

UV and Visible Raman Spectroscopic Study of the Reduction Behavior of VO_x/θ-Al₂O₃ Catalysts

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Introduction

Supported vanadium oxide catalysts are widely used in a variety of industrial applications and show great potential in a number of redox reactions (1). Vanadia catalysts are usually reduced to some extent during redox reactions, and the reduced vanadia species have been proposed as the active sites (1,2). Therefore, information on the valence state and molecular structure of the reduced vanadia catalysts is of great interest. However, the issue still remains unclear and intriguing to people in this field.

Although Raman spectroscopy is a powerful tool for characterization of the molecular structure of supported vanadia, it has been very difficult to obtain Raman spectra from reduced supported vanadia species with conventional (visible) Raman measurements (3). Our recent UV Raman studies of VO_x/θ-Al₂O₃ during butane dehydrogenation (4) and Cr/Al₂O₃ reduced by hydrogen (5) suggest that UV Raman may be capable of detecting reduced, supported metal oxides. Moreover, the UV and visible Raman study of VO_x/θ-Al₂O₃ systems (6) suggest that excitation wavelengths can give information on different surface VO_x species: Monovanadate and polyvanadate species are selectively resonance enhanced by UV and visible excitation, respectively. Therefore, a study of the reduction process of VO_x/θ-Al₂O₃ using multi-excited Raman spectroscopy may provide us more insight into the reduction behavior of surface VO_x species.

Experimental

Supported VO_x samples were prepared via incipient wetness impregnation of alumina (θ-Al₂O₃; Johnson Matthey, UK) with aqueous NH₄VO₃ solutions. Surface VO_x density varied in the range 0.01 – 14.2 V/nm². In the Raman study of hydrogen-reduced V/θ-Al₂O₃ catalysts, samples were first calcined at 823 K for 2 h and cooled to room temperature in He before reduction in flowing 5% H₂/N₂ at different temperatures (473 – 973 K) for 1 h. Raman spectra were collected with both UV (244 nm) and visible (488 nm) excitations using a fluidized bed reactor and a UV Raman instrument built at Northwestern University (4-6). UV-Vis DRS and H₂-TPR were also measured to help elucidate the reduction behavior of surface VO_x species.

Results and Discussion

UV Raman spectra of VO_x/θ-Al₂O₃ with low surface VO_x density (0.06 and 0.16 V/nm²) show that the bands due to θ-Al₂O₃ become stronger relative to those of surface VO_x species after hydrogen treatment at 673 K and above, an indication of the reduction of surface

VO_x species. In-situ UV-Vis DRS measurements from V/θ-Al₂O₃ also show decreasing absorbance in the UV region upon hydrogen reduction which indicates the increased Raman intensity from θ-Al₂O₃ is due to lower self-absorption. A new feature was observed near 880 cm⁻¹ after reduction at 873 K, and the intensity of bands due to oxidized VO_x species decreased greatly. A change in the relative intensity of the band due to V=O and V-O-Al bonds as a function of reduction temperature shows that the V-O-Al interface bond is much easier to reduce than the V=O bond.

Hydrogen-reduction of VO_x/θ-Al₂O₃ samples with intermediate VO_x density (1.2 and 4.4 V/nm²) was studied by both UV and visible Raman spectroscopy. The bands due to VO_x species totally disappear in visible Raman spectra after hydrogen reduction above 573 K, consistent with previous visible Raman studies (17,25-31). However, Raman bands, e.g., at ~1020 cm⁻¹, due to monovanadate are still observable, and a new band at ~870 cm⁻¹ is evident in UV Raman spectra even after hydrogen treatment at 973 K. This apparent difference between the two excitation wavelengths suggests that the VO_x species detected by visible excitation are much easier to reduce than those detected by UV excitation, i.e. polyvanadate is more easily reduced than monovanadate. This is confirmed by TPR results. Considering the structural differences between monovanadate and polyvanadate species, it is reasonable to deduce that V-O-Al bond is more difficult to reduce than the V-O-V bond. The new UV Raman band centered at 870 cm⁻¹, similar to the band observed on 0.16V after high temperature hydrogen treatment, is attributed to reduced VO_x species, most likely V₂O₃ as supported by the UV and visible Raman spectra of bulk vanadium oxides including V₂O₅, VO₂, and V₂O₃. This broad feature is also observed on VO_x/θ-Al₂O₃ samples with higher VO_x density (8 and 14.4 V/nm²) after hydrogen-reduction at high temperatures. Moreover, the reduction of V₂O₅ on these samples is found to be much easier than surface VO_x species.

Significance

The UV- and visible-excited Raman studies of VO_x/θ-Al₂O₃ materials reduced in hydrogen show that polyvanadate and V₂O₅ are more easily reduced than monovanadate species. UV Raman exhibits higher sensitivity toward reduced vanadia species than visible Raman, mainly due to decreased self-absorption and resonance enhancement in the UV region. Comparison of the UV Raman spectra from reduced V/θ-Al₂O₃ with bulk vanadium oxide compounds suggests that reduced VO_x species have a V₂O₃-like structure.

References

1. Weckhuysen, B.M. and Keller, D.E. *Catal. Today* 78, 25 (2003).
2. Argyle, M. D., Chen, K. D., Iglesia, E., and Bell, A.T. *J. Phys. Chem. B* 109, 2414 (2005).
3. Wachs, I.E., Jehng, J.M., Deo, G., Weckhuysen, B.M., Gulians, V.V., Benziger, J.B., and Sundaresan, S. *J. Catal.* 170, 75 (1997).
4. Wu, Z. and Stair, P.C. *J. Catal.* 237, 220 (2006).
5. Sullivan, V.S., Jackson, S.D., and Stair, P.C. *J. Phys. Chem. B* 109, 352 (2005).
6. Wu, Z., Kim, H.K., Stair, P.C., Rugmini, S., and Jackson, S.D. *J. Phys. Chem. B* 109, 2793 (2005).