

In-situ and Time-Resolved Resonance Raman Spectroscopy in Catalysis

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Introduction

Raman spectroscopy is one of the most important tools for characterization of heterogeneous catalytic systems because it can provide molecular-level information about both catalyst and reagents under reaction conditions. The ability to tune the excitation wavelength in Raman spectroscopy opens the possibility of selecting the species detected, i.e. active phase, support, reactants, products, or intermediates, by means of the resonance enhancement effect. With the proper corrections for self-absorption and scattering cross section, Raman intensities can be quantified. Using a rapid heat-quench sequence to activate catalytic reactions, the limitations imposed by the duration of signal averaging can be overcome to achieve time-resolution for reactions in the range of microseconds or below.

Here we demonstrate the advantages of selective excitation and quantification using resonance Raman spectroscopy in catalysis. We also show the utility of rapid activation and quenching of reactions using infrared laser heating combined with in-situ Raman spectroscopy to unravel complex reaction pathways.

Materials and Methods

A variety of catalytic materials have been studied, including vanadium oxide supported on alumina powder and on nanostructured membrane scaffolds, TiO₂ films and as supports for vanadia, and zeolite H-MFI. Catalytic species have been deposited by wet impregnation and by atomic layer deposition. The catalytic materials have been measured in-situ under oxidizing, reducing, reaction, and ambient conditions and at both elevated and cryogenic temperatures.

Raman spectra have been excited at a number of wavelengths in the visible and ultraviolet regions using both a cw argon ion laser and a tunable pulsed laser (Ti:Sapphire oscillator pumped by a diode-pumped, intracavity frequency-doubled Nd:YLF laser). Spectra were recorded by single-stage and triple-stage spectrometers coupled to liquid nitrogen-cooled CCD detectors.

In-situ cells make use of a fluidized bed method to minimize interference by laser-induced heating and photochemistry on the measurements. Rapid heating and quenching are accomplished using an infrared laser and sample motion in the fluidized bed.

Results and Discussion

Using diffuse reflectance as an external standard, Raman intensity measurements of

V/ θ -Al₂O₃ were corrected for the self-absorption. By selectively detecting monovanadate (UV-excited), polyvanadate (visible-excited), and V₂O₅ (visible-excited) in resonance Raman measurements, the distribution of monovanadate, polyvanadate and V₂O₅ present on dehydrated V/ θ -Al₂O₃ samples was quantified as a function of surface VO_x density. Monovanadate species are present at all VO_x densities studied but are the dominant species at low density. Polyvanadate and V₂O₅ are also present and predominate at intermediate and high surface VO_x density. Both the nature and amount of coke formed during butane dehydrogenation are related to the nature of VO_x species. Monovanadates make chainlike polyaromatics while polyvanadates mainly produce sheet-like (2D) polyaromatics that are detrimental to the catalytic activity. The amount of coke formed from butane DH follows the sequence: polymeric VO_x > monomeric VO_x > V₂O₅, Al₂O₃. The Raman spectrum following hydrogen reduction is consistent with the formation of V₂O₃.

Raman spectra for hydrated and dehydrated VO_x supported on θ -alumina exhibit not only the fundamental VO stretching vibrations in the 900-1100 cm⁻¹ region, but also overtone bands in the 1800-2100 cm⁻¹ region. The V=O bond dissociation energies estimated from the band positions of dehydrated VO_x on θ -alumina are two-times larger than typical ranges of V=O bond dissociation energies for crystalline V₂O₅ and isolated VO_x on silica or on α -Al₂O₃. This indicates that reduction of vanadyl O atoms on θ -alumina is much more difficult.

UV Raman measurements of amorphous TiO₂ with and without vanadia overlayers demonstrate that VO_x enhances the restructuring of TiO₂ to form the anatase structure.

The Raman spectra of Al-O stretching vibrations were measured for γ -alumina with 220 nm excitation. Spectra for other phases of alumina support have also been measured and significant effects on Al-O band intensities by surface VO_x species were observed.

Infrared laser heating can successfully activate reactions inside zeolite pores. With increasing laser power, reactants disappear and products appear. Because heating and cooling is very rapid the escape of adsorbed species from the pore structure is undetectable. Consequently the formation of carbonaceous deposits is exclusively in the pores. Reaction intermediates are trapped and observed by in-situ Raman spectroscopy.

Significance

This work provides a number of examples of how Raman spectroscopy can be used to dissect and identify the species present in a complex catalytic reaction mixture. Moreover, new information is obtained about the nature of catalytic active sites and reaction pathways.