Structure and operando catalysis of silica SBA-15 supported molybdenum oxide catalysts

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Introduction

Supported molybdenum oxide catalysts have been shown to be active in partial oxidation of alkanes. The active sites in such systems are considered to be dispersed molybdenum oxide surface species. The nature of these species supported on silica has been discussed for a long time in the literature [1-3]. In this contribution we elucidate the structure dispersed molybdenum oxide using IR-, UV/Vis-, X-ray absorption spectroscopy as well as in situ/operando Raman spectroscopy. Our results show the existence of Mo-O-Mo containing i.e. dimeric/oligomeric species besides monomeric species even at low molybdenum oxide loadings (1.0 Mo/nm²) in the hydrated and dehydrated state [4,5]. Furthermore, our in situ and operando experiments reveal that the ratio of tetrahedral dioxo and square-pyramidal monooxo molybdenum oxide changes with temperature and gas-phase composition [6,7].

Experimental

The silica SBA-15 supported molybdenum oxide catalysts (MoOₓ/SBA-15) were synthesized by ion-exchange of ammonium heptamolybdate using functionalized silica SBA-15 as described elsewhere [4,5]. For IR experiments ¹⁷NO and ¹⁸NO were used as probe molecules [5]. In situ/operando Raman experiments were conducted using a new setup with 514 nm laser excitation combined with MS for product analysis. In situ Raman studies were conducted in the presence of steam (O₂/N₂/H₂O = 10/45/45). Propylene selective oxidation was studied for C₃H₆/O₂/N₂ = 3/790 at 500°C (total flow rate: 90 ml/min) [6,7].

Results and Discussion

FTIR spectra of MoOₓ/SBA-15 5.9 wt% Mo (0.8 Mo/nm²) using ¹⁷NO and ¹⁸NO adsorption followed by oxidation (Fig. 1) show bidentate and bridging nitrate bands at 1575 and 1618 cm⁻¹ (¹⁷NO: 1592 and 1533 cm⁻¹), indicating the presence of monomeric and connected molybdenum oxide centers [5]. This result is supported by UV/Vis experiments showing significant intensity at 300 to 350 nm, which originate from connected tetrahedral or connected octahedral molybdenum oxide centers [4].

The detailed EXAFS analysis of dehydrated MoOₓ/SBA-15 shows a peak at typical Mo-Mo distances in the radial distribution function FT(χ(k) k²), which implies the presence of connected molybdenum centers. Moreover, the Mo K pre-edge of the supported molybdenum oxide species is decreased compared to α-MoO₃. A fit of the Mo K pre-edge peak with octahedral and tetrahedral reference compounds (α-MoO₃ and Na₂MoO₄) exhibits an O₈ : T₄ ratio of 1 : 3 [4].

The Raman spectra of silica supported molybdenum oxide show that the molybdenum oxide structure is significantly influenced by the presence of steam. Based on a recent theoretical study [8], the bands at 969 and 991 cm⁻¹ are assigned to the asymmetric stretching mode of tetrahedral dimolybdyl (dioxo) species and the stretching mode of square pyramidal (monooxo) molybdenum oxide species. Upon exposure to steam a decrease in the intensity ratio I₉₉₁/I₉₆₉ in redshift from 991 to 983 cm⁻¹ of the monooxo species is attributed to the presence of hydrogen-bonded oxo ligands in the dioxo species [6,7]. Using DFT comparable frequency shifts have been calculated for MoO stretch vibrations of dioxo species [9].

The Raman spectra of silica supported molybdenum oxide at 500°C under oxidative (A), reactive (B) and oxidative (C) conditions strongly resemble each other and show a higher intensity of the monooxo-related Raman band as compared to the dioxo-related band under all conditions. Switching to reactive conditions (B) by propene addition to the feed results in a redshift of the monooxo-related Raman band from 991 to 983 cm⁻¹, indicating the conversion of monooxo to dioxo species. The observed 8 cm⁻¹ redshift from 991 to 983 cm⁻¹ of the monooxo species is attributed to the presence of hydrogen-bonded oxo ligands in the dioxo species [6,7]. Using DFT comparable frequency shifts have been calculated for MoO stretch vibrations of dioxo species [9].

Using IR-, UV/Vis-, X-ray absorption spectroscopy it is demonstrated that dispersed molybdenum oxide is present on silica as monomeric and di- or oligomeric species in the hydrated and dehydrated state. Furthermore, in situ/operando Raman spectroscopy shows under reactive and non-reactive conditions that the detailed structure of dispersed molybdenum oxide consists of monooxo and dioxo species in agreement with theory.

Fig. 1: IR spectra of oxidized 5.9 wt.% Mo (0.8 Mo/nm²) MoOₓ/SBA-15 (black), after treatment with NO (2.0 mbar) and O₂ (7.3 mbar) at RT (red), after evacuation to 10⁻⁵ mbar at RT (blue), after treatment at 100°C at 10⁻⁵ mbar and subsequent cooling to RT (green).

References