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Bismuth Molybdate-Based Catalysts for Selective Oxidation of Hydrocarbons

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Abstract

Bismuth molybdate materials (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6) are well-known in the field of catalysis due to their excellent activity for one of the most important industrial processes: the oxidation/ammoxidation of lower olefins. These processes play an important role in society since the production of one quarter of the most important industrial organic chemicals and intermediates (such as acrolein, acrylic acid, propylene oxide, etc.) used in the manufacture of industrial products and consumer goods is based on these reactions. Although the materials were developed since the 1960s, the topic still attracts many attentions; new catalysts with different additive elements to enhance catalytic activity are still explored. Advanced researches on bismuth molybdate-based catalysts have been performed not only with the change in composition but also in the synthesis methods. This book chapter summarizes recent researches on the development of bismuth molybdate-based catalysts with new achievements in catalysis field.

Keywords: selective oxidation, hydrocarbons, catalysts, bismuth molybdates, reaction mechanism

1. Introduction

Since they were developed by SOHIO company in 1959, bismuth molybdates have received a large attention owing to their high selectivity and activity for partial oxidation and ammoxidation of lower olefins to essential intermediate products for industrial applications. Aspects of these compounds such as structure, catalytic property, conductivity, etc. have been thoroughly investigated. Most studies are concentrated on the catalytic property of bismuth molybdates. Here, the reactions, the mechanism, and all related aspects have been explored

although there are still a lot of controversies. Among many other selective oxidation catalysts, bismuth molybdates are the most extensively studied and serve as the basis for today's many highly active and selective commercial catalyst systems [1]. There are many kinds of bismuth molybdates with different Bi/Mo atomic ratios, but those which have been quite thoroughly investigated and exhibit good catalytic properties are in the range of composition Bi/Mo = 2/1–2/3.

Three phases of bismuth molybdates, α, β, and γ, exhibit good catalytic properties for oxidation of propylene. Their catalytic activities decrease in the following generally accepted order, $Bi_2Mo_2O_9$ (β) $\geq Bi_2Mo_3O_{12}$ (α) $> Bi_2MoO_6$ (γ), which is reported by many authors [1–5]. However, there are some authors who reported the opposite trend: $\gamma \geq \beta > \alpha$ [6, 7], $\beta > (\alpha = \gamma)$ [8], $\alpha > \beta > \gamma$ [9].

Catalysts based on bismuth molybdates can be divided into the following components:

Primary bismuth molybdate system: These catalysts are mixed oxide constituted from Bi_2O_3 and MoO_3 at specified ratios as mentioned above.

Multicomponent bismuth molybdate system: These catalysts were developed by the modification of primary bismuth molybdates by replacing or adding other metal elements. The first replacement of half of the amount of the bismuth molybdate by iron in $Bi_9P_1Mo_{12}O_{52}$ increased the catalytic activity for the ammoxidation of propylene noticeably. The Bi-Fe-Mo-O system consists of several different composite oxides including bismuth molybdate, iron molybdate, and $Bi_3FeMo_2O_{12}$. Following this improvement, divalent transition metal cations such as Co^{2+} and Ni^{2+} were also found to enhance the catalytic activity and selectivity significantly [4].

The catalyst $Bi_{1-x/3}\phi_{x/3}V_{1-x}Mo_xO_4$, which form a solid solution with composition limits of bismuth vanadate, x = 0, and the α phase of bismuth molybdate, x = 1, attracted many attentions [10, 11] since it is a good system to investigate the diffusion of lattice oxide. The participation of the lattice oxide ion into the reaction is quite prominent in this catalyst system, but the degree of the participation depends on the catalyst composition.

2. Phase diagram of bismuth molybdates

To understand on the bismuth molybdate catalysts, it is necessary to explore the phase diagram of this system since three catalytic active phases of bismuth molybdates exhibit some unique properties. The phase diagram established by Egashira et al. (**Figure 1**) [12] is the most well known in literature. In this phase diagram, three main phases of bismuth molybdates can be found.

2.1. The Scheelite (α) phase

This phase has the nominal composition $Bi_2Mo_3O_{12}$ (written in short as the 2/3 phase). The α phase forms a eutectic with MoO_3 at 615°C and at 71 atom% Mo:

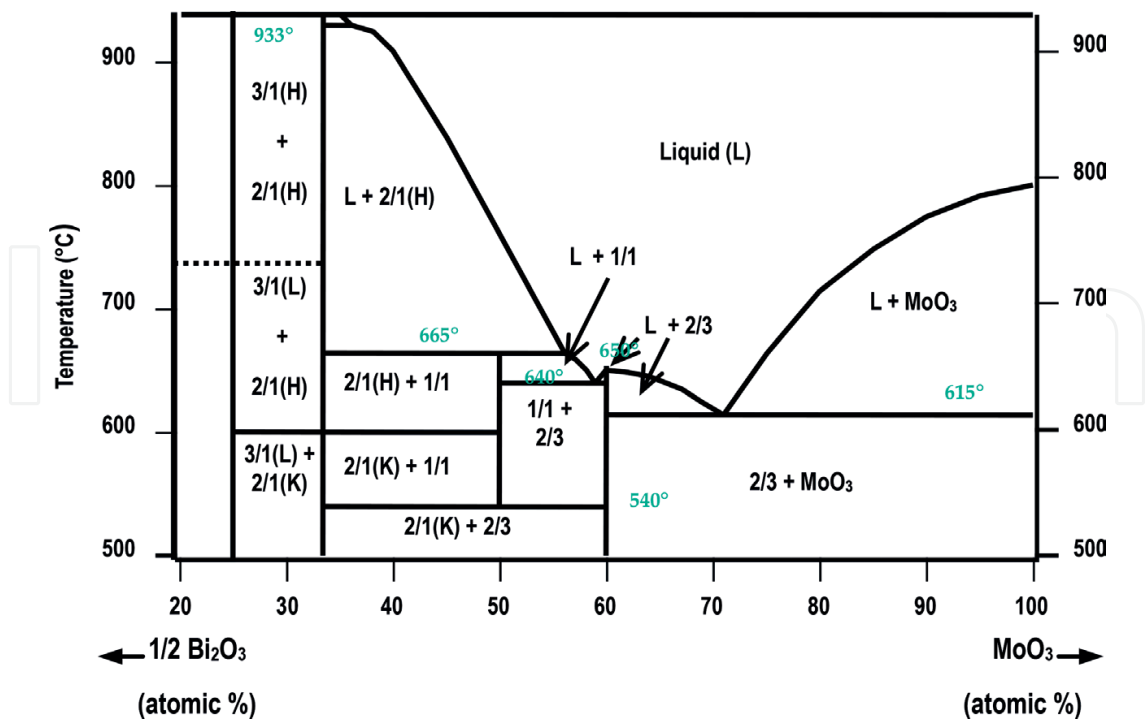$$\text{liq.} \rightarrow Bi_2Mo_3O_{12} + MoO_3 \tag{1}$$

Figure 1. Phase diagram for the bismuth molybdate system by Egashira [12].

The α phase also forms a eutectic with 1/1 at 640°C and at 59 atom% Mo:

$$\text{liq.} \rightarrow \text{Bi}_2\text{Mo}_3\text{O}_{12} + \text{Bi}_2\text{Mo}_2\text{O}_9 \tag{2}$$

The α phase has been reported to be stable in a large temperature range between room temperature and 650°C [13]. The α phase congruently melts at 650°C.

The α phase has a monoclinic structure (a = 0.789 nm, b = 1.170 nm, c = 1.224 nm, β = 116°20′) which was related to the Scheelite-type structure with space group P21/c.

2.2. The Erman (β) phase

This phase has the nominal composition $\text{Bi}_2\text{Mo}_2\text{O}_9$ (written in short as the 1/1 phase). The β phase is only stable in the relatively narrow temperature range of 665–540°C. The β phase is formed by the peritectic reaction of liquid MoO_3 with the high-temperature form of the γ phase at 665°C:

$$\text{MoO}_3\,(\text{liq.}) + \text{Bi}_2\text{MoO}_6\,(\text{H}) \rightarrow \text{Bi}_2\text{Mo}_2\text{O}_9 \tag{3}$$

but disproportionates into 2/1 (K) and 2/3 below 540°C:

$$2\,\text{Bi}_2\text{Mo}_2\text{O}_9 \rightarrow \text{Bi}_2\text{MoO}_6\,(\text{K}) + \text{Bi}_2\text{Mo}_3\text{O}_{12} \tag{4}$$

However, since the rate of reaction (Eq. 4) is very low, $\text{Bi}_2\text{Mo}_2\text{O}_9$ can exist even at room temperature as a metastable phase. There are two metastable modifications: β' and β'' [14].

The β phase of bismuth molybdate which was first identified by Erman et al. [14] has an ortho-rhombic crystal structure with lattice parameters: a = 1.079 nm, b = 1.189 nm, c = 1.186 nm, and space group Pnmm or Pnm21.

2.3. The Koechlinite (γ) phase

This phase has the nominal composition Bi_2MoO_6 (written in short as the 2/1(K) phase). The high-temperature modification of this phase is indicated by γ′ - Bi_2MoO_6 (2/1(H)). The intermediate metastable polyform between γ and γ′ is γ″ (or 2/1(I)). The formation of Bi_2MoO_6 (H) from liquid is also due to a peritectic reaction as in the case of the β phase. The solid which takes part in this reaction is indicated to be the high-temperature form of $3Bi_2O_3 \cdot 2MoO_3$ (3/1):

$$MoO_3 \text{ (liq.)} + 3Bi_2O_3.2MoO_3 \text{ (H)} \rightarrow 3\left[Bi_2O_3 . MoO_3(H)\right] \tag{5}$$
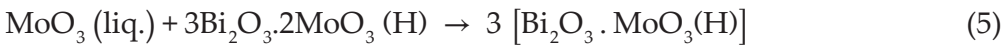
The high-temperature phase Bi_2MoO_6 (H) is transformed into Bi_2MoO_6 (K) at 600°C, but the rate of this transition is low so that Bi_2MoO_6 (H) can exist even at room temperature [12, 15].

Earlier reports by Zemann and Aykan [16, 17] showed that the crystal structure of natural koechlinite, Bi_2MoO_6, was orthorhombic, a = 0.550 nm, b = 1.624 nm, c = 0.549 nm, and space
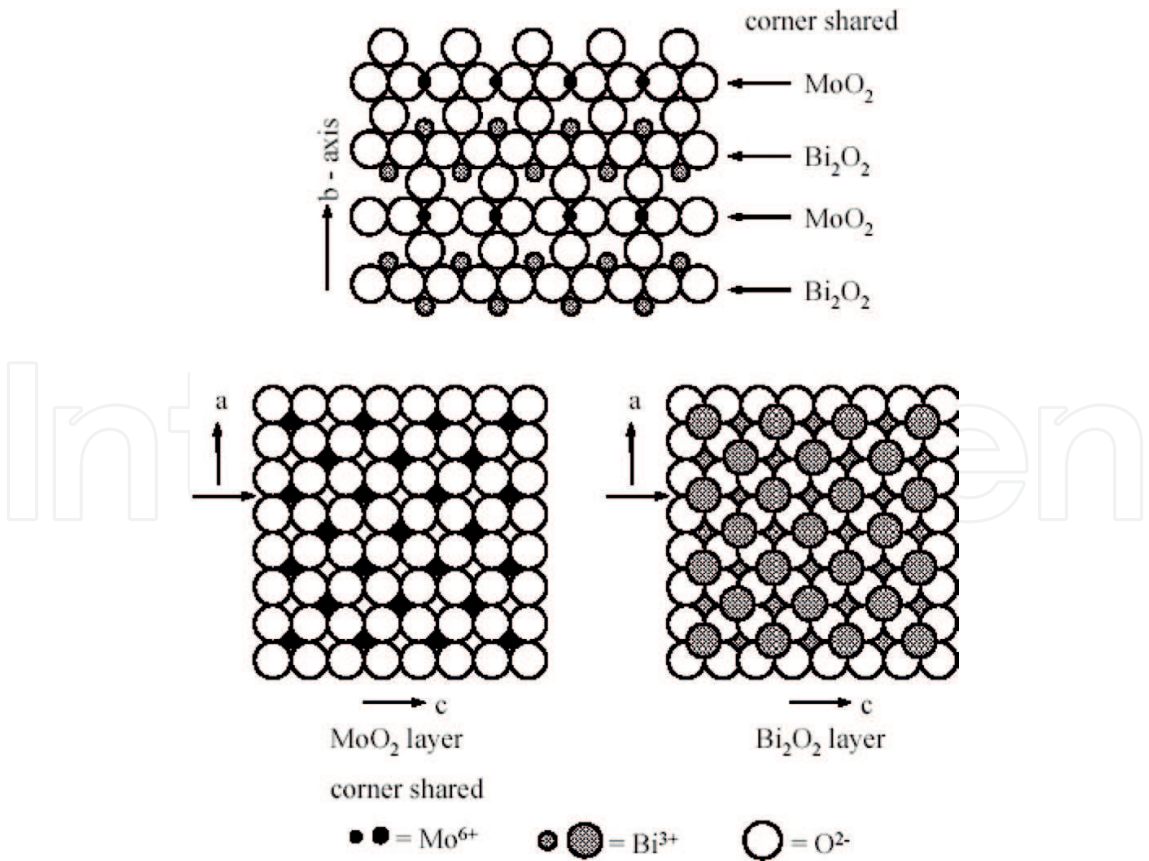

Figure 2. Layered structure of Bi_2MoO_6 [19].

group Cmca (D2h18); Van den Elzen and Rieck [18] reported the same lattice parameters but different space groups: Pca21.

The structure was described as alternate layers of $(BiO^+)_{2n}$ and $(MoO_4^{2-})_n$ perpendicular to the y direction. The $(MoO_4^{2-})_n$ layer consists of deformed oxo-molybdenum octahedra, sharing four corners with neighboring oxo-molybdenum octahedra in the same layer perpendicular to the y direction. The molybdenum-oxygen bond distances in such a layer can be divided in two classes, the first with bond lengths of approximately 0.224 nm. The two other apical ions of the oxo-molybdenum octahedra point toward a $(BiO^+)_{2n}$ layer, one below and one above.

Thus, if a $Bi_2O_2^{2+}$ = B layer and a MoO_2^{2+} = A layer, in crystals they will be connected via layers of oxygen anions denoted by O. Schematically, therefore, the schemata of three bismuth molybdate phases can be written as the following [8]:

- α phase=(BOAOAOAO)m.
- β phase=(BOAOAO)m.
- γ phase=(BOAO)m.

The structure of the γ phase can be seen in **Figure 2** [19]. The position of bismuth and molybdenum atoms in the unit cell is shown together with their bonds to oxygen.

3. Synthesis of bismuth molybdates

Bismuth molybdates can be obtained via different methods, for example, co-precipitation [9, 20], solid-state reaction [21], spray drying [22–24], hydrothermal [25, 26], solution combustion [27], and solgel route [28].

3.1. Co-precipitation

The most popular method to prepare bismuth molybdates is co-precipitation. Almost all authors [7, 29, 30] follow this method although there are some modifications. The starting reactants are typically a solution of $Bi(NO_3)_3.5H_2O$ in water, a suitable quantity of HNO_3, and a solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ in water. The solution of bismuth nitrate is added to ammonium molybdate or vice versa. pH is adjusted in the range of about 1–9 by adding NH_3 or HNO_3, depending on each author. The precipitate is filtered and dried or the liquid is directly evaporated. Some other modifications of precipitation synthesis use $Bi(NO_3)_3.5H_2O$ and H_2MoO_4 or $BiONO_3.H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ as starting materials [7, 31]. Precipitates are calcined at some given temperature, normally from 450 to 580°C.

3.2. Solid-state reaction

Another conventional method to prepare bismuth molybdate is a solid-state reaction from mixtures of bismuth oxide and molybdenum oxide powders [12, 29, 32] or a mixture of $Bi(NO_3)_3.5H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ powders [33] at the temperature range of 500–650°C.

3.3. Solgel

This method is used by a few authors. Godard et al. [28] prepared bismuth molybdates by a citrate-based method from aqueous solutions of Bi^{3+} and Mo^{6+} and citric acid in equivalent amounts. Wildberger et al. [34] used an alkoxide method to prepare bismuth molybdates supported by titania. The gelation occurs at low temperatures and results in amorphous materials with unique morphology and extraordinary dispersion of the active compound. Bismuth molybdates are obtained by calcining these materials at about 500°C.

Solgel method was considered as an effective pathway to afford pure phases of these catalysts. However, it requires acidic conditions in general, which is harsh and less suitable for practical applications [28]. A solgel synthesis of bismuth molybdates as thin film has been reported at quite neutral pH conditions [35], but the synthesis proved to be effective at different pH values. However, at neutral and basic pH conditions, it turns difficult to obtain pure phases of bismuth molybdates. The gelation process is considered to be entirely different at pH 1 and 5. With increasing content of bismuth, the formation of the impure Bi_2O_3 phases turns more difficult to be avoided. Among different catalysts, sample $Bi_2Mo_3O_{12}$ synthesized at pH 5 displayed high conversion and selectivity. Additionally, it can be synthesized in more convenient manner, making it suitable for the applications in practical technical processes [36].

3.4. Hydrothermal method

The hydrothermal method has been applied to prepare bismuth molybdates by Beale and Sanka [37, 38]. Stoichiometric amounts of acidified bismuth nitrate solutions were mixed with ammonium heptamolybdate dissolved in ammonium hydroxide. The pH of this mixture was adjusted to a specific range (2–6) before introducing this mother liquor into a Teflon-lined autoclave. The autoclave was placed in a preheated furnace (140°C) for several hours. After a specific period (20 h), the contents were washed and dried. Thus, this method requires very low temperatures (except the β phase which needs to be calcined further at 560°C) and results in high surface area (9–10 m^2/g).

3.5. Spray drying

As known, bismuth molybdates can be prepared by conventional methods such as precipitation and solid-state reaction, which have been used for long and are widely applied for laboratory scale and industrial processes. However, pure bismuth molybdates prepared by conventional methods are not often obtained, and all commercial oxidation catalysts are multiphase [39].

Spray drying was applied to synthesize many multi-metal oxides, which exhibit good characteristics [40]. Homogeneity, stoichiometry, uniformity of product size, hardness, and abrasiveness are advantages of spray drying. Spray drying can be applied to replace conventional synthesis methods, which opens interesting industrial applications. To synthesize bismuth molybdates, the precursor solution for spray drying was prepared from a solution of $(NH_4)_6Mo_7O_{24}$ and a solution of $Bi(NO_3)_3$ with the addition of few milliliters of concentrated

HNO_3 in order to keep the Bi-salt dissolved. This precursor solution was spray dried using a laboratory spray dryer with a reasonable nozzle and feeding rate at a suitable temperature (about 200°C). Spray drying is one of the best methods to prepare pure phases of bismuth molybdates. It is a versatile method which is able to prepare mixtures of bismuth molybdates with desired Bi/Mo ratio in accordance with the phase diagram, which is very useful for preparing mixed catalysts with higher activity than the pure one owing to the synergy effect. Spray drying confirmed its reputation as a reliable method for the synthesis of pure catalysts [41]. Therefore, the XRD patterns of the spray drying bismuth molybdate samples with different Bi/Mo ratios (**Figure 3** [42]) are considered as the standard to determine the phase composition of these compounds.

3.6. Solution combustion

The solution combustion synthesis is a quite simple method and presents several advantages. It is based on highly exothermic redox chemical reactions between metallic compounds and nonmetallic ones. The first step of the solution combustion synthesis is the preparation of an aqueous solution of suitable metal salts, e.g., nitrates (bismuth nitrate, ammonium molybdate), because of their high solubility in water and the oxidizing potential of NO_3^- groups. An organic molecule such as urea, glycine, hydrazine, or precursors containing a carboxylate anion is then added to form complexes with the metal ions. The organic molecule works as a fuel as its combustion enables to release a huge amount of heat in a short period of time. The
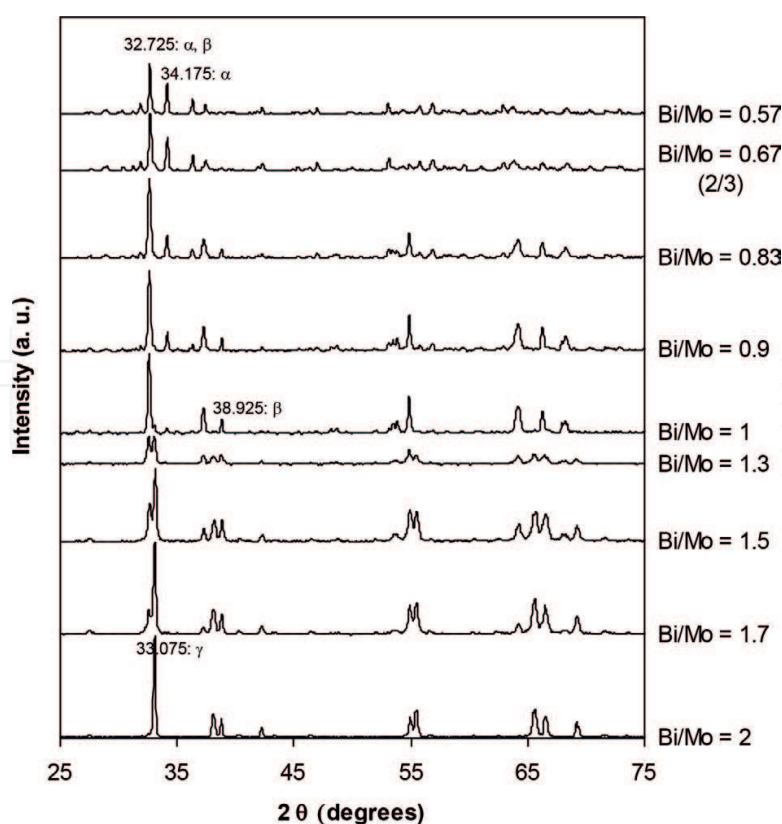

Figure 3. XRD patterns of bismuth molybdate samples with 0.57 < Bi/Mo < 2 [42].

final solution is then heated until reaching temperatures in the range of 300–450°C for a very short residence time to avoid sintering, which brings the solution to ebullition. The resulting mixture then becomes dry and in a matter of minutes ignites that sets off highly exothermic, self-sustaining, and fast redox reactions that generate a dry, usually crystalline, fine powder. The obtained powders can be calcined or not since the uncalcined powders are crystallized well already. The products possess a relatively high specific surface area. The rapidity of the method may also allow the formation of metastable phases [27, 43–46].

4. Selective oxidation of light hydrocarbons on catalysts

Selective oxidation and ammoxidation of hydrocarbons play an important role in society since the production of one quarter of the most important industrial organic chemicals and intermediates used in the manufacture of industrial products and consumer goods is based on these reactions [55]. Hence, they contribute significantly to the gross national products of industrial countries and afford future opportunities for developing countries. They also present opportunities for significant fundamental research.

The selective oxidation of light hydrocarbons, especially propylene, is the most significant and well-studied process. Its products include important intermediates such as acrolein, acrylic acid, propylene oxide, etc. The catalytic process was first discovered in 1948 by Hearne and Adams [47] with the use of cuprous oxide catalysts. In 1959 and in 1962, Idol [48] and Callahan [49], respectively, improved the yield of the reaction with the discovery of bismuth molybdate catalysts. Shortly after that, this process was industrialized by SOHIO company and has then been developed and improved year by year by this company [3]. Drastic and empirical changes have been introduced to the catalyst composition and preparation as well as to the reaction process. As a result, the reaction yield has been increased over the past 40 years from 50% to over 80% [50].

4.1. Reaction and products

Since selective oxidation of propylene is the most popular process among those of other light hydrocarbons, it is chosen to be described here as an example. The product of the reaction, acrolein, is formed from propylene in a two-step process through the allylic alcohol intermediate (**Figure 4**). The second step is more exothermic ($\Delta H = -195.5$ kJ, mol^{-1}) than the first one
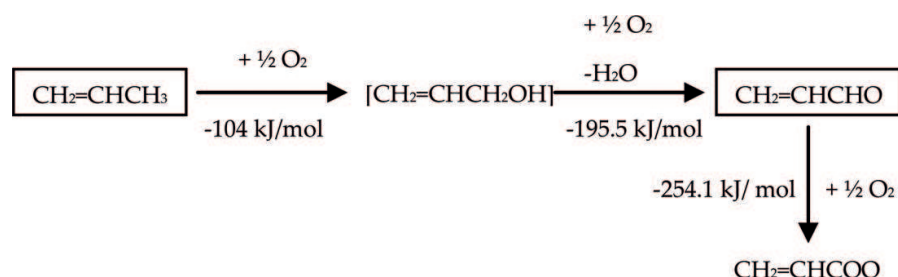

Figure 4. Reaction pathway of the selective oxidation of propylene.

($\Delta H = -104$ kJ mol^{-1}), probably due to the stabilization energy of the conjugated electronic system of acrolein [4].

By-products of this reaction are acrylic acid and carbon oxides in addition to minor products such as acetaldehyde, acetic acid, formaldehyde, and polyacrolein. The yield of acrylic acid is only 10% mol, while the yield of acrolein is more than 70%. If acrylic acid is to be obtained, it must be synthesized from the oxidation of acrolein in a second-stage reactor with a different catalyst [51]. Carbon oxides are the products of the complete oxidation of acrolein or acrylic acid as well as parallel complete oxidation of propylene [52]. Acetaldehyde and formaldehyde formation during the reaction is due to the oxidative breaking of the propylene C=C bond:

$$CH_3CH = CH_2 + O_2 \rightarrow CH_3CHO + CH_2O \tag{6}$$
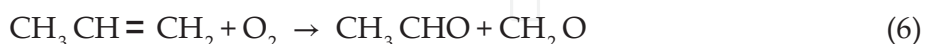
Acetaldehyde and formaldehyde can also be oxidized further [4].

In the industry, the reaction is carried out in a fluidized bed reactor to facilitate the heat transfer and allow good temperature control, which is important for maintenance of selectivity. The silica support provides mechanical stability for the catalyst in the abrasive environment of the fluidized bed. Pressures are low (about atmospheric) and temperatures are in the range 400–500°C [5].

4.2. Catalysts

Catalysts which exhibit above properties for selective oxidation are usually mixed systems in which transition metal oxides of group B (most often Mo or V) are combined with oxides of groups IVA, VA, and VIA (Bi, Sb, Sn, P, Te) or group VIIIB (Fe, Co, Ni). Favored structures are scheelites, fluorites, rutiles, trirutiles, pyrochlores, and perovskites. Industrial catalysts contain as a rule small amounts of promoters: alkali or alkaline earth metals are commonly reported in the catalyst formula, and several other elements of variable valency and rare earth metals can be also found therein.

These catalysts can be divided into following system:

• Antimonate system included (i) the uranium antimonate system based on USb_3O_{10} (UO_3 + Sb_2O_4) catalyst which was developed in 1966; (ii) the iron antimonate system, $Fe_{10}Sb_{25}Si_{50}$, consisting of the active components $FeSbO_4$, Sb_2O_4, and SiO_2; and (iii) the tin antimonate systems based on SbSnO which were studied since 1969 [53] and attracted attention during the 1980s [54]. Although the in-tank acrylonitrile yields of the above antimonate catalyst compositions are respectable, they do not measure up to the productivities of the best molybdate catalysts. In addition, the antimonate-based catalysts are much more fragile than the molybdate-based systems under commercial operation. Therefore, it is imperative to operate the antimonate systems under rigidly controlled operating conditions, in order to prevent possible plant upsets and irreversible reduction which leads to the destruction of the antimonate catalysts. In contrast, the later-generation molybdate-based catalysts are almost indestructible and can easily withstand inadvertently plant upsets, including severe reductions. It is for these reasons that the complex mixed metal molybdates are currently the industrially preferred catalysts for the ammoxidation of propylene to acrylonitrile [55].

- The cuprous oxide system: Cu_2O powder is obtained by CuO reduction at about 400°C. This system is more accurately defined as a multiphase (Cu-Cu_2O-CuO) system. Consequently, it has proven to be very difficult to characterize. The catalyst undergoes changes in its bulk chemical composition, activity, and selectivity during oxidation of propylene; therefore, its activity is less stable than the other catalyst system. Anyway, the simple oxide Cu_2O is reported to exhibit significant activity and selectivity and has been often chosen as a model catalyst for the determination of the involved reaction mechanism [4]. It was reported that catalytic activity of Cu_2O catalyst system is lower than that of bismuth molybdate catalysts; therefore, the Cu_2O catalyst is less popular [56].

- Bismuth molybdate system: Catalysts based on bismuth molybdates are the most efficient class of catalyst for oxidation and ammoxidation of propylene and olefin. They are also most thoroughly investigated. This system will be described more detailed in the next section.

4.3. Mechanism of the reaction

Mechanism of selective oxidation of propylene to acrolein over bismuth molybdate catalyst was proposed by Burrington et al. [54, 57] (**Figure 5**). Details about active sites are shown in **Figure 6**.

According to Burrington [57] and Grasselli [58], initial chemisorption of propylene occurs on molybdenum dioxo groups bridged to bismuth-oxygen group 1, followed by allylic abstraction by Bi oxygens to form a π-allyl complex 2, which then undergoes C–O bond formation resulting
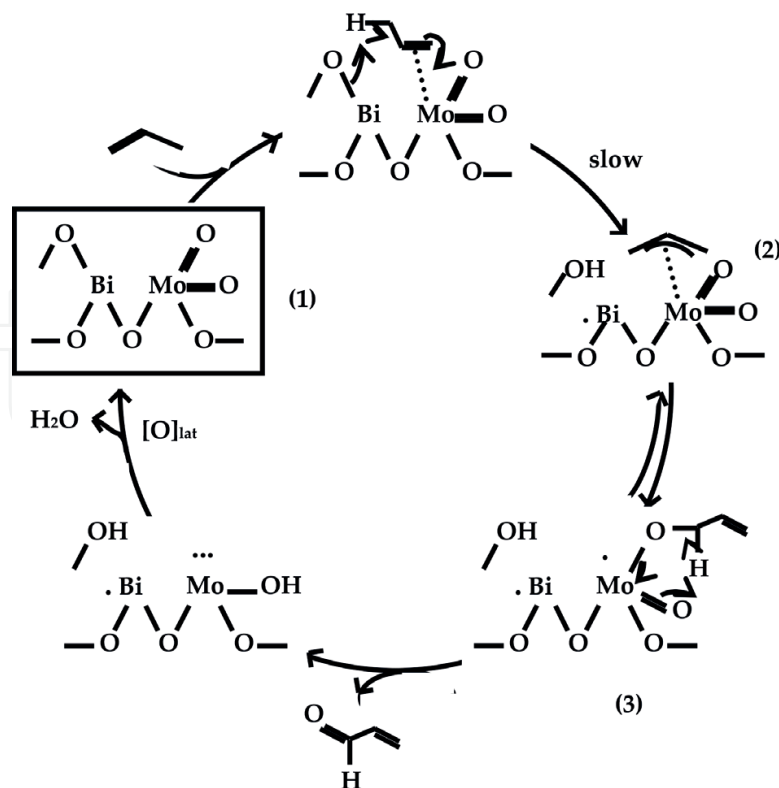

Figure 5. Mechanism of selective oxidation of propylene to acrolein over bismuth molybdate catalyst by Burrington et al. [57].
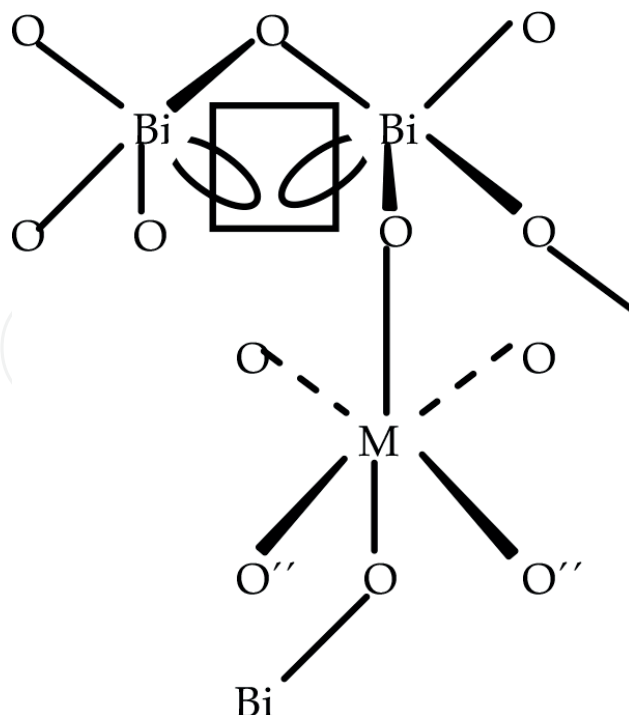
Figure 6. Schematic representation of the catalytic site for partial oxidation of propylene on Bi_2MoO_6 [58]. The oxygen designated O′ is believed to be responsible for the α-hydrogen abstraction; that designated O″, associated with Mo, is believed to be responsible for oxygen insertion into the allylic intermediate to give acrolein. Square (two lone pairs of electron associated with Bi–O–Bi surface groups) designates the center for O_2 reduction and dissociative chemisorption.

in a σ-O-allyl molybdate 3, the acrolein precursor, and Mo(V) analog to Mo(VI) esters formed from allyl alcohol and $Bi_2O_3.MoO_3$. Lattice oxygen removed from the catalyst during the surface oxidation of propylene to form acrolein must be replenished by gaseous oxygen in order to reconstitute the active site 1 and complete the redox cycle. Thus, the reaction occurs via a Mars and Van Krevelen mechanism in which propylene adsorbs reversibly and then reacts with an oxygen atom of the catalyst. This rate-limiting step leads to cleavage of one of the C–H bonds of the methyl group of the adsorbed propylene and results in the formation of an adsorbed OH group and a loosely adsorbed allyl radical that is rapidly stabilized as an adsorbed vinylalkoxide [59]. The sites for chemisorption and dissociation of gaseous oxygen molecule are spatially and structurally distinct from the active sites, at which adsorption and oxidation of propylene take places. These sites are singly coordinated unsaturated metal cations on the surface. These sites may reduce molybdenum cations because molybdenum is known to form various multivalent coordinate compounds containing oxygen and molybdenum is also stable in its lower valence states [60]. Therefore, the partially reduced catalysts are good catalysts (rule of "site isolation" [61]).

This mechanism can be applied to explain the difference in activity noted in the three phases of bismuth molybdates. The γ phase and Bi_2O_3 have too few chemisorption sites, while MoO_3 has no α-hydrogen abstracting sites, and, thus, these catalysts are the least active ones. The α and β phases have a favorable balance of these two sites necessary to effect the rate-determining first hydrogen abstraction. The multicomponent system possesses the greatest number of active surface sites having the proper structure and composition and a solid-state structure with the ability to rapidly reconstitute these surface sites with bulk lattice oxygen [1].

However, experiments using gaseous O^{18} showed that 16% of the lattice oxygen in the α phase and 100% of lattice oxygen in the γ phase were involved in the formation of both acrolein and carbon dioxide at 430°C [6]. On the other hand, the layer structure of γ phase results in low-energy pathways than the more closed parked structure of α phase so that oxygen anions can diffuse easier [1]; for example, in the reoxidation cycle, γ phase can be more active than the others. These may support for the opposite observation of some authors about the order of catalytic activity of three phases.

5. Catalytic properties of bismuth molybdate system

The most popular industrial catalysts for selective oxidation of propylene are based on multicomponent metal oxides containing mainly Bi/Mo(W)-O phases modified by various metal elements such as Fe, Co, and Ni. Commercial catalysts introduced by SOHIO for the ammoxidation of propylene to acrylonitrile are summarized in **Table 1** [50].

These commercial catalysts, however, were developed based on the fundamental researches on basic types of bismuth molybdate catalysts.

5.1. Catalytic activity of different primary bismuth molybdate phases

Three phases of bismuth molybdates, α, β, and γ, exhibit good catalytic properties for oxidation of propylene. Their catalytic activities decrease in the following generally accepted order: $Bi_2Mo_2O_9$ (β) $\geq$ $Bi_2Mo_3O_{12}$ (α) > Bi_2MoO_6 (γ). Although this order is reported by many authors [1, 2, 28, 60, 62], there are some papers in which the opposite trend is stated: $\gamma \geq \beta > \alpha$ [6, 7] or $\beta > (\alpha = \gamma)$ [8] or $\alpha > \beta > \gamma$ [9], $\beta > \alpha > \gamma$ [41], $\gamma > \alpha$ [63]. These reports, however, are not exhaustive, but it shows the large divergence of opinion. All these catalysts were not prepared in the same manner nor were the reaction conditions equivalent. In addition, some of the early results were reported on a per-gram basis and not per unit surface area. Some authors explain the higher activity of α and β phases compared to γ phase that α and β phases possess more molybdenum dioxo groups than γ phase does; for example, they possess more active sites for propylene chemisorption [41]. The higher activity γ phase compared to α phases was assigned for the facile oxygen mobility of γ [63]. Especially, the conflicting results on the activity of Bi_2MoO_6 found in the literature were explained by a surface enrichment with bismuth during prolonged calcination or reaction, resulting in a deactivation of the catalyst.

Year	Catalysts	Acrylonitrile yield (%)
1960–1963	$Bi_9PMo_{12}O_{52}/SiO_2$	55
1963–1965	$Bi_{4.5}Fe_{4.5}PMo_{12}O_{52}/SiO_2$	65
1969–1970	$K_{0.1}(Ni,Co)_9Fe_3BiPMo_{12}O_x/SiO_2$	75
1975–1991	$(K,Cs)_a(Ni,Co,Mn)_{9.5}(Fe,Cr)_{2.5}Bi/Mo_{12}O_x/SiO_2$	78–80
1992–1995	$(K,Cs)_a(Ni,Mg,Mn)_{7.5}(Fe,Cr)_{2.3}Bi_{0.5}Mo_{12}O_x/SiO_2$	>80

Table 1. Commercial catalysts introduced by SOHIO [50].

It was found that the activity and selectivity of Bi_2MoO_6 catalysts, in the selective oxidation of propylene to acrolein, are very sensitive to the presence of small amounts of excess bismuth. This excess leads to a surface enrichment with bismuth and thereby to a low-active and low-selective catalyst. However, such catalysts with a Bi/Mo slightly above 2 do show reasonable activities and selectivities after calcination at moderate temperatures and/or for a short period of time. These catalysts loose their activity after calcination at a higher temperature or for a longer period of time. This makes that the activity and selectivity of these catalysts are strongly dependent on the calcination time and temperature. The reasonable initial activities of catalysts with a Bi/Mo slightly above 2 are ascribed to relative low Bi/Mo ratios at parts of the surface after calcination for a short period of time. The excess bismuth merges with the active parts of the surface during calcination, leading to the deactivation of the catalyst. The sublimation of molybdenum from the catalyst may play a minor role in the deactivation process. The deactivated samples can be reactivated by reduction, while the activity of the active samples is hardly affected by reduction. This reactivation is a result of the formation of bismuth particles leading to a decrease in the Bi/Mo ratio at other parts of the surface. The deactivation during calcination and after reduction occurs at similar rates indicating that these deactivation processes are similar [64].

5.2. Synergy effect in the mixtures of bismuth molybdates

The synergy effect is expressed as the enhancement of the catalytic activity when two or three phases are present in the catalysts. One of the best-known examples of the synergy effect is the cooperation between α and γ phases obtained by chemical decomposition at about 540°C of the β phase [9, 65, 66]. However, types of cooperation and explanations offered are different among authors (**Table 2**).

In general, due to the presence of the synergy effect in the mixtures of bismuth molybdates, the catalytic activity of these catalysts may be influenced strongly if the samples are not pure bismuth molybdate phases (alpha, beta, or gamma, corresponding to Bi/Mo ratios of 2/3, 1/1, and 2/1, respectively). Samples with other Bi/Mo ratios (Bi/Mo ratios of 1.5, 1.3, etc.) even exhibited higher activity since they are mixtures of these bismuth molybdate phases. Thus, the catalytic activity of bismuth molybdate samples depends significantly on the Bi/Mo ratio of the samples. Catalytic activity of bismuth molybdate samples with different Bi/Mo ratio is presented in **Figure 7** [42].

The synthesis method also influences on the catalytic activity of bismuth molybdate catalysts since different synthesis methods may result in different purities of the catalysts and different surface areas. Samples synthesized by solid-state reaction and precipitation sometimes exhibit unexpected catalytic activity due to the formation of other unexpected bismuth molybdate phases and even MoO_3 or Bi_2O_3. Due to the presence of unexpected bismuth molybdate phases, the samples may possess the synergy effect which increase catalytic activity [68].

5.3. Multicomponent bismuth molybdate catalysts

Synergy effect in the mixtures of bismuth molybdate phases may be one of the reasons for the plentiful researches on multicomponent bismuth molybdates. Many different metals have been added to bismuth molybdate to increase their activities such as Fe, V, Ni, Sn, Zr, etc.
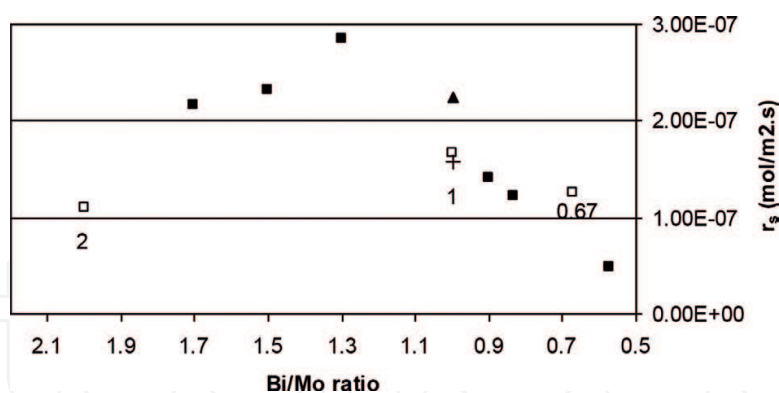
Figure 7. Reaction rate for acrolein formation of bismuth molybdates with Bi/Mo ratio from 0.57 to 2 (synthesized by spray drying): □, pure samples; ▲, Bi/Mo = 1 (47% γ, 47% α, 6% β); +, Bi/Mo = 1 (29% γ, 29% α, 42% β).

Multicomponent $Ni_xFe_3Bi_1Mo_{12}O_{42+x}$ catalysts were applied to the oxidative dehydrogenation of C_4 raffinate-3 to 1,3-butadiene. Conversion of n-butene, selectivity for 1,3-butadiene, and yield for 1,3-butadiene over $Ni_xFe_3Bi_1Mo_{12}O_{42+x}$ catalysts showed volcano-shaped curves with respect to nickel content. Among the catalysts tested, $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ showed the best catalytic performance. The conversion of n-butene was increased with increasing surface acidity of the catalyst. The largest surface acidity of the $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst was responsible for its enhanced catalytic performance in the oxidative dehydrogenation of C_4 raffinate-3. The facile oxygen mobility of the Bi_2MoO_6 phase in the $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst also played an important role in enhancing the catalytic performance of the $Ni_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst [69].

Bismuth molybdenum titanium oxides containing 14 or 25 wt% of bismuth molybdate were prepared in a highly dispersed state by the solgel method. Their catalytic performance in propene oxidation to acrolein was studied. The increase in activity of BiMoTi oxides in propene

Authors	Type of cooperation	Explanation
Matsuura et al. [62]	$\alpha + \gamma$ in n-C4 = ODH	Formation of a phase similar to β
Carson et al. [9]	$\alpha + \gamma$ in n-C3 = Ox	Decomposition of α or γ
Weng et al. [67]	α + various oxides in n-C4 = Ox	Action of spillover oxygen
Godard et al. [28]	$\alpha + \gamma$ in n-C4 = ODH	Dual role
Soares et al. [20]	$\beta + \gamma$ in selective catalytic oxidation of 1-butene	The high oxygen mobility in the lattice of the γ phase that allows the migration of oxygen species from the γ to the β phase
Le et al. [42]	$\alpha/\beta + \gamma$ in the selective oxidation of propylene to acrolein	High conductivity of $\gamma + \alpha/\beta$ possesses more active sites to absorb α-hydrogen atoms of propylene
Jung et al. [63]	$\alpha + \gamma$ in the oxidative dehydrogenation of C4 raffinate-3 to 1,3-butadiene	A combination of the facile oxygen mobility of γ and the abundant adsorption sites of α for n-butene

Table 2. Explanation given in the literature for the cooperative effects between bismuth molybdates.

oxidation as compared to that of bulk bismuth molybdate can be tentatively related to the stabilization of small aggregates of Bi- and Mo-containing phases due to the beneficial presence of the titania matrix. The catalytic performance of the samples is significantly depended on the crystal size of bismuth molybdate phase; an optimum size (23 nm) should exist to enhance the catalytic performance [70].

Several investigations have shown that the apparent activation energy for propylene oxidation to acrolein can be reduced by the replacement of Mo by V for catalysts maintaining a scheelite structure with the composition $Bi_{1-x/3}V_{1-x}Mo_xO_4$ (x = 0–1), which was first reported by Sleight et al. in the 1970s [71]. Cesari and coworkers also obtained this compound, which forms a solid solution with composition limits of bismuth vanadate (x = 0) and the α phase of bismuth molybdate (x = 1) [72]. The authors found that the V^{5+} ion in $BiVO_4$ can be replaced by Mo^{6+} until x = 1, forming cationic vacancies without changing its original structure. Catalytic activity for the reactions producing both acrolein and acrylonitrile in the oxidation or ammoxidation of propylene increases drastically with increasing concentration of cationic vacancies of $Bi_{1-x/3}V_{1-x}Mo_xO_4$. The lattice parameter changed regularly with x, and it was concluded that the replacement of vanadium by molybdenum atoms resulted in random vacancies of the bismuth cations in order to balance the difference in negative charges between the tetrahedral anion groups VO_4^{3-} and MoO_4^{2-}. The selectivity of the reaction is also improved with the degree of substitution to some extent [73]. It was also reported that the activation barrier for the rate-limiting step is well described by the band-gap of such catalysts, the activation energy decreases with the band gap [3]. Among the multicomponent metal oxide system $Bi_{1-x/3}V_{1-x}Mo_xO_4$, $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ exhibited the highest catalytic activity due to combining a high ability to adsorb propylene and abstract α-hydrogen to convert propylene to incomplete oxidized organic compounds while having a high conductivity to allow mobility of lattice oxygen [74].

Recently, an investigation of propylene oxidation was conducted over Bi, Mo, and V oxides having the aurivillius structure with the composition $Bi_4V_{2-x}Mo_xO_{11+x/2}$ (x = 0–1). The activity of the aurivillius structure was compared with oxides having the scheelite structure. The aurivillius-phase catalysts again show a correlation between the apparent activation energy and the band gap of the oxide, and the only difference being that for a given band gap is that the apparent activation energy for the aurivillius-phase catalysts is 1.5 kcal/mol higher than that of the scheelite-phase catalysts. This difference is attributed to the lower heat of propene adsorption on the aurivillius-phase catalysts. A further finding is that for catalysts with band gaps greater than 2.1 eV, the acrolein selectivity is 75% for the conditions used and independent of the propylene conversion. When the band gap falls below 2.1 eV, the intrinsic selectivity to acrolein decreases rapidly and then decreases further with increasing propylene conversion. This pattern shows that when the activity of oxygen atoms at the catalyst surface becomes very high, two processes become more rapid—the oxidation of the intermediate from which acrolein is formed and the sequential combustion of acrolein to CO_2 [59].

In the most recent work on multicomponent bismuth molybdate catalysts, other components including conductive materials (SnO_2, ZrO_2) and nonconductive materials (MgO) were added to beta-bismuth molybdates (β-$Bi_2Mo_2O_9$). Comparison of the catalytic activities of these samples showed that the addition of a suitable amount (10% mol) of SnO_2 improved
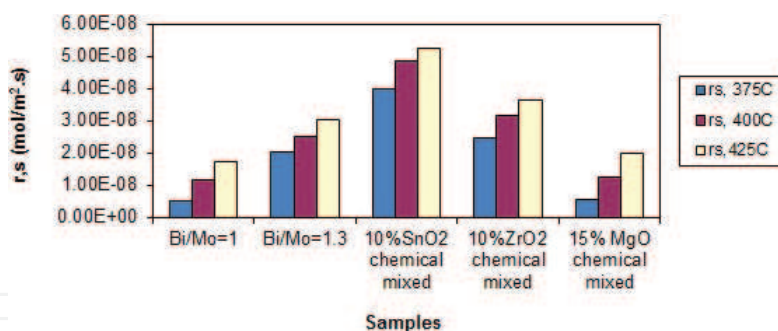
Figure 8. Comparison of the catalytic activities (reaction rates for acrolein formation based on catalyst surface area, r_s, mol/m²s) of different catalysts based on beta-bismuth molybdate with other oxides.

significantly the catalytic activity of beta-bismuth molybdate to an unprecedented high level for any known single bismuth molybdate catalyst phase or other highly active bismuth molybdate mixtures (bismuth molybdate with Bi/Mo ratio of 1.3). When adding ZrO_2 to beta-bismuth molybdate, the catalytic activity of the sample increases slightly. In contrast, adding MgO to beta-bismuth molybdate does not increase the catalytic activity of the samples (**Figure 8**). SnO_2 was found to exhibit much higher conductivity than ZrO_2, leading to bismuth tin molybdate catalyst also exhibiting high conductivity, while MgO is a nonconductive material. This is evidenced that the increase of the conductivity of the bismuth tin molybdate could be one of the reasons for the increase of their catalytic activity resulting in a synergy effect in its catalytic activity [75].

6. Conclusions

Although bismuth molybdate catalysts have been studied and developed for many years, nowadays, they still attract many research interests worldwide not only due to the importance of the chemical processes that they catalyze in industry but also due to the interesting aspects raised during the researches such as the involvement of lattice oxygen during the catalytic processes or the synergy effects occurring in the mixtures of bismuth molybdate phases. There are many factors influenced on the catalytic properties of these materials including synthesis methods and addition of other elements on the multicomponent systems. The recent studies show that the addition of Sn or V in the basic bismuth molybdate catalysts increase significantly or the mobility of lattice oxygen or the ability to adsorb α-hydrogen in reacted hydrocarbons and, thus, increase their catalytic activity. The increase of surface area of bismuth molybdate catalysts using advanced synthesis methods such as hydrothermal, solgel, and solution combustion also contributes on the increase of catalytic activity. Catalytic performance of the recently developed bismuth molybdate-based catalysts generally reaches to more than 80% conversion of hydrocarbons and 75% selectivity of the desired products. However, the wish to increase selectivity and yield of desired products in these popular chemical processes will still continue to attract worldwide researchers to study to improve catalytic performances of these popular catalyst compounds.

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References

[1] Grasselli RK, Burrington JM. Selective oxidation and ammoxidation of propylene by heterogeneous catalysis. Advances in Catalysis. 1981;**30**:133

[2] Keulks GW, Krenzke LD. Selective oxidation of propylene. Notermann TM. Advances in Catalysis. 1978;**27**:183

[3] Moro-oka Y, Ueda W. Multicomponent bismuth molybdate catalyst: A highly functionalized catalyst system for the selective oxidation of olefin. Advances in Catalysis. 1994;**40**:233-273

[4] Bettahar MM. On the partial oxidation of propane and propylene on mixed metal oxide catalysts. Applied Catalysis A: General. 1996;**145**:1

[5] Gates BC. Catalytic Chemistry. 1992. pp. 403

[6] Krenzke LD, Keulks GW. The catalytic oxidation of propylene: VI. Mechanistic studies utilizing isotopic tracers. Journal of Catalysis. 1980;**61**:316

[7] Batist PA, Bouwens JFH, Schuit GCA. Bismuth molybdate catalysts. preparation, characterization and activity of different compounds in the Bi- Mo- O system. Journal of Catalysis. 1972;**25**:1

[8] Batist PA, Der Kinderen AHWM, Leeuwenburgh Y, Metz FAMG, Schuit GCA. The catalytic oxidation of 1-butene over bismuth molybdate catalysts: IV. Dependence of activity on the structures of the catalysts. Journal of Catalysis. 1968;**12**:45

[9] Carson D, Coudurier G, Forissier M, Vedrine JC. Synergy effects in the catalytic properties of bismuth molybdates. Journal of Chemical Society, Faraday Transactions. 1983;**I**(79):1921

[10] Ueda W, Asakawa K, Chen CL, Moro-Oka Y, Ikawa T. Catalytic properties of tricomponent metal oxides having the scheelite structure: I. Role of bulk diffusion of lattice oxide ions in the oxidation of propylene. Journal of Catalysis. 1986;**101**:360

[11] Porta P, Jacono ML, Valigi M, Minelli G, Anichini A, De Rossi S, Gazzoli D. Structural, surface, and catalytic properties of bismuth molybdovanadates containing foreign atoms: I. X-ray characterization of iron-containing bismuth molybdovanadate catalyst. Journal of Catalysis. 1986;**100**:86

[12] Egashira M, Matsuo K, Kagawa S, Seiyama T. Phase diagram of the system Bi_2O_3. MoO_3. Journal of Catalysis. 1979;**58**:409

[13] Gates BC, Katzer JR, Schuit GCA. Chemistry of Catalytic Processes. 1st ed. New York: McGraw-Hill; 1979

[14] Erman LY, Gal'perin EL, Kolchin IK, Dobrzhanskii GF, Chernyshev KS. Russian Journal of Inorganic Chemistry. 1964;**9**:1174

[15] Snyder TP, Hill CG Jr. Stability of bismuth molybdate catalysts at elevated temperatures in air and under reaction conditions. Journal of Catalysis. 1991;**132**:536

[16] Zemann Journal of Structure Reports. 1948;**11**:305

[17] Aykan K. Reduction of Bi_2O_3. MoO_3 catalyst during the ammoxidation of propylene in the absence of gaseous oxygen. Journal of Catalysis. 1968;**12**:281

[18] Van den Elzen AF, Rieck GD. Redetermination of the structure of Bi_2MoO_6. Koechlinite-Acta Crystallographia, Section B. 1973;**29**:2436

[19] Van den Elzen AF, Rieck GD. The crystal structure of $Bi_2(MoO_4)_3$ Acta Crystallographia, Section B. 1973;**29**:2433

[20] Soares APV, Dimitrov LD, de Oliveira MC-RA, Hilaire L, Portela MF, Grasselli RK. Synergy effects between β and γ phases of bismuth molybdates in the selective catalytic oxidation of 1-butene. Applied Catalysis, A: General. 2003;**253**(1):191-200

[21] Rastogi RP, Singh AK, Shukla CS. Kinetics and mechanism of solid-state reaction between bismuth (III) oxide and molybdenum (VI) oxide. Journal of Solid State Chemistry. 1982;**42**(2):136-148

[22] Le MT, Van Well WJM, Van Driessche I, Hoste S. Influence of organic species on surface area of bismuth molybdate catalysts in complexation and spray drying methods. Applied Catalysis, A: General. 2004;**267**(1-2):227-234

[23] Schuh K, Kleist W, Høj M, Trouillet V, Jensenc AD, Grunwaldt J-D. One-step synthesis of bismuth molybdate catalysts via flame spray pyrolysis for the selective oxidation of propylene to acrolein. Chemical Communications. 2014;**50**(97):15404-15406

[24] Le MT, Van Well WJM, Van Driessche I, Hoste S. Spray drying, a versatile synthetic method to control purity in single phases and mixed phases of bismuth molybdates. Canadian Journal of Chemical Engineering. 2005;**83**(2):336-343

[25] Schuh K, Kleist W, Høj M, Trouillet V, Jensenc AD, Beato P, Jensen AD, Grunwaldt J-D. Bismuth molybdate catalysts prepared by mild hydrothermal synthesis: Influence of pH on the selective oxidation of propylene. Catalysts. 2015;**5**(3):1554

[26] Schuh K, Kleist W, Høj M, Trouillet V, Beato P, Jensen AD, Patzke GR, Grunwaldt J-D. Selective oxidation of propylene to acrolein by hydrothermally synthesized bismuth molybdates. Applied Catalysis A. 2014;**482**:145-156

[27] Farin B, Alessandro HA, Videla M, Specchia S, Gaigneaux EM. Bismuth molybdates prepared by solution combustion synthesis for the partial oxidation of propene. Catalysis Today. 2015;**257**(Part 1):11-17

[28] Godard E, Gaigneaux EM, Ruiz P, Delmon B. New insights in the understanding of the behaviour and performances of bismuth molybdate catalysts in the oxygen-assisted dehydration of 2-butanol. Catalysis Today. 2000;**61**(1-4):279-285

[29] Trifiro F, Hoser H, Scarle RD. Relationship between structure and activity of mixed oxides as oxidation catalysts: I. Preparation and solid state reactions of Bi-molybdates. Journal of Catalysis. 1972;**25**:12

[30] Grzybowska B, Haber J, Komorek J. The chemistry of Bi-Mo oxide catalysts: I. Phase composition of catalysts and its relation to the structure of precursors. Journal of Catalysis. 1972;**25**:25

[31] Boon L, Metselaar R. Electrical transport properties of beta-bismuth molybdate $Bi_2Mo_2O_9$. Journal of Solid State Inorganic Chemistry. 1990;**27**:381

[32] Buttrey DJ, Vogt T, White BD. High-temperature incommensurate-to-commensurate phase transition in the Bi_2MoO_6 catalyst. Journal of Solid State Chemistry. 2000;**155**:206

[33] Wragg RD, Ashmore PG, Hockey JA. Heterogeneous selective ammoxidation over bismuth molybdate catalysts. Journal of Catalysis. 1973;**31**:293

[34] Wildberger MD, Grunwaldt JD, Maciejewski M, Mallat T, Baiker A. Sol–gel bismuth–molybdenum–titanium mixed oxides I. Preparation and structural properties. Applied Catalysis A: General. 1998;**175**:11

[35] Le MT, Kovanda M, Myslik V, Vrnata M, Van Driessche I, Hoste S. Pulsed laser deposition and dip-coating techniques in the fabrication of bismuth molybdate gas sensors. Thin Solid Films. 2006;**497**(1-2):284-291

[36] Le MT, Do VH, Truong DD, Pham NN. Sol–Gel Synthesis of Bismuth molybdate catalysts for the selective oxidation of propylene to acrolein: Influence of pH value and theoretical molar atomic ratio. Journal of the Chinese Chemical Society. 2017;**64**:1326-1332

[37] Beale AM, Sanka G. In situ study of the formation of crystalline bismuth molybdate materials under hydrothermal conditions. Chemistry of Materials. 2003;**15**:146

[38] Beale AM, Sanka G. In situ characterization of iron phosphate and bismuth molybdate catalysts prepared by hydrothermal methods: An EDXRD and combined XRD/XAS study. Nuclear Instruments and Methods in Physics Research, Section B. 2003;**199**:504

[39] Grasselli RK. Comments on the papers on selective oxidation catalysis. Catalysis Today. 1987;**1**:337

[40] Van Driessche I, Mouton R, Hoste S. Rapid formation of the Bi_2-xPbxSr$_2$Ca$_2$Cu$_3$Oy high Tc-phase, using spray-dried nitrate precursor powders. Materials Research Bulletin. 1996;**31**:979

[41] Le MT, Van Craenenbroeck J, Van Driessche I, Hoste S. Bismuth molybdate catalysts synthesized using spray drying for the selective oxidation of propylene. Applied Catalysis A: General. 2003;**249**:355-364

[42] Le MT, Van Well WJM, Stoltze P, Van Driessche I, Hoste S. Synergy effects between bismuth molybdate catalyst phases (Bi/Mo from 0.57 to 2) for the selective oxidation of propylene to arcrolein. Applied Catalysis A: General. 2005;**282**:189-194

[43] Specchia S, Galletti C, Specchia V. Solution combustion synthesis as intriguing technique to quickly produce performing catalysts for specific applications. Studies in Surface Science and Catalysis. 2010;**175**:59-67

[44] Specchia S, Finocchio E, Busca G, Specchia V. Combustion synthesis. In: Lackner M, Winter F, Agarwal AK, editors. Handbook of Combustion. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2010. pp. 439-472

[45] Moore JJ, Feng HJ. Combustion synthesis of advanced materials: Part II. Classification, applications and modelling. Progress in Materials Science. 1995;**39**:243-273

[46] Moore JJ, Feng HJ. Combustion synthesis of advanced materials: Part II. Classification, applications and modelling. Progress in Materials Science. 1995;**39**:275-316

[47] Hearne GW, Adams ML. U.S. Patent 2451485; 1948

[48] Idol Jr JD. U.S. Patent 2904508; 1959

[49] Callahan JL, Gertisser B. Mixed antimony oxide-uranium oxide oxidation catalyst. U.S. Patent 3,198,750; 1965

[50] Grasselli RK. Fundamental principles of selective heterogeneous oxidation catalysis. Topics in Catalysis. 2002;**21**:79

[51] Ullmann's Encyclopedia of Industrial Chemistry. Vol. A1. 1985. p. 149

[52] Grzybowska B. Thirty years in selective oxidation on oxides: What have we learned? Topics in Catalysis. 2000;**11**(/12):23

[53] Godin GW, Mac Cain CC, Porter EA. On the partial oxidation of propane and propylene on mixed metal oxide catalysts. In: Hightower JW, editor. Proceedings of the 4th International Congress on Catalysis. Vol. 1. Moscow; 1968; Elsevier. 1969. p. 347

[54] Burrington JD, Kartisek CT, Grasselli RK. Surface intermediates in selective propylene oxidation and ammoxidation over heterogeneous molybdate and antimonate catalyst. Journal of Catalysis. 1984;**87**:363

[55] Grasselli RK. Advances and future trends in selective oxidation and ammoxidation catalysis. Catalysis Today. 1999;**49**:141

[56] Song W, Ferrandez DMP, van Haandel L, Liu P, Nijhuis TA, Hensen EJM. Selective propylene oxidation to acrolein by gold dispersed on $MgCuCr_2O_4$ spinel. ACS Catalysis. 2015;**5**:1100-1111

[57] Burrington JD, Kartisek CT, Grasselli RK. Mechanism of nitrogen insertion in ammoxidation catalysis. Journal of Catalysis. 1983;**81**:489

[58] Glaeser LC, Brazdil JF, Hazel MAS, Mehecic M, Grasselli RK. Identification of active oxide ions in a bismuth molybdate selective oxidation catalyst. Journal of the Chemical Society, Faraday Transactions. 1985;**1**(81):2903

[59] Zhai Z, Wütschert M, Licht RB, Bell AT. Effects of catalyst crystal structure on the oxidation of propene to acrolein. Catalysis Today. March 2016;**261**(1):146-153

[60] Brazdil JM, Suresh DD, Grasselli RK. Redox kinetics of bismuth molybdate ammoxidation catalysts. Journal of Catalysis. 1980;**66**:347

[61] Grasselli RK. Genesis of site isolation and phase cooperation in selective oxidation catalysis. Topics in Catalysis. 2001;**15**:93

[62] Matsuura I, Shut R, Hirakawa K. The surface structure of the active bismuth molybdate catalyst. Journal of Catalysis. 1980;**63**:152

[63] Jung JC, Kim H, Kim YS, Chung Y-M, Kim TJ, Lee SJ, Oh S-H, Song IK. Catalytic performance of bismuth molybdate catalysts in the oxidative dehydrogenation of C4 raffinate-3 to 1, 3-butadiene. Applied Catalysis A: General. 2007;**317**:244-249

[64] van Well WJM, Le MT, Schiodt NC, Hoste S, Stoltze P. The influence of the calcination conditions on the catalytic activity of Bi_2MoO_6 in the selective oxidation of propylene to acrolein. Journal of Molecular Catalysis A: Chemical. 2006;**256**:1-8

[65] Carson D, Forissier M, Vedrine JC. Kinetic study of the partial oxidation of propene and 2-methylpropene on different phases of bismuth molybdate and on a bismuth iron molybdate phase. Journal of the Chemical Society, Faraday Transactions. 1980;**1**(84):1017

[66] Bing Z, Pei S, Shishan S, Xiexian G. Cooperation between the α and γ phases of bismuth molybdate in the selective oxidation of propene. Journal of the Chemical Society, Faraday Transactions. 1990;**86**:3145

[67] Weng LT, Sham E, Doumain N, Ruiz P, Delmon B. In: Centi G, Trifiro F, editors. New developments in selective oxidation. Amsterdam: Elsevier; 1990. p. 757

[68] Le MT. Synthesis and application of bismuth molybdate. [PhD thesis]. Ghent University; 2005

[69] Jung JC, Lee H, Kim H, Chung Y-M, Kim TJ, Lee SJ, Oh S-H, Kim YS, Song IK. Catalytic performance of multicomponent bismuth molybdates ($NiXFe_3Bi_1Mo_{12}O_{42}+X$) in the oxidative dehydrogenation of C4 raffinate-3 to 1,3-butadiene: Effect of nickel content and acid property. Catalysis Communications. 2008;**9**:447-452

[70] Carrazán SRG, Martín C, Mateos R, Rives V. Influence of the active phase structure Bi-Mo-Ti-O in the selective oxidation of propene. Catalysis Today. 2006;**112**:121-125

[71]   Sleight AW, Aykan K, Rogers DB. New nonstoichiometric molybdate, tungstate, and vanadate catalysts with the scheelite-type structure. Journal of Solid State Chemistry. 1975;**13**:231

[72]   Cesari M, Perego G, Zazzetta A, Manara G, Notari B. The crystal structures of the bismuth molybdovanadates and of the α-phase bismuth molybdate. Journal of Inorganic and Nuclear Chemistry. 1971;**10**:3595

[73]   Kim YC, Ueda W, Moro-oka Y. Selective oxidation of propane to acrolein and ammoxidation to acrylonitrile over Ag-doped bismuth vanadomolybdate catalysts. Studies in Surface Science and Catalysis. 1990;**55**:491

[74]   Nguyen TT, Le TM, Truong DD, Fehrmann R, Riisager A, Van Driessche I. Synergy effects in mixed Bi_2O_3, MoO_3 and V_2O_5 catalysts for selective oxidation of propylene. Research on Chemical Intermediates. 2012;**38**(3):829-846

[75]   Le MT, Do VH, Truong DD, Bruneel E, Van Driessche I, Riisager A, Fehrmann R, Trinh QT. Synergy effects of the mixture of bismuth molybdate catalysts with SnO_2/ZrO_2/ MgO in selective propene oxidation and the connection between conductivity and catalytic activity. Industrial and Engineering Chemistry Research. April 12, 2016;**2016, 55**(17):4846-4855