

# Structure of vanadium oxide catalysts supported on nanostructured SiO<sub>2</sub>

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## Introduction

Investigating supported vanadium oxide catalysts has received much attention in recent years because of their activity and selectivity for several oxidation and dehydrogenation reactions of light alkanes [1]. Hence, it is very important to determine the type and structure of the vanadium oxide species involved. From Raman and X-ray absorption spectroscopy (XAS) experiments, it has been suggested that vanadium oxide on SiO<sub>2</sub> is present in a hydrated state whose structure may be similar to that of V<sub>2</sub>O<sub>5</sub>. Here, vanadium oxide catalysts supported on SBA-15, a nanoporous siliceous molecular sieve having a high surface area (> 800 m<sup>2</sup>/g) were investigated by XAS. The aim of this study was to determine the structure of the hydrated state and the dehydrated state before and after thermal treatment, respectively.

## Experimental

XAS measurements at the V K edge (5.465 KeV) were performed at beamline E4 at HASYLAB (DESY, Hamburg, Germany) in the transmission mode. The VO<sub>x</sub>/SBA-15 samples and the references V<sub>2</sub>O<sub>5</sub> (Alfa Aesar, >99.8%), NH<sub>4</sub>VO<sub>3</sub> (Riedel, >99.5%), and Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> were pressed into pellets (5 mm diameter, pressing force 1 t for 30 s) containing 0.5-2.0 mg sample and 15 mg BN. The VO<sub>x</sub>/SBA-15 samples (2.7, 5.4, 10.8 wt% V) were prepared via a grafting/anion exchange method by Hess et al. [2]. Combined XAS/MS measurements were performed in an in situ cell, which was heatable and closed with Kapton windows. For dehydration of the VO<sub>x</sub>/SBA-15 sample the cell was flowed with 20% O<sub>2</sub> and 80% He and was heated with a rate of 5 K/min from 25 °C to 350 °C. Ex situ measurements were performed in He atmosphere at room temperature. Data analysis was conducted using the software WinXAS v3.1.

## Results and Discussion

In Figure 1 the V K edge XANES spectra of hydrated VO<sub>x</sub>/SBA-15 is shown. A comparison of the FT[χ(k)k<sup>3</sup>] with references shows the similarity between the hydrated VO<sub>x</sub>/SBA-15 sample and V<sub>2</sub>O<sub>5</sub>. Apparently, the structure in this state is comparable with the polymeric structure of V<sub>2</sub>O<sub>5</sub>. This was reinforced by an EXAFS refinement based on the V<sub>2</sub>O<sub>5</sub> structure.

Dehydration of the VO<sub>x</sub>/SBA-15 sample is correlated with the loss of water measured by MS. This process is completed around 120 °C and is followed by a change in structure. A detailed analysis of this process is on-going.

The V K edge XANES spectra and the FT[χ(k)k<sup>3</sup>] of dehydrated VO<sub>x</sub>/SBA-15 are comparable to those of NH<sub>4</sub>VO<sub>3</sub> and Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub>. The height of the pre-edge peak and the similarity of the XANES region is indicative of a tetrahedral coordination of vanadium by oxygen in the dehydrated state. EXAFS analysis of the dehydrated state showed that vanadium oxide on SBA-15 consists of dimeric V<sub>2</sub>O<sub>7</sub> units comparable to the structures of Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> or NH<sub>4</sub>VO<sub>3</sub>. The assembly of these dimeric V<sub>2</sub>O<sub>7</sub> units on the SiO<sub>2</sub> support appears to be regular and the single units have to be in spatial proximity. An EXAFS refinement of a corresponding model structure to the experimental spectrum of the dehydrated material yielded a good agreement (Figure 2). A schematic representation of the arrangement of the V<sub>2</sub>O<sub>7</sub> dimers on SBA-15 is depicted in Figure 2.

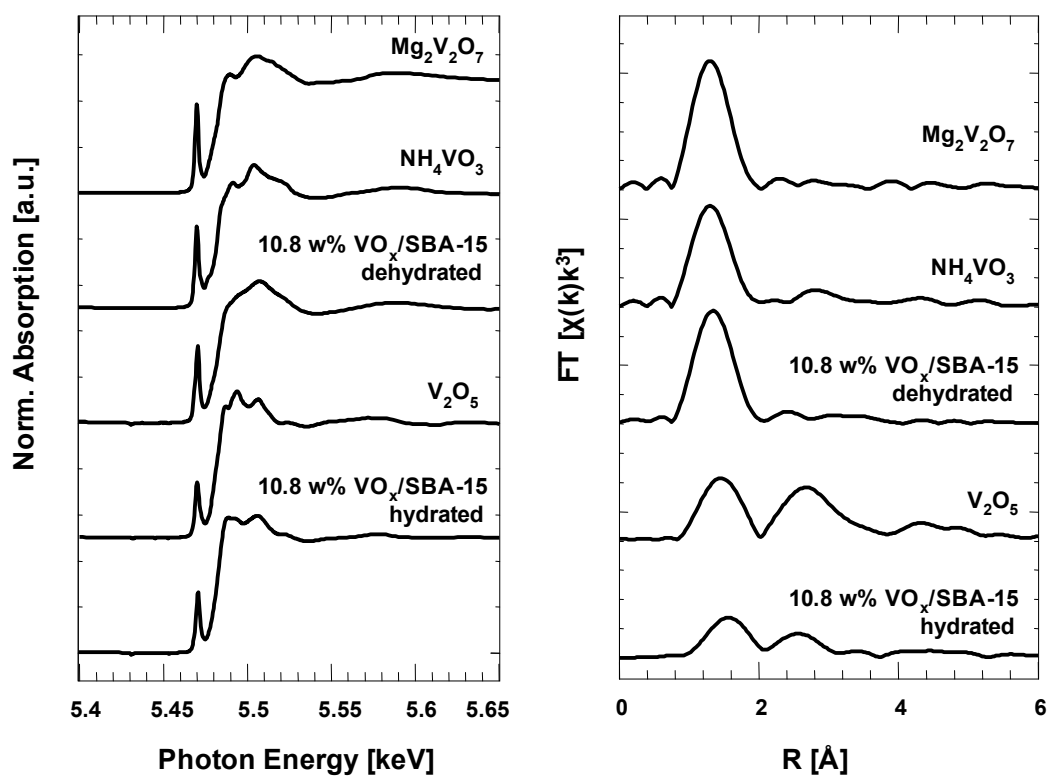


Figure 1 V K edge XANES (left) and  $FT[\chi(k)k^3]$  (right) of  $VO_x/SBA-15$  in the hydrated and dehydrated state compared to various references

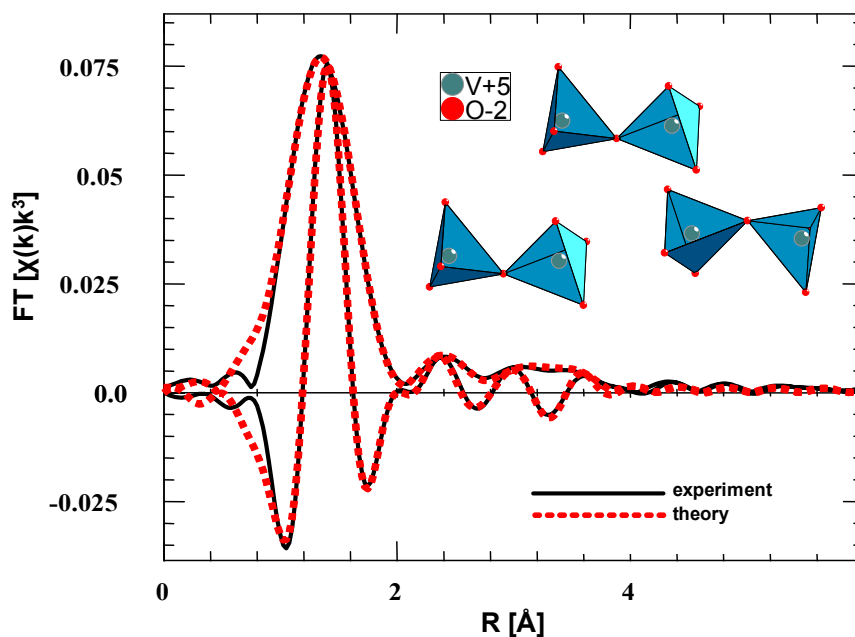


Figure 2 EXAS refinement of a suitable model structure (inset) to the V K edge  $FT[\chi(k)k^3]$  of dehydrated  $VO_x/SBA-15$ .

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### References

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