



Selective oxidation of propylene to acrolein by hydrothermally synthesized bismuth molybdates



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ABSTRACT

Hydrothermal synthesis has been used as a soft chemical method to prepare bismuth molybdate catalysts for the selective oxidation of propylene to acrolein. All obtained samples displayed a plate-like morphology, but their individual aspect ratios varied with the hydrothermal synthesis conditions. Application of a high Bi/Mo ratio during hydrothermal synthesis afforded γ -Bi₂MoO₆ as the main phase, whereas lower initial bismuth contents promoted the formation of α -Bi₂Mo₃O₁₂. Synthesis with a Bi/Mo ratio of 1:1 led to a phase mixture of α - and γ -bismuth molybdate showing high catalytic activity. The use of nitric acid during hydrothermal synthesis enhanced both propylene conversion and acrolein yield, possibly due to a change in morphology. Formation of β -Bi₂Mo₂O₉ was not observed under the applied conditions. In general, the catalytic performance of all samples decreased notably after calcination at 550 °C due to sintering.

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1. Introduction

The typical commercial catalyst for the selective oxidation of propylene to acrolein and for propylene ammoxidation to acrylonitrile is based on bismuth molybdates as the active species in combination with additional elements such as Co, Ni, Fe, Cr, Al or alkali metals [1,2]. Transition metal molybdates, especially CoMoO₄ or Fe₂(MoO₄)₃ and their solid solutions, increase the ability to exchange electrons and oxygen anions due to the effective activation of molecular oxygen by Co²⁺ and Fe³⁺. They change the morphology of the catalyst under the reaction conditions along with recently reported synergistic effects of the different phases [3–5]. Other elements, including alkali metals, W, V, Nb, etc. are usually added to enhance the catalyst life time and its mechanical strength. They also lead to minor improvements in activity and selectivity [6,7].

Various bismuth molybdates including α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ have been prepared and tested as oxidation catalysts [8]. Whereas γ -Bi₂MoO₆ exhibits an Aurivillius-type structure with alternating [Bi₂O₂]²⁺ slabs and layers of corner sharing MoO₆ octahedra, both the α - and the β -phase can be considered as defective fluorite structures consisting of tetrahedral MoO₄ motifs. At temperatures above 570 °C the metastable γ'' -phase is formed which is further transferred to the high-temperature γ' -phase at 640 °C. γ' -Bi₂MoO₆, which is also known as the γ (H)-phase, also has a fluorite-like structure based on MoO₄ tetrahedra [9]. The metastable phase β -Bi₂Mo₂O₉ can usually be accessed in the temperature range from 540 to 665 °C [10].

Despite extensive preceding studies, there is an ongoing debate in literature about the relative catalytic activity of these phases [11,12]. The group of Keulks [4,11] found the γ -Bi₂MoO₆ phase to be most active, whereas Burrington and Grasselli [13] stated that the β -phase showed the highest rates for propylene oxidation. Carson et al. [14] prepared the different bismuth molybdate phases by co-precipitation at pH = 7 and found that the catalytic activity for propylene oxidation decreased in the following order: $\alpha > \gamma > \beta$. They further concluded that a mechanical mixture of α -Bi₂Mo₃O₁₂

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and γ - Bi_2MoO_6 was more active and selective in propylene oxidation to acrolein than the according pure phases. This synergistic effect was confirmed by Bing et al. [12], who suggested that the γ -phase generated the active oxygen species, while the α -phase contributed the selective sites for acrolein formation. According to Le et al. [15] the synergistic effect was only observed in mixtures containing the γ -phase in close contact to the other phases.

The most common method to prepare bismuth molybdate catalysts is co-precipitation [16,17] followed by calcination or solid-state reaction [18] at temperatures up to 1000 °C, but also sol-gel synthesis [19] or spray drying [20] were applied. These synthesis routes require harsh conditions and high temperatures to obtain crystalline products, which may influence the catalytic activity of the resulting phase. van Well et al. [21] found that the activity of γ - Bi_2MoO_6 prepared by co-precipitation and spray drying strongly depended on the calcination conditions. Alternatively γ - Bi_2MoO_6 has been synthesized under hydrothermal conditions applying cetyltrimethylammonium bromide (CTAB) as a surfactant [22] or using sodium, chlorine or fluorine containing reactants [23,24], which may remain in the product and influence its catalytic performance. Hydrothermal processes are typical soft chemistry ('chimie douce') approaches which provide convenient access to advanced materials of high crystallinity, high purity, narrow size distribution and a low degree of aggregation [8]. Beale and Sankar [25] prepared α - and γ -bismuth molybdate in a one step hydrothermal synthesis from Bi_2O_3 dissolved in nitric acid and ammonium molybdate dissolved in ammonium hydroxide. Synthesis with β -phase stoichiometry (Bi/Mo = 2:2) and variation of the pH value did not yield β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ under hydrothermal conditions so that heat treatment was required [8].

In the present study, mild hydrothermal techniques were applied to produce various bismuth molybdate phases with different morphologies and corresponding phase mixtures. The influence of calcination on the phase composition and the catalytic activity for propylene oxidation to acrolein has been studied in detail. However, to the best of our knowledge hydrothermally synthesized bismuth molybdates have not yet been applied for the selective oxidation of propylene to acrolein. In the following, we compare the properties of catalysts emerging from this flexible synthetic route to samples synthesized by conventional co-precipitation.

2. Experimental

2.1. Synthesis

The bismuth molybdate materials were synthesized by hydrothermal synthesis, while reference samples were obtained from conventional co-precipitation. All chemicals were analytical grade and used without further purification.

In a typical hydrothermal synthesis 10 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and the stoichiometric amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Bi/Mo ratios in the range of 0.5–3) were dissolved in 100 ml deionized water. These samples will be referred to here as HT.BixMoy with x/y being the Bi/Mo molar ratio. Additionally for a ratio of Bi/Mo = 1:1 the pH was adjusted from 0.9 to 4 by addition of ammonium nitrate solution (HT.Bi1Mo1.pH4). 5 ml of nitric acid was added to the solution containing a Bi/Mo ratio of 1:1 and 2:1 referred to as HT.BixMoy.HNO₃. Precursors with a Bi/Mo = 2:1 ratio were moreover dissolved in 80 ml of 25 vol.% acetic acid to lower the pH value from 0.8 to 0.2 (HT.Bi2Mo1.HOAc). The resulting solutions were heated in sealed 250 ml autoclaves (Berghof) with Teflon inlays at 180 °C for 24 h in an oven. After cooling to room temperature, the solid product was separated by filtration, washed with water, ethanol and finally with acetone. The resulting powder was dried at room temperature and ambient pressure. The samples prepared with a Bi/Mo ratio in the range 0.5–2 in water were also calcined at 550 °C for 4 h.

The corresponding co-precipitated samples were synthesized according to Carrazán et al. [6] using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in NH_4OH and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ dissolved in HNO_3 at pH = 7. The resulting solid material was calcined at 450 °C to yield the α - and the γ -phases and at 680 °C to obtain the β -phase. Experiments are referred to as CP.BixMoy_CT where CT is the calcination temperature in °C.

2.2. Characterization

Powder X-ray diffraction (PXRD) measurements were recorded using a Bruker D8 Advance powder diffractometer in the range $2\theta = 8\text{--}80^\circ$ (step size 0.016°) with $\text{Cu K}\alpha$ radiation (Ni-filter, 45 mA, 35 kV) on rotating sample holders. Raman spectra were recorded with a Horiba Jobin Yvon spectrometer (LabRam) attached to an Olympus microscope (BX 40) using a 632.8 nm laser in the range $100\text{--}1100\text{ cm}^{-1}$ on an object slide without pretreatment of the sample.

The specific surface area (SSA) was measured by nitrogen adsorption at its boiling point (Belsorp II mini, BEL Japan Inc.) using multipoint BET theory in the $p/p_0 = 0.05\text{--}0.3$ range.

For scanning electron microscopy (SEM), performed on a Quanta 200 ESEM (FEG) microscope at the Centre of Electron Nanoscopy (CEN) at DTU, samples were deposited on a carbon foil on aluminium stubs and coated with carbon to improve the conductivity.

Surface analysis by X-ray photoelectron spectroscopy (XPS) was performed with a K-Alpha spectrometer (ThermoFisher Scientific) using a microfocused $\text{Al K}\alpha$ X-ray source (400 μm spot size). Data acquisition and processing using Thermo Avantage software is described elsewhere [26]. Charge compensation during analysis was achieved using electrons of 8 eV energy and low energy argon ions to prevent any localized charge build-up. Spectra were fitted with one or more Voigt profiles (binding energy uncertainty: $\pm 0.2\text{ eV}$) [27,28]. Scofield sensitivity factors were applied for quantification [29]. The energy scale was calibrated to the binding energy of C 1s (C–C, C–H) at 285.0 eV controlled by means of the well known photoelectron peaks of metallic Cu, Ag and Au, respectively.

The bulk composition of the catalysts was determined by optical emission spectrometry with inductively coupled plasma (ICP-OES, Agilent 720/725-ES). The plasma was created by a 40 MHz high-frequency generator and argon was applied as the plasma gas. For the ICP-OES each sample was dissolved in 6 ml concentrated HNO_3 , 2 ml concentrated HCl and 0.5 ml H_2O_2 in a microwave (at 600 Watt for 45 min).

Quantitative nitrogen analysis was carried out using hot gas extraction method (LECO TC 600). The samples were heated in a graphite crucible under flowing helium and thermally decomposed. The amount of N_2 gas was determined by a heat conductivity detector. Each measurement was repeated twice and a standard deviation was calculated.

2.3. Catalytic test reaction

Catalytic activities were measured in a continuous flow fixed bed reactor, a U-shaped quartz reactor with 4 mm inner diameter. The catalyst powders were crushed and sieved to 150–300 μm particles and 500 mg of sample was loaded in the reactor and stabilized with quartz wool. The quartz reactor was connected to a commercial test unit (ChimneyLab Europe) with calibrated mass flow controllers (Brooks) and placed in an oven (Watlow) [30]. A thermocouple was placed inside the reactor just touching the catalyst bed to measure the reaction temperature and a pressure transducer placed upstream of the reactor measured the actual reaction pressure. The catalysts were pre-oxidized in dry air at 550 °C for the calcined hydrothermally synthesized samples and at

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