



Molybdenum oxide supported on nanostructured MgO: Influence of the alkaline support properties on MoO_x structure and catalytic behavior in selective oxidation



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ABSTRACT

Local structure and catalytic activity of molybdenum oxide supported on alkaline, nanostructured support materials were investigated. The structure of the surface oxide catalysts was significantly affected by the properties of the support. The support material was prepared via two different routes. A direct MgO synthesis approach was compared to SBA-15 coated with magnesium oxide. The structure of the support materials was investigated by XRD and N₂ physisorption. Both materials exhibited a high specific surface area with a narrow pore size distribution. The MgO-coated SBA-15 (*MgO/SBA-15*) exhibited a similar alkaline character as pure nanostructured MgO (*nano-MgO*) but was more stable under catalytic conditions. The highly dispersed molybdenum species on the support was characterized by XRD, XAS and DR-UV-Vis spectroscopy. The catalytic activity for selective oxidation of propene was investigated by gas chromatography. A considerably different species was present on the alkaline support, compared to more acidic support materials like SBA-15. The structure of the supported molybdenum oxide consisted of predominantly isolated [MoO₄] tetrahedra and was largely independent from Mo loadings. The supported catalysts with isolated [MoO₄] tetrahedra exhibited only poor catalytic activity compared to the higher polymerized Mo species supported on silica SBA-15.

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1. Introduction

Molybdenum oxide based catalysts are frequently used in selective oxidation of light alkanes and alkenes [1]. The most simple molybdenum oxide, orthorhombic α -MoO₃, exhibits only poor catalytic activity. Addition of further metal centers like tungsten or vanadium leads to an increase in catalytic activity and selectivity towards selective oxidation products [2]. Mixed oxides usually consist of interlinked polyhedra with cations of different valences. However, the origin of the promoting effect of additional metal centers is still under debate [3–6]. The use of supported metal oxides instead of bulk material simplifies the investigation of particular metal oxide structures, which are otherwise not available under reaction conditions. Supported oxides function as model systems, which allow correlating local structural motifs with catalytic behavior without considering bulk oxide properties. Hence, supported molybdenum oxides are frequently used to investigate binary metal oxide structures. The material used as support is known to influence the metal-support interaction. Al₂O₃ and silica type

support materials like SBA-15 are well-established and the interactions with the supported oxides are reasonably understood [7–11]. Only few studies report on molybdenum oxide supported on magnesium oxide [12–15]. MgO exhibits alkaline properties, which is in contrast to the acidic silica SBA-15. According to Wachs et al. the structure of supported metal oxides is correlated to the net pH at the point of zero charge of the oxide support. They investigated the structural dependency of vanadium oxides supported on different oxide materials on the net pH and predicted a tetrahedral molybdenum oxide species on the surface of an alkaline support [16]. This has later been confirmed by Aritani et al. for MgO-supported molybdenum oxides [15]. Furthermore, Bare et al. reported an isolated tetrahedral molybdenum species for uncalcined samples between weight loadings of 5–20 wt.%. Accordingly, calcination led to a transformation of the tetrahedral molybdenum oxide to an octahedral species. They correlated the structural change to the loss of surface hydroxyl groups during calcination [13,14]. Stampf et al. detected the formation of [MoO₄] tetrahedra by simply mixing MoO₃ with MgO mechanically, which indicated that Mo ions very easily diffuse from the MgO surface into the bulk material [17]. Llorente et al. considered the bulk diffusion of the Mo ions to be temperature dependent, thus leading to the formation of MgMoO₄ at temperatures above 1093 K and highly dispersed MoO₃ at moderate calcinations temperatures

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[12]. Here, we investigated Mo oxides supported on two different high surface area materials with alkaline properties on the basis of magnesium oxide. The materials exhibited a high specific surface area generated through an open pore structure similar to SBA-15. To further elucidate the structure–activity correlation, structural differences of molybdenum species depending on the support material were investigated.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of support material

Mesoporous magnesium oxides were prepared by two different routes. MgO-coated SBA-15, denoted as “MgO/SBA-15”, was synthesized using the mesoporous, hexagonally ordered silica SBA-15 as structural template [18]. SBA-15 was prepared according to Zhao et al. [19]. Hydrothermal treatment was performed at 403 K for 24 h. However, unlike the procedure described by Zhao et al., calcination was carried out in two steps. Initially, calcination temperature was kept for 3 h at 453 K, followed by a second calcination step at 823 K for 5 h. The resulting SBA-15 was impregnated with magnesium nitrate. Typically 2.0 g of SBA-15 were stirred for 5 h at room temperature in 20 ml of a 1-M $\text{Mg}(\text{NO}_3)_2$ (hexahydrate, Alfa Aesar, 98%) solution with an $\text{H}_2\text{O}/\text{EtOH}$ ratio of 1:1. The $\text{Mg}(\text{NO}_3)_2$ to SBA-15 ratio of the resulting dispersion was approximately 3:1. The product was filtered off and dried under a flow of synthetic air at room temperature for 6 h. Calcination of $\text{Mg}(\text{NO}_3)_2$ on SBA-15 was carried out under the same gas flow for 3 h at 723 K. The heating rate was kept at 2 K/min.

Nanostructured magnesium oxide, denoted as “nano-MgO”, was synthesized for comparison and verification of the alkaline properties of both support materials. Nano-MgO was synthesized using a hydrothermal approach with triblock copolymer P-123 (Aldrich) as template reagent. A similar synthesis procedure has already been reported for mesoporous zinc oxide [20]. Typically 5.37 g of $\text{Mg}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 98%) and 30.03 g of $\text{CO}(\text{NH}_2)_2$ (Roth, 99.6%) were dissolved in 400 ml of deionized water. 154 mg of P-123 were added to the solution and the pH value was adjusted to 4.6 using acetic acid. The solution was stirred for 24 h at room temperature and then kept at 363 K under hydrothermal conditions for 48 h. The solid product was filtered off, washed with deionized water to neutral pH, and dried for 2 h at 388 K. The resulting white spherules were calcined under static atmosphere at 673 K for 2 h.

2.1.2. Synthesis of supported Mo oxides

Subsequently, both nano-MgO and MgO/SBA-15 were loaded with molybdenum oxide. The amount of molybdenum was adjusted to 5 wt.%. Preparation of the samples was done by incipient wetness. An aqueous solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (AHM, Fluka, 99.0%) was used. Calcination was carried out under static conditions at 723 K for 5 h.

2.2. Sample characterization

2.2.1. X-ray absorption spectroscopy (XAS)

In situ and ex situ transmission XAS experiments were performed at the Mo K edge (20.0 keV) at beamline X1 at the Hamburg Synchrotron Radiation Laboratory, HASYLAB, using a Si(311) double crystal monochromator. Transmission XAS measurements were performed in an in situ cell described earlier [21]. Powder samples were pressed into self-supporting pellets (5 mm in diameter). The sample weight (30–50 mg) was calculated to result in an edge jump of $\Delta\mu(d) = 1.0$. Reference materials and samples for ex situ

measurements were diluted with 200–250 mg of polyethylene (PE, Induchem Switzerland) and pressed into self-supporting pellets of 13 mm in diameter. XAFS spectra at the Mo K edge (19.9–20.8 keV, to 14.5 \AA^{-1}) were measured in approximately 3 min. In situ measurements were conducted in 5% propene and 5% oxygen in helium (total flow 40 ml/min) in a temperature range from 293 K to 723 K at a heating rate of 4 K/min. The gas atmosphere was analyzed using a non-calibrated mass spectrometer in a multiple ion detection mode (Omnistar, Pfeiffer).

X-ray absorption fine structure (XAFS) analysis was performed using the software package WinXAS v3.2 [22]. Background subtraction and normalization were carried out by fitting linear polynomials to the pre-edge and third degree polynomials to the post-edge region of an absorption spectrum, respectively. The extended X-ray absorption fine structure (EXAFS) $\chi(k)$ was extracted by using cubic splines to obtain a smooth atomic background $\mu_0(k)$. The $\text{FT}(\chi(k) * k^3)$ was calculated by Fourier transformation of the k^3 -weighted experimental $\chi(k)$ function, multiplied by a Bessel window, into the R space.

2.2.2. Powder X-ray diffraction (XRD)

Powder X-ray diffraction patterns were obtained using an X'Pert PRO MPD diffractometer (PANalytical) in theta/theta geometry. Cu K alpha radiation (40 kV and 40 mA) and a solid state multi-channel PIXcel[®] detector were used.

Low-angle diffraction patterns were measured in the transmission mode between 0.4° and $6^\circ 2\theta$ and -0.4° and $-4^\circ 2\theta$ in steps of $0.013^\circ 2\theta$ with a sampling time of 90 s/step. The positive and negative values for the (10l) diffraction line were averaged. Wide-angle diffraction patterns were measured in reflection mode in a range of 5 – $120^\circ 2\theta$ in steps of $0.013^\circ 2\theta$ with a sampling time of 60 s/step. A programmable slit was used to obtain an active irradiation length of 12 mm/step. Diffraction refinements were carried out by using the program X'Pert HighScore Plus (v2.2d, PANalytical).

2.2.3. X-ray fluorescence analysis (XRF)

Elemental analysis by X-ray fluorescence analysis was carried out on an AXIOS X-ray spectrometer (2.4 kW model, PANalytical) equipped with a Rh K alpha source, a gas flow detector and a scintillation detector. Samples were diluted with wax (Hoechst wax C micropowder, Merck) and pressed into 13 mm pellets. Quantification was performed by standardless analysis with the SuperQ 5 software package (PANalytical).

2.2.4. Diffuse reflectance UV–Vis spectroscopy (DR–UV–Vis)

UV–Vis measurements were conducted on a two-beam spectrometer (V670, JASCO) with a diffuse reflectance attachment containing an integration sphere coated with barium sulfate. Powder samples were measured in the spectral region of 200–2000 nm. Baseline correction was done with the help of a white standard. The pure support material was used as white standard for the supported molybdenum oxides. Reference materials were diluted with commercial magnesium oxide (ABCR, 99.95%). It was also used as white standard for the references.

The DR–UV–Vis spectra were transferred into the Kubelka–Munk function $F(R_\infty)$. According to Gao et al. data were plotted $(F(R_\infty) * hv)^2$ against hv . The edge energy was determined from the intercept of the straight line in the low-energy rise [23]. The uncertainty of this approach was estimated to be approximately 3%.

2.2.5. Nitrogen physisorption

Nitrogen adsorption/desorption isotherms were measured at 77 K using a BELSORP-Mini II (BEL Inc. Japan). Prior to measurement samples were degassed under reduced pressure at 383 K

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