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Structure and catalytic activity characterization of bismuth molybdate catalysts

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We present a study of Bi–Mo catalysts prepared from pure oxides (MoO_3 and Bi_2O_3) by solid state reaction methods. The structure characterization by X-ray diffraction shows only the low temperature (koechlinite) and high temperature (γ(H)) phases in varying proportions depending on the calcination temperature. The carbon monoxide oxidation shows a synergetic effect for mixed oxides as compared to pure oxides. Significant differences in catalytic activity, surface morphology and surface concentration were observed when the molybdenum precursor was changed from molybdenum trioxide to ammonium heptamolybdate in the catalyst preparation.

Keywords: Bismuth-molybdate catalysts; characterization of bismuth molybdates

1. Introduction

Bismuth-molybdate based catalysts are currently used for selective olefin oxidation and ammoxidation processes [1]. The main characteristic of Bi–Mo mixed oxides in these reactions is their ability to use lattice oxygen to oxidize hydrocarbons and be reoxidized in presence of gaseous oxygen [2]. These catalysts can form several phases ($Bi_2Mo_2O_9$ (β), $Bi_2Mo_3O_{12}$ (α), Bi_2MoO_6 (γ), etc.), depending on the reaction temperature and the Bi/Mo ratio [3]. $Bi_2Mo_2O_9$ (β) produces the best catalyst in terms of activity and selective oxidation [4]. However, the instability of β phase at high temperatures greatly limits its use in such applications as automobile emission control catalysts.

On the other hand, transition metal oxides (TMO) and base metal oxides are often used in the oxidation of carbon monoxide [5,6], in contrast with the bismuth-molybdate system. In general, for CO and hydrocarbon oxidation, high activity requires metal ions that can take up more than one valence state in order to participate in reduction–oxidation (redox) reactions [7]. Both of these requirements are fulfilled by the γ(H) phase of Bi_2MoO_6.

The aim of this work is to characterize the structure and to evaluate the CO oxidation activity of the high temperature form of Bi_2MoO_6. The catalyst characterization was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Auger electron spectroscopy (AES).

2. Experimental procedure

Catalysts were prepared by solid state reaction of molybdenum and bismuth precursors at high temperatures (above 800 K). In method A, powders of Bi_2O_3 and MoO_3 (99.9% purity) were thoroughly mixed (in an agate mortar) in the appropriate proportions to give the atomic ratio Bi/Mo = 2. After obtaining a very uniform mixture, three samples were prepared by calcining them in an alumina crucible at 823, 923 and 1123 K for 40 h. Catalysts were allowed to cool to room temperature inside the oven. In method B, ammonium heptamolybdate was used as precursor, instead of MoO_3; other steps were identical in both cases. The final specimens had a distinct yellow color, regardless of the preparation method.

X-ray diffractograms were obtained with a General Electric XRD6 diffractometer, using Cu Kα radiation at 40 kV and 20 mA. SEM micrographs were obtained using a Jeol JSM-5300 microscope.

Surface areas were determined by the BET method using nitrogen as adsorbate at 77 K. Samples were outgassed under high vacuum at 423 K during one hour, prior to surface area measurements.

The carbon monoxide oxidation was used as a test reaction for Bi–Mo catalysts. That reaction was carried out at temperatures in the range of 483–773 K, in a conventional flow system under atmospheric pressure. The partial pressures of oxygen and carbon monoxide were changed in order to obtain different CO/O_2 ratios (0.5, 1.0, 2.0, 5.0, 10.0 and 20.0). The products were analyzed by thermal conductivity gas chromatography using a 3 m stainless steel column filled with 3A molecular sieve at 343 K. The reaction rates were calculated at conversions of 5% (around 573 K). The catalysts were heated in air to 473 K for 1 h, before the reaction test.

The surface composition was determined using Auger electron spectroscopy (AES) with a scanning Auger microprobe (Perkin-Elmer, PHI 595). The energy of the incident electron beam was 3 keV at 150 nA current. Auger spectra were recorded at different points on the surface and the standard Multiple Technique

Analytical Computer System (MACS) software for this particular instrument was used to obtain a semiquantitative analysis of the spectra, following the relative elemental sensitivity factors given by MACS [8].

3. Results and discussion

Bismuth molybdate, Bi_2MoO_6, has three polymorphs which are usually known as γ(L), γ(H) and γ''. γ(L) (koechlinite) is the low temperature form, γ(H) is the high temperature form, and γ'' is the metastable intermediate between them [1,2]. Chen et al. [9] showed a structure with $a = 1.725, b = 2.242$, and $c = 0.585$ nm, and angle β of 89.5°, for a solid obtained by fusion at 1200 K. On the other hand, Watanabe et al. [10] reported a "similar" structure with very close a, b and c lattice parameters, and angle β of 90.48°, for samples prepared at 928 K. Their calculations agreed fairly well with Chen's structure, except for changes in relative intensities in some peaks. They claim that those differences are due to planar defects introduced by the lower solid state reaction temperature.

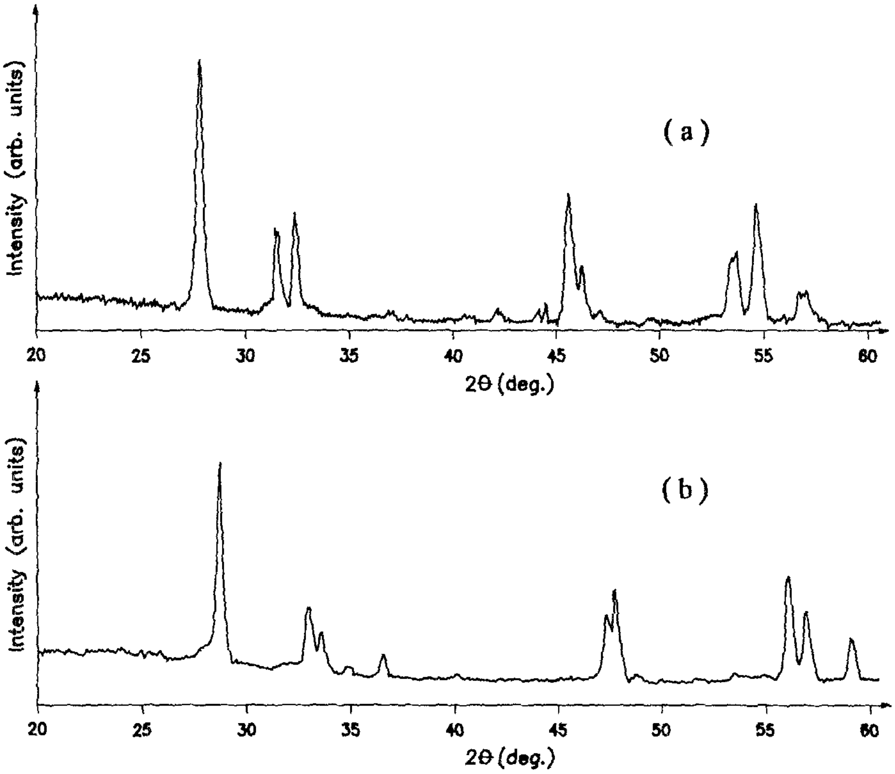

Fig. 1. X-ray spectra from samples prepared by method A and calcined at 823 (a) and 1123 K (b).

X-ray diffraction was used to assess the phases involved in these catalysts as a function of the temperature and the type of molybdenum precursor. Figs. 1a and 1b show X-ray spectra for samples prepared by method A, and calcined at 823 and 1123 K, respectively. Figs. 2a and 2b show equivalent X-ray spectra for samples prepared by method B, calcined at the same temperature as those in fig. 1. At low calcination temperature (823 K) we obtained the well characterized koechlinite phase (fig. 1a). For higher temperature (1123 K) the observed XRD patterns (figs. 1b and 2b) were very similar to the ones reported by Watanabe [10], and thus, inconsistent with those reported by Chen [9] for similar compounds. For intermediate temperature (923 K) a mixture of koechlinite and Watanabe phases is observed, as expected. This sample was further used for surface analysis and catalytic studies.

The surface morphology of catalysts obtained at 923 K was studied by SEM. Figs. 3a and 3b show SEM images of samples before the reaction test. Samples A (fig. 3a) showed fused-like platelets in the size range of 25 μm. Samples B (fig. 3b) also exhibit needle-like crystals, some of them very sharp and thin, in

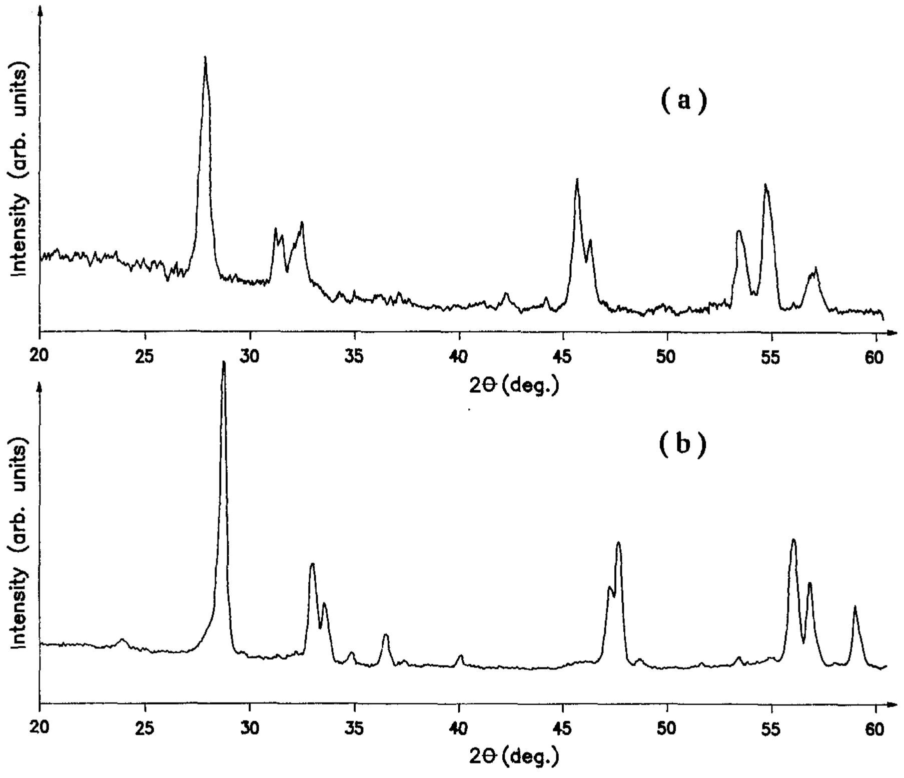

Fig. 2. X-ray spectra from samples prepared by method B and calcined at 823 (a) and 1123 K (b).

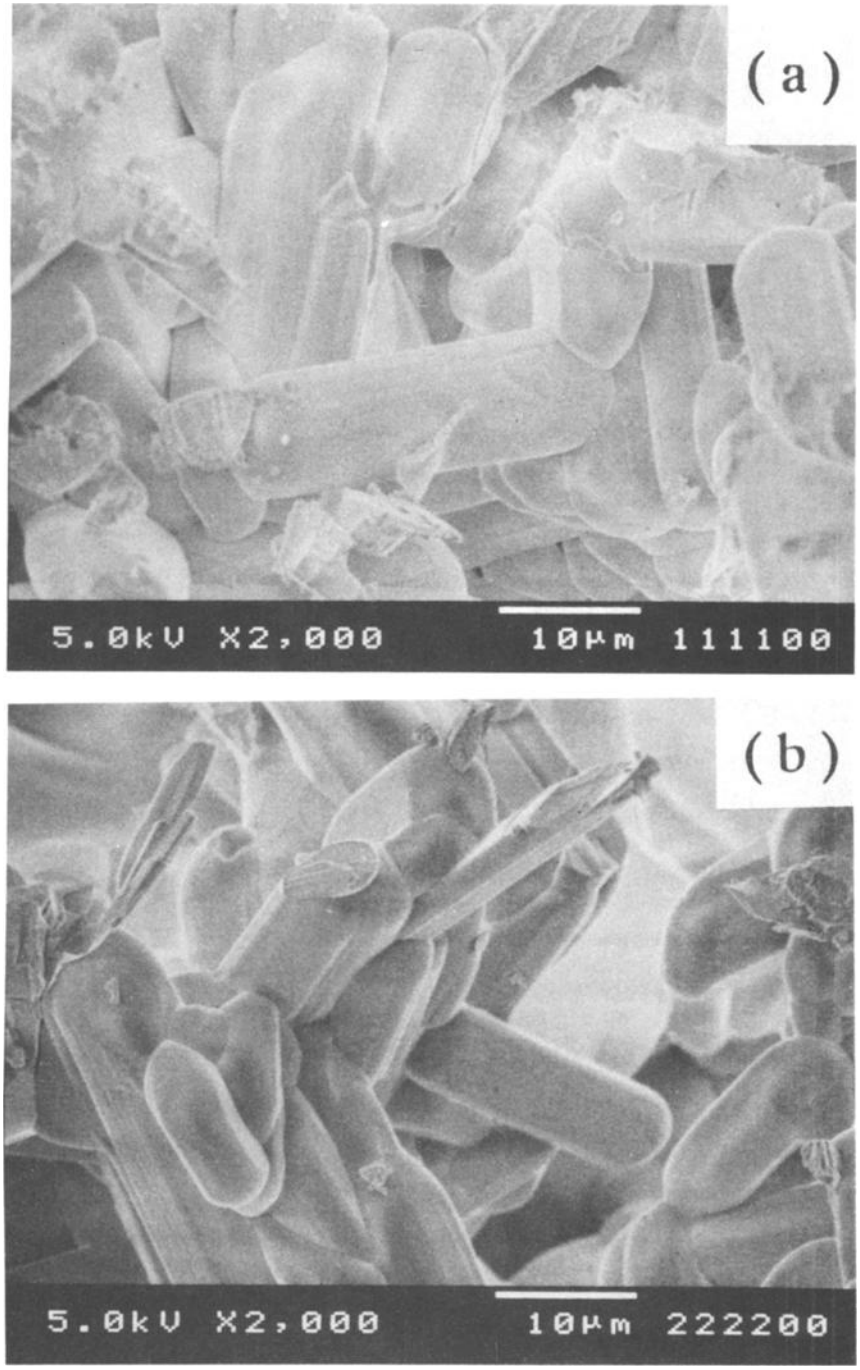

Fig. 3. SEM micrographs from samples before the reaction test. (a) Prepared by method A and (b) prepared by method B.

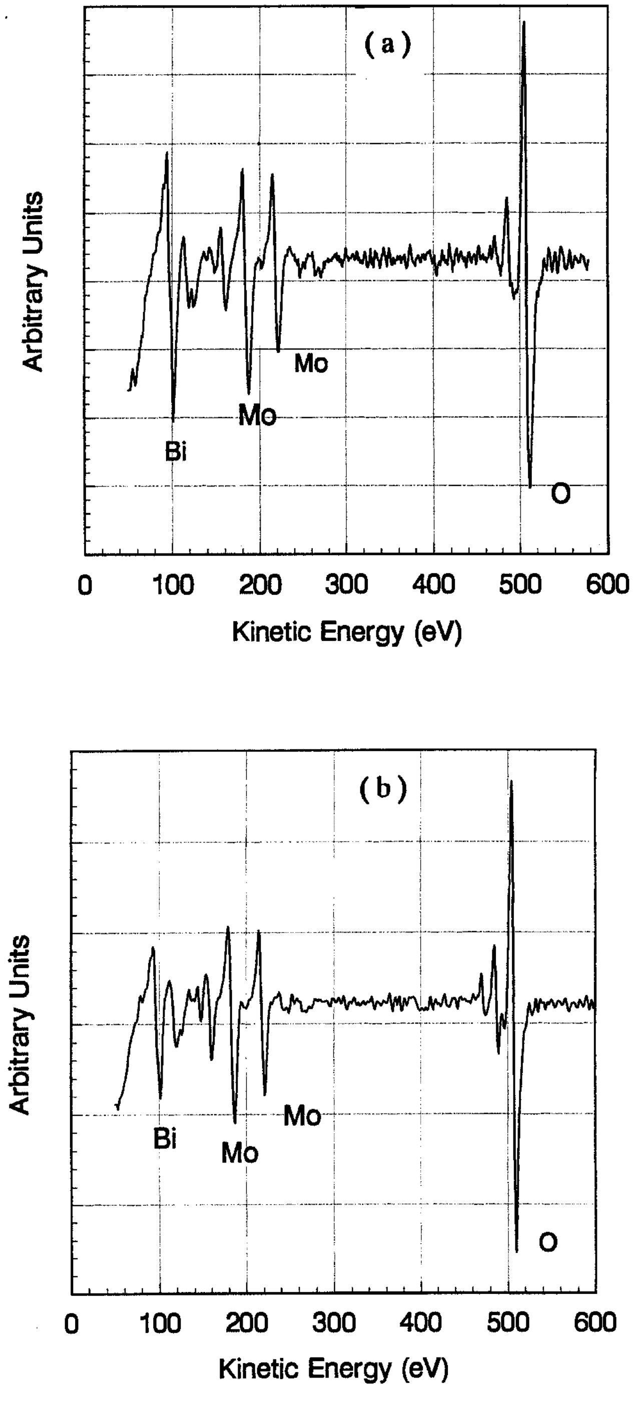

Fig. 4. Auger spectra from corresponding samples shown in fig. 3.

Table 1
Atomic concentration (%) of Bi and Mo from AES analysis, for samples A and B, before and after reaction

	Bi	Mo	Bi/Mo
Sample A before	43.24	25.52	1.69
Sample A after	32.70	28.52	1.15
Sample B before	20.91	29.49	0.71
Sample B after	22.93	30.06	0.76

the same size range. These results suggest that samples obtained from MoO_3 reach an equilibrium form more rapidly than samples derived from ammonium heptamolybdate.

The surface Bi/Mo ratio was determined by Auger analysis. The AES spectra of these platelets is shown in figs. 4a and 4b. A summary of the results concerning Bi and Mo concentrations, is presented in table 1. As we can see, samples A have more bismuth at the surface as compared to samples B. The Bi/Mo ratio is higher for sample A (1.69) than for sample B (0.71); however, the surface for both types of samples is bismuth deficient in comparison with the stoichiometric compound.

The catalytic activity as a function of the reaction temperature was evaluated in the temperature range of 483–773 K for the single (MoO_3 or Bi_2O_3) or mixed oxides (A and B), at the molar ratio $CO/O_2 = 5$ where the maximum activity was observed. Fig. 5 shows the "light-off" type scheme for the yield of CO (defined as moles CO_2/moles CO) as a function of increasing temperature for all catalysts.

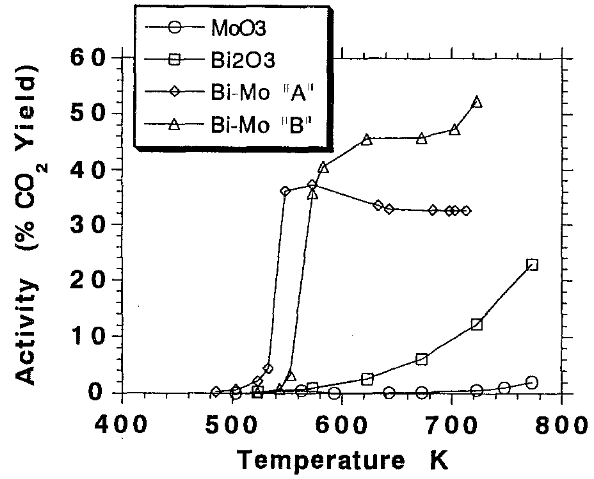

Fig. 5. Oxidation of CO as a function of temperature for MoO_3, Bi_2O_3 and Bi_2MoO_6 (A and B).

The comparison shown in this figure is made under the same conditions of mass (0.5 g), flow (2.4 ℓ/h) and CO/O_2 ratio [5], which is where the maximum conversion was found for Bi–Mo oxides. Under these conditions, MoO_3 was almost inactive, yielding only 2% of CO at 773 K; on the other hand, Bi_2O_3 yields 23% of CO at the same temperature. Mixed oxides showed a significant increase in activity at low temperatures (523–573 K), making evident a strong synergetic effect.

Catalyst A was more active than B on the low temperature zone (523–563 K). However, the reverse was true for temperatures higher than 573 K. Catalyst A reached very rapidly the maximum yield (40% at 540 K) allowed by the concentration of oxygen in the feed. The maximum yield was maintained at higher temperatures. On the other hand, catalyst B surpassed the maximum yield for temperatures higher than 575 K. Such a behavior indicates that besides the oxygen in the feed, oxygen from the lattice is being consumed by the reaction. This suggests a mechanism similar to the olefin oxidation mechanism [11], where the reactive oxygen is provided by the catalyst, which is further re-oxidized by adsorption–dissociation of molecular oxygen.

The reaction rates were calculated after 1 h, when a steady state was reached. By comparing the reaction rate obtained for these Bi–Mo oxides with other results for mixed oxides, we found that they have the same order of activity as cobalt perovskites (6–8 ml CO_2 s^{-1} g^{-1}), although they are less active than copper chromites [12]. The surface area of these mixed catalysts was about 0.5 m^2/g, and similar for all samples. This low surface value is mainly due to the high temperature used during preparation. Efforts will be made to support these oxides in order to increase their surface area and stability.

4. Conclusions

The structure of Bi–Mo mixed oxides based on the solid state reactions of single MoO_3 and Bi_2O_3 has been presented. XRD results show different structures, depending on the calcination temperature.

The koechlinite form (low temperature form) was identified for the samples calcined at 823 K. Increasing the temperature between 923 and 1123 K produces mainly the γ(H) phase which has been reported by Watanabe [9]. No significant differences were observed in the catalyst structure when the sample was synthesized using ammonium heptamolybdate in place of MoO_3. However, the surface Bi/Mo atomic ratios were different between both samples.

The activity yield of these Bi_2MoO_6-γ(H) catalysts for CO oxidation was comparable to the activity of $CoLaO_3$ or $BaCoO_3$ spinels, showing a considerable synergetic effect with respect to the single Bi_2O_3 or MoO_3 oxides. Further studies are needed to evaluate other catalytic parameters in these samples, as well as the role of defects in the microstructure of the γ(H) phase.

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