Electronic Supporting Information (ESI)

One-step synthesis of bismuth molybdates via flame spray pyrolysis used in the selective oxidation of propylene


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This electronic supporting information gives additional description of the preparation, characterization and the catalytic activity tests as well as on the evaluation of the test data. Moreover, X-ray absorption near edge structure (XANES) spectra of the as prepared and a used sample, transmission electron microscopy (TEM) images of the three flame made samples and powder X-ray diffraction (PXRD) pattern of the used samples are given. Where not sufficiently described in the paper some further explanation is given as well.

1. Experimental details

1.1. Preparation

The high surface area samples bismuth molybdates with Bi/Mo ratios of 1:1, 2:1 and 2:3 were prepared by flame spray pyrolysis (FSP) from Bi(III)- and Mo(VI)-2-ethylhexanoate dissolved in xylene (total concentration of 0.15 mol/l). 50 ml syringes are used, which are placed in a syringe pump (World Precision Instruments) and the precursor solution was pumped with a speed of 5 ml/min. Oxygen was used as dispersion gas (5 Nl/min) to create the spray and the supporting flame was a mixture of oxygen (1.6 Nl/min) and methane (750 Nml/min). The gas flows were controlled by mass flow controllers (Bronkhorst). The spray was ignited by the oxygen/methane supporting flame and the products were collected on water cooled glass fiber filter (Ø 240 mm; Whatman GF6) by means of a vacuum pump (R5, Busch).
1.2. Materials characterization

The structure of the different samples was determined by powder X-ray diffraction (PXRD) using a Bruker D8 Advance diffractometer in the range 2θ = 8 - 80° (step size 0.016 °) with Cu Kα radiation (Ni-filter, 45 mA, 35 kV) in Bragg-Brentano geometry on rotating sample holders.

X-ray absorption spectroscopy (XAS) was performed at the beamline BM01B at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The samples were diluted with boron nitride and pressed as pellets for ex situ measurement in transmission mode at the Mo K edge (20.0 keV) using a continuously scanning Si(111) double crystal monochromator and a gold-coated mirror for the rejection of higher harmonics. A Mo foil was measured as an energy-calibration reference. XAS data were processed using the IFFEFIT software package 1.

Bright field transmission electron microscopy (Tecnai T20) was measured on the as-prepared powders supported on lacey carbon copper grids. The oxidic catalyst powder in the sieve fraction < 150 µm was transferred to the grid by dipping it several times in the powder and removing loosely bound excess.

Nitrogen physisorption at the boiling point of nitrogen was used to determine the specific surface area (SSA) of the various samples with a Belsorp II mini (BEL Japan Inc.) using multipoint BET theory in the p/p₀ = 0.05 – 0.3 range.

For analysis of the surface composition XPS was performed with a K-Alpha spectrometer (ThermoFisher Scientific) using a microfocused Al Kα X-ray source (400 µm spot size), data acquisition and processing was performed using the Thermo Avantage software 2. Charge compensation during analysis was achieved using electrons of 8 eV energy and low energy argon ions to prevent any localized charging. Spectra were fitted with one or more Voigt profiles (binding energy uncertainty: ±0.2 eV). Scofield sensitivity factors were applied for quantification. 3 The energy scale was shifted to the binding energy of C 1s (C-C, C-H) at 285.0 eV and was calibrated by means of the peaks of metallic Cu 2p, Ag 3d and Au 4f, 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 HNO₃, 2 ml concentrated HCl and 0.5 ml H₂O₂ in a microwave (at 600 Watt for 45 minutes).

1.3. Catalytic test measurements

In a typical test of the catalytic performance the FSP-derived powders were pressed, crushed and sieved to 150 – 300 µm sized particles, 500 mg of sample was loaded in the reactor without dilution and stabilized with quartz wool (see analogous procedure in ref. 4). The catalysts were pre-oxidized in dry air at 300 °C in the reactor. Activity tests were performed using a gas composition of C₃H₆/O₂/N₂ = 5/25/70 and flows of 50, 80 and 120 Nml/min at 360 °C. Gas analysis was performed using a dual channel GC–MS (Thermo Fisher) with a TCD detector to quantify N₂, O₂, CO and CO₂ and a FID detector parallel with the MS to identify and quantify light hydrocarbons and oxygenated products.

The measured concentrations were corrected for expansion of the gas due to combustion using the nitrogen signal as internal standard, before calculating the conversion of propylene ($X_{Propylene}$), the selectivity to acrolein ($S_{Acrolein}$) and the acrolein yield ($Y_{Acrolein}$).

$$X_{Propylene} = 1 - \frac{c_{C_3H_6}^{bypass}}{c_{C_3H_6}}$$

$c_{C_3H_6}$ propylene concentration detected in the product stream [vol.%]

$c_{C_3H_6}^{bypass}$ propylene concentration detected in the bypass [vol.%]

$$S_{Acrolein} = \frac{c_{C_3H_4O}^{bypass}}{c_{C_3H_6}^{bypass} - c_{C_3H_6}}$$

$c_{C_3H_4O}$ propylene concentration detected in the product stream [vol.%]

$$Y_{Acrolein} = X_{Propylene} \cdot S_{Acrolein} = \frac{c_{C_3H_4O}^{bypass}}{c_{C_3H_6}^{bypass}}$$
2. Additional results from characterization and catalytic tests

Figure S1 shows X-ray absorption near edge structure (XANES) spectra measured at the Mo K edge of two FSP-derived samples which are compared to Na$_2$MoO$_4$·2H$_2$O (tetrahedral Mo) and α-MoO$_3$ (octahedral Mo). According to Reilly et al. the features A and B correspond to 1s-4d (A) and 1s-5p (B) transitions, respectively. The pre-edge feature A is larger for sodium molybdate containing tetrahedrally coordinated Mo(VI) compared to orthorhombic MoO$_3$, which incorporates Mo(VI) in an octahedral environment, because the 1s-4d transition is more allowed in tetrahedral symmetry.

![XANES spectra](image)

**Fig. S1** X-ray absorption near edge structures (XANES) of the flame made samples with Bi/Mo = 2:1 and Bi/Mo = 1:1 as well as two reference spectra measured at the Mo K edge (Na$_2$MoO$_4$·2H$_2$O: tetrahedral Mo; α-MoO$_3$: octahedral Mo).

XANES spectra of the sample synthesized with Bi/Mo = 1:1 are similar to those of Na$_2$MoO$_4$·2H$_2$O indicating that β-Bi$_2$Mo$_2$O$_9$ was formed by flame spray pyrolysis, given that the β-phase contains tetrahedral Mo(VI) species. The spectra measured for the sample with Bi/Mo = 2:1 exhibited a stronger peak in the B region sensitive for octahedral Mo(VI) and lower intensity for A, which agreed well with reference data for octahedrally coordinated Mo (reference here α-MoO$_3$).
XPS spectra of the FSP samples with Bi/Mo ratio of 1:1 and 2:1 around the Mo 3d- and Bi 4f-region are shown in Figure S2.

**Fig. S2** XP spectra including the according Voigt fits (red and green line) of the flame made samples with Bi/Mo = 2:1 and 1:1. For a better visualization all spectra are normalized to maximum intensity.
Selected electron microscopy images are given in Figure S3 and the catalytic performance in Figure S4.

**Fig. S3** Transmission electron microscopy (TEM) images of the samples synthesized with Bi/Mo = 2:1 (a, b), Bi/Mo = 1:1 (c, d) and Bi/Mo = 2:3 (e, f).

TEM images evidenced that the samples with initial Bi/Mo ratio of 1:1 and 2:3 yielded larger particles with smaller spherical particles with a diameter < 10 nm on top.
Fig. S4 Performance of the flame made materials in the selective oxidation of propylene to acrolein at 400 °C (a and b) and at 440 °C (c and d). Clear deactivation of the sample synthesized with Bi/Mo = 1:1 is observed since the conversion at 440 °C is almost the same as at 400 °C, in line with the decomposition of $\beta$-Bi$_2$Mo$_3$O$_9$ to $\alpha$-Bi$_2$Mo$_3$O$_12$ and $\gamma$-Bi$_2$MoO$_6$ occurring at 440 °C and upwards (Fig. 2). The samples synthesized with Bi/Mo = 2:1 does not deactivate since higher conversion is observed at 440 °C than at 400 °C.
Fig. S5 X-ray diffraction pattern of the samples after application in the selective oxidation of propylene to acrolein at 360 °C and heating up to 520 °C. The samples synthesized with Bi/Mo = 2:1 and 2:3 did not change their phase composition during the catalytic activity tests at higher temperatures, whereas β-Bi$_2$Mo$_3$O$_9$ decomposed into α-Bi$_2$Mo$_3$O$_{12}$ and γ-Bi$_2$MoO$_6$ at T > 440 °C.
Fig. S6: XANES of the flame made $\gamma$-Bi$_2$MoO$_6$ and $\beta$-Bi$_2$Mo$_2$O$_9$. A phase change of the sample synthesized with Bi/Mo = 1:1 at temperatures above 440 °C is indicated by the spectra (compare green and black line).

XANES obtained after normalization indicated $\gamma$-Bi$_2$MoO$_6$ for the sample synthesized with Bi/Mo = 2:1, which contains octahedral Mo(VI) species. The spectrum for the sample synthesized with Bi/Mo = 1:1 is more dominant in the region A but the intensity is less in the region B, which is in well agreement with $\beta$-Bi$_2$Mo$_2$O$_9$, containing tetrahedral Mo(VI) species. The spectrum of the used sample lies in between, which fits well with the results obtained from the X-ray diffraction pattern suggesting the presence of a mixture of $\alpha$- and $\gamma$-bismuth molybdate.

References