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Propene oxidation on substituted 2:1 bismuth molybdates and vanadates

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Abstract

The oxidation of propene over mixed metal oxide catalysts based on cation substituted 2:1 bismuth molybdates ($Bi_2Mo_{1-x}Me_xO_{6-y}$, Me = Ni ($x = 0.0, 0.25$)) and vanadates $Bi_2V_{1-x}Me_xO_{5.5-y}$, Me = Mn($x = 0.25$), and Mo($x = 0.0, 0.25$ and 0.50) has been studied. At atmospheric pressure and temperatures of 350–550°C, the Mo:V containing catalysts are more selective for acrolein production than either Bi_2MoO_6, or $Bi_2VO_{5.5}$, but Ni and Mn substitutions produced less selective catalysts. Small quantities of propylene oxide were observed, but attributed to gas-phase reactions which are partially quenched by all the catalysts investigated.

Keywords: Bismuth molybdate; Bismuth vanadate; Substitution; Propene oxidation

1. Introduction

Bismuth molybdates are the basic catalysts for the oxidation of propylene to acrolein. Their properties and the mechanism of acrolein production on these materials have been extensively studied [1–11]. Several of the various Bi/Mo binary oxides, $Bi_2Mo_xO_{3+3x}$ ($x = 1, 2, 3$) are effective catalysts for propene oxidation, and the γ-phases, with composition Bi_2MoO_6, have received much attention. The low temperature γ-phase has the layered Aurivillius structure, but converts to the fluorite-related γ' phase (through an intermediate γ'' phase) at temperatures above 600°C [12–15]. Some confusion remains regarding the catalytic effectiveness of these phases – the catalyst synthesis procedures (calcination at 600°C) in some studies of effective bismuth molybdate catalysts [16] would suggest the presence of some γ', while statements that γ' is inactive also appear [14]. The generally accepted mechanism of propene oxidation on bismuth molybdates assigns the initial allylic H-abstraction [7] to oxygen atoms associated with Bi. There is strong evidence that the O donated to the allyl intermediate to form acrolein is associated with Mo sites, although conflicting interpretations remain [1,9,10].

The use of aliovalent cation substitutions to alter the bulk and surface properties of oxide materials, including bismuth molybdate catalysts [17–22], has long been applied towards improving their performance in a variety of applications and to the understanding of the relationship between structure and reactivity. Commercial catalysts make use of many additional elements. The resulting changes in bulk characteristics

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such as electronic and ionic conductivity [17,19] have also been implicated in oxidation catalysis. In a study of ternary (Bi, Mo, V) oxides having the scheelite structure (related to α-bismuth molybdate), Ueda et al. showed that the ternary materials have improved catalytic activity and selectivity when compared to the binary end members, $Bi_2Mo_3O_{12}$ and $BiVO_4$ [20]. In addition, these improvements correlated with the oxygen mobility in the lattice, as determined by isotopic exchange with gas-phase O_2. This corresponds to previous suggestions [5,11] that rapid migration of lattice oxygen to fill the surface vacancies generated by the reaction is necessary for good catalytic selectivity.

Recently, new ternary oxides have been synthesized based on cation substitutions in $Bi_2VO_{5.5}$, which adopt a similar (Aurivillius-phase) crystal structure to γ-Bi_2MoO_6 [23,24]. Some of these Bi*Me*VO$_x$ (*Me* = Cu, Mn, e.g.) materials exhibit outstanding oxide ion conductivity [23]. Because of the structural homology between these materials and γ-bismuth molybdate, the oxidation of propene over these materials is of considerable interest. Of particular interest is the effect of cation substitution in the lattice positions thought to be responsible for oxygen donation and the result on the scheelite materials. We present here propene oxidation results on selected ternary compounds of this class; $Bi_2Mo_{1-x}V_xO_{6-y}$ ($x = 0$, 0.25, 0.50, 0.75 and 1.00), $Bi_2Mo_{1-x}Ni_xO_{6-y}$ ($x = 0.25$), and $Bi_2V_{1-x}Mn_xO_{5.5-y}$ ($x = 0.25$).

2. Experimental

2.1. Catalyst synthesis

Standard high temperature methods were used to synthesize the desired materials. Bismuth molybdate–vanadate compositions were prepared by reaction of stoichiometric mixtures of Bi_2O_3, MoO_3 and V_2O_5. The starting mixtures were heated in air in alumina crucibles at 550°C, 700°C and 810°C, typically for 16 h at each temperature. Samples were cooled to room temperature and reground between firings. The reactions were monitored by powder X-ray diffraction and the heating–grinding cycles continued until no further changes were observed. The samples of $Bi_2Mo_{0.75}Ni_{0.25}O_y$ and $Bi_2V_{0.75}Mn_{0.25}O_y$ were prepared similarly using NiO and MnO_2 as starting materials and with final heating temperatures of 860°C and 880°C, respectively. $Bi_2Mo_{1-x}V_xO_y$, ($x = 0.0, 0.75, 0.5, 1.00$) were also prepared by ultrasonic spray pyrolysis (UPS) [25]. Stoichiometrically correct solutions were prepared by dissolving ammonium heptamolybdate and ammonium metavanadate in distilled water. The resulting solution was acidified with HNO_3 and the required quantity of bismuth nitrate added. The resulting clear solution was fed to a Sonotek 120 ultrasonic nozzle to form a fine mist, which was then entrained in an air stream (3 l min^{-1}) and carried through a tube furnace. The dried particles were captured on a filter and subsequently calcined in flowing air for 1 h at 700°C. Bi_2MoO_6 material was also purchased from Johnson–Matthey. The materials were all characterized by X-ray diffraction (Scintag XDS2000 (HT materials), Siemens D5000 (USP materials)). Surface area measurements were made by BET methods as well as by analysis of SEM images. All materials used as catalysts were pelletized, ground, and sieved to 80–200 mesh size (75–180 μm).

Catalytic rates and selectivities were measured in a single pass, differential down-flow packed bed quartz reactor (hot zone volume, 2 cm^3), which has been described previously [26]. The catalysts (0.15–0.5 g samples) were supported on quartz wool within the 4 mm i.d. quartz tube with a type *K* thermocouple in a 1 mm o.d. quartz sheath embedded in the catalyst charge. Rates were measured by on-line GC analysis of the reactor effluent: connection to a quadruple mass spectrometer afforded GC–MS for product identification. The reactant gases used were UHP grade O_2 and polymer grade (99.5+%) propylene from Matheson Gas Products; both used without further purification. The propene conversion and reaction selectivity (reported herein on a carbon atom basis) on each catalyst, as well as the empty reactor were obtained between 350°C and 550°C with a standard gas mixture (C_3H_6:O_2=2:1, 1 atm total pressure) and total gas flow rate of 10 ml min^{-1} at STP. Variation of the gas residence time (by flow rate changes) was used to test that the results represent differential rates and initial selectivities.

In some cases, because of small catalyst samples and low surface areas, the homogeneous reaction was a significant portion (20%) of the propene conversion, and had to be subtracted to obtain catalytic rates. This was done by three different methods. In the first, the contribution of the empty reactor at the same conditions was subtracted from the results. This method results in an overestimate of the gas-phase contributions because the catalyst interferes with at least some aspects of the gas-phase chemistry. The second method assumed constant selectivities in the gas-phase processes, which then provided a correction of the CO_2 rates (no acrolein production occurs without a catalyst). All the data point to only two significant catalytic products, acrolein and CO_2, for all catalysts. A final check on the gas-phase corrections involved the variation of the gas-phase volume after the bed by a movable quartz rod, and extrapolation of the results to zero gas-phase volume. This gave results which agreed with the second method. All three methods gave catalytic acrolein selectivities which for the conditions reported here agreed to within 2–3%.

3. Results

3.1. Catalyst synthesis and characterization

Table 1 lists the materials used in this study and some of their characteristics. The high temperature preparation method produces Bi_2MoO_6 in the high temperature fluorite-related γ' phase, which is also the structure of the Bi_2MoO_6 purchased from Johnson Matthey. $Bi_2VO_{5.5}$, on the other hand, forms the Aurivillius phase analogous to low temperature γ-Bi_2MoO_6. The X-ray powder diffraction patterns of the ternary compounds $Bi_2Mo_{1-x}V_xO_{6-x/2}$ show evidence of limited solid solution behaviour in the end members. Outside these limits (values of x from 0.15 to 0.75), the diffraction patterns show evidence of an intermediate compound, $Bi_4MoVO_{11.5}$, and miscibility gaps. The intermediate compound is the only phase visible by XRD in the Mo50V50 material. While the complete crystal structure of this compound is not yet determined, single crystal X-ray diffraction data indicate a monoclinic unit cell with lattice parameters, $a = 11.64(4)$ Å, $b = 5.78(3)$ Å, $c = 24.43(8)$ Å, $\beta = 101.29°$, and a probable space group $P2_1/c$. The powder X-ray diffraction pattern can be indexed from the single crystal data and the general pattern of peak intensities strongly suggests that the cation positions in the structure are fluorite related. The sample with $x = 0.75$ is near the solubility limit of Mo in $Bi_2VO_{5.5}$, reported by Vannier et al. [24], while the material with $x = 0.25$ has diffraction lines of both the 50:50 structure and γ'-Bi_2MoO_6. The $Bi_2Mo_{1-x}Ni_xO_y$ series also contains an intermediate at $x \approx 0.25$, which appears also to be fluorite related. At higher levels of Ni substitution diffraction features of NiO are observed as a second phase. The $Bi_2V_{1-x}Mn_xO_y$ materials have the Aurivillius structure for $x \leq 0.25$. The powder diffraction pattern of the $Bi_2V_{0.75}Mn_{0.25}O_y$ used in the catalytic experiments was completely indexed with a tetragonal unit cell, with lattice parameters $a = 3.913(1)$ Å, $c = 15.522(2)$ Å. USP synthesis produced single-phase Bi_2MoO_6 and $Bi_2VO_{5.5}$. The mixed $Bi_2Mo_{1-x}V_xO_y$, USP materials consisted of a mixture with the same phases as those synthesized by high temperature techniques, but in different proportions. The $x = 0.5$ compound contained small amounts of both binary end members

Table 1
Catalytic materials synthesized for this study

Label [a]	Nominal composition	Surface area (BET)	Surface area (SEM)
Mo100	γ'-Bi_2MoO_6	0.7	—
Mo50V50 (HT)	$Bi_2Mo_{0.05}V_{0.05}O_y$	0.08	0.13
Mo50V50 (USP)	$Bi_2Mo_{0.05}V_{0.05}O_y$	—	—
Mo25V75 (HT)	$Bi_2Mo_{0.25}V_{0.75}O_y$	—	—
Mo25V75 (USP)	$Bi_2Mo_{0.25}V_{0.75}O_y$	0.3	0.95
V100 (USP)	$Bi_2VO_{5.5}$	0.3	0.8
V75Mn25 (HT)	$Bi_2V_{0.75}Mn_{0.25}O_y$	—	—
Mo75Ni25 (HT)	$Bi_2Mo_{0.75}Ni_{0.25}O_y$	—	—

[a] HT denotes high temperature synthesis and USP denotes ultrasonic pyrolysis synthesis (see text for details).

as well as $Bi_4MoVO_{11.5}$. Evidently, during drying of the droplets and the subsequent nitrate decomposition, phase separation occurred which the relatively mild calcination step (700°C) did not remove. These necessarily brief characterization results show that none of these ternary compounds form a complete homotactic solid solution series. The catalytic rate measurements were restricted to materials with compositions within single-phase regions.

The surface area of the Bi_2MoO_6 sample obtained from Johnson Matthey was determined by BET methods to be 0.4 $m^2\,g^{-1}$. BET determinations of the surface areas were uncertain and in some cases unavailable because of the low specific areas. The surface areas of some of the high temperature and USP materials were also estimated from SEM images of the synthesized powders, which consisted of irregular particles with rectangular facets. The USP particles, which consisted of spheres, cenospheres and fragments before calcination, converted to rectangular crystal habits upon calcination. The external appearance of the particles suggests some internal surface area. The calculated external surface areas of these particles were approx. 0.1–0.2 $m^2\,g^{-1}$ for the high temperature materials, and near 1 $m^2\,g^{-1}$ for USP materials. Although the SEM values should provide lower limits to the total surface area, some of the BET measurements were even lower. Therefore, the surface specific rates are uncertain by factors of 3 or more. Previous results on bismuth molybdates shown in Table 2 indicate the difficulties in obtaining reproducible rates. Surface area measurements of the Ni and Mn substituted materials were not pursued.

3.2. *Catalytic activity*

Only acrolein and CO_2 are significant catalytic products. Other minor products, formaldehyde, ethene, propene oxide, acetaldehyde, and methane, are associated with gas-phase reactions and are excluded from the analysis here. Differential reaction conditions were assured by low conversions (< 10% in all cases) and the lack of rate or selectivity variation with space velocity. Table 2 compares the catalytic rates at standard conditions for the series of catalysts. Previously reported activities of bismuth molybdates and selected Bi–Mo–V scheelite materials are also included in Table 2 for comparison. The measured rate behaviour is similar to previous reports (first-order propene dependence, zero-order oxygen dependence) as are the measured activation energies. The catalytic activities for all the materials are within an order of magnitude of each other although higher activities are suggested for the ternary Bi–Mo–V compounds, a trend which agrees with the findings for the scheelite materials. The Ni and Mn substitu-

Table 2
Rates for propene oxidation over various bismuth-based binary and ternary oxides

Catalyst	Rate [a] ($\mu mol\,s^{-1}\,g^{-1}$)	Rate ($\mu\,mol\,s^{-1}\,m^{-2}$)	E_{act} ($kJ\,mol^{-1}$)	Catalyst mass (g)
Literature				
α-$Bi_2Mo_3O_{12}$ [b]	—	5.3, 7.8, 5.0 [c]	83, 120, 79	—
γ-Bi_2MoO_6 [b]	—	1.1, 39, 4.7	83	—
$BiVO_4$ [c]	—	0.37	79	—
$BiMo_{0.45}V_{0.55}O_y$ [c]	—	15	79	—
This work				
γ'-Bi_2MoO_6	2.4	3.5	82(7)	0.24
Mo50V50 (HT)	0.72	5–9	89(10)	0.25
V100 (USP)	0.9	1–3	87(4)	0.10
Mo25V75 (USP)	1.85	2006	75(7)	0.04
V75Mn25 (HT)	0.72	—	63(2)	0.21
Mo75Ni25(HT)	0.29	—	71(6)	0.22

[a] Reaction conditions: 450°C, 110 kPa total pressure, propene/O_2 = 2.0. Conversions were all less than 10% and showed no dependence on space velocity.

[b] The 400°C values compiled in Tables 2 and 3 of Ref. [1] were extrapolated by the method described therein to our conditions.

[c] Values for our conditions extrapolated (first-order propene dependence) from Ref. [20].

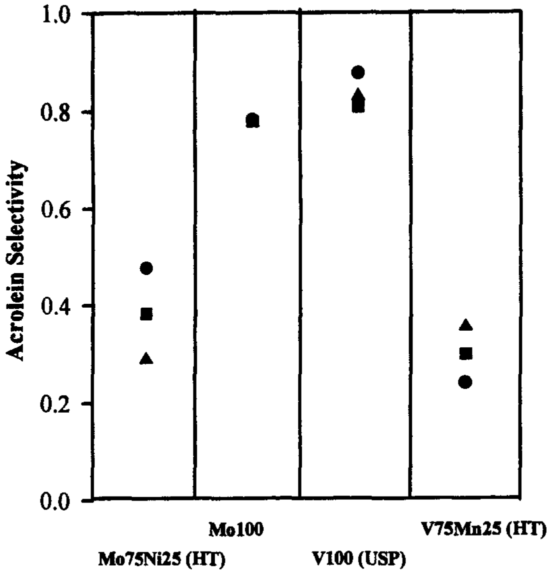

Fig. 1. Acrolein selectivity (carbon atom basis) for Ni-substituted Bi_2MoO_6 and Mn-substituted $Bi_2VO_{5.5}$ at several temperatures. Propene/O_2=2, 110 kPa, conversions less than 10%. ●=450°C, ■=475°C, ▲=500°C.

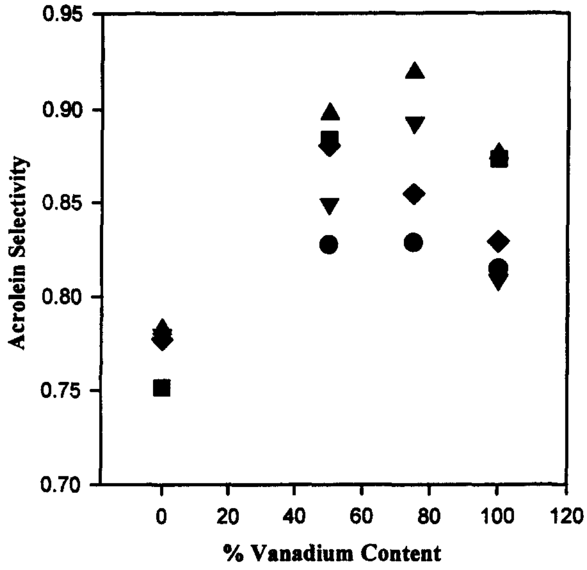

Fig. 2. Acrolein selectivity (carbon atom basis) for ternary $Bi_2Mo_{1-x}V_xO_{6-x/2}$ catalysts. Reaction conditions: propene/O_2=2, 110 kPa, conversions less than 10%. ■=400°C, ▲=450°C, ▼=475°C, ◆=500°C.

tions produce no great changes in the catalytic activity, however, levels of Ni higher than the solubility limit did result in higher rates (results not shown), which we attribute to the presence of the additional NiO phase.

3.3. *Catalytic selectivity*

Catalytic acrolein selectivity data are summarized in Figs. 1 and 2. The acrolein selectivity of the ternary compounds differ from their binary counterparts. As Fig. 1 shows, substitutions of Ni into Bi_2MoO_6 and Mn into $Bi_2VO_{5.5}$ both result in substantially lower selectivities. Higher Ni/Mo ratios (not shown) results in further decreasing acrolein selectivity and higher rates, due to NiO. Increased acrolein selectivities, however, are seen with Mo/V combinations when compared to the binary end members, with selectivities greater than 90% in some conditions (see Fig. 2). The ordering of the catalysts with respect to acrolein selectivity is Mo25V75>Mo50V50>V100>Mo100. As the data in Fig. 2 shows, the temperature dependence of the acrolein selectivity is rather mild in this gas composition, with a maximum for each catalyst near 450°C. The selectivities of the USP generated materials were (within experiment uncertainty) similar to those for the HT materials despite the differences in the phase distributions, and exhibit the same increase in selectivity for the ternary compounds. A synergic effect of physical mixtures has been reported [27–29].

3.4. *Propene oxide*

Propene oxide, and other minor products were also observed and attributed to gas-phase processes [30,31]. There are previous suggestions that surface processes, e.g., the desorption of radicals, can increase the rate of the gas-phase processes in similar systems [32–35]. As Fig. 3 shows, however, the presence of each of our catalysts lowers the production of propene oxide (and other products of the homogeneous chemistry) in the reactor. Destruction of propene oxide by the catalyst could account for some of this effect. Additionally, peroxy radicals, which are the chief epoxidation reagents in the gas-phase, can also be quenched by the presence of the catalyst. The interruption of gas-phase oxidative processes by various oxides has been demonstrated to play a major role in methane coupling (Ref. [26] and A.J.J., data not shown).

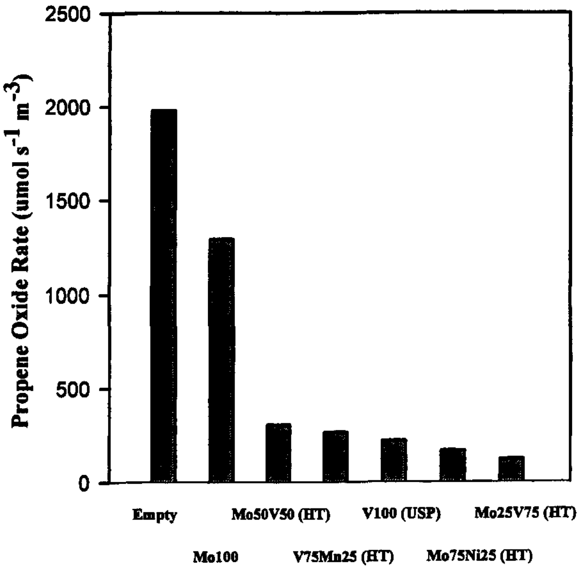

Fig. 3. Propene oxide production rates in the empty reactor and with various oxide catalysts at standard conditions (450°C, propene/O_2=2, 110 kPa total pressure).

4. Discussion

Our observations extend the picture which has evolved from extensive study of bismuth molybdate based catalysts for propene oxidation. All four bismuth molybdate structures (α, β, γ, γ') and the binary bismuth vanadates show similar acrolein selectivities. The reported activities are scattered, but are generally within an order of magnitude of one another, a trend continued in our results. It is generally agreed that the initial allylic H-abstraction step is rate limiting and is associated with bismuth sites. The catalytic performance is, therefore, not particularly sensitive to structural variations in the materials such as the bulk co-ordination of bismuth. The catalytic activity can vary as other cations are substituted for molybdenum and even more widely with substitutions on the bismuth sites.

Acrolein selectivity is governed by the fate of the allylic reaction intermediate and both Mo and V in the various binary oxides guide the reaction towards acrolein formation. Our findings, as well as that of Ueda [20] on scheelite analogues, have shown that ternary (Bi–Mo–V) materials are more selective than the binary end members. An increase in acrolein selectivity from 80 to 90% implies a twofold decrease in the probability of deep oxidation of the allyl intermediate. The causes of these differences are not clear since many aspects of the catalyst structure, such as oxygen defect formation energies, will affect the competition between the desirable acrolein pathway and other undesirable ones. The energetics of oxygen donation depend on an interplay between electronic and ionic effects, the dependence of which on structure and composition is not well understood. Even more uncertainty surrounds the surface structure of these oxides. The parallel enhancement of H-abstraction and O-donation (both redox steps) continues to explain the failure to find oxide catalysts capable of direct propene epoxidation from molecular oxygen.

It has been proposed that an increase in oxygen mobility allows the surface vacancies produced in both reaction steps to be more rapidly reconstituted and that lattice substitutions aid this step. Oxygen exchange measurements on the Bi–Mo–V scheelite materials agree with this hypothesis. While this ability could certainly affect the reaction selectivity by 'healing' vacancies which might lead to deep oxidation, this step cannot dominate the reactivity since a bottleneck at this stage would displace H-abstraction as the rate limiting step and thus, not preserve the first-order propene dependence observed in the kinetic rate law. A correlation between mobility and catalytic performance is not apparent in our materials, which span a wide range of conductivities (Refs. [23,36] and A.J.J., data not shown). For example, $Bi_2V_{0.75}Mn_{0.25}O_y$ has the highest conductivity among them, yet is a poor catalyst. The conductivities of $Bi_2Mo_{0.50}V_{0.50}O_y$ and Bi_2MoO_6, which differ in selectivity, are not significantly different. Additionally, the various bismuth molybdates have widely varying conductivities [37], yet have very similar catalytic performance. A better correlation, such as observed for the scheelites [20], might be obtained between catalytic selectivity and gas–solid oxygen exchange, which involves both bulk mobility and oxygen activation.

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