Structure and properties of Mo oxide catalyst supported on hollow carbon nanofibers in selective propene oxidation

T. Ressler¹, A. Walter¹, J. Scholz¹, J.-P. Tessonnier², D.S. Su²

¹ Institut für Chemie, TU Berlin, Sekr. C2, Straße des 17. Juni 135, 10623 Berlin, Germany
² Fritz-Haber-Institut der MPG, Abteilung Anorganische Chemie, Faradayweg 4-6, D-14195 Berlin, Germany

Introduction

Mixed oxide catalysts containing metals from group 5 or 6 of the Periodic Table are active in selective oxidation of propane to acrolein and acrylic acid. Detailed studies on the correlations between structure and performance are required to reveal the role of catalyst structure and composition. The reduced chemical complexity of binary oxides makes them preferred model systems to distinguish between structural and compositional effects on catalytic performance. Unfortunately, most binary molybdenum oxides (like Mo₄O₁₁, Mo₈O₂₃, etc.) are not stable under reaction conditions and transform into $\alpha$-MoO₃. In order to modify the structure of binary molybdenum oxides while maintaining structural stability above 673 K, supporting oxide species on various oxidic or carbonaceous supports is currently employed extensively by many researchers. Recently, we have shown that hexagonal MoO₃ supported on nanostructured SiO₂ is stable under selective oxidation conditions up to 773 K. Moreover, it was possible to correlate the local structure around the metal centers with their catalytic performance [1].

Here, we have performed in situ XAS investigations of molybdenum oxide supported on carbon nanofibers. Our approach focused on elucidating both the local structure around the Mo centers in the as-prepared and the activated model catalysts and the structural dynamics under changing reaction conditions [2].

Experimental

Deposition of molybdenum on to open, hollow vapor-grown carbon nanofibers (VGCNFs, Pyrograf Products Inc.) was done by incipient wetness procedure using an aqueous (NH₄)₆Mo₇O₂₄ • 4H₂O (Fluka) solution adjusted to pH 3 with nitric acid. After calcination (298 K, 10 h; 373 K, 5 h; 623 K, 2 h) the final 7 wt. % Mo containing MoₓOᵧ-VGCNF was obtained. Samples treated at temperature higher than 623 K are denoted as activated MoₓOᵧ-VGCNF [2,3].

Structural and functional analyses of MoₓOᵧ-VGCNF in 3 % propene and 10 % oxygen were performed by combined in situ transmission XAS-MS experiments at the Hamburg Synchrotron Radiation Laboratory, HASYLAB [2].

Results and discussion

The local structure of as-prepared MoₓOᵧ-VGCNF was very similar to that of hexagonal MoO₃. Compared to silica based supports which may stabilize hex-MoO₃ at temperatures above 673 K [1], the presence of hex-MoO₃ on VGCNF resulted from moderate temperatures (< 623 K) during catalyst preparation (Figure 1, left). During heat-treatment in propene and oxygen containing atmosphere as-prepared MoₓOᵧ-VGCNF (Figure 1, middle) transformed into activated MoₓOᵧ-VGCNF above 623 K. The local structure around the Mo centers in activated MoₓOᵧ-VGCNF was similar to that of $\alpha$-MoO₃ (Figure 1, right). A slightly reduced amplitude is indicative of Mo oxide support interaction and small, layer-like MoO₃ species supported on VGCNF.
Temperature and time-dependent XAS measurements showed a rapid transformation from hexagonal MoO$_3$ to $\alpha$-MoO$_3$ supported on VGCNF under reaction conditions (Figure 2, left). Subsequently, the resulting activated Mo$_{x}$O$_{y}$-VGCNF catalyst exhibited a slowly increasing average oxidation state. The latter coincided with the formation of acrylic acid, which is hardly detectable during catalysis on regular, binary $\alpha$-MoO$_3$ (Figure 2, right). Moreover, activated Mo$_{x}$O$_{y}$-VGCNF was much more active in the selective oxidation of propene compared to $\alpha$-MoO$_3$. Apparently, the particular local structure of “$\alpha$-MoO$_3$” like molybdenum oxide species supported on VGCNF permitted a complete re-oxidation under reaction conditions in contrast to regular $\alpha$-MoO$_3$. The correlation between catalytic selectivity and average oxidation state as a result of suitable reduction-oxidation kinetics corroborates the importance of structural complexity rather than chemical complexity [2].

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**References**