Structure and reactivity of supported vanadium oxide catalysts in selective oxidation

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Introduction

One of the most important ways to functionalize hydrocarbons is the selective oxidation of alkanes and alkenes with vanadium based oxide catalysts. Industrially used catalysts exhibit a highly complex chemical composition. To optimize catalytic processes it is essential to study model systems under simplified conditions. Nanostructured oxide materials are often used as support to create suitable model systems for detailed simultaneous investigations of catalysts structure and performance. The structure of the surface oxide catalysts is determined by the properties of the support material.[1, 2] Thus, it is possible to generate a variety of molecular model catalyst structures. Here, we investigated the influence of MgO-coated SBA-15 (MgO/SBA-15) with alkaline surface properties on the structure of supported vanadium oxide catalysts. To gain deeper insight into structure-activity correlation, we used a combination of spectroscopic techniques and simultaneous determination of catalytic activity under selective propene oxidizing conditions.

Experimental

The high surface area support material was obtained by synthesis of silica SBA-15 and subsequent coating with magnesium oxide. Vanadium oxide based catalysts were prepared by incipient wetness of the support MgO/SBA-15 with an aqueous solution of a suitable catalyst precursor. In situ transmission XAS-MS experiments were performed at the V K edge at the Hamburg Synchrotron Radiation Laboratory, HASYLAB. Additionally, in situ DR-UV-Vis measurements were conducted on a JASCO V-670 spectrometer equipped with a “praying mantis” in situ cell. Catalysis measurements were performed in 5 % propene, 5 % oxygen in helium atmosphere between 25 °C and 450 °C. Catalytic activity was determined by GC-MS.

Results and discussion

The alkaline character of the MgO/SBA-15 support led to the formation of low polymerized, tetrahedral vanadium oxide units. X-ray absorption spectroscopy (XAS) and diffuse reflectance UV-Vis (DR-UV-Vis) spectroscopy measurements allowed the determination of the polymerization degree at different catalyst loadings. Figure 1 depicts the pseudo-radial distribution function FT(\(\gamma(k)k^2\)) derived from EXAFS. Fitting of a theoretical model to the experimental data revealed an increasing polymerization degree of the [VO₄] units with increasing vanadium surface coverage. However, the connectivity of the catalyst units was low compared to oxides supported on silica SBA-15.[2] Temperature programmed reduction of the vanadium oxide catalysts was investigated by in situ XAS experiments in propene containing atmosphere (Figure 2, inset). At an onset temperature of 250 °C a decrease in pre-edge peak intensity was observed (Figure 2), indicating a reduction of the vanadium oxide species. Reducibility of the supported V oxides was directly correlated to catalytic activity in selective propene oxidation.

References

Figure 1: Experimental (red) V K edge $\text{FT}(\chi(k)k^3)$ of supported V oxide catalysts on $\text{MgO/SBA-15}$ together with a theoretical XAFS function (blue).

Figure 2: V K edge pre-edge peak height of $\text{V/MgO/SBA-15}$ as a function of temperature during reduction in propene (RT $\rightarrow$ 440 °C, 4 K/min, 5 % propene in helium). Inset: Evolution of V K edge XANES spectra during temperature programmed reduction.

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