Molybdenum and vanadium based oxide catalysts supported on mesoporous magnesium oxide – structure and catalytic activity –

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Introduction

Molybdenum and vanadium oxides are active in the heterogeneously catalyzed selective oxidation of light alkenes and alkanes. Nanostructured oxide materials constitute suitable supports for model oxide catalysts. The structure of the Mo or V oxides on the surface of the support is governed by treatment and reaction conditions. Here, we present the formation of different structures of supported Mo or V oxide catalysts caused by varying calcination conditions and catalyst loadings. The catalytic activity of the various molybdenum and vanadium oxides is determined for the selective oxidation of propene.

Experimental

Nanostructured mesoporous magnesium oxide was prepared by nanocasting [1]. The molybdenum and vanadium oxide based catalysts were formed by incipient wetness of the MgO support. Catalyst loadings were chosen between 1-10 wt.% Mo, and V, respectively. In situ transmission XAS-MS experiments were performed at the Mo K edge and V K edge at the Hamburg Synchrotron Radiation Laboratory, HASYLAB. Additionally, combined in situ DR-UV-Vis-MS measurements were conducted. Mo K edge EXAFS calculations were refined to the Fourier transformed \( k^3 \)-weighted \( \chi(k) \). Coordination numbers CN and amplitude reducing factor \( S_0^2 \) were kept invariant, while disorder parameters \( \sigma^2 \) and distances \( R \) of single scattering paths were allowed to vary.

Results

The mesoporous magnesium oxide consists of hexagonally arranged mesopores with a high specific surface area (between 100 and 250 m\(^2\)·g\(^{-1}\)). Structural formation of the supported catalysts was strongly correlated to calcination conditions. Preliminary investigation on Mo catalysts supported on commercially purchased MgO (ABCR) showed an increasing distortion of the tetrahedral structure of Mo catalyst with increasing calcination temperature \( T_{calc} \). The increasing disorder parameter \( \sigma^2 \) resulting from EXAFS refinements is displayed in Fig. 1. A correlation between calcination temperature and Mo catalyst structure was confirmed by DR-UV-Vis measurements. The influence of water in the calcination atmosphere played an important role. The acid-base characteristics of the support material MgO strongly depends on binding of water molecules, forming hydroxyl groups on the MgO surface. As a result the catalyst structure changed with varying acid-base character. The observed catalyst structure can be correlated to the pH depended molybdate and vanadate formation in aqueous solution. For the supported Mo oxides the structure is largely independent of Mo loading. Conversely, the supported V oxides underwent structural changes at higher loadings. The amplitude of the pronounced peak in the pseudo radial distribution function \( FT(\chi(k)k^3) \) decreased with increasing V loading, indicating a structural distortion (Fig. 2). Furthermore, DR-UV-Vis spectra revealed a significant shift of the edge energy to lower values for higher V loading. Therefore, a larger number of V-O-V bonds at higher loadings can be assumed [2]. Under reaction conditions (RT \( \rightarrow \) 450 °C, 5% propene, 5% O\(_2\) in helium), a change in the XANES spectra due to reduction of the catalyst was observed (Fig. 3 and 4). The reduced pre-edge peak in the XANES of the Mo species may indicate a deformation of the tetrahedral coordination (Fig. 3).
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References