XAS Characterisation of VO_x supported on SBA-15

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Introduction

Vanadia supported catalysts play an important role in heterogeneous catalysis. Having a high activity and selectivity for several oxidation reactions in organic chemistry they are used for a number of reactions, e.g. the partial oxidation of methane to formaldehyde. Hence it is very important to determine the kind and structure of the involved vanadium oxide species. There are several publications in which the existence of a gel like V_2O_5 structure on SiO_2 supports, mostly on the basis of Raman investigations, is suggested for the hydrated state [1,2]. In this study VO_x supported on SBA-15, a mesoporous siliceous molecular sieve having a high surface area (> 800 m^2/g), was measured using X-ray absorption spectroscopy (XAS). To observe the change in structure between the hydrated and dehydrated state during oxidation an in situ measurement was performed during heating.

Experimental

The XAS-measurements at the V K-edge (5.465 KeV) were performed at beamline E4 in Hasylab (Hamburg, Germany) using transmission mode. The reference V_2O_5 (Riedel, >99.5%) was pressed into a pellet (13mm diameter, pressing force 1 t for 30 s) containing substance for an absorption step around one and PE for stabilizing. The reference was investigated in a measurement cell at room temperature under vacuum. The VO_x/SBA-15 (3wt%) sample, which was prepared via a grafting/anion exchange method [1], was pressed into a pellet (5mm diameter, pressing force 1 t for 30 s) containing 1:100 sample and BN for stabilizing. The measurement was performed in an in situ cell which was heatable and closed with Kapton windows. The cell was flowed with 80% O_2 and 20% He and was heated with a rate of 5 K/min from room temperature to 350 °C. To yield a better absorption a tunnel with Kapton windows at the end and connections for gas flow (in that case He) was installed in front of the cell. The data analysis was performed using the software WinXAS v3.1. The temperature resolved measurement was evaluated using a Principle Component Analysis (PCA).

Results and Disscusion

The obtained XANES spectra from XAS measurement are shown in Figure 1 and 2. It was found a similarity in pre-edge height, position and the formation of the XANES features of hydrated VO_x/SBA-15 (3 wt%) and the reference V_2O_5. Due to the high sensibility of the XANES region to the geometric structure and the specific bonding situation around the absorber atom it is concluded that the hydrated VO_x/SBA-15 structure is similar to the V_2O_5 structure. This is consistent with the literature [2]. After dehydration the similarity with V_2O_5 is not found in XANES. The position and height of the pre-edge peak implies a change in geometry, from octahedral to tetrahedral, like it is described in literature [2]. But a detailed analysis of the electronic and geometric structure of dehydrated VO_x on SBA-15 is on-going and will be presented elsewhere.

The change in structure can be observed in the temperature resolved measurement (Figure 3). A good indicator for the dehydration process is the height of the pre-edge peak presented in Figure 4. From that data the process of dehydration seems to be completed at ~150 °C. Looking at the XANES it may be possible that a third component is involved. This assumption is also resulting from the PCA. But further analysis is still in progress.

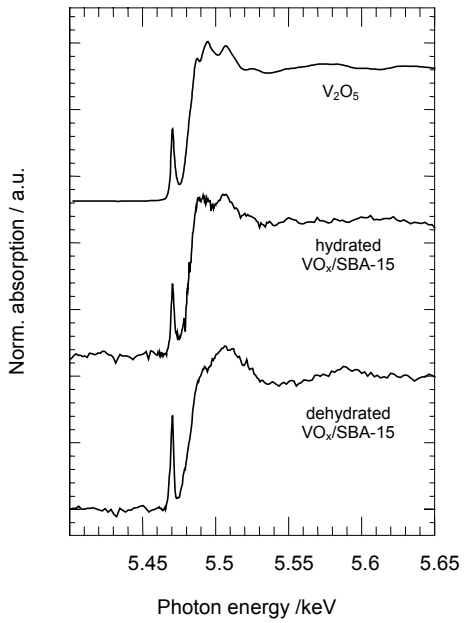

Figure 1: XANES spectra of V_2O_5 and VO_x/SBA-15

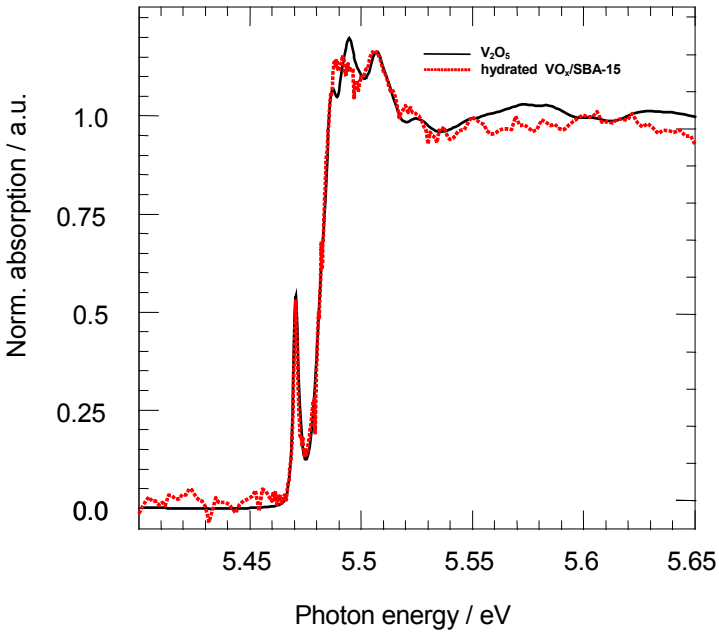

Figure 2: Comparison in XANES spectra of V_2O_5 and hydrated VO_x/SBA-15

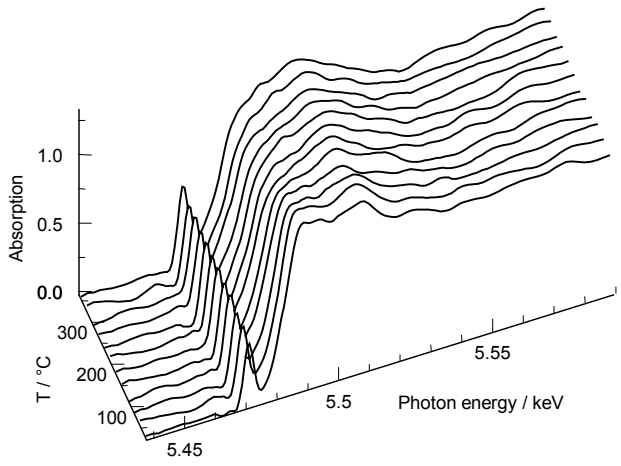

Figure 3: Temperature resolved measurement during Oxidation

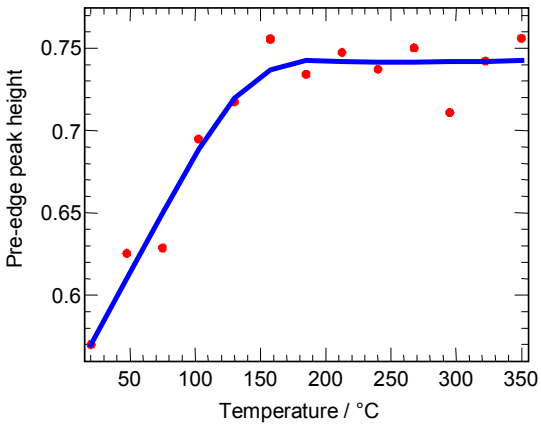

Figure 4: Change in pre-edge Peak height during Oxidation

References

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[2] X. Gao, S.R.Bare, B.M. Weckhuysen, and I.E. Wachs, Phys. Rev. B 102, 10842 (1998)