X-ray Diffraction and Vibrational Spectroscopy of Catalysts for Exhaust Aftertreatment

Roger England and Howard Fang, Cummins Inc., Columbus, IN 47201
Thomas R. Watkins, Michael J. Lance and Douglas Blom, Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Abstract
Raman vibrational spectroscopy was used to characterize surface adsorbing species during catalyst nitration and sulfation as well as particle size effects of precious metal additives during sintering. The study of these surface species is critical in understanding the thermodynamic and kinetic parameters necessary for catalytic model development and design. In this study, the Raman response was calibrated to a known physical measurement of the crystallite size in the bulk material via X-ray diffraction (XRD)\(^1\) and transmission electron microscopy (TEM). Once calibrated, the Raman technique was used as a particle size probe to delineate catalyst degradation pathways, which are critical in developing a fundamental understanding of aging mechanisms in NO\(_x\)/SO\(_x\) absorbers.

Background
The surface area of certain active components controls catalytic activity. Upon extended operation at high temperatures, the surface area of some of these components decreases, reducing the activity of the catalyst. Transition frequencies and bandwidths of Raman bands from the support materials are sensitive to the surface area and particle size of these active components. A change of one weight percent doping of Pt can significantly alter the Raman bands of the titania substrate or support. The observed band broadening is an indication of the relaxation process with surrounding lattice modes, and the correlation length is a function of the crystallite size of the Pt. The titania 146 cm\(^{-1}\) Raman band can be used to characterize the lattice relaxation and sintering effect of Pt on catalytic activity. Applications for this measurement technique include selective catalytic reduction of NO\(_x\)/SO\(_x\) (for TiO\(_2\) and V\(_2\)O\(_5\)) and oxygen storage materials (such as CeO\(_2\)). This study seeks a correlation between this Raman bandwidth and the Pt particle size to other reference methods such as XRD and TEM.

Experimental
For this study, all samples were impregnated with Pt and calcined at 400°C. The XRD measurements were made using a Philips X’Pert Pro MPD Diffractometer using Cu K\(_\alpha\) radiation with 1° incident divergence, soller slits, and a 0.1mm receiving slit height. The instrumental and size broadening were determined from \(\Theta–2\Theta\) scans (20 seconds per 0.02° step) of the (200) of a silicon reference powder and the (200) peak of platinum on the catalyst, respectively. This platinum peak was selected due to a lack of interference with substrate reflections (see Figure 1). Full width half maximum values were calculated using Jade. The Scherrer formula\(^3\) was used to calculate the mean crystallite size: \(t = (0.9\lambda)/(B \cos\Theta_B)\) where \(t\) is the crystallite size, \(B\) is the peak breadth in radians, \(\Theta_B\) is the Bragg angle, and \(\lambda\) is the wavelength of the radiation. This calculation was used with the assumption that there were no significant nm length scale strains present in the Pt crystals.
Raman spectra were obtained with a DilorXY800 Raman microprobe (JY, Inc., Edison, NJ) using a Innova 308C Ar⁺ ion laser (Coherent, Inc., Santa Clara, CA) at 515 nm and 300mW output power. The spot diameter and penetration depth were both ~10 µm in size. Peak position and bandwidth were determined by fitting the spectra with a pseudo-Voigt curve fit.

**Results and Discussion**

The anatase-to-rutile phase transition temperature and the titania sintering temperature are both platinum content dependent. The theoretical phase transformation temperature between anatase and rutile is ~1000°C.² Raman spectra of the commercial titania used in this study are shown in Figure 2 where the phase transition of anatase/rutile in titania initiated around 750°C. Raman bands attributed to anatase (ρ ~ 3.8 g/cm³) are located at 146, 399, 518 and 640 cm⁻¹ while the rutile bands are located at 238, 450 and 613 cm⁻¹ (ρ ~ 4.26 g/cm³). The transition frequencies and bandwidths of TiO₂ bands are invariant with temperature.

The Pt content alters Raman behavior of titania. Here, approximately one weight percentage of Pt significantly altered Raman bands of support materials (see figure 3). The transition frequency shifts from 146.2 cm⁻¹ to 153.4 cm⁻¹ and the bandwidth increases from 9 cm⁻¹ to 18.3 cm⁻¹ (~100 % change). Raman bandwidth is very sensitive to particle dispersion and size of Pt, even for low Pt loading. Raman scattering has been used to estimate particle/crystallite size on catalysts,¹ and can be more sensitive to sintering than XRD when the Pt particle size is <15 nm.

Impurities and the addition of Pt lowers the titania sintering initiation temperature. As shown in Figure 3(b) between 600- 650°C, the surface area of the sample containing 1.66 % Pt reduces from 50 to 20 m²/g due to sintering. Both Raman frequency and bandwidth increase slightly with calcination temperature, before decreasing at 725°C due to the anatase/rutile phase transition (see Figure 3).

A good correlation between Raman and XRD measurements is shown in Figures 6 and 7. The Raman responses increase with temperature and appear correlated to increasing Pt crystallite size. This suggests that the small Pt particles are sintering to form bigger particles. The net effect is the reduction of Pt metal surface area/catalytic activity. Figure 4 shows a typical full width half-maximum measurement from XRD used in the Scherrer equation. Figure 5 shows an order of magnitude agreement between the 10nm particles in the electron micrograph and those calculated by XRD.

**Summary**

These measurements are first steps in the effort to delineate S-poisoning mechanisms in NOₓ absorbers by monitoring either adsorbed species or functionality of the support materials. XRD and TEM measurements correlate with Raman bandwidth measurements of substrates, providing a measure of the active component crystallite size and sintering effects.
References

Acknowledgements
• M. Sanders, Goal Line Environmental Technologies, Knoxville, TN.
• Research sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User and Fellowship Programs, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725. MJL supported in part by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, Department of Energy.
• This research was supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and Oak Ridge Institute for Science and Education.

Figure 1  The influence of the Pt on the anatase/rutile transition temperature.
Figure 2  The change in the Raman response due to addition of 1.66% Pt.

Figure 3  The change of Raman transition frequency and bandwidth as a function of calcination temperature
Figure 4  Typical FWHM measurement, values were calculated using Jade.
Figure 5  TEM image of the dispersion of the ~10 nm Pt particles on the surface of the 600°C TiO₂ sample
Figure 6 Correlation of the Raman frequency response to the XRD measured crystallite size is evident.

Figure 7 Correlation of the Raman bandwidth response to the XRD measured crystallite size also evident.