

# Synchrotron and simulations techniques applied to problems in materials science: catalysts and Azul Maya pigments

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Development of synchrotron techniques for the determination of the structure of disordered, amorphous and surface materials has exploded over the past 20 years owing to the increasing availability of high-flux synchrotron radiation and the continuing development of increasingly powerful synchrotron techniques. These techniques are available to materials scientists who are not necessarily synchrotron scientists through interaction with effective user communities that exist at synchrotrons such as the Stanford Synchrotron Radiation Laboratory. In this article the application of multiple synchrotron characterization techniques to two classes of materials defined as 'surface compounds' is reviewed. One class of surface compounds are materials like  $\text{MoS}_{2-x}\text{C}_x$  that are widely used petroleum catalysts, used to improve the environmental properties of transportation fuels. These compounds may be viewed as 'sulfide-supported carbides' in their catalytically active states. The second class of 'surface compounds' are the 'Maya blue' pigments that are based on technology created by the ancient Maya. These compounds are organic/inorganic 'surface complexes' consisting of the dye indigo and palygorskite, common clay. The identification of both surface compounds relies on the application of synchrotron techniques as described here.

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## 1. Introduction

The availability of high-quality synchrotron radiation and the ability to apply synchrotron techniques routinely to problems in materials science has greatly enhanced our ability to solve materials problems that involve highly disordered, amorphous or surface states. The application of synchrotron techniques to materials problems has been reviewed recently (Gerson *et al.*, 1999; Yoshiki, 2002; Montano & Hiroyuki, 1999). Techniques such as WAXS (wide-angle X-ray scattering), XAFS (X-ray absorption fine structure) and XANES (X-ray absorption near-edge structure) have become routine techniques for the materials scientist, improving our ability to understand difficult issues related to the structure and function of modern poorly crystalline materials. *In situ* techniques and surface techniques including surface scattering are developing rapidly and will become routine in the near future to help us further understand complex materials. It is the high intensity and stability of synchrotron radiation sources, along with the

possibility to select the wavelength of the beam, that make synchrotron techniques so valuable for the problems described here.

An example of how a simple synchrotron technique such as synchrotron XRD (X-ray diffraction) can yield new insight into an old problem can be found in a recent paper about the magnetic structure of *Aurivillius* ceramics (Fuentes *et al.*, 2002). Members of this class such as  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  are of interest because of the high-temperature ferroelectricity and their potential as magnetoelectric sensors. The crystalline structure of these materials is formed by perovskite octahedra, sandwiched between bismuth oxide layers. For temperatures above the Curie point,  $T_c$  (873–1073 K), *Aurivillius* crystals adopt centrosymmetric tetragonal structures, with space group *Fmmm*. In the ferroelectric temperature domain  $T < T_c$ , tetragonal symmetry breaks down to orthorhombic or monoclinic, with lattice parameters slightly different from those corresponding to the high-temperature configuration. Determining the crystal symmetry group is difficult, but it is

important, because symmetry is a decisive factor in the structure polarization relationship. This symmetry breakdown is clearly seen by synchrotron diffraction as described in the publication cited above (Fuentes *et al.*, 2002), but has been difficult or impossible to see by conventional in-house X-ray methods.

In addition, synchrotrons have become 'friendlier' places to work owing to the presence of user support groups and synchrotron support staff who are encouraged to interact with users who may not be familiar with synchrotron techniques. This follows from the pioneering work of synchrotron scientists that made possible the high-quality beam and experiments that materials scientists enjoy today (Doniach *et al.*, 1997). Here we discuss two classes of surface compounds: the sulfide-supported carbides of type  $\text{MoS}_{2-x}\text{C}_x$  and Maya blue pigments. The application of synchrotron techniques to these classes of materials has greatly enhanced our understanding of them.

### 2. Synchrotron studies and sample preparation

All synchrotron studies reported here were performed at Stanford Synchrotron Radiation Laboratory (SSRL) from 2000 to 2003 under a grant from the DoE (Department of Energy) BES (Basic Energy Sciences) called the 'Gateway Program'. It is designed to bring students from the United States/Mexico border into the synchrotron community.

Sample preparation techniques can be found in the cited references. The X-ray scattering data were collected at SSRL on beamline 2-1. The vertical collimation and high brightness of the synchrotron beam allowed use of a Si(111)-based detector able to resolve lattice changes of the order of 0.1%. The size of the focused beam was  $2\text{ mm} \times 1\text{ mm}$  and approximately  $10^{10}$  photons  $\text{s}^{-1}$  are incident on the sample. The XRD patterns were collected in the  $5\text{--}75^\circ$   $2\theta$  range with X-rays tuned to the energy of the Zn *K*-edge (9.659 keV). The NEXAFS (near-edge X-ray absorption fine-structure experiments) were carried by Joachim Stöhr on beamline 8-2. Samples were pressed into In foil. The spectra were recorded as a function of incident X-ray photon energy in the vicinity of the C *K*-edge (275–325 eV). The partial electron-yield was measured; selecting secondary electrons with a mean free path of about 1 nm were measured. The method is sensitive only to the surface layers yielding information very similar to Auger electron and X-ray photoelectron techniques. Samples and standards for Fe XAFS were loaded into 0.5 mm-thick aluminium sample holders that were sealed using Mylar tape. The samples were placed on rods and frozen under liquid nitrogen prior to being placed into the cryostat. Fe *K*-edge absorption spectra for the various samples were collected on SSRL beamline 7-3 (1.8 T wiggler field) using a Si (220) double-crystal monochromator and a 13-element solid-state germanium array detector. The SPEAR storage ring was normally operating at 55–100 mA at 3.0 GeV. Harmonics were rejected by detuning the two-crystal monochromator to 50% of the maximum intensity. During data collection, samples were maintained at approximately 10 K using an Oxford

Instruments CF1204 liquid-helium flow cryostat. Further details can be found in the references cited later.

### 3. Surface compounds

Many compounds that have a practical importance are most effective as small particles. Heterogeneous catalysts are a prime example. Catalysts that can be stabilized as small particles have a greater active surface area for performing the desired reactions. As the particles become smaller, the way in which the particle terminates its surface becomes more extensive and easier to characterize. Atomically clean surfaces reconstruct in a vacuum. However, catalysts are in reactive environments and may terminate their surfaces by chemistry that integrates the surrounding reactants. This is especially true in catalytic environments at temperatures lower than 673 K, where kinetic hindrance often prevents the formation of the bulk equilibrium phase. These non-equilibrium catalytic surface compounds can be thought of as three-dimensional polymers with terminating groups that reflect the environment in which they operate.

Perhaps the most extensively studied and understood example of this is the industrially important Ziegler-Natta polymerization catalyst (Cerruti, 1999). Originally, based on small particles of  $\text{TiCl}_3$ , it was recognized that the desirable polymerization properties could be enhanced by modifying the surface of the  $\text{TiCl}_3$  with agents such as  $\text{AlCl}_3$  or alkyl aluminium compounds.  $\text{TiCl}_3$  crystallites are terminated with Al compounds that interface with the growing polymers.  $\text{TiCl}_3$  provides the appropriate redox (electron) substrate and the Al surface provides the proper polymerization stereochemistry for the desired reaction. The enhancement of the Ziegler-Natta polymerization catalyst progressed by reduction in the particle size and therefore the enhancement of the contribution of the surface structure, until finally the 'single site' metallocene catalyst emerged. The reference cited above discusses the 'control of the architecture or three-dimensional structure of the catalyst' that has not only enabled the success of the polymer industry but also opened 'the way to the creation of new and completely revolutionary families of materials'. The author describes the catalyst as a 'reactor granule . . . with its own energy and materials balance'. Today we might call it a nano-reactor with all of the elements of the chemical reactor on the nanoscale. The examples of surface compounds given in this report include a catalyst similar to that just described and an entirely unexpected example in the Maya blue pigments.

### 4. Transition-metal sulfide catalysts

Catalysts based on transition-metal sulfides (TMS) such as  $\text{MoS}_2$  and  $\text{WS}_2$  are used by refineries around the world to meet environmental requirements for heating and transportation fuels through the removal of sulfur, nitrogen and other pollutants. It is expected that, as the world petroleum reserves dwindle, heavy crudes containing larger amounts of sulfur, nitrogen and metals will become a major source of petroleum

hydrocarbons. Faced with increasing reliance on high sulfur crudes and increasingly strict regulations regarding sulfur content of fuels, better HDS (hydrodesulfurization), HDN (hydrodenitrogenation) and HDM (hydrodemetallization) catalysts are sought. In addition, it has been found recently that the TMS catalysts are very effective anodes for hydrogen activation in fuel cells, especially for high-sulfur-content fuels (Zhang *et al.*, 2002). In order to meet the increasing environmental demands and to develop new uses for the TMS, a deeper understanding of their structure and function in stable operating conditions is necessary.

The most important basic aspect of catalysis by the TMS is the determination of the catalytic stable state as a function of position in the periodic table. The first report of the periodic effect in catalysis by TMS emphasized the importance of determining the 'catalytic stable state' (Pecoraro & Chianelli, 1981). This paper established the bulk crystalline structure of the transition-metal sulfide catalysts for the HDS reaction and was the first paper to place the extremely active  $\text{RuS}_2$  catalyst at the peak of the 'volcano plot' for HDS activity.  $\text{RuS}_2$  catalysts have also been recently shown to be very effective anodes for hydrogen activation in fuel cells. Both the HDS activity and the hydrogen activation activity point to the importance of the  $4d$  and  $5d$  electrons in catalysis by the TMS, particularly in reactions involving hydrogen. This is the most fundamental rule in catalysis by TMS and this phenomenon has been underpinned theoretically in recent studies (Chianelli *et al.*, 2002). Commercial catalysts are the more complex 'promoted systems', based on  $\text{MoS}_2$  or  $\text{WS}_2$  that are 'promoted' by Co or Ni but not by Fe or Cu. This effect is also explained by the concept of 'pseudo-binary' catalysts. Catalysts based on Co/Mo, Ni/Mo, Co/W and Ni/W behave as 'pseudo-binaries' because they achieve  $4d$  and  $5d$  electron configurations that mimic noble-metal configurations by creating 'surface compounds' with the promoter phase at the surface of the 'support phase'. Thus, Co supported on  $\text{MoS}_2$  has enhanced activity and performs like a noble-metal sulfide, though  $\text{RuS}_2$  activity is not achieved. A complete discussion on this subject is beyond the scope of this report but is another example of the importance of surface compounds in catalysis (Chianelli *et al.*, 1994).

## 5. TMS surface compounds

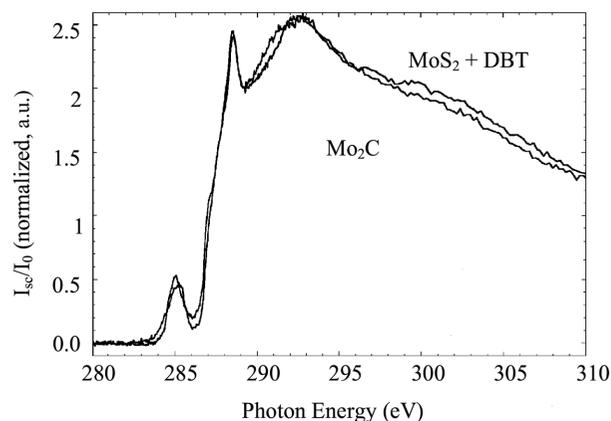
Recent results indicate that the surfaces of the TMS in their catalytic stable state (CSS) contain carbon directly bonded to the catalytic metals (Berhault *et al.*, 2001; Kelty *et al.*, 1999). Carbon XANES spectra described in these references clearly show that the transition metal is bound directly to carbon on the surface of the catalyst. The Auger electron-yield NEXAFS spectrum is shown for a  $\text{MoS}_2$  catalyst in Fig. 1. The Auger electron yield comes from the first nanometer of the surface; the fluorescent yield spectrum that is dominated by bulk phase (not shown) has very little indication of carbon. This key information, elucidating the existence of the surface compounds, comes from synchrotron studies, and is confirmed by EELS, IR and other techniques confirming the existence of

the carbon surface compounds. These compounds are shown schematically in Fig. 2. In this figure,  $\text{RuS}_{2-x}\text{C}_x$  is shown as a cross section of a spherical particle with the carbide phase covering the surface of the sphere.  $\text{MoS}_{2-x}\text{C}_x$  is shown as a cylindrical particle with the surface of the cylinder covered with the carbide phase.

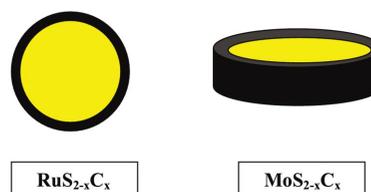
Thus, the CSS for Mo is  $\text{MoS}_{2-x}\text{C}_x$  and for Ru is  $\text{RuS}_{2-x}\text{C}_x$ . For example, a catalyst that was originally  $\text{RuS}_2$  with the pyrite structure and an average particle size of 10 nm was used to hydrodesulfurize the model compound DBT for over 1000 h. The resulting catalysts retained the bulk pyrite structure and particle size but had lost sulfur and gained carbon such that the stoichiometry was now  $\text{RuS}_{1.7}\text{C}_{0.3}$ . This corresponds to removing the surface layer of sulfur and replacing it with carbon in a 10 nm particle (Chianelli & Berhault, 1999). This is an example of a description of the CSS of a TMS catalyst. This description is the proper starting point for a discussion on the 'active sites' in a stabilized TMS catalyst.

A similar situation exists for Mo and W catalysts that are promoted with Co or Ni. Thus, any description of TMS catalysts that neglects the important role of carbon stabilization is incomplete and inadequate. It is also true that promotion must be treated as a symmetrical synergism, rather than promotion of one phase by another, in order to understand the true nature of the effect (Berhault *et al.*, 2002).

Demonstration of the existence of surface compounds in operating catalysts has long been overdue, especially in the



**Figure 1**  
Carbon Auger electron-yield NEXAFS spectrum from a  $\text{MoS}_2$  catalyst stabilized under HDS conditions, showing similarities to the surface of  $\text{Mo}_2\text{C}$  (see Berhault *et al.*, 2001).



**Figure 2**  
Cross-sectional schematics of surface compounds (in black)  $\text{RuS}_{2-x}\text{C}_x$  and  $\text{MoS}_{2-x}\text{C}_x$  formed, respectively, on a spherical particle of  $\text{RuS}_{2-x}\text{C}_x$  and a cylinder of  $\text{MoS}_{2-x}\text{C}_x$ . Both particles have a maximum dimension of about 10 nm.

field of TMS catalytic materials. Understanding of discrete surface phases in operating catalysts adds important information for process operation. For example, refinery operators have for many years recognized the existence of ‘hard carbon’ (carbide surface phase) and ‘soft carbon’ (coke) in hydro-treating catalysts. Soft carbon can be removed through regeneration processes but hard carbon cannot. Indeed, attempts to remove hard carbon result in destruction of the catalyst owing to the removal of surface phases during the catalysts activation process. Fresh TMS catalysts exhibit a slow induction of catalytic activity when first put on line in catalyst reactors again because of the formation of the surface compounds described above (Chianelli, 2004). We again emphasize the importance of understanding the catalyst structure stable under operating conditions to understanding the fundamental basis for catalyst activity.

6. CSS for industrial catalysts

Industrial MoS<sub>2</sub> HDS catalysts are usually supported on Al<sub>2</sub>O<sub>3</sub> and promoted with Co or Ni depending on the petroleum feedstock being treated. The main role of Al<sub>2</sub>O<sub>3</sub> is probably to nucleate and stabilize TMS particles that are too small to exist in its absence. Thus, a typical commercial HDS catalyst is Co/Mo/Al<sub>2</sub>O<sub>3</sub> and this catalyst, used in an industrial reactor, might remain active for years, again depending on the petroleum feedstock being treated. The catalysts will deactivate more rapidly if the petroleum feedstock is heavy, containing high quantities of sulfur, nitrogen, aromatic compounds and metals such as vanadium. The evolution and the structure of the CSS, and the mechanism for its deactivation, have been the subject of controversy for many years.

In order to illuminate this subject, industrial catalysts have been studied that were operated in commercial HDS units for more than four years, leading to a new understanding of the catalytic phases that are stabilized under these conditions (Perez De la Rosa *et al.*, 2004). In these studies, three commercial Co/Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, that had been run in an industrial reactor for one week, one month and four years, were studied using synchrotron XRD techniques. A catalyst was removed from the industrial reactor after four years in a ‘regularly scheduled turn around’ and was still active as confirmed by model compound reaction studies. Fig. 3 shows the wide-angle X-ray scattering from these catalysts in the range ~6–20° 2θ. The 002 reflection of the MoS<sub>2</sub> bulk structure can be seen just below 12° 2θ. The intensity of the 002 reflection from the MoS<sub>2</sub> sample reflects the degree of stacking of the MoS<sub>2</sub> anisotropic layers. Analysis of the ‘excess’ (diffuse) scattering under the 002 reflection led to an estimate of the number of stacked *versus* single layers (Fig. 4). The term ‘excess scattering’ refers to the scattering that is above the background but not part of the specifically Bragg 002 reflection. This is due to single layers and appears in all catalysts included in this study (Liang *et al.*, 1986). It is obvious from Fig. 3 that the stacking height decreases as the catalyst is subject to longer times in the reactor. Analysis of the excess scattering owing to single layers shows that single layers

predominate after four years in the reactor, as indicated in Fig. 5. The study also indicates that previous HRTEM studies of these catalysts overlooked the single layers that are responsible for the excess scattering measured by synchrotron diffraction. Thus, industrial hydrotreating conditions induce a ‘destacking’ process resulting in the stabilization of single-layered nanoparticles with the MoS<sub>2</sub> structure indicated

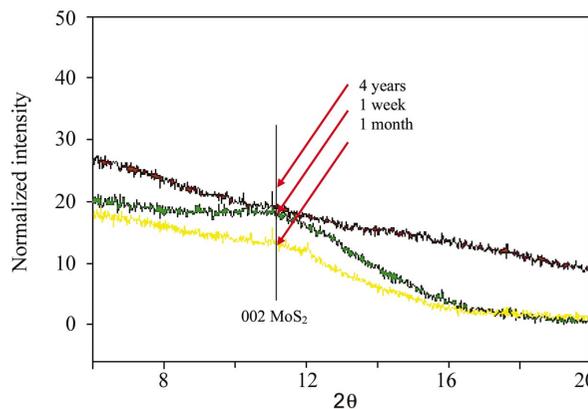


Figure 3 XRD data from three catalysts: 1 week, 1 month and 4 years run times in the range from 6 to 20° 2θ.

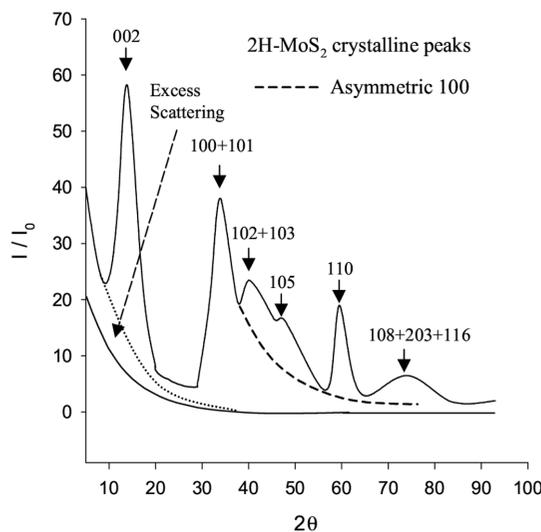


Figure 4 XRD pattern of poorly crystalline MoS<sub>2-x</sub>C<sub>x</sub> (see Perez de la Rosa *et al.*, 2004).

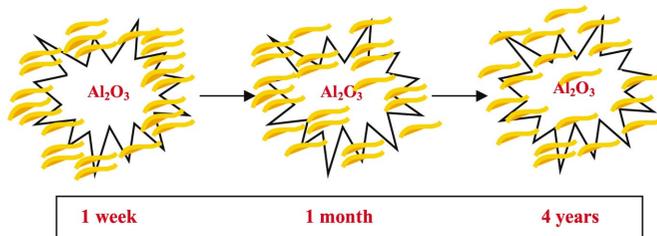


Figure 5 Schematic representation of promoted MoS<sub>2-x</sub>C<sub>x</sub> spreading across the Al<sub>2</sub>O<sub>3</sub> support with time under operating conditions.

schematically in Fig. 5. This surprising conclusion is made possible by the application of synchrotron radiation and radically alters the way in which the aging of these catalysts is viewed. These results are summarized:

(i) Scattering dominated by the active phases is easily isolated by subtraction of the alumina support contribution. This operation is only successful with data showing a high signal-to-noise ratio.

(ii) Analysis of the active phase scattering indicates that the catalyst equilibrated under reaction conditions consists of mainly single layers of  $\text{MoS}_2$ , overlooked by HRTEM studies that ‘see’ only stacked layers.

(iii) Catalysts that have been run for long periods of time under high-pressure conditions tend to ‘destack’.

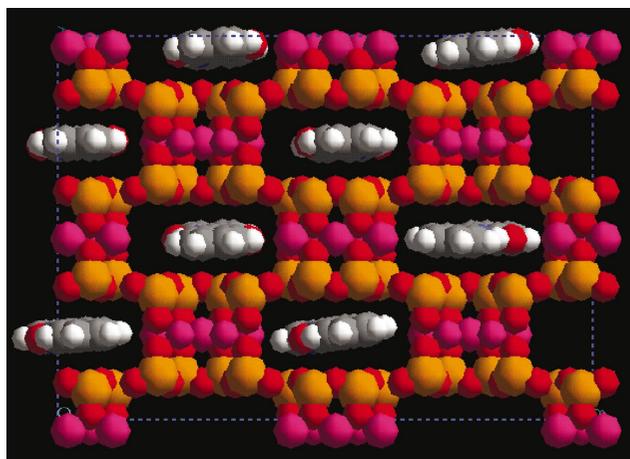
Future work will focus on the change in structure with deactivation and selectivity of the HDS reaction that has been associated with stacking in  $\text{MoS}_2$ -based catalysts (Daage & Chianelli, 1994).

## 7. Maya blue: an ancient organic/inorganic pigment

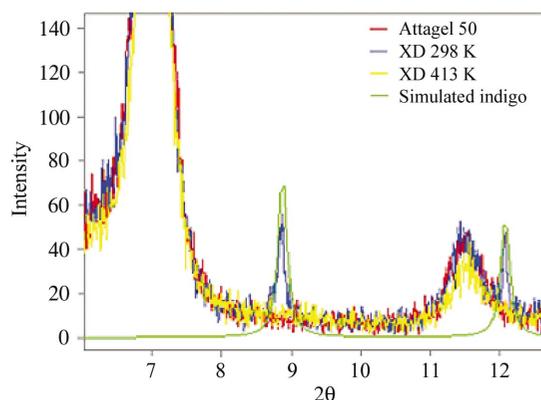
The ancient Maya people who inhabited Mesoamerica approximately 1000 years ago produced a remarkable blue pigment known today as Maya blue. This pigment was used to produce beautiful murals and pottery that survive in many places in Mexico and Central America (Polette *et al.*, 2002). The longevity and stability of the color are due to an unusual chemical composition that brings together an organic dye (indigo) and an inorganic clay (palygorskite). The exact nature of the complex organic/inorganic material has only recently been deciphered using advanced probes and simulation.

Synchrotron techniques, XAFS and WAXS have been combined with simulation modeling to develop an understanding of this fascinating material (Polette *et al.*, 2000). These studies found that Maya blue is a ‘surface compound’ with the indigo molecule inserted into channels at the clay surface and bonded to chemical sites in the channels. CERIUSt<sup>2</sup> (Accelrys) simulation shows how the indigo molecules slip into the exposed surface channels (Fig. 6). This channel binding and the resulting charge transfer is responsible for the stability of the complex and its remarkable color. Maya blue becomes a prototype for useful complex organic/inorganic materials with potential application as environmentally friendly pigments.

Experimental verification of the structure of the surface complex comes from XRD studies. The low-angle region of the WAXS data is shown in Fig. 7. The major diffraction peaks are due to the inorganic clay, palygorskite. Indigo (6 wt%) is mixed with palygorskite and gives the composite pattern shown in the Fig. 7. Two diffraction peaks owing to the indigo occur just below  $9^\circ 2\theta$  and just above  $12^\circ 2\theta$  and are compared with a simulated indigo pattern. When heated to 413 K the surface compound is formed and the two indigo peaks disappear. This surface compound is ‘Maya blue’. The success of the synchrotron XRD technique in demonstrating the existence of the surface compound has opened the way for



**Figure 6**  
CERIUSt<sup>2</sup> ‘sorption’ simulation of Maya blue.



**Figure 7**  
WAXS XRD data in the region from 6 to  $13^\circ 2\theta$ . The red line is the inorganic clay, palygorskite (Attagel 50), the green line is the simulated diffraction pattern of indigo, the blue line is a mixture of 6% indigo and 94% palygorskite, not heated, and the yellow line is the same mixture heated to 413 K.

future developments in extending the ancient knowledge of the Maya into modern materials science.

## 8. Conclusions

The examples described above demonstrate the usefulness of synchrotron techniques in helping to solve complex materials problems. The examples of ‘surface compounds’ are particularly powerful examples of understanding how useful compounds may terminate their surfaces as the particle size is reduced. Surface and poorly crystalline phases are broadly resistant to chemical characterization by more traditional approaches. Surface compounds are becoming more important as the world of materials delves further into regions of nanoscale materials. The importance of understanding their structure and behavior is a challenge for materials scientists and is greatly assisted by synchrotron techniques.

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## References

- Berhault, G., Cota Araiza, L., Duarte Moller, A., Mehta, A. & Chianelli, R. R. (2002). *Catal. Lett.* **78**, 81–90.
- Berhault, G., Mehta, A., Pavel, A., Yang, J., Rendon, L., Jose Yacaman, M., Cota Araiza, L., Moller, L. & Chianelli, R. R. (2001). *J. Catal.* **198**, 9–19.
- Cerruti, L. (1999). *Int. J. Philos. Chem.* **5**, 3–41.
- Chianelli, R. R. (2004). Personal communication.
- Chianelli, R. R. & Berhault, G. (1999). *Catal. Today*, **53**, 357–366.
- Chianelli, R. R., Berhault, G., Raybaud, P., Kasztelan, S., Hafner, J. & Toulhoat, H. (2002). *Appl. Catal. A*, **227**, 83–96.
- Chianelli, R. R., Daage, M. & Ledoux, M. J. (1994). *Adv. Catal.* **40**, 177–232.
- Daage, M. & Chianelli, R. R. (1994). *J. Catal.* **149**, 414–427.
- Doniach, S., Hodgson, K., Lindau, I., Pianetta, P. & Winick, H. (1997). *J. Synchrotron Rad.* **4**, 380–395.
- Fuentes, M. E., Mehta, A., Lascano, L., Camacho, H., Chianelli, R., Fernández, J. F. & Fuentes, L. (2002). *Ferroelectrics*, **269**, 159–164.
- Gerson, A. R., Halfpenny, P. J., Pizzini, S., Ristic, R., Roberts, K. J., Sheen, D. B., Sherwood, J. N. (1999). *X-ray Characterization of Materials*, edited by E. Lifshin, pp. 105–169. Weinheim: Wiley-VCH.
- Kelty, S. P., Chen, J. G., Ruppert, A. F., Chianelli, R. R., Ren, J. & Whangbo, M.-H. (1999). *J. Phys. Chem.* **103**, 4649–4655.
- Liang, K. S., Chianelli, R. R., Chien, F. Z. & Moss, S. C. (1986). *J. Non-Cryst. Solids*, **79**, 251–273.
- Montano, P. A. & Hiroyuki, O. (1999). *MRS Bull.* **24**, 13–16.
- Pecoraro, T. A. & Chianelli, R. R. (1981). *J. Catal.* **67**, 430–445.
- Perez De la Rosa, M., Texier, S., Berhault, G., Camacho, G., José Yácaman, M., Mehta, A., Fuentes, S., Montoya, A., Murrieta, F. & Chianelli, R. R. (2004). *J. Catal.* **225**, 288–299.
- Polette, L. A., Meitzner, G., José Yacamán, M. & Chianelli, R. R. (2002). *Microchem. J.* **71**, 167–174.
- Polette, L. A., Ugarte, N., José Yacamán, M. & Chianelli, R. R. (2000). *Discov. Archeol.* pp. 46–53.
- Yoshiki, S. (2002). *Toyota Chuo Kenkyusho R&D Rebyu*, **37**, 37–42.
- Zhang, H., Verde-Gómez, Y., Jacobson, A. J., Ramirez, A. & Chianelli, R. R. (2002). *Proceedings of the MRS Fall Meeting*, Boston, MA, USA.