



Red-ox Properties of Vanadium Ions in VO_x/SBA-15: An FTIR Spectroscopic Study



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Introduction

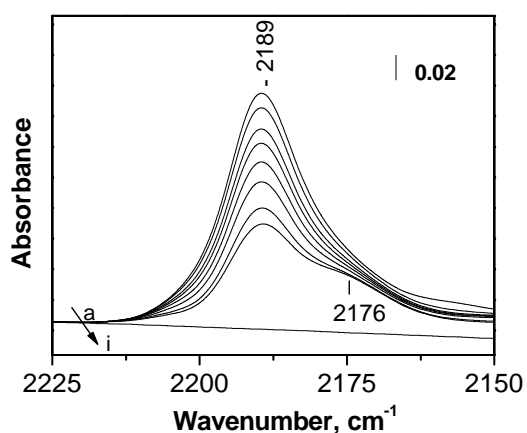
Catalysts consisting of oxidic vanadium species supported on SBA-15 (VO_x/SBA-15) exhibit excellent performance in several reactions such as oxidative dehydrogenation of propane [1] and oxidation of methane [2] or methanol [3] for production of formaldehyde. The potential of SBA-15 for catalytic applications arises from the uniformly sized hexagonally ordered pores, high hydrothermal stability and large surface area, which allows for highly dispersed vanadium species in the channels of the SBA-framework. Little is reported on the nature of vanadium in such materials; and the goal of this work is to investigate the state and redox properties of vanadium supported on SBA-15. The vanadium sites were characterized by CO adsorption after different sample pretreatments, and the adsorbate complexes were studied by FTIR spectroscopy.

Experimental

VO_x/SBA-15 was prepared from silica SBA-15 as described in [4]; the V content was 2.7 wt%. Self-supporting pellets were obtained by pressing the powders at 10 MPa. Samples were treated in a vacuum system connected to the IR cell. Samples were evacuated at 673 K for 1 h before CO or H₂ was adsorbed at 77 K. H₂ treatments lasted 1 h at 573 and 673 K, respectively, and were followed by evacuation at the same temperature. FTIR spectra were recorded using a Perkin Elmer S 2000 at 2 cm⁻¹ resolution.

Results and Discussion

CO interacted with the OH groups of activated VO_x/SBA-15, but no additional bands were observed that indicated adsorption on vanadium sites. Such behaviour is consistent with literature reports on vanadium supported on “normal” SiO₂, and has been attributed to the coordinative saturation of V⁵⁺ ions and the covalent character of the V⁵⁺=O bond. However, after reduction of the sample with H₂ at 673 K the V⁵⁺ ions were reduced to two different kinds of V³⁺ sites, as manifested by carbonyl bands at 2189 and 2177 cm⁻¹.



CO adsorbed on VO_x/SBA-15 treated in H₂ at 673 K. a)-h), evacuation during a gradual increase to RT; i) evacuation at 373 K.

showing carbonyl bands at 2202 and 2190 cm⁻¹. Contrary to the V³⁺-CO species the bands of the V⁴⁺-CO carbonyls disappeared completely after evacuation of the sample at low temperatures, which could be explained by the σ - character of the V⁴⁺-CO bond. In the presence of O₂ at room temperature the V³⁺ ions were fully oxidized to V⁵⁺.

To unravel the reasons for the heterogeneity of the vanadium ions, additional CO and H₂ adsorption experiments were made with the pure SBA-15 support. Only a fraction of the OH groups were disturbed even at 77 K and 400 hPa H₂, indicating that two different types of terminal Si⁴⁺-OH groups may exist in the channels of the SBA-15 framework. The heterogeneity of vanadium in VO_x/SBA-15 could thus either be due to (i) the presence of isolated and associated vanadium sites or (ii) different surroundings of the vanadium ions, which may be attached at or near the silanol group sites.

Conclusions

Vanadium that is dispersed in the framework of SBA-15 forms two different types of sites.

Literature

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2. H.H. López and A. Martínez, *Catal. Lett.*, 83 (2002) 37.
3. C. Hess, I.J. Drake, J.D. Hoefelmeyer, T.D. Tilley and A.T. Bell, *Catal. Lett.*, 105 (2005) 1.
4. C. Hess, J.D. Hoefelmeyer, T.D. Tilley, *J. Phys. Chem. B*, 108 (2004) 9703.

The respective V³⁺-CO carbonyls are characterized by very high stability and their bands disappeared from the spectra only after evacuation at 373 K, which is an indication for synergism between σ - and π - components of the bond between the V³⁺ ions and the CO molecules. In the presence of O₂ at low temperatures the V³⁺ ions from the initially reduced sample are partly oxidized to V⁴⁺ sites