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REPORT CP 368

DETERMINATION BY X-RAY ABSORPTION SPECTROSCOPY OF  
PLATINUM VALENCE IN ORGANOMETALLIC COMPLEXES INVOLVED IN  
GEL MAMMARY IMPLANT MATERIALS

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## Final Report

- Project Title** Determination by X-ray Absorption Spectroscopy of Platinum Valence in Organometallic Complexes involved in Gel Mammary Implant Materials
- Project No.** CP368
- Study Director** Robert A. Scott, Ph.D., Department of Chemistry, University of Georgia, Athens, GA
- Testing Facility** Stanford Synchrotron Radiation Laboratory
- Sponsor** Mentor Corporation
- Objective** We have utilized synchrotron radiation-based X-ray absorption spectroscopy to determine the valence state of Pt in the hydrosilylation catalyst used to polymerize siloxane materials for gel mammary implants
- Rationale** X-ray absorption spectroscopy uses synchrotron radiation as a source of X-rays to probe the electronic and molecular structures surrounding unique elements in amorphous samples. The source X-rays cause photoionization of core electrons (Pt  $2p_{3/2}$  in this case) generating photoelectrons that scatter from nearby electron density surrounding neighboring atoms. The energy of the photon required to dissociate these core electrons (the core electron binding energy) is sensitive to the valence electron configuration and can thus be used to directly probe the valence state of the element [1-3]. By recording x-ray absorption spectra of known-valence Pt model compounds, we can identify the spectral difference between Pt(0) and Pt(II), allowing us to measure the valence state of the Pt hydrosilylation catalyst.
- Protocol** X-ray absorption spectroscopic data were collected by fluorescence excitation techniques on beamlines 7-3 or 9-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) at the Pt  $L_3$  edge (ca. 11565 eV) on gel implant material catalysts. Samples of ca. 50 microliter volume were loaded into polycarbonate cuvetts and contained within a cryostat for data collection at sample temperatures of ca. 10 K. X-ray Absorption Near-Edge Structure (XANES) data from the Pt  $L_3$  edge were compared with data from known-valence Pt compounds to determine the average valence of Pt species in each sample.
- Samples** The Pt catalyst used [REDACTED] contains vinyl siloxane monomers bound to Pt through the C=C functionality. Known-valence Pt model compounds were chosen with similar bonding. Specifically, the Pt(0) model compound examined was [REDACTED] and it was prepared as a 0.1-M solution in poly(dimethylsiloxane), vinyl terminated. The Pt(II) model compound was Pt(1,5-cyclooctadiene)Cl<sub>2</sub> (CAS#12080-32-9; Aldrich P/N 24,493-7), also prepared in silicone fluid.

For each of the three compounds, two independently prepared samples were examined by XAS on three separate beamline visits.

368003	Pt Catalyst	2000ppm	BL7-3	07-Mar-2003
368108	Pt Catalyst	2000ppm	BL9-3	08-Apr-2004
368-4	Pt(0) Model	26.4ppm	BL9-3	13-Dec-2002
368101	Pt(0) Model	25.3ppm	BL9-3	08-Apr-2004
368-2	Pt(II) Model	26.8ppm	BL9-3	13-Dec-2002
368102	Pt(II) Model	23.0ppm	BL9-3	08-Apr-2004

**Results** X-ray absorption spectra for all six samples are compared in Figure 1 in the energy range that contains the Pt L<sub>3</sub> edge. The comparison in Figure 1 shows that these spectra can be reproducibly obtained, but that the appearance is quite similar for the different samples. Our ability to distinguish Pt valence states will require careful comparison of edge energies. We therefore have chosen to compare only spectra of the three samples collected during the same run on the same beamline (368101, 368102, 368108).

Pt L<sub>3</sub> edges of these three samples are directly compared in an expanded scale in Figure 2. The effect of differing valence states is most clearly observed in the inflection point of the main edge. cursory examination of this comparison shows that the Pt catalyst sample (368108) exhibits essentially identical valence to the Pt(0) model compound (368101).

**Conclusion** The comparison of Pt L<sub>3</sub> edge spectra in Figure 2 shows that essentially all of the Pt in the SiTech Pt catalyst is in the Pt(0) valence state. To quantify this qualitative statement, we have employed several different data smoothing/differentiation routines to determine the inflection points for these spectra. The Pt(II) model yields an inflection point of  $11563.89 \pm 0.05$  eV, while the Pt(0) model yields an inflection point of  $11565.06 \pm 0.04$  eV. The Pt catalyst sample yields an inflection point of  $11565.02 \pm 0.05$  eV. With these uncertainties in our measurements, we can conclude that the Pt catalyst contains at least 95% Pt(0). Given that the total Pt concentrations in these samples are approximately 25 ppm, this implies that there must be less than 1.2 ppm Pt(II) in the Pt catalyst sample.

- References**
1. Stein, J, Lewis, LN, Gao, Y, Scott, RA "In Situ Determination of the Active Catalyst in Hydrosilylation Reactions Using Highly Reactive Pt(0) Catalyst Precursors" *J. Am. Chem. Soc.* **1999**, *121*, 3693-3703.
  2. Lewis, LN, Colborn, RE, Grade, H, Bryant, GL, Jr., Sumpter, CA, Scott, RA "Mechanism of Formation of Platinum(0) Complexes Containing Silicon-Vinyl Ligands" *Organomet.* **1995**, *14*, 2202-2213.
  3. Lewis, LN, Stein, J, Smith, KA, Messmer, RP, LeGrand, DG, Scott, RA In *Progress in Organosilicon Chemistry* Marciniak, B, Chojnowski, J, Eds., Gordon and Breach: Amsterdam, 1995, pp. 263.

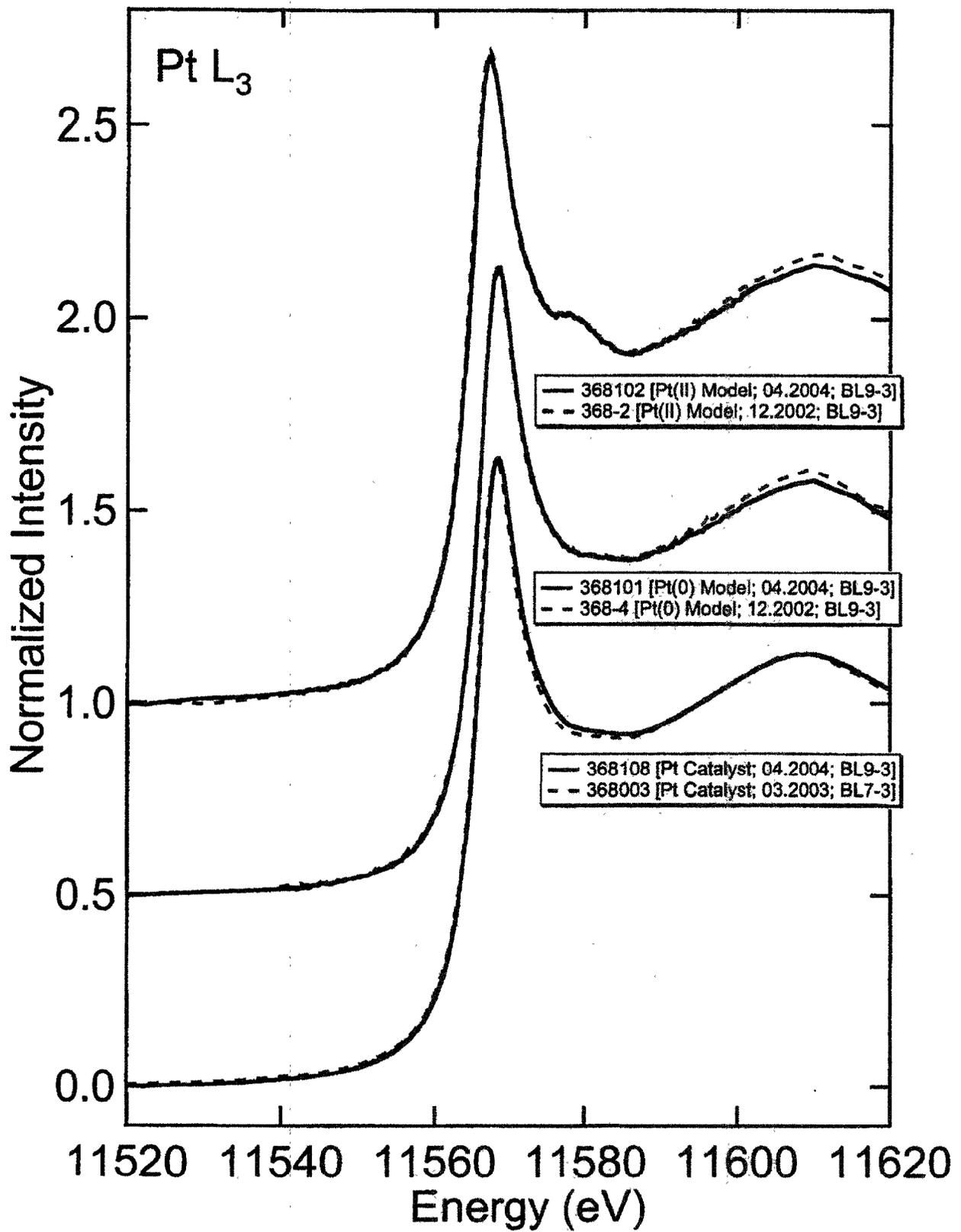


Figure 1

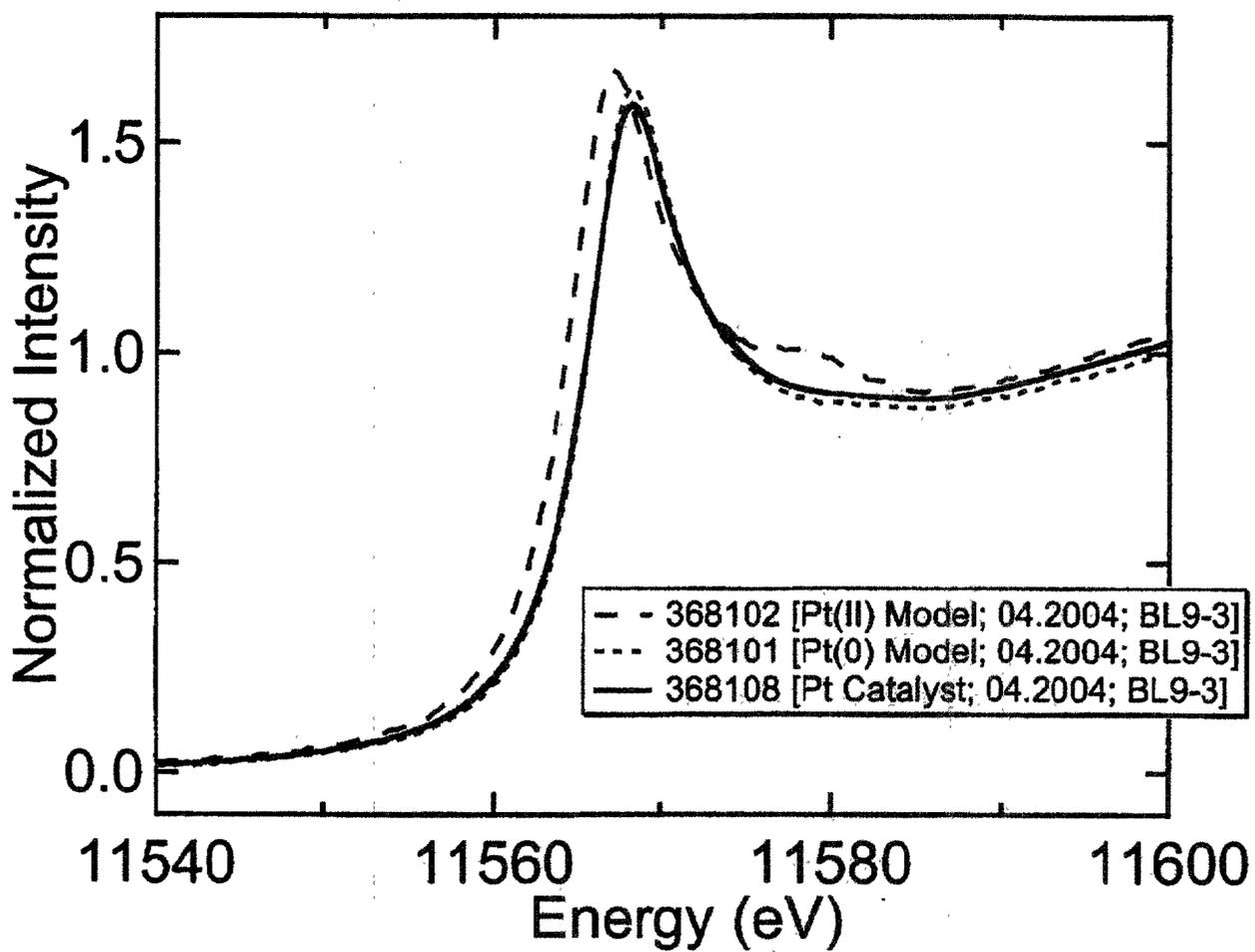


Figure 2