged in a supercell with monoclinic symmetry. The resulting monoclinic structure has large cation sites distinguished by a local environment that consists of vacant cation sites as well as other large cations. Specifically, the resulting empirical formula is  $\text{A}_2\Box(\text{BO}_4)_3$ , where  $\Box$  indicates a cation vacancy. The defect structure retains the scheelite packing arrangement but with one third of the large cation sites vacant.

Three distinct structural variants exist for defect scheelite  $\text{A}_2\Box(\text{BO}_4)_3$  as represented by their respective parent compounds:  $\text{Bi}_2\Box\text{Mo}_3\text{O}_{12}$  (space group  $\text{P}2_1/c$  see Figure 2)<sup>16</sup>,  $\text{La}_2\Box\text{Mo}_3\text{O}_{12}$  (space group  $\text{C}2/c$  see Figure 3)<sup>17</sup> and  $\text{Eu}_2\Box\text{Mo}_3\text{O}_{12}$  (space group  $\text{C}2/c$ ).<sup>18</sup> Each structure type is characterized by a unique ordering of the trivalent cations and cation vacancies on the A site in the  $\text{ABO}_4$  scheelite structure. In the case of bismuth molybdate, there are three scheelite subcells per unit cell and the cations and vacancies are uniquely ordered within the scheelite structure framework in such way as to give rise to tetrahedral pairs of  $\text{Mo}_2\text{O}_8$  groups.<sup>14</sup> This specific ordering is driven by the asymmetric nature of the  $\text{Bi}^{3+}$  cation with its directionally oriented lone pair of electrons in a hybridized orbital having p character.<sup>19</sup> This lone pair effect dictates the cation size exhibited by  $\text{Bi}^{3+}$  relative to other large trivalent cations such as lanthanum.<sup>20</sup> This is an important factor to take into account in the case of solid solutions that contain bismuth. When the lone pair character of  $\text{Bi}^{3+}$  is constrained in a site,  $\text{Bi}^{3+}$  will appear smaller than  $\text{La}^{3+}$  in the same structure. This typically can occur when the lattice site is highly symmetrical and the presence of nearest neighbor atoms inhibits distortion or expansion of the lattice site occupied by bismuth. However, when  $\text{Bi}^{3+}$  lone pair character dominates, then  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  appear to be similar in size. This occurs when the lattice site is asymmetric and allows for distortion to accommodate the bismuth lone pair. For the other two structure types, the cation and vacancy ordering are a consequence of the relative size ( $\text{La}^{3+} \geq \text{Bi}^{3+} > \text{Eu}^{3+}$ ) absent asymmetry for trivalent lanthanum and europium cations compared to bismuth. Therefore, in the case of scheelite molybdate solid solutions the relative size of these large trivalent cations and the lone pair effect of  $\text{Bi}^{3+}$  are expected to impact materially the features (including cation/vacancy site occupancy and ordering) of the bulk and thus also the surface structures. These effects will, in turn, govern any catalytic properties of such mixed metal molybdates.

## 2. Bismuth molybdate based scheelite catalysts

### 2.1 $\alpha$ - $\text{Bi}_2\Box\text{Mo}_3\text{O}_{12}$

The commercially most important and the most studied of the scheelite structure selective oxidation catalysts is  $\alpha$ -bismuth molybdate. From studies of the catalytic properties of this single phase, most of the essential components of the surface and solid state mechanisms of selective alkene oxidation catalyst have been determined. The rate determining step in the case of

propylene oxidation and ammoxidation over bismuth molybdate is  $\alpha$ -hydrogen abstraction to form the symmetric allyl intermediate followed by sequential oxygen (or nitrogen from ammonia) insertion and further hydrogen abstraction producing acrolein or acrylonitrile, respectively. This mechanism was initially developed by Adams and Jennings<sup>21</sup> and then further expanded by Burrington.<sup>22</sup> An additional mechanistic requirement that must be considered involves the lattice oxide ions of the catalyst<sup>23</sup> according to the Mars and van Krevelen<sup>24</sup> mechanism. This mechanism is greatly influenced by the solid state structure and redox chemistry of the oxide catalyst. Therefore, the key solid state structural characteristics for a successful selective oxidation catalyst are:

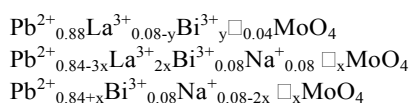
1. Lattice oxide ions having the optimal metal-oxygen bond strength to effect single insertion of oxygen (or NH from ammonia) into the allylic intermediate.
2. Rapid restructuring of the reduced active site through facile migration of oxide ions from the bulk to the surface active for regeneration of the active site.
3. Separate surface sites for reduction of oxygen, incorporation of the oxide ion into the lattice and transport of this oxide ion through the lattice to be available for regeneration of the surface hydrocarbon activation site.

For  $\alpha$ -bismuth molybdate, the structure appears to be a propitious template that integrates both the cations necessary for the hydrocarbon activation and transformation (e.g. bismuth and molybdenum) with the characteristics necessary for redox activity.<sup>9</sup> However, another important characteristic that needs to be taken into account is an understanding of any linkage between the solid state features of the defect (i.e. cation vacancy) scheelite structure extant with  $\alpha$ -bismuth molybdate and its catalytic behavior.

## 2.2 Role of bismuth and cation vacancies

The first attempt to discern a possible catalytic role for structural vacancies using the scheelite structural template examined the solid solution series  $A^{2+}_{1-3x}Bi^{3+}_{2x}\square_xMoO_4$   $0 \leq x \leq 1/3$  having the ideal  $CaWO_4$  structure with divalent cations ( $A^{2+}$ ) of the correct ionic size substituting for calcium to create a controlled concentration of cation vacancies in the structure.<sup>25,26</sup> Using the solid solution series  $Pb^{2+}_{1-3x}Bi^{3+}_{2x}\square_xMoO_4$  as catalysts for the selective ammoxidation of propylene to acrylonitrile, it was found that the catalytic activity increased sharply by isomorphous substitution of bismuth for lead in the single phase scheelite  $PbMoO_4$  structure and the concomitant formation of cation vacancies in the structure as shown in Figure 4. The same finding was made using the single phase solid solution series  $Na^{+}_{0.5-3x}Bi^{3+}_{0.5+x}\square_{2x}MoO_4$   $0 \leq x \leq 1/6$  with catalytic activity increasing abruptly with the addition of bismuth to  $Na_{0.5}Bi_{0.5}MoO_4$  and the commensurate creation of cation vacancies. The conclusion the authors drew from this study was that cation vacancies were responsible for the rate determining  $\alpha$ -hydrogen abstraction from propylene to form an allylic intermediate. This was proposed to be accomplished by the ability of cation vacancies to stabilize the surface hydroxyl groups formed from hydrogen abstraction from propylene. However, what was lacking in these first studies was the recognition that in all cases bismuth was present when high yields were achieved because the formation and amount of cation vacancies was concomitant with the amount of bismuth in the structure. Thus, it was not possible from the solid solution series selected for these initial studies to independently determine the catalytic role of cation vacancies from that of bismuth.

In order to decouple the presence of bismuth and cation vacancies and independently assess their catalytic roles, the activity for propylene ammoxidation to acrylonitrile was compared using the following scheelite single phase solid solution series as catalysts<sup>27</sup>:



The results, also shown in Figure 4, clearly demonstrate that both bismuth and cation vacancy concentration affect activity for conversion of propylene to acrylonitrile. However, key is the observation that in the absence of bismuth, vacancies alone will not result in the selective conversion of propylene to acrylonitrile. The catalytic behavior of the bismuth-free single phase scheelite solid solution  $Pb^{2+}_{1-3x}La^{3+}_{2x}\square_xMoO_4$  has only limited catalytic activity with no discernible trend with the concentration of cation vacancies presence. Thus, in the absence of bismuth, the presence of cation vacancies is not sufficient to provide selective transformation of propylene to acrylonitrile to the extent that occurs when bismuth is also present. Clearly then high yield to the allylic product acrylonitrile is proportional to the amount of bismuth present, not the presence of cation vacancies alone. This establishes again that bismuth is a necessary constituent of the active site responsible for the rate determining  $\alpha$ -hydrogen abstraction step, directly or indirectly.

## 2.3 Redox promotion: $Bi_3FeMo_2O_{12}$

As mentioned previously, in the ongoing development of commercially competitive catalysts for industrial application in propylene ammoxidation to acrylonitrile and propylene oxidation to acrolein/acrylic acid, the catalytically active phase for multicomponent catalysts is bismuth molybdate, present in its scheelite  $\alpha$ - $Bi_2\square Mo_3O_{12}$  form. In the development of these

multiphasic, multicomponent mixed metal oxide catalysts, iron was among the first identified as, and continues to be, an essential promoter additive.<sup>7</sup>

An iron containing scheelite bismuth molybdate single phase with the composition  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$  was first synthesized and characterized and found to have the scheelite crystal structure with a unique and very specific cation substitution arrangement.<sup>28,29</sup> Unconventionally, trivalent iron incorporates into the scheelite bismuth molybdate structure through substitution for molybdenum while for charge balance additional bismuth fills the normally vacant cation sites. This results in a non-defect  $\text{ABO}_4$  scheelite with the stoichiometry  $\text{Bi}(\text{Fe}_{1/3}\text{Mo}_{2/3})\text{O}_4$ . Two polymorphs are evident with this phase. One has the iron and molybdenum ordered on the B site. The other has iron and molybdenum randomly occupying the B site. The monoclinic superstructure formed by the ordered structure consists of three scheelite subcells. Iron is trivalent in the structure and since it substitutes into the B site occupied by molybdenum, it is tetrahedrally coordinated by oxygen. All four oxygens bound to iron are shared with molybdenum and/or bismuth in the structure which is expected to be beneficial for lattice oxygen transfer and redox activity in the Mars-van Krevelen catalytic cycle for hydrocarbon oxidation. The evidence of the redox promoting effect of iron incorporation into the scheelite bismuth molybdate structure is the observation that the rate of oxidation as measured by the oxidative dehydrogenation of 1-butene to butadiene was observed to be three times greater for the iron-substituted scheelite.<sup>30</sup> In addition, this phase has in fact been specifically identified in a patent disclosure<sup>31</sup> as a beneficial component of a complex mixed metal oxide catalyst for the selective oxidation and ammoxidation of an alcohol and/or alkene for the production of unsaturated nitriles, aldehydes or olefins including the production of acrylonitrile by propylene ammoxidation.

From the perspective of the chronology of the design and development of heterogeneous selective oxidation catalysts, the  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$  phase is the first explicit example of co-incorporation of a redox active element (i.e.  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ ) with the catalytically active cations (i.e.  $\text{Bi}^{3+}$  and  $\text{Mo}^{6+}$ ) into a single phase structure. This fact manifestly exemplifies the versatility of the scheelite phase as a structural template for, in this case, catalytic materials.

#### 2.4 Redox promotion: $\text{Bi}_x\text{Ce}_{2-x}\square\text{Mo}_3\text{O}_{12}$

Cerium-doped bismuth molybdate having the stated composition of  $\text{Bi}_9\text{CeMo}_{12}\text{O}_{52}$  was first studied and reported as an effective catalyst for selective ammoxidation of propylene.<sup>32</sup> Further advanced and patented for commercial application in the 1980s,<sup>33</sup> bismuth-cerium molybdate has become a ubiquitous constituent of complex multicomponent catalyst designed for commercial application.<sup>34-38</sup> It was found that the scheelite structure with bismuth and molybdenum can accommodate another redox active element, cerium, but in a much different way than iron is as discussed above. This work examined a significantly broad composition range covering the entire defect scheelite stoichiometry,  $\text{Bi}_x\text{Ce}_{2-x}\square\text{Mo}_3\text{O}_{12}$  with  $0 \leq x \leq 2$ . A phase diagram was constructed showing that two solid solutions exist across this composition range. One solid solution consists of cerium dissolved in the  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$  structure for  $x$  greater than about 1.8. The second solid solution having bismuth dissolved in the cerium molybdate structure when  $x$  is less than about one. The enhanced catalytic activity was attributed to the presence of the  $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$  redox couple in the presence of the catalytically necessary  $\text{Bi}^{3+}$  responsible for rate determining  $\alpha\text{-H}$  abstraction of adsorbed propylene. The incorporation of this redox couple into both the surface and the bulk structure facilitates lattice oxygen transfer to the bismuth-containing active site as required by the operative Mars-van Krevelen mechanism for selective propylene ammoxidation. In addition to the example of the  $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$  phase discussed above, this is analogous to the redox promotion observed by redox active iron in the solid solution series  $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$  that coexists with the  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$  phase in multiphasic molybdate selective oxidation catalysts. However, in the case of the  $\text{Bi}_x\text{Ce}_{2-x}\square\text{Mo}_3\text{O}_{12}$  solid solution series, the redox active promoter, cerium, is incorporated in the same phase as the catalytically active component, bismuth, rather than as a separate phase that must then interact with the catalytically active bismuth-containing phase through a synergistic mechanism such as surface wetting/spreading of phases or even structural epitaxy.<sup>39</sup> From the perspective of catalytic efficacy and simplicity, the single phase form of the catalyst is typically preferred when possible.

Both bismuth-cerium molybdate solid solutions exhibit high catalytic activity for the selective ammoxidation of propylene to acrylonitrile at the compositions corresponding to the phase boundaries where the solubility limits of cerium in bismuth molybdate and bismuth in cerium molybdate occur. These specific compositions maximize the number of neighboring bismuth and cerium cations in a single phase structure. This provides the optimum interaction between these two critical components to create a more effective catalytic site for selective activation and oxidative transformation of propylene than a site having only bismuth as occurs with  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$ .

X-ray and neutron diffraction analyses along with Rietveld data analysis were used to characterize of a solid solution of cerium in  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$  having the nominal composition of  $\text{Bi}_{1.8}\text{Ce}_{0.2}\text{Mo}_3\text{O}_{12}$  which corresponds to the low cerium solubility limit in the phase diagram.<sup>41</sup> The results confirm previous work that a solid solution is formed in which cerium occupies a portion of the bismuth cation sites of the  $\text{A}_2\square(\text{BO}_4)_3$  defect scheelite structure. However, cerium preferentially occupies one of the two A cation sites as well as occupying a portion of the vacancies giving the following stoichiometry for site occupancy  $(\text{Bi}_{0.94}\text{Ce}_{0.03})_a(\text{Bi}_{0.88}\text{Ce}_{0.12})_b(\text{Ce}_{0.04})_c\text{Mo}_3\text{O}_{12}$  where “a” and “b” are the two A sites in  $\alpha\text{-Bi}_2\square\text{Mo}_3\text{O}_{12}$  and “c” is the cation vacancy site. The apparent reason for this site preferences is that coordination sphere of the “a” site is distorted in such a way that it can more readily accommodate the bismuth lone pair than that present in the distorted coordination sphere of the “b” site as shown in



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Figure 5. Thus, the more symmetric  $Ce^{3+}$  cation mostly occupies the uniform coordination sphere of the “b” cation site in the structure.

The most recent advance in the understanding and application of the scheelite structure to the design of catalysts for selective alkene (amm)oxidation is the cerium-rich solid solution phase of the mixed metal oxide  $Bi_xCe_{2-x}Mo_3O_{12}$  series.<sup>41</sup> This new generation of acrylonitrile catalysts is a marked structural and chemical variant of those based originally on the  $\alpha$ - $Bi_2Mo_3O_{12}$  active phase. Characterization of this solid solution series typically would presume a random distribution of the trivalent cations across all the trivalent the cation sites of the scheelite-derived structure. This is suggested by the systematic change in unit cell volume as function of the Bi/Ce content (See Table 1). However, as seen with structural analysis of the cerium-doped bismuth molybdate, a similar cation substitution mechanism occurs with the cerium-rich solid solution as well that presumably is a reason for its enhanced catalytic properties. Based on Rietveld analysis of diffraction data collected using laboratory and synchrotron X-ray sources, bismuth preferentially occupies one of the three crystallographically distinct sites in the cerium molybdate structure as shown in Table 2. This single phase series is, thus, not a conventional solid solution. The site preferentially occupied by bismuth is designated Ce(3) in the La/Ce molybdate structure based on the cation occupancy determination from Rietveld analysis.

It is, thus, possible to describe the catalytically active center for this unique solid solution series taking into account that the site preference for bismuth is driven by need to accommodate its lone pair of electrons by being next to a vacant cation site as shown as shown in Figure 6. The function of bismuth in the catalytic redox cycle is promoted by having a redox active element in a neighboring structural site that serves as a shuttle for lattice oxidation pursuant to the Mars-van-Krevelen mechanism. This is expected to promote reoxidation/reconstruction of the bismuth active site in the catalytic cycle. This active site structure can serve as a basis for a new class of selective olefin oxidation catalyst with the promise of higher activity, yield, productivity and longer catalyst life and stability in commercial operation compared to current state-of-the art catalysts.

### 3 Conclusions

Numerous structural types of metal oxides have been examined as classes of solid state materials for a wide range of applications in addition to catalysis. These other applications include solid oxide ion conductors, high temperature superconductors and ceramics among many others.<sup>42</sup> In the case of selective oxidation and ammoxidation of alkenes, two structural types stand out as the basis for the most efficient and commercially applied: scheelite molybdate, and rutile antimonate. Based on patent citations for catalysts used in the manufacture of acrylonitrile from propylene, the majority of patents claim the former indicating its greater commercial interest.<sup>43</sup> Both scheelite bismuth molybdate and rutile iron antimonate are used commercially as admixtures of multiple metal oxides which act in various ways to promote these catalytically active phases.<sup>7</sup> Bismuth molybdate-based selective oxidation catalysts have proven to be highly amenable to improvement by chemical promotion which is attributable to the unique structural features of the defect scheelite structure discussed above. One can then expect that its potential for commercial application, including further enhancements for acrylonitrile production from propylene, will grow and extend to areas of alkane oxidation and ammoxidation (propane oxidation to acrylic acid and ammoxidation to acrylonitrile), alkenes from alkanes (propane oxidative dehydrogenation to propylene) and commercially advantaged catalytic processes for manufacture of butadiene from butene and butane feedstocks.

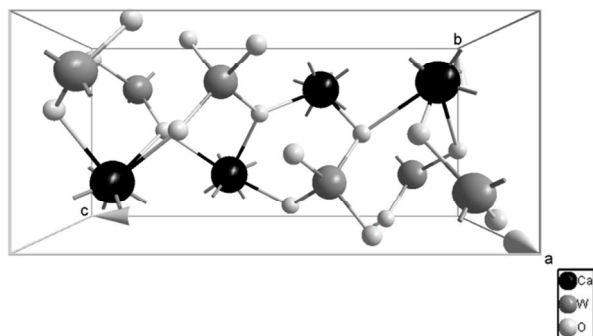


Figure 1.  $CaWO_4$  scheelite structure.

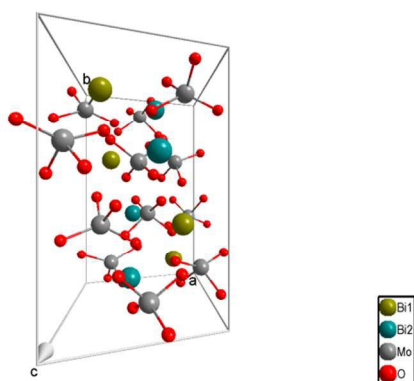
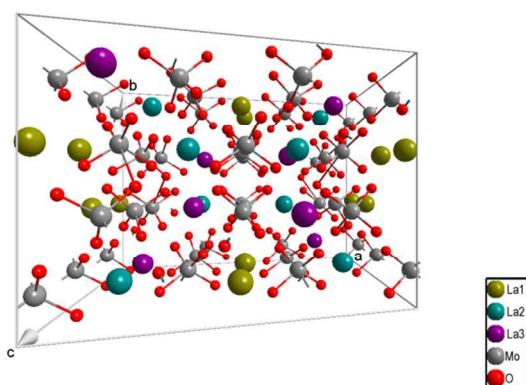
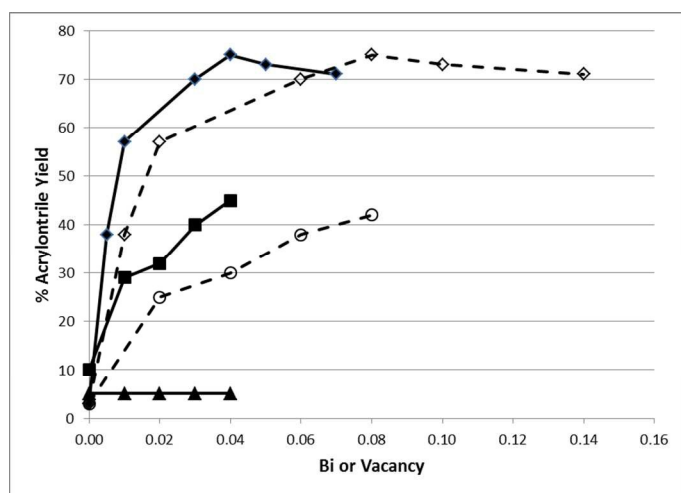
Figure 2.  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  scheelite-derived structure.Figure 3.  $\text{La}_2\text{Mo}_3\text{O}_{12}$  scheelite-derived structure.

Figure 4. Acrylonitrile yield from propylene for various defect scheelite molybdates catalysts. Solid = Vacancy; Open = Bismuth for:

(◇)  $\text{Pb}^{2+}_{1-3x}\text{Bi}^{3+}_{2x}\square_x\text{MoO}_4$ ; bismuth and vacancy varied

(○)  $\text{Pb}^{2+}_{0.88}\text{La}^{3+}_{0.08-y}\text{Bi}^{3+}_y\square_{0.04}\text{MoO}_4$ ; bismuth only varied

(□)  $\text{Pb}^{2+}_{0.84-3x}\text{La}^{3+}_{2x}\text{Bi}^{3+}_{0.08}\text{Na}^+_{0.08}\square_x\text{MoO}_4$ ; vacancy only varied

(△)  $\text{Pb}^{2+}_{1-3x}\text{La}^{3+}_{2x}\square_x\text{MoO}_4$ ; vacancy only varied/no bismuth present

Source of data: References (1, 2, 25-27).

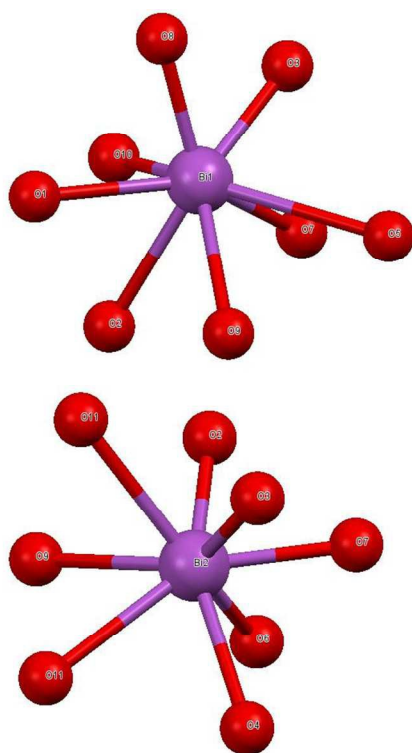


Figure 5. Site coordination of the “a” Bi(1) and “b” Bi(2) site coordination spheres of  $\text{Bi}_{1.8}\text{Ce}_{0.2}\text{Mo}_3\text{O}_{12}$ .



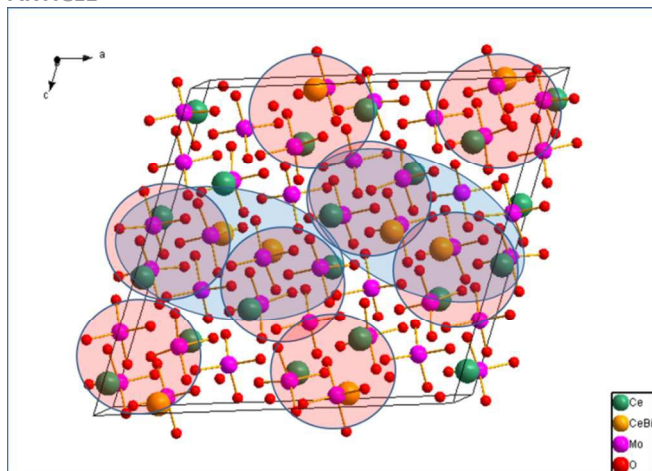


Figure 6. Model of active sites for propylene ammoxidation in bismuth-cerium molybdate solid solution having the cerium molybdate structure. Source: Reference (41) with permission.

Table 1. Summary of unit cell parameters for the series  $\text{Bi}_x\text{Ce}_{2-x}\text{Mo}_3\text{O}_{12}$   $0 \leq x \leq 2$ .

x	$\text{Ce}_2\text{Mo}_3\text{O}_{12}$ phase					$\text{Bi}_2\text{Mo}_3\text{O}_{12}$ phase				
	a (Å)	b(Å)	c(Å)	$\beta$ in degree	cell volume (Å <sup>3</sup> )	a (Å)	b(Å)	c(Å)	$\beta$ in degree	cell volume (Å <sup>3</sup> )
0.25	16.8858(5)	11.8397(3)	15.9858(5)	108.528(2)	3,030.27(13)					
0.5	16.8715(4)	11.8440(3)	15.9604(5)	108.645(2)	3,021.92(13)					
0.75	16.8698(5)	11.8377(3)	15.9430(6)	108.813(2)	3,013.71(17)					
1	16.8732(6)	11.8250(4)	15.9306(6)	108.988(2)	3,005.61(17)	7.674(1)	11.573(2)	11.924(2)	114.74(1)	961.7(2)
1.25	16.8686(6)	11.8348(4)	15.9239(6)	108.982(2)	3,006.11(17)	7.690(0)	11.574(1)	11.925(1)	114.91(0)	962.6(1)
1.5	16.8508(9)	11.8295(5)	15.9583(9)	109.068(4)	3,006.52(19)	7.697(0)	11.564(0)	11.940(0)	115.04(0)	962.9(0)
1.75	16.8648(32)	11.8229(18)	15.9757(28)	109.178(13)	3,008.62(65)	7.704(0)	11.551(0)	11.952(0)	115.19(0)	962.5(0)

Table 2. Lattice parameters and site occupancies from Rietveld refinement of synchrotron X-ray diffraction data.

Composition	a (Å)	b(Å)	c(Å)	$\beta$ in degree	Ce(1) (frac)	Ce(2) (frac)	Ce(3) (frac)	cell volume (Å <sup>3</sup> )
$\text{Bi}_{0.5}\text{Ce}_{1.5}\text{Mo}_3\text{O}_{12}$	16.8762(2)	11.8402(4)	15.9742(9)	108.679(1)	1	1	0.778	3023.79(2)

## ARTICLE

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**Notes and references**

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