# Resonance Raman Spectroscopy of Catalysts and Supports

Hack-Sung Kim[1, 2], Jeffrey Elam[3], Zili Wu[1], and Peter C. Stair[1, 2]*
[1] *Department of Chemistry, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208, USA*
[2] *Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[3] *Energy Systems Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
* pstair@northwestern.edu

## Introduction

Raman spectroscopy has been extensively used to characterize supported catalytic oxide species, but its application to the supporting oxide is relatively rare because the spectra are generally dominated by bulk signals. The ability to select the excitation wavelength in Raman spectroscopy makes it possible to control the species detected: supported phases, support films, or bulk support, by avoiding or taking advantage of the resonance enhancement effect as well as to minimize fluorescence interference.

Here we present examples of selecting the excitation wavelength for Raman spectroscopy of catalyst materials: 1) Detection of a thin-film, $TiO_2$ support and influence of vanadia ($VO_x$) monolayers on the titania structure. 2) The observation of V=O second and third harmonic bands in resonance Raman spectra which leads to an estimate for the V=O dissociation energy. 3) Raman spectroscopy of weakly scattering alumina supports, including γ-, δ-, θ-, and α-$Al_2O_3$ and the effect of surface vanadia on the *alumina* vibrational spectra.

## Materials and Methods

Catalysts consisting of a 1 nm $TiO_2$ film and $VO_x$ supported on the $TiO_2$ film were synthesized in nanostructured anodic aluminum oxide (AAO) membrane channels by atomic layer deposition (ALD) using $Al(CH_3)_3$, $TiCl_4$, $OV(OC_3H_7)_3$, and water.[1] $VO_x$ on θ-alumina was prepared by incipient wetness impregnation using $NH_4VO_3$. γ-, δ-, θ-, and α-$Al_2O_3$ supports were obtained from Aldrich or Johnson-Matthey.

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

Fig. 1 compares Raman spectra for coated AAO membranes excited at 287 nm. Only fluorescence is detectable with excitation at 430 nm. In spectrum (a) the AAO has been coated with 1-nm $Al_2O_3$ and 1-nm $TiO_2$. A broad, featureless band with a maximum at about 650 $cm^{-1}$ indicates the presence of an amorphous $TiO_2$ film. Spectra (b) and (c) show that the amorphous $TiO_2$ converts to the anatase and brookite structures at <120°C when 1 ML of vanadia is present. Generally, anatase $TiO_2$ is the support for vanadia catalysts because of a good crystallographic fit between the oxides. The spectra in Fig. 1 show that the presence of the $VO_x$ strongly influences the structure of the $TiO_2$ support. Further phase transformations from anatase/brookite to rutile $TiO_2$ depends on catalytic reaction conditions and possibly the method of $VO_x$ deposition method.

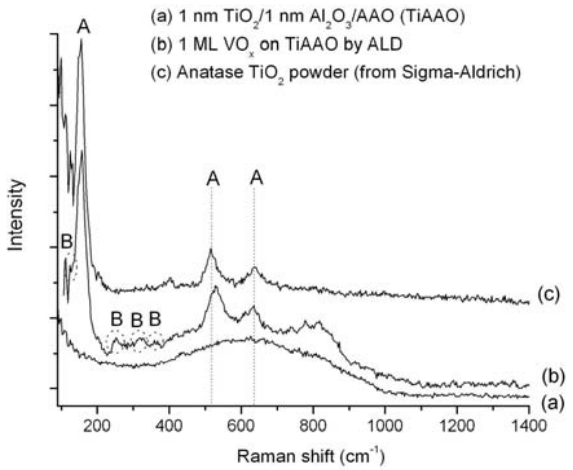


**Figure 1.** UV Raman spectra: (a) 1 nm ALD $TiO_2$ on 1 nm ALD $Al_2O_3$ on AAO membrane, (b) 1 ML $VO_x$ on (a), (c) anatase $TiO_2$ powder. Raman bands of anatase and brookite $TiO_2$ are marked with 'A' and 'B', respectively.

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 $V_2O_5$ and isolated $VO_x$ on silica or on α-$Al_2O_3$. This indicates that the vanadyl O atoms on θ-alumina are much more difficult to remove.

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.

## Significance

This work shows the first successful Raman measurements for $VO_x$ on titania/alumina/AAO membranes and for γ-alumina. Also shows the first observation of overtone Raman bands associated with the surface VO species on alumina.

## References

1. Stair, P. C.; Marshall, C.; Xiong, G.; Feng, H.; Pellin, M. J.; Elam, J. W.; Curtiss, L.; Iton, L.; Kung, H.; Kung, M.; Wang, H.-H., *Top. Catal.* **2006,** 39, (3-4), 181-186.