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Bismuth molybdates prepared by solution combustion synthesis for the partial oxidation of propene

Benjamin Farin [a], Alessandro H.A. Monteverde Videla [b], Stefania Specchia [b,*], Eric M. Gaigneaux [a,**]

[a] Institute of Condensed Matter and Nanosciences – MOlecules, Solids and reactiviTy (IMCN/MOST), Université catholique de Louvain, Croix du Sud 2 box L7.05.17, 1348 Louvain-La-Neuve, Belgium
[b] Green Energy & Engineering (Gre.En^2) Group – Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

ABSTRACT

The solution combustion method (SCS) is demonstrated as an easy and fast alternative method allowing the synthesis of mixed oxides with thermally sensitive metals, still keeping a good control on their stoichiometry and phase composition. Bismuth molybdates with different theoretical Bi/Mo atomic ratios, namely α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6 were synthesized by the SCS, fully characterized by XRD, Raman, SEM/EDX, BET and XPS analyses, and tested in the partial oxidation of propene to acrolein. The SCS method allowed obtaining crystalline catalysts with Bi/Mo atomic ratios close to the theoretical values and very good catalytic properties namely high propene conversion (from 13.4 to 23.4%) and acrolein selectivity (from 71.5 to 80.0%) at 425 °C. A high purity of the SCS prepared bismuth molybdates was obtained by means of a subsequent calcination treatment. Such treatment did not alter the high catalytic activity of the catalysts, which slightly increased (from 12.3 to 25.5%), but induced a marked loss of acrolein selectivity (from 66.2 to 48.4%) at 425 °C. This effect is due to a strong increase of the oxidation states of Mo and Bi and reduction of the specific surface area during the calcination.

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1. Introduction

Co-precipitation, high temperature solid-state reactions, spray drying or sol–gel syntheses are the most common methods used to prepare mixed oxide catalysts [1–8]. These routes require severe conditions and long calcination treatments at high temperatures to prepare crystalline materials. This is why the morphology and surface texture of the as-prepared catalysts and thus their resulting catalytic activity are not easily controlled. On this point of view, the solution combustion synthesis (SCS) appears as an elegant alternative protocol. This method is quite simple and presents several advantages. It is based on highly exothermic redox chemical reactions between metallic compounds and non-metallic ones.

The first step of the SCS involves the preparation of an aqueous solution containing suitable metal salts. Nitrates are chosen as metals precursors because of their high solubility in water and the oxidizing potential of NO_3^- groups. An organic molecule is then added to the mixture to form complexes with the metal ions and to facilitate the obtaining of a homogeneous solution. The organic molecule works as a fuel as its combustion enables to release a huge amount of heat in a short period of time. Various organic compounds can be used such as urea, glycine, hydrazine or precursors containing a carboxylate anion. The two first compounds are the most convenient ones since they are cheap and readily available commercially. The second step of the SCS process thus consists in heating the final solution until reaching temperatures in the range of 300–450 °C, which brings the solution to ebullition. The resulting mixture then becomes dry and in a matter of minutes ignites what sets off highly exothermic, self-sustaining and fast redox reactions that generate a dry, usually crystalline, fine powder.

The exothermicity of these redox reactions allows reaching temperature peaks that vary from 700 to 1500 °C [9–15]. The very short residence time at high temperature enables synthesizing solid with a minimized occurrence of sintering. Compounds having a relatively high specific surface area can thus be prepared. The rapidity of the method may also allow the formation of metastable phases [9–12]. Finally, a rapid crystallization could favour defects which sometimes enable improving the selectivity of catalysts towards the wished product. The SCS method, in fact, has been favourably used to produce cheaply a huge variety of nanomaterials, such as

catalysts, phosphors, pigments and refractories, for many different applications [16–22].

However, severe conditions as the high-temperatures that are reached during the SCS method appear conflicting with the synthesis of materials made of temperature sensitive metals like molybdenum, rhenium and ruthenium. Among these, MoO_3 indeed sublimates starting from 800 °C [23]. The opportunity to generate temperature sensitive oxides with relatively high specific surface area via the SCS method is then here broached through the synthesis of bismuth molybdates. Three main crystallographic phases of BiMo-mixed oxides are distinguished at atmospheric pressure: $Bi_2Mo_3O_{12}$ (the α-phase), $Bi_2Mo_2O_9$ (the β-phase) and Bi_2MoO_6 (the γ-phase) [24–26]. These phases are generally prepared via a solid co-precipitation within an aqueous solution having a Bi/Mo molar atomic ratio equal to 2/3, 1/1 and 2/1, respectively. In the present study, these materials are prepared via the SCS method. A first key question is to evaluate to what extent the SCS method allows preparing bismuth molybdates keeping the control of the stoichiometry and homogeneity of the prepared solids. After their synthesis, the bismuth molybdates are used as catalysts in the propene partial oxidation to acrolein. The second key question is to check whether the simple SCS method is able to produce highly efficient catalysts. This reaction was selected because of the well-known efficiency of bismuth molybdates for the allylic oxidation of olefins. In fact, the reaction's products are important intermediates involved in numerous downstream chemical processes [6,27]. In a world where sustainability and the development of environmentally friendly chemical processes has become a major concern, this work is thus also in line with the efforts trying to improve the valorization of light olefins [28].
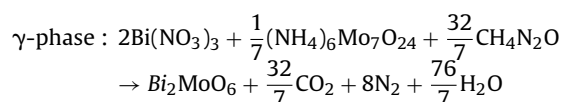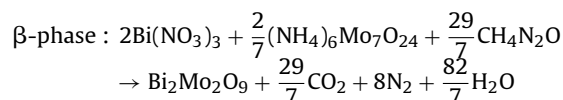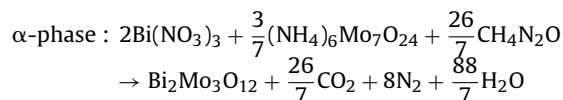
2. Experimental

2.1. Chemicals

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, >98% purity), ammonium molybdate tetrahydrate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$, >99% purity), and urea (NH_2CONH_2, > 99% purity), were purchased from Sigma–Aldrich. Nitric acid (HNO_3, 65 wt.%) was purchased from Merck. All aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q system with a resistivity > 18 MΩ cm^{-1}. Technical grade propene (99.5%), research oxygen and nitrogen (99.999% purity) gases were provided by Praxair and used as received.

2.2. Synthesis of materials

The bismuth molybdates were prepared by the SCS method according to the following stoichiometric reactions:

$$\alpha\text{-phase}: 2Bi(NO_3)_3 + \frac{3}{7}(NH_4)_6Mo_7O_{24} + \frac{26}{7}CH_4N_2O$$
$$\rightarrow Bi_2Mo_3O_{12} + \frac{26}{7}CO_2 + 8N_2 + \frac{88}{7}H_2O$$

$$\beta\text{-phase}: 2Bi(NO_3)_3 + \frac{2}{7}(NH_4)_6Mo_7O_{24} + \frac{29}{7}CH_4N_2O$$
$$\rightarrow Bi_2Mo_2O_9 + \frac{29}{7}CO_2 + 8N_2 + \frac{82}{7}H_2O$$

$$\gamma\text{-phase}: 2Bi(NO_3)_3 + \frac{1}{7}(NH_4)_6Mo_7O_{24} + \frac{32}{7}CH_4N_2O$$
$$\rightarrow Bi_2MoO_6 + \frac{32}{7}CO_2 + 8N_2 + \frac{76}{7}H_2O$$

To prepare 500 mg of each type of catalyst, Bi and Mo precursors, and urea were used in a stoichiometric amount, according to the α-, β-, or γ-phase, and dissolved in ultrapure distilled water. For each catalyst, the obtained solution was thoroughly stirred at 80 °C to ensure the complete dissolution of all reagents. It was then transferred in a ceramic dish and placed into an electric oven set at 430 °C. After water evaporation and a significant increase in the system viscosity, the heat released in the fast reaction allowed the formation of the catalytic powders. The total time necessary to produce the powder was approximately 20 min. Subsequently, after grinding in an agate mortar, half of the prepared powders were calcined in an oven at 425 °C for 4 h in static air, to favour the decomposition of the eventually unreacted nitrate precursors and improve the formation of the desired α, β, or γ crystalline phases. The samples obtained right after the SCS are noted with _F at the end of their label (F for fresh), whereas the calcined ones are noted with _C at the end of their label (C for calcined).

A reference sample ($Bi_2Mo_2O_9$-Cop) having a Bi/Mo ratio of 1 was also prepared via the co-precipitation method, as described by Carrazan et al. [29]. $Bi(NO_3)_3 \cdot 5H_2O$ (0.04 mol) was dissolved in a distilled water solution (1 L) heated at 50 °C by using concentrated HNO_3 (0.05 L). ($NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.006 mol) dissolved in distilled water (0.35 L) was added to the bismuth solution before adjusting the pH at 5 with diluted NH_3 (5 mol L^{-1}). The final solution was stirred for 2 h, aged 24 h and filtered. The recovered solid was dried overnight at 110 °C and calcined at 550 °C, for 4 h, in static air and in a muffle oven. A 5 °C min^{-1} ramp was used to reach the desired calcination temperature.

2.3. Characterization

X-ray diffraction measurements (XRD) were performed on a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 0.15418 nm). The 2θ diffractograms were recorded at a rate of 1.2° min^{-1} between 5 and 75°. The ICDD-JCPDS database was used to identify the detected crystalline phases.

Nitrogen physisorption was performed at −196 °C on a Micromeritics ASAP 2020 instrument. Before the measurement, each sample (about 100 mg) was outgassed overnight at 150 °C in vacuum (7 Pa). The specific surface area was evaluated by the BET method between 0.05 and 0.30 p/p°. The pore diameter distribution was evaluated by the Barrett–Joyner–Halenda (BJH) method, calibrated for cylindrical pores according to the improved Kruk–Jaroniec–Sayari (KJS) method, with the corrected form of the Kelvin equation, from the desorption branches of the isotherms.

Confocal Raman spectroscopy was performed on an InVia Raman microscope (Renishaw) equipped with a diode light (785 nm). The spectra were recorded between 100 and 3500 cm^{-1} with a 4 cm^{-1} resolution. 10 scans were recorded and averaged for each sample. Moreover, an acquisition time of 10 s was selected, a laser power was set to 10 mW and the 50× objective was used to focus the apparatus.

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EXD FEI-Quanta^{TM} Inspect 200 with EDAX PV 9900 instrument working at 15 kV) was performed to analyze the morphology and evaluate the average chemical composition of the prepared samples. EDX spectra were analyzed with the Genesis Spectrum v. 6.04 (EDAX Inc.) software.

X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronics PHI 5800 Versa Probe electron spectrometer system with monochromated Al Kα X-ray source at 1486.60 eV operated at 25 W, 15 kV, with 100 micron X-rays spot. To reduce any possible charging effects of X-rays, a dual beam charge neutralization method was applied, combining both low energy ions and electrons. The samples were previously outgassed in an ultra-high vacuum chamber at 2.5×10^{-6} Pa for 12 h. Survey scans were recorded from 0 to 1200 eV. The narrow Bi 4f spectra were collected from 148 to 170 eV, the narrow Mo 3d spectra from 218 to 240 eV, and the narrow O 1s spectra from 524 to 536 eV. The samples were analyzed under identical conditions and corrections