

Direct correlation of the structure and dispersion of SBA-15 supported vanadia model catalysts using multi *in situ* spectroscopy

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Introduction

Multiple *in situ* spectroscopy allows to obtain information from various spectroscopic methods applied to one catalyst sample. A direct correlation of spectroscopic results is possible as any influence of both the particular sample and the reaction cell geometry, which may affect the heating and gas flow conditions, is removed. Here, we introduce a new experimental setup which combines Raman, UV-VIS and X-ray photoelectron spectroscopy (XPS). To the best of our knowledge this is the first setup which couples XPS with optical spectroscopic methods. In addition, fiber probes are used for both the Raman and UV-VIS part, which may avoid problems associated with the passage of light through additional optical components (windows/reactor walls) and their contribution to the overall signal. This multiple spectroscopic approach is widely applicable to study changes in the structure and dispersion of heterogeneous catalysts. This is illustrated by a study of the effects of water on the structure and dispersion of silica SBA-15 supported vanadia. Water is a common product of selective oxidation reactions. Also, water vapour is often added to the feed to improve the catalyst performance or open new reaction pathways such as acrylic acid formation in the partial oxidation of propane [1].

Materials and Methods

We have used a novel synthesis approach based on controlled grafting/ion exchange to prepare highly dispersed vanadium oxide supported on mesoporous silica SBA-15 (V/SBA-15) [2]. The focus of this study was a V/SBA-15 catalyst with a loading of 3.3 wt% V, a specific surface area of 490 m²/g and mean pore diameter of 5 nm. The experiments were carried out using a modified XPS apparatus. The spectrometer was attached to a reaction cell allowing for continuous gas flow as well as Raman and UV-VIS fiber probes to be inserted.

Results and Discussion

The UV-Vis spectrum shows that the fully hydrated vanadia catalyst is slightly reduced but consists mainly of V⁵⁺ species. The corresponding Raman spectrum is in excellent agreement with that of the water containing V₂O₅ gel (xerogel) V₂O₅·1.2H₂O, which consists of polymerized pyramidal VO₅ units similar as in V₂O₅. Upon catalyst dehydration by treatment in oxygen flow at 300°C dramatic changes in all spectra are observed (UV-Vis, Raman, XPS). As demonstrated by UV-Vis and Raman spectroscopy, a highly dispersed V⁵⁺ species is formed, which consists of tetrahedrally coordinated vanadium. Figure 1 shows the V2p_{3/2} emission of hydrated (bottom spectrum) and dehydrated (top spectrum) SBA-15 supported vanadia together with a least-square fit to the data. After dehydration a dramatic shift in intensity to higher BE is observed. Quantitative analysis (see Table 1) yields an intensity increase of the band around 518.7 eV from 42% to 82%, whereas the band centered at

517.3 eV shows an intensity decrease from 44% to 12%. It is evident that the band around 518.7 eV can not solely be described by a change in oxidation state. However, final state effects are known to result in size-dependent BE shifts for small conducting particles on insulating substrates. This situation applies to small vanadia particles with V ions in oxidation state 3+, which are known to be formed under high-vacuum conditions. In accordance with these results the V ions in our SBA-15 supported vanadia particles are reduced from 5+ to 3+ upon transfer to the analysis chamber, which only renders possible the analysis of their size changes. These results highlight the great potential of XPS to differentiate and quantify vanadia species of different dispersion [3]. In particular, by combining XPS with UV-Vis and Raman spectroscopy within one setup information on both the structure and dispersion of highly dispersed vanadia can be obtained.

Significance

Using a new experimental setup the correlation between changes in structure and dispersion has been studied directly for the first time as demonstrated for the dehydration of a well-defined SBA-15 supported vanadia catalyst.

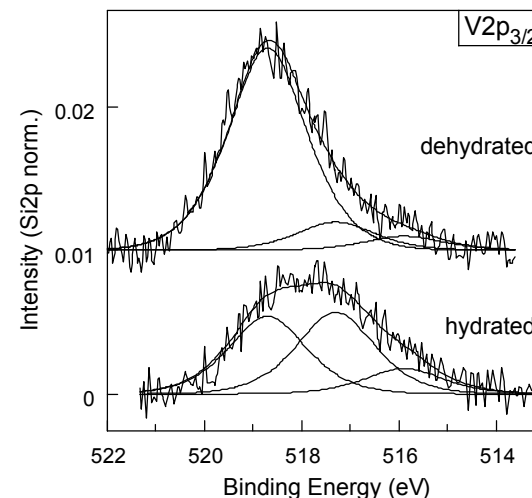


Figure 1. XP spectra of the V2p_{3/2} region of hydrated (bottom) and dehydrated (top) SBA-supported vanadia together with the results of the fit analysis. The spectra are offset for clarity.

References

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