UV and Visible Raman Spectroscopic Study of the Reduction Behavior of VOx/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 VOx/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 VOx/θ-Al2O3 systems (6) suggest that excitation wavelengths can give information on different surface VOx species: Monovanadate and polyvanadate species are selectively resonance enhanced by UV and visible excitation, respectively. Therefore, a study of the reduction process of VOx/θ-Al2O3 using multi-excited Raman spectroscopy may provide us more insight into the reduction behavior of surface VOx species.

Experimental
Supported VOx samples were prepared via incipient wetness impregnation of alumina (θ-Al2O3: Johnson Matthey, UK) with aqueous NH4VO3 solutions. Surface VOx 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 VOx species.

Results and Discussion
UV Raman spectra of VOx/θ-Al2O3 with low surface VOx density (0.06 and 0.16 V/nm²) show that the bands due to θ-Al2O3 become stronger relative to those of surface VOx species after hydrogen treatment at 673 K and above, an indication of the reduction of surface VOx 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 VOx 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 VOx/θ-Al2O3 samples with intermediate VOx density (1.2 and 4.4 V/nm²) was studied by both UV and visible Raman spectroscopy. The bands due to VOx 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 VOx 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. 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 VOx/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 VOx/θ-Al2O3 systems (6) suggest that excitation wavelengths can give information on different surface VOx species: Monovanadate and polyvanadate species are selectively resonance enhanced by UV and visible excitation, respectively. Therefore, a study of the reduction process of VOx/θ-Al2O3 using multi-excited Raman spectroscopy may provide us more insight into the reduction behavior of surface VOx species.

Significance
The UV- and visible-excited Raman studies of VOx/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 VOx species have a V2O3-like structure.

References