

Resonance Raman spectroscopic study of alumina supported vanadium oxide catalysts

Hack-Sung Kim* and Peter C. Stair

Department of Chemistry, Center for Catalysis and Surface Science and Institute for Catalysis and Energy Processes, Northwestern University, Evanston, IL 60208, USA; Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

*hskim@anl.gov

Introduction

The core bonds in supported metal oxide catalysts that affect the heterogeneous catalytic reactions are the M=O, M-O-M, and M-O-S bonds (M= V, Mo, W, etc, S= Al, Si, Ti, etc).¹⁻³ The M-O vibrational bands are typically weak or undetected by IR or normal (non-resonance) Raman spectroscopy. With resonance enhancement, the detection sensitivity of Raman spectroscopy increases enormously. For example, intense M-O stretching bands can be observed by resonance Raman spectroscopy under proper resonance conditions. Besides the enhanced fundamental bands, overtone and combination bands can be observed which provide additional information.

Resonance Raman spectroscopic application to the supported metal oxides is rare. Here we present the first extensive analysis of UV resonance Raman spectra for alumina-supported vanadium oxide catalysts. It is also a powerful tool for assigning the electronic transitions observed in UV-VIS absorption spectra because of the direct link to the specific stretching vibrations that are enhanced.

Materials and Methods

The preparation method is described in detail elsewhere.⁴ Briefly, VO_x supported on θ -alumina (BET Surface area = 101 m²/g) was prepared by incipient wetness impregnation using ammonium metavanadate. After impregnation, the samples were dried and calcined at 823 K.

Raman spectra were measured using a tunable laser (Ti:Sapphire oscillator pumped by a diode-pumped, intracavity frequency-doubled Nd:YLF laser) with second, third, fourth harmonic conversion to produce wavelengths 210 nm to 900 nm and a triple-stage spectrometer coupled to a liquid nitrogen-cooled CCD.

Results and Discussion

The Raman spectra for θ -Al₂O₃ and vanadia supported on θ -Al₂O₃ (Figure 1) make possible the identification of VO_x-associated overtones and combinations as well as fundamentals. The resonance Raman spectra excited at 220 nm are in general agreement with previously published spectra⁴ excited at 244 nm and 488 nm, but the new spectra include additional features such as overtones, combinations, and OH stretching. From a detailed analysis of the spectra, several vibrational parameters for V=O and V-O were obtained.

With 220 nm excitation, the Raman spectra for dehydrated vanadia samples are characterized by the selective enhancement of V=O stretching bands, which allows us to assign the higher-energy charge transfer band in the UV-VIS spectra to the V=O transition. The assignment is significant because the higher-energy charge transfer band has never been identified.

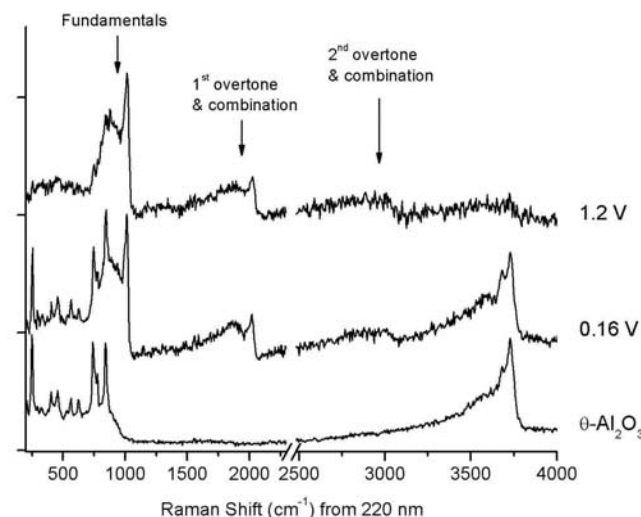


Figure 1. Resonance Raman spectra excited at 220 nm obtained at dehydrated conditions for θ -Al₂O₃ and X V/nm² on θ -Al₂O₃ (X= 0.16 and 1.2).

Significance

This work shows a clear assignment of UV-VIS absorption bands using resonance Raman spectroscopy. Also shows the first detailed analysis of UV resonance Raman spectra for alumina-supported vanadium oxide catalyst

References

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