Research Note

Direct correlation of the dispersion and structure in vanadium oxide supported on silica SBA-15

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Abstract

Raman, UV–vis, and X-ray photoelectron spectroscopy were combined in one experimental setup to directly study the interplay between the structure and dispersion of SBA-15-supported vanadium oxide during dehydration. The fully hydrated catalyst is slightly reduced but consists mainly of V^{5+} species with pseudo-octahedral V coordination strongly resembling the xerogel $V_2O_5 \cdot 1.2H_2O$. After dehydration, a highly dispersed surface vanadium oxide species with tetrahedrally coordinated vanadium and significantly smaller ensemble size is formed.
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1. Introduction

Water is a common product of selective oxidation reactions. In addition, water vapor is often added to the feed to improve catalyst performance. Despite its importance and extensive research on the influence of water on supported metal oxide catalysts, some fundamental aspects, including changes in catalyst dispersion and their potential correlation with structural changes, still have not been addressed in the literature in adequate proportion to their importance [1]. X-ray photoelectron spectroscopy (XPS) can provide direct information on the dispersion of supported metal oxide catalysts, such as vanadium oxide supported on SiO_2, Al_2O_3, and TiO_2 [2]. However, many of the previous studies were performed on samples exposed to air before being introduced into the XPS chamber without further treatment. Despite the well-known influence of water, XPS has been applied only recently to study the effect of dehydration on vanadium oxide dispersion [3].

Multiple in situ spectroscopy can provide information from various spectroscopic methods applied to one catalyst sample. A direct correlation of spectroscopic results is possible, because any influence of both the particular sample and the reaction cell

geometry, which may affect the heating and gas flow conditions, is removed. Recently, three spectroscopic techniques, including Raman and UV–vis spectroscopy, were combined for characterization of supported metal oxide catalysts [4,5].

In the present work, the effect of water on both structure and dispersion was studied for a silica SBA-15-supported vanadium oxide model catalyst. In particular, by combining Raman, UV–vis, and XPS within one experimental setup, we show for the first time a direct correlation between changes in structure and dispersion and the extent of dehydration. This multiple spectroscopic approach is the first to couple XPS with optical spectroscopic methods. A cross-sectional view of the setup is shown in the inset of Fig. 1; details are given below.

Previous Raman, UV–vis, and EXAFS studies have demonstrated that the presence of water can influence the molecular structure of surface vanadium oxide species [6–9]. The structure of the fully hydrated state of silica-supported vanadium oxide species closely resembles that of $V_2O_5 \cdot nH_2O$ gels, with vanadium in pseudo-octahedral coordination forming layers of two-dimensional polyvanadates. Dehydrated vanadium oxide at low V coverage (i.e., below the coverage at which V_2O_5 is formed) has been proposed to be present as isolated tetrahedral VO_4 [7–9]. However, a recent IR study has provided evidence for the presence of V–O–V, implying vanadia dimers or polymers [10]. Previously, the presence of polymeric species on
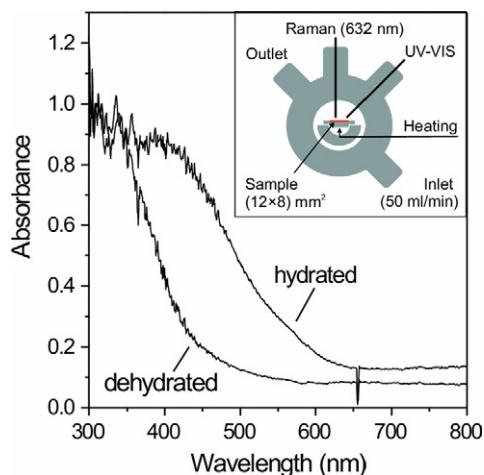
Fig. 1. UV–vis spectra of hydrated and dehydrated V/SBA-15. The inset shows a cross-sectional scheme of the experimental setup illustrating the UV–vis and Raman capabilities.

silica SBA-15-supported vanadia had been suggested on the basis of UV–vis results [11–14].

For a detailed understanding of catalyst properties, the use of materials with well-defined structure is necessary. Therefore, we have prepared vanadium oxide model catalysts via controlled grafting/anion exchange resulting in highly dispersed vanadium oxide supported on the inner pores of the well-ordered mesoporous matrix of silica SBA-15 [14]. Recently, we demonstrated the excellent catalytic properties of this catalyst system in the propane partial oxidation to acrylic acid as well as methanol partial oxidation to formaldehyde [15].

2. Experimental

Details of the catalyst preparation and characterization are described elsewhere [14]. Briefly, functionalization of SBA-15 was achieved by adding 3-aminopropyltrimethoxysilane to a suspension of SBA-15 in toluene at 65 °C. The contents were filtered, washed, and stirred in 0.3 M HCl. For SBA-15-supported vanadium oxide catalysts (V/SBA-15), appropriate amounts of butylammonium decavanadate were added to a suspension of functionalized SBA-15 in water. The resulting yellowish powder was calcined at 550 °C. The SBA-15 reference material was prepared according to the above procedure; however, in the ion-exchange step potassium oxalate monohydrate (Fluka, >99.5%) instead of decavanadate was used. The V/SBA-15 (SBA-15) material had a loading of 3.3 wt% V, a specific surface area of 490 m^2/g (472 m^2/g), and mean pore diameter of 5 nm (5.1 nm), as determined from the adsorption branch of the isotherm using BJH analysis. V_2O_5 (Riedel-de Haen; 99.5%) was used as purchased.

The measurements were carried out using a LHS/SPECS EA200 MCD system. An evacuation cell of this XPS apparatus was modified to allow for continuous gas flow as well as Raman and UV–vis fiber probes to be inserted into the cell (see inset of Fig. 1). Powder samples were introduced as is into a stainless steel sample holder with a 0.6-mm-deep rectangular well covering an area of (12×8) mm^2. Raman spectra (Kaiser Optical)

were measured at 5 cm^{-1} spectral resolution using 632-nm excitation at 5 mW measured at the position of the sample. The spot size at the sample had a diameter of ca. 30 μm. The spectrometer was calibrated before the experiments using a neon lamp. Sampling times were typically 15 min. UV–vis spectra were recorded on a HR2000CG (Ocean Optics) using D_2 and halogen light sources. The spectrometer was calibrated using $BaSO_4$ as white standard. The sampling time was 1 min. The XPS system was equipped with a MgK_α source (1253.6 eV, 168 W). The binding energy scale was calibrated using Au4f$_{7/2}$ = 84.0 eV and Cu2p$_{3/2}$ = 932.67 eV from foil samples. Spectra were recorded at room temperature. Data acquisition time was 60 min. Charging of the samples was accounted for by setting the peak of the Si2p signal to 103.6 eV [14]. Further data reduction included satellite deconvolution and subtraction of a Shirley background. Quantitative data analysis was performed on the basis of peak areas by fitting with 30/70 Gauss–Lorentz product functions. Atomic ratios were calculated using empirical cross sections [16]. The transfer to/from the analysis chamber was performed without air exposure (quasi in situ).

3. Results and discussion

Fig. 1 shows the UV–vis spectrum of fully hydrated SBA-15-supported vanadium oxide. The spectrum is characterized by a broad O → V charge transfer band extending up to ca. 650 nm and a small offset at higher wavelengths (650–800 nm) with respect to the dehydrated sample [17]. The presence of absorption above 400 nm is typical for highly polymerized vanadium oxide species. The offset may indicate the presence of d–d transitions of reduced vanadium oxide. The Raman spectrum of the hydrated V/SBA-15 sample recorded at 632 nm excitation is depicted in the bottom panel of Fig. 2 together with a spectrum of V_2O_5 as reference. The spectrum of V/SBA-15 shows some similarity to that of crystalline V_2O_5, but additional bands at 268 and 1021 cm^{-1} are present. However, the spectrum of V/SBA-15 is in excellent agreement with that of $V_2O_5 \cdot 1.2H_2O$ recorded by Abello et al. at 647 nm excitation [18]. After recording the UV–vis and Raman spectra, the sample was transferred to the XPS analysis chamber. At the bottom of Fig. 3, the V2p$_{3/2}$ emission together with a least squares fit to the data is shown. A comparison with literature data on V2p$_{3/2}$ binding energies (BEs) for well-ordered vanadium oxide films allows us to assign the bands at 515.9 eV and 517.3 eV to V^{3+} and V^{5+}, respectively [19]. Quantitative analysis was performed using three fit functions with constant widths (FWHM = 2.1 eV), which are even lower than those used to describe the well-ordered vanadium oxide films [19], confirming the homogeneity of our powder model system. EPR experiments on the fully hydrated V/SBA-15 sample gave a V^{4+} signal corresponding to only 0.3% of the total amount of vanadium. Therefore, XPS confirms the UV–vis results and identifies the reduced vanadium oxide as V^{3+} species.

After XPS analysis, the sample was transferred back into the reaction cell, heated to 300 °C, and treated at 300 °C for 30 min in 20% O_2/He flow. After dehydration, dramatic changes were observed in all spectra. The Raman and UV–vis spectra are de-
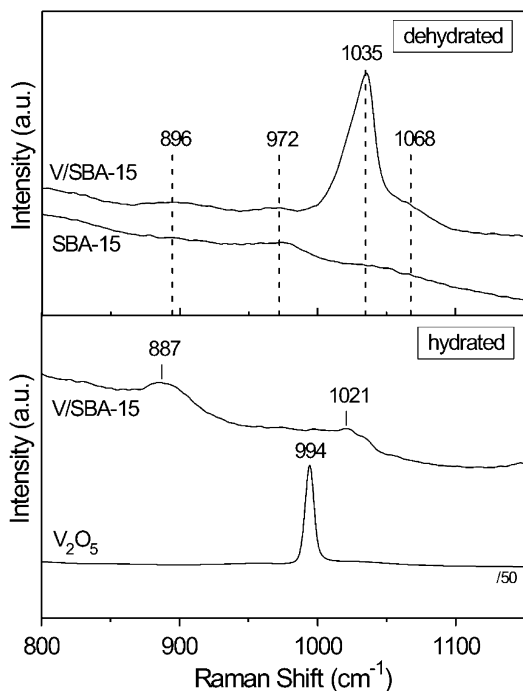
Fig. 2. Top panel: Raman spectra of dehydrated V/SBA-15 (top) and bare SBA-15 (bottom). Bottom panel: Raman spectra of hydrated V/SBA-15 (top) and V_2O_5 (bottom). The spectra are offset for clarity.
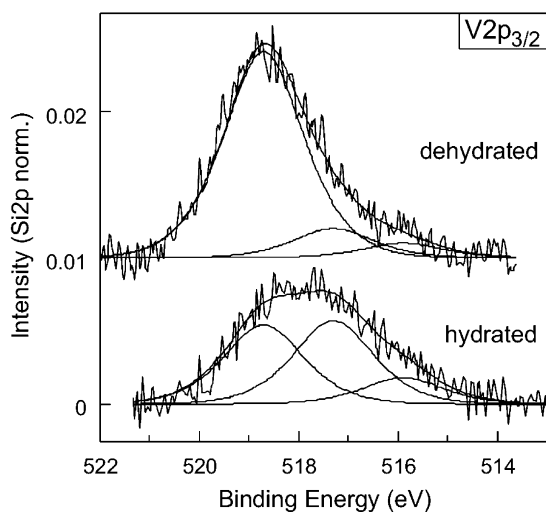

Fig. 3. XPS $V2p_{3/2}$ spectra of hydrated (bottom) and dehydrated (top) V/SBA-15 together with the results of the fit analysis. The spectra are offset for clarity. For details see text.

Table 1
Results of the XPS $V2p_{3/2}$ analysis of SBA-15-supported vanadium oxide

	Position (eV)	Width (eV)	% ($t = 60$ min)	% ($t = 0$ min)
3.3 wt% V/SBA-15 (hydrated)	518.7	2.1	41.6	44.0
	517.3	2.1	44.4	53.2
	515.9	2.1	14.0	2.8
3.3 wt% V/SBA-15 after O_2 treatment (dehydrated)	518.7	2.1	82.3	83.4
	517.3	2.1	11.9	16.4
	515.9	2.1	5.8	0.2

ditional feature at 972 cm^{-1} is characteristic of the Si–OH stretching mode of surface hydroxyls [20]. On grafting of vanadium oxide, its intensity decreases as a result of the reaction of Si–OH with the vanadium oxide precursor. The Raman band around 1035 cm^{-1} has an asymmetric band shape with a shoulder at 1068 cm^{-1} [21]. It is assigned to the V=O stretch vibration of tetrahedrally coordinated V ions. The feature at 896 cm^{-1} can be due to either vibrations of the surface vanadium oxide species or changes related to the silica surface on grafting of vanadium oxide. In summary, the UV–vis and Raman data suggest that after dehydration, both isolated and small aggregates of polymerized VO_4 units with tetrahedrally coordinated V ions are present [10].

After the Raman and UV–vis analysis, the sample was cooled to room temperature and transferred to the XPS chamber. Fig. 3 shows the $V2p_{3/2}$ emission of dehydrated SBA-15-supported vanadium oxide (top spectrum) together with a least squares fit to the data. After dehydration, a dramatic shift in intensity to higher BE is observed. Quantitative analysis 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%. The presence of 6% V^{3+} in dehydrated V/SBA-15 is a result of the sample reduction by UHV/X-ray. However, time-dependent XPS analysis shows that for the dehydrated sample at $t = 0$, no significant amount of V^{3+} is present (see Table 1) [3]. It is evident that the band at around 518.7 eV cannot be described solely by a change in oxidation state (see above). However, final state effects are known to result in size-dependent BE shifts for small conducting particles on insulating substrates [22]. This situation applies to small vanadium oxide particles with V ions in oxidation state 3+ and vanadyl groups at the surface, which are known to be formed under reduced-pressure conditions [23]. In accordance with these results, the V ions in our SBA-15-supported vanadium oxide particles are suggested to be partly reduced from 5+ to 3+ on transfer to the analysis chamber, which makes possible an analysis of their size changes.

In summary, our XPS results directly show that dehydration of the catalyst is accompanied by a strong decrease in cluster size, that, is, an increase in the dispersion of the catalyst. Our results strongly suggest that on dehydration, most of the surface vanadium oxide is subject to a significant decrease in cluster size. The fact that the band at 518.7 eV is also present for the hydrated sample indicates that water from ambient significantly reduces the dispersion of part, but not all, of the surface vanadium oxide species.

picted in Fig. 1 and the top panel of Fig. 2, respectively. The UV–vis spectrum shows absorption due to O → V charge transfer bands, which extend up to ca. 450 nm. Such an absorption behavior is typical for reference compounds with tetrahedrally coordinated vanadium, such as $Mg_2V_2O_7$ or NH_4VO_3. In contrast, orthovanadate reference compounds, such as $Mg_3V_2O_8$, exhibit an absorption band extending only up to ca. 400 nm. The Raman spectrum of V/SBA-15 shows strong features at around 1035 and 1068 cm^{-1}, along with smaller features around 896 and 972 cm^{-1}. The Raman bands at 896, 1035, and 1068 cm^{-1} are observed only after deposition of vanadium oxide. The ad-

4. Conclusion

In conclusion, 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 vanadium oxide catalyst. The dehydrated state of our model catalyst serves as a perfect starting point to study catalyst changes associated with the transition into its active state with the hydrated catalyst resembling an upper limit in the water-containing catalyst environment during partial oxidation reactions.

Acknowledgments

References

[1] B. Gryzbowska-Swierkosz, Top. Catal. 11/12 (2000) 23.

[2] K. Inumaru, M. Misono, T. Okuhara, Appl. Catal. A 149 (1997) 133;
G.C. Bond, J.P. Zurita, S. Flamerz, Appl. Catal. 27 (1986) 353.

[3] C. Hess, R. Schlögl, Chem. Phys. Lett. 432 (2006) 139.

[4] A. Brückner, Chem. Commun. (2005) 1761.

[5] A.M. Beale, A.M.J. van der Eerden, K. Kervinen, M.A. Newton, B.M. Weckhuysen, Chem. Commun. (2005) 3015.

[6] M. Schraml-Marth, A. Wokaun, M. Pohl, H.L. Krauss, J. Chem. Soc. Faraday Trans. 87 (1991) 2635.

[7] S. Xie, E. Iglesia, A.T. Bell, Langmuir 16 (2000) 7162.

[8] X. Gao, S.R. Bare, B.M. Weckhuysen, I.E. Wachs, J. Phys. Chem. B 102 (1998) 10842;
J.-M. Jehng, G. Deo, B.M. Weckhuysen, I.E. Wachs, J. Mol. Catal. A 110 (1996) 41.

[9] D.E. Keller, T. Visser, F. Soulimani, D.C. Koningsberger, B.M. Weckhuysen, Vib. Spectrosc. 43 (2007) 140.

[10] T.V. Venvov, C. Hess, F.C. Jentoft, Langmuir 23 (2007) 1768.

[11] V. Fornes, C. Lopez, H.H. Lopez, A. Martinez, Appl. Catal. A 249 (2003) 345.

[12] Y.-M. Liu, Y. Cao, N. Li, W.-L. Feng, W.-L. Dai, S.-R. Yan, H.-Y. He, K.-N. Fan, J. Catal. 224 (2005) 417.

[13] P. Kustrowski, Y. Segura, L. Chmielarz, J. Surman, R. Dziembaj, P. Cool, E.F. Vansant, Catal. Today 114 (2006) 307.

[14] C. Hess, J.D. Hoefelmeyer, T.D. Tilley, J. Phys. Chem. B 108 (2004) 9703;
C. Hess, U. Wild, R. Schlögl, Microporous Mesoporous Mater. 95 (2006) 339, and references therein.

[15] C. Hess, M.H. Looi, S.B. Abd Hamid, R. Schlögl, Chem. Commun. (2006) 451;
C. Hess, I.J. Drake, J.D. Hoefelmeyer, T.D. Tilley, A.T. Bell, Catal. Lett. 105 (2005) 1;
C. Hess, Surf. Sci. 600 (2006) 3695.

[16] D. Briggs, M.P. Seah, Practical Surface Analysis, Wiley, Chichester, 1990.

[17] The sharp feature at 656 nm is an artifact of the UV–vis spectrometer.

[18] L. Abello, E. Husson, Y. Repelin, G. Lucazeau, J. Solid State Chem. 56 (1985) 379.

[19] A.-C. Dupuis, M. Abu Haija, B. Richter, H. Kuhlenbeck, H.-J. Freund, Surf. Sci. 539 (2003) 99.

[20] R.H. Stolen, G.E. Walrafen, J. Chem. Phys. 64 (1976) 2623.

[21] The presence of a vanadia-related band with significant intensity at 1068 cm^{-1} was confirmed by preliminary UV-Raman experiments in collaboration with Peter Stair.

[22] G.K. Wertheim, Z. Phys. B 66 (1987) 53.

[23] S. Guimond, M. Abu Haija, S. Kaya, J. Lu, J. Weissenrieder, S. Shaikhutdinov, H. Kuhlenbeck, H.-J. Freund, J. Döbler, J. Sauer, Top. Catal. 38 (2006) 117.