

New insight into the structure and dispersion of silica supported molybdenum oxide catalysts

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Introduction

Rational design of selective oxidation catalysts such as silica supported molybdenum oxide requires knowledge on the relation of structure and activity. New spectroscopic evidence for the presence of both monomeric *and* connected centers in dispersed molybdenum oxide is provided. *In situ* Raman spectra during propylene selective oxidation underline the relevance for catalysis. Detailed XPS analysis reveals new insight into the molybdenum oxide dispersion.

Experimental

Controlled synthesis of silica supported molybdenum oxide catalysts (Mo/SBA-15) was based on ion-exchange of heptamolybdate using functionalized silica SBA-15 [1,2]. Structural insight was obtained by vibrational (IR, Raman) spectroscopy [1] and supported by UV-Vis and X-ray absorption (XA) spectroscopy [3]. For *in situ* Raman experiments a new setup based on variable excitation (488, 514, 632 nm) combined with MS for product analysis was used. Propylene selective oxidation was studied for C₃H₆/O₂/N₂ = 3/7/90 at 500°C (total flow rate: 90 ml/min). For dispersion studies *quasi in situ* XPS was employed as described previously [4].

Results/Discussion

Using silica as an inert support we studied structural aspects of dispersed molybdenum oxide still debated in the literature. FTIR spectra of 5.9 wt% Mo/SBA-15 (0.8 Mo/nm²) using NO adsorption followed by oxidation (Fig. 1, left) show bidentate and bridged nitrate bands at 1575 and 1618 cm⁻¹, respectively, implying the presence of monomeric *and* connected molybdenum oxide centers [1]. These findings are supported by recent results from Raman, UV-Vis and XA spectroscopy [3]. By using *in situ* Raman spectroscopy during propylene selective oxidation at 500°C the relevance of these structural results is underlined. At higher loadings (7.6 Mo/nm²) Raman spectra in the presence of the reaction mixture reveal local structural dynamics of the supported molybdenum oxide (Fig. 1, right) as indicated by the appearance of a new Raman

band at 970 cm⁻¹ due to the formation of dispersed species. Besides, typical α -MoO₃ Raman bands at 666, 819 and 995 cm⁻¹ are observed.

Regarding molybdenum oxide dispersion detailed XPS analysis reveals that besides the cation/support ratio also the cation binding energy (BE) value gives insight into the state of dispersion due to size-dependent BE shifts [4]. Compared to the BE value of bulk α -MoO₃ (232.6 eV) the spectra show bands at higher BE indicating the presence of small aggregates of dispersed molybdenum oxide species (Table 1). The combination of XPS analysis with Raman results allows us to establish a correlation of the changes in structure and dispersion of the supported molybdenum oxide species.

Table 1. Results of the Mo 3d_{5/2} analysis and Mo/Si atomic ratios of Mo/SBA-15 samples

Loading (Mo/nm ²)	Mo/Si	BE (eV)
0.8	0.039	234.0
2.4	0.091	234.1
9.8	0.123	233.9, 232.6

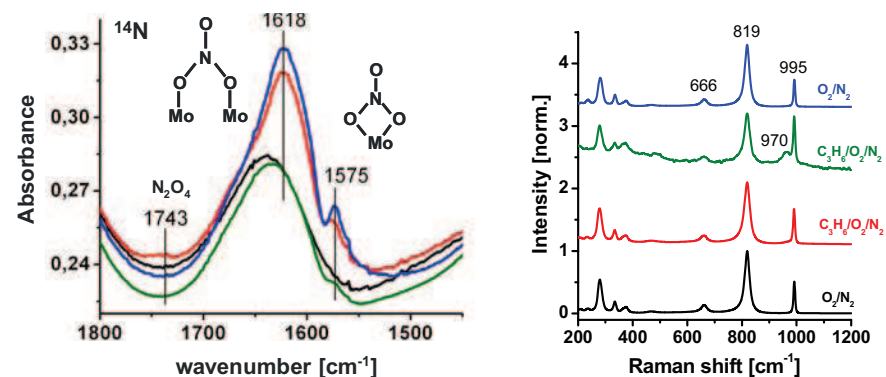


Figure 1. Left: IR spectra of Mo/SBA-15 (0.8 Mo/nm²) after nitrate formation. Right: *In situ* Raman spectra of Mo/SBA-15 (7.6 Mo/nm²) at 500°C in the presence of the gas mixtures indicated. For details see text.

References.

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