

# Influence of the active phase structure Bi-Mo-Ti-O in the selective oxidation of propene

S.R.G. Carrazán, C. Martín, R. Mateos, V. Rives\*

*Departamento de Química Inorgánica, Universidad de Salamanca, 37008-Salamanca, Spain*

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## Abstract

Bismuth molybdenum titanium oxides were prepared in a highly dispersed state by the sol–gel method and in a largely crystallized state by coprecipitation and impregnation. The catalysts contained 14 or 25 wt.% of bismuth molybdate. Their catalytic performance in propene oxidation to acrolein was studied. The increase in activity of Bi-Mo-Ti oxides in propene oxidation as compared to that of bulk bismuth molybdate can be tentatively related, in the case of the sol–gel samples, 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 prepared by coprecipitation or impregnation is enhanced once a crystal size of bismuth molybdate close to 23 nm is reached, i.e., the crystal size should not be too small (samples prepared by the sol–gel method) nor too large (samples prepared by impregnation and coprecipitation), but an optimum size should exist to enhance the catalytic performance.

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## 1. Introduction

Different commercial multicomponent catalysts have been developed to improve the efficiency of bismuth molybdate catalysts for acrolein and acrylonitrile synthesis via Mars and van Krevelen redox mechanism [1]. The active phase is bismuth molybdate in the  $\alpha$  ( $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ ),  $\beta$  ( $\text{Bi}_2\text{Mo}_2\text{O}_9$ ) or  $\gamma$  ( $\text{Bi}_2\text{MoO}_6$ ) forms [2,3]. Most of these studies attempt to relate the physicochemical properties of these solids with their catalytic activity [4,5]. However, it is not clear enough which of the phases ( $\alpha$ ,  $\beta$  or  $\gamma$ ) is more active and selective in allylic oxidation. On the other hand, several groups [6,7] have tested the effect of several supports (e.g., silica, alumina and titania) on the precise phase of bismuth molybdate formed and the interaction/collaboration between that phase and the support, aiming to find beneficial effects for the catalytic performance.

In this paper we report the synthesis of a series of Bi-Mo-Ti oxides following different routes (sol–gel, coprecipitation and impregnation) in order to analyse how the preparation method (and changes in several preparation parameters, such as

bismuth molybdate loading, time and the calcination temperature) and the presence of the titania matrix modify the structure of the active phase in the partial oxidation of propene to acrolein. Moreover, we also try to relate the catalytic performance with the solid-state properties of the catalysts, especially from the structural point of view.

## 2. Experimental

### 2.1. Preparation of the catalysts

Catalysts Bi-Mo-Ti-O were prepared following three routes, namely coprecipitation (sample C1), impregnation (samples I1 and I2) and sol–gel (sample SG2). To prepare sample C1, a solution containing 0.35 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (hereafter BiN) in 4 M  $\text{HNO}_3$  was added to a suspension of 2 g of  $\text{TiO}_2$  (Degussa P-25, ca. 80% anatase,  $50 \text{ m}^2 \text{ g}^{-1}$ ) in a solution containing 0.1949 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{12} \cdot 4\text{H}_2\text{O}$  (hereafter AHM) in a 5 wt.% ammonia solution; the concentration of the BiN solution was that necessary to obtain a molar Mo/Bi ratio of 3/2 and final pH was adjusted to 7 with the same ammonia solution above described; in this way, precipitation of bismuth molybdate is achieved. The mixture was vigorously stirred and gently heated in a water bath to dryness. The solid thus obtained was dried in an open oven at  $100^\circ\text{C}$  for 19 h, and finally calcined in an open

\* Corresponding author. Fax: +349 23 29 45 74.

E-mail address: [vrives@usal.es](mailto:vrives@usal.es) (V. Rives).

oven at 500 °C for 3 h. Samples I were obtained by adding first a AHM aqueous solution (containing 0.1954 or 0.3908 g) to 2 g of TiO<sub>2</sub>; after evaporation of the solvent the solid was calcined in an open oven at 500 °C for 3 h and then it was suspended in a BiN/HNO<sub>3</sub> solution (containing 0.35 or 0.71 g BiN); drying and calcination were performed as above described. In this case two different samples were obtained: sample I1 containing 14 wt.% of bismuth molybdate (hereafter BM) and sample I2 containing 25% BM. Finally, to prepare sample SG2 by the sol-gel method, 7.34 g of Ti tetraisopropoxide were dissolved in 27.5 ml of isopropanol and, while vigorously stirred (500 rpm), solutions of AHM, BiN and HNO<sub>3</sub> (4 M) were simultaneously added. The molar water:alkoxide:acid ratio was 6:1:0.5 and the molar Mo/Bi ratio was 3/2, the total BM content was equivalent to 25%. Gelation took place in 2–3 min at room temperature and the gel was aged for 20 h. After that it was dried under vacuum at room temperature. The solid obtained was calcined in O<sub>2</sub> flow at 250 °C for 30 min to remove organic residues and then at 500 °C for further 30 min (in all cases, the heating schedule was 5 °C min<sup>-1</sup>). The solid was cooled to room temperature under the oxygen flow.

In order to analyse the effect of the calcination time, portions of catalysts I2 and SG2 were calcined for 8 or 20 h, respectively, at 500 °C, leading to samples I2c and SG2c, respectively. Bulk  $\alpha$ -Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> (sample  $\alpha$ -BM) was prepared by precipitation from aqueous AHM and BiN/HNO<sub>3</sub> solutions, as described elsewhere [8]: a portion of 10 g of BiN was dissolved in 42 ml of aqueous HNO<sub>3</sub> (4 M) to avoid bismuth hydrolysis. This solution was dropwise added on a 5% NH<sub>3</sub> aqueous solution of AHM containing the stoichiometric amount of AHM) and pH was also adjusted to 7, thus precipitating bismuth molybdate. Finally, the precipitate was dried and the solid was calcined in flowing oxygen at 5 °C min<sup>-1</sup> up to 250 °C; this temperature was maintained for 30 min and then was raised up to 500 °C at the same heating rate, and this temperature was also maintained for 30 min. Then the sample was cooled to room temperature under oxygen flow.

## 2.2. Experimental techniques

Element chemical analyses were carried out by atomic absorption in a Mark-2 ELL 240 apparatus at Servicio General de Análisis Químico Aplicado (University of Salamanca, Spain). The powder X-ray diffraction (PXRD) patterns were obtained with a Siemens D-500 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) interfaced to a DACO-MP data acquisition microprocessor, the identification of the phases was achieved by using a database software (JCPDS files). The average crystallite sizes were estimated using the Scherrer equation and the width of selected diffraction peaks were fitted by a Pearson-type profile function. An instrumental line broadening of  $2\theta = 0.23^\circ$  was taken into account. The FT-Raman spectra were recorded in a RFS 100/S Bruker spectrophotometer using the 1064 nm line from a Nd:YAG laser as the excitation line, with an output laser power of 150 mW; the resolution was 4 cm<sup>-1</sup> and a backscattering geometry was chosen. Specific surface area, following the BET

method, and porosity assessment were determined from nitrogen adsorption–desorption isotherms, recorded at –196 °C in a Gemini apparatus from Micromeritics.

## 2.3. Catalytic tests

Selective oxidation of propene was studied under atmospheric pressure conditions in a conventional fixed-bed reactor equipped with a jacket furnace. A PID controller with a coaxial thermocouple was used to control the temperature, and the reactions were carried out at 400 and 420 °C; the reaction mixture consisted of He:O<sub>2</sub>:propene (molar ratio 10:10:80, corresponding to partial pressures of 76, 76 and 608 Torr, respectively), the flow (total 30 ml min<sup>-1</sup>) being measured with mass flow controllers. Fifty milligrams of catalyst was dispersed with glass balls (diameter 200–315  $\mu$ m). Analysis of the products was made on-line with an Intersmat IGC 121 ML gas chromatograph with a thermal conductivity detector and Hayesep Q (1.5 m length, 1/8 in. diameter) and Tenax (2.5 m length, 1/8 in. diameter) columns. Acrolein, CO<sub>2</sub> and water were the only reaction products.

## 3. Results and discussion

### 3.1. Characterisation

As the solids were not filtered after synthesis, the chemical analysis data indicate that the Bi, Mo and Ti content, and the molar Mo/Bi ratio (3/2) are coincident with the expected values.

The PXRD pattern of bulk bismuth molybdate (sample  $\alpha$ -BM, Fig. 1) corresponds to monoclinic  $\alpha$ -Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, which most intense peaks are recorded at 3.19  $\text{\AA}$  (2 2 1) planes, 3.06  $\text{\AA}$  (0 2 3) planes and 2.88  $\text{\AA}$  (0 4 0) planes. These peaks are also recorded in the diagrams of samples C and I2, together with sharp intense peaks due to anatase (1 0 1) planes at 3.52  $\text{\AA}$  and rutile (1 0 0) planes at 3.26  $\text{\AA}$ , but are absent on the diagram of

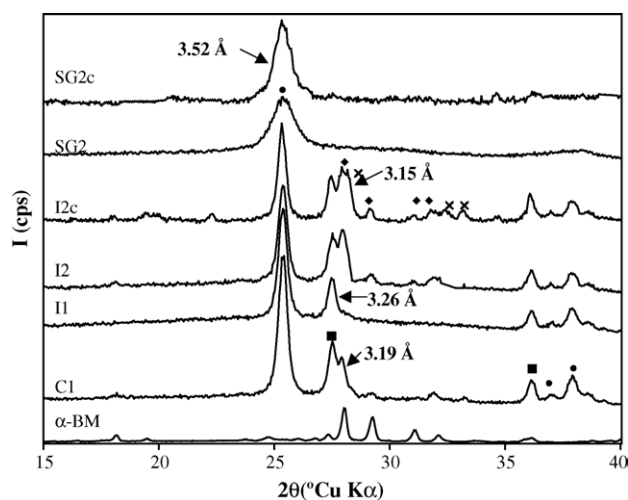


Fig. 1. X-ray diffraction patterns of Bi-Mo-Ti-O samples prepared by coprecipitation (C1), impregnation (I) and sol-gel (SG) methods. (◆)  $\alpha$ -Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, (×)  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, (●) anatase and (■) rutile.

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