

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 twenty years due 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 (SSRL). In this article we review the application of multiple synchrotron characterization techniques to two classes of materials defined as “surface compounds.” 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” is 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, a common clay. The identification of both surface compounds relies on the application of synchrotron techniques as described in this report.

Keywords: XAFS, WAXS, SAXS, XANES, Catalysts, Maya Blue.

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 recently reviewed^{1,2,3}. Techniques such as WAXS (Wide Angle X-ray Scattering), XAFS (X-ray Adsorption Fine Structure) and XANES (X-ray Adsorption 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 advanced 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 signal-to-noise ratio of synchrotron sources along with the tenability of the beam that make synchrotron techniques so valuable for the problems described in this report

An example of how a simple synchrotron technique such as XRD (X-Ray Diffraction) can add new insight into an old problem can be found in a recent paper about the magnetic structure of *Aurivillius' ceramics*⁴. Members of this class such as $BaBi_4Ti_4O_{15}$ 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 (600°C ~ 800°C), Aurivillius crystals adopt centro-symmetrical 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 in synchrotron diffraction as described in the publication but has been difficult or impossible to see by conventional in-house x-ray methods.

In addition, synchrotrons have become “friendlier” places to work due to the presence of user support groups and synchrotron support staffs 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 today⁵. In this report we discuss two classes of surface compounds: The SSC (Sulfide Supported Carbides) of the 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 were performed at Stanford Synchrotron Radiation Laboratory from 2000 to 2003 under a grant from the DoE (Department of Energy) BES (Basic Energy Sciences). The grant is a training grant called the “Gateway Grant” 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 beam line 2-1. The vertical collimation and high brightness of the synchrotron beam allowed use of a Si (111)-based detector suitable to resolve lattice changes of the order of 0.1 %. The size of the focused beam was 2 X 1 mm and approximately 10^{11} photons/sec are incident on the sample. The XRD patterns were collected in the 5° - 75° 2θ range at the Zn K-edge (9.659 keV). The NEXAFS (Near Edge X-ray Adsorption Fine Structure) experiments were carried by Joachim Stöhr on beam line 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 with a mean free path of about 1nm was measured. The method is sensitive only to the surface layers yielding information very similar to Auger Electron and X-ray Photoelectron techniques. XAFS samples and standards were separately loaded into 0.5 mm – thick aluminum 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. Appropriate K-edge absorption spectra for the various samples were

collected on SSRL beamline SB07-3 (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 55–90 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 practical importance are most effective as small particles. Heterogeneous catalysts are a prime example. Catalysts that can be stabilized as small particles have more effective surface area to perform 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 vacuum. However, catalysts are in reactive environments and may terminate their surfaces by chemistry involving the surrounding reactants. This is especially true in catalytic environments at temperatures lower than 400°C. Higher temperatures may be required to obtain bulk equilibrium phases. 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 catalyst⁶. Originally, based on small particles of TiCl_3 , it was recognized that the desirable polymerization properties

could be enhanced by modifying the surface of the TiCl_3 with agents such as AlCl_3 or alkyl aluminum compounds. The TiCl_3 crystallites are terminated with Al compounds that interface with the reacting polymers. The TiCl_3 provides the appropriate redox (electron) substrate and the Al surface provides the proper polymerization stereochemistry for the desired reaction. The field progressed until the particle became smaller and smaller and the surface structure more important, until finally the “single site” metallocene catalyst emerged. The reference cited above discusses “control of the architecture or three-dimensional structure of the catalyst” that has enabled not only the success of the polymer industry but also “opening the way to the creation of new and completely revolutionary families of materials.” The author describes the catalyst as a “reactor granule...with it’s own energy and materials balance”. Today we might call it a nano-reactor with all of the elements of a 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 TMS (Transition Metal Sulfides) such as MoS_2 and 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 heavy crudes containing larger amounts of sulfur, nitrogen and metals will become the major source of petroleum hydrocarbons in the future. Faced with increasing amounts of heavier 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 promising sulfur tolerant fuel cell anodes⁷. 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 required.

The most important basic aspect of catalysis by the TMS (transition metal sulfides) is the determination of the CSS (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 “stable catalytic state”⁸. This paper established the bulk crystalline structure of the transition metal sulfides for the HDS reaction and was the first paper to describe the extremely active RuS₂ catalyst as the peak of the ‘volcano plot’ for HDS catalysis. RuS₂ catalysts also have recently been 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 studies⁹. Additionally, commercial catalysts are “promoted systems”: catalysts based on MoS₂ or WS₂ that are “promoted” with 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 a “surface compound” with the promoter phase at the surface of the “support phase.” Thus, Co supported on MoS₂ has enhanced activity and behaves as a noble metal sulfide, though RuS₂ activity is not achieved. A complete discussion of this subject is beyond the scope of this report but is another example of the importance of surface compounds in catalysis¹⁰.

5. Transition Metal Sulfide 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^{11,12}. 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 is shown for a MoS₂ catalyst in figure 1. The Auger electron yield comes from the first nanometer of the surface and the fluorescence yield comes from the bulk phase (not shown) but has very little indication of carbon. This key information coming from synchrotron studies is confirmed by EELS, IR and other techniques confirming the existence of the surface compounds. These compounds are shown schematically in figure 2. In this figure RuS_{2-x}C_x is shown schematically as a cross section of a spherical particle with the carbide phase covering the surface of the sphere and MoS_{2-x}C_x is shown as a cylindrical particle with the edge of the cylinder covered with the carbide phase.

Thus, the CSS for Mo is MoS_{2-x}C_x and for Ru is RuS_{2-x}C_x. For example, a catalyst that is originally RuS₂ with the Pyrite structure and an average particle size of 10 nm was run in an HDS reactor with the model compound DBT for over 1000

hours. 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 particle¹³. This is an example of a description of the CSS of a TMS catalyst. It is this description that is the proper starting point for a discussion of 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 fail to take into account the important role of carbon in stabilized HDS catalysts cannot give an accurate description of the fundamental origin of catalytic properties in these catalysts. It is also true that promotion must be described as a symmetrical synergism, rather than promotion of one phase by another, for example, in order to understand the true nature of the effect¹⁴.

The demonstration of the existence of surface compounds in operating catalysts has long been overdue, especially in the 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 carbon) and “soft carbon” (coke) in hydrotreating catalysts. Soft carbon, but not hard carbon can be removed through regeneration processes. However, attempts to remove hard carbon result in destruction of the catalyst and this can be explained by the development of surface phases during the catalysts activation process. Catalysts particularly unsupported

TMS catalyst tend to activate when first put on line in catalyst reactors again because of the formation of the surface compounds described above¹⁵. It is also important to again emphasize the importance of understanding the total catalyst structure stable under active operating conditions to understand the basis for catalyst activity in a fundamental way.

6. CSS for Industrial Catalysts

Industrial MoS₂ HDS catalysts are usually supported on Al₂O₃ and promoted with Co or Ni depending on the petroleum feedstock being treated. Thus, a typical HDS catalyst is Co/Mo/Al₂O₃ 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 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 catalytically stabilized active phase has been the subject of controversy for many years including the mechanism for their deactivation.

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 conditions¹⁶. In these studies three commercial Co/Mo/Al₂O₃ 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. Figure 3 shows the wide-angle scattering from these catalysts in the region from approximately $6 - 20^\circ 2\theta$. In this region the 002 reflection of the MoS_2 bulk structure can be seen just below 2θ . The intensity of the 002 reflection from the MoS_2 bulk structure reflects the degree of stacking of the MoS_2 anisotropic layers. Analysis of the excess (diffuse) scattering under the 002 reflection led to an estimate of the number of stacked layers verses single layers (figure 4). The term excess scattering refers to the scattering that is above the background but not part of the Bragg 002 reflection. This excess scattering is due to single layers and appears in all catalysts described¹⁷. It is obvious from figure 3 that the stacking decreases as the catalyst is subject to longer times in the reactor. Analysis of the excess scattering due to single layers shows that single layers predominate after four years in the reactor as indicated in figure 5. Furthermore, the study also indicates that previous HRTEM studies of these catalysts over looks the single layers that are determined by 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_2 structure indicated schematically in (figure 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:

1. Scattering from the active phases is easily by subtraction of the alumina support contribution.

2. Analysis of the active phase scattering indicates that the catalyst consists of mainly single layers of MoS₂ in contrast to HRTEM studies that “see” only stacked layers.
3. 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 MoS₂ based catalysts¹⁸

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 survives today in many places in Mexico and Central America¹⁹. Its longevity and stability are due 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 elaborated using advanced probes and simulation.

Synchrotron techniques, XAFS and WAXS have been combined with simulation modeling to develop an understanding of this fascinating material²⁰. 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. CERIOUS² (Accerlyrus Inc.) simulation shows how the indigo molecules slip

into the exposed surface channels (figure 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 figure 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 figure 7. Two diffraction peaks due to the indigo occur a just below $9^{\circ} 2\theta$ and just above $12^{\circ} 2\theta$ and are compared with a simulated indigo pattern. When heated to 140°C 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 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 help 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 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 that is greatly assisted by synchrotron techniques.

9. Acknowledgements

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Figure 6: CERIOUS² “Sorptions” simulation of Maya Blue.

Figure 7: WAXS XRD data in the region from 6 to 13° 2θ. 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 140°C.

Figure 1:

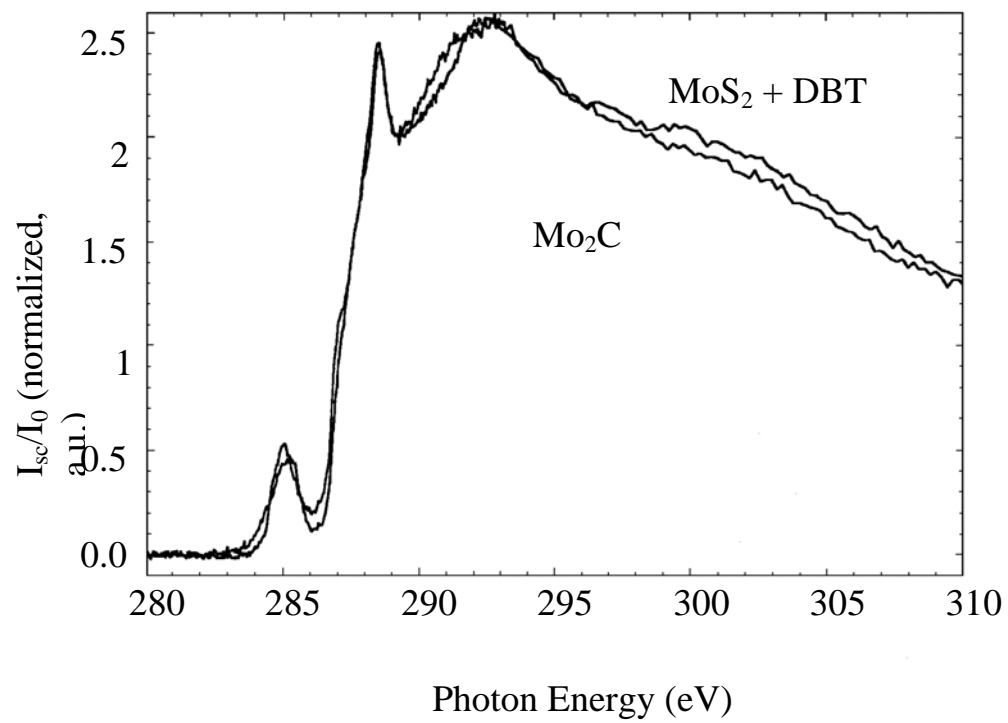


Figure 2:

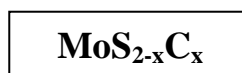
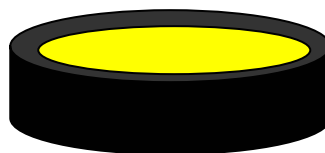
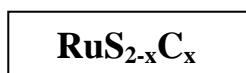
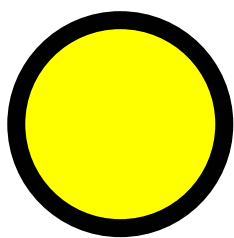


Figure 3

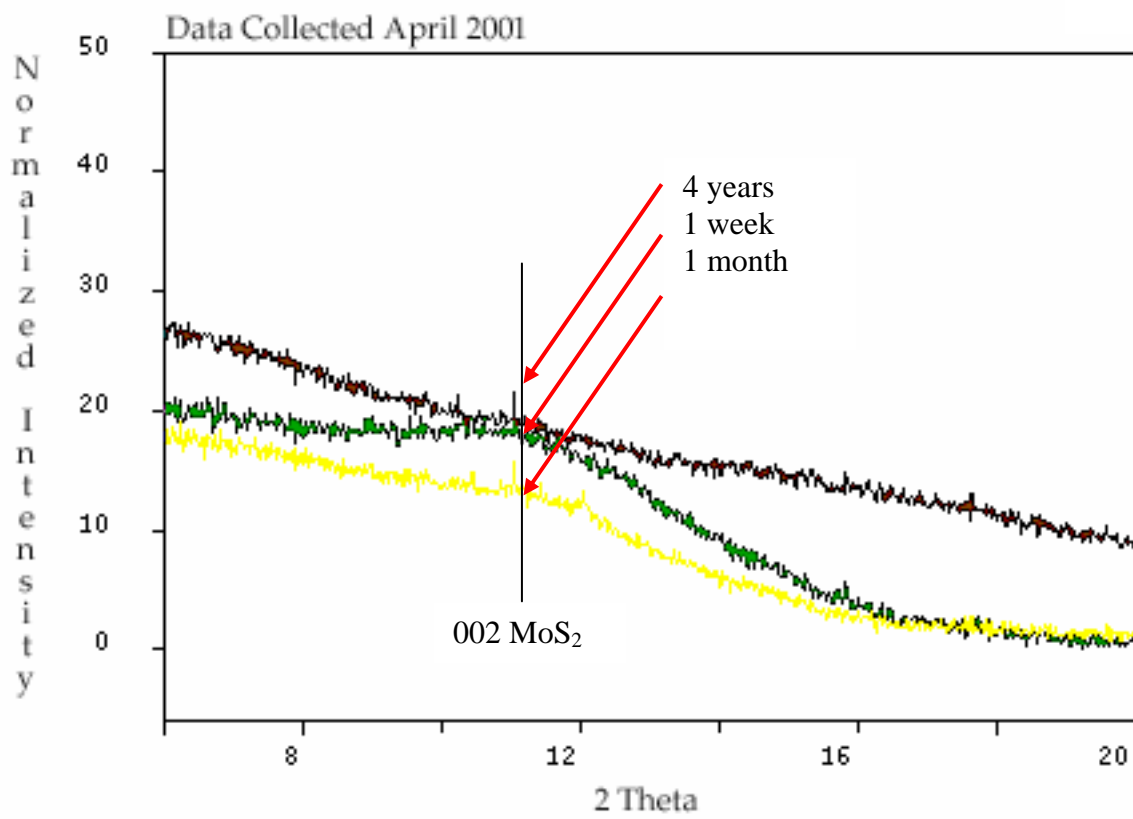


Figure 4

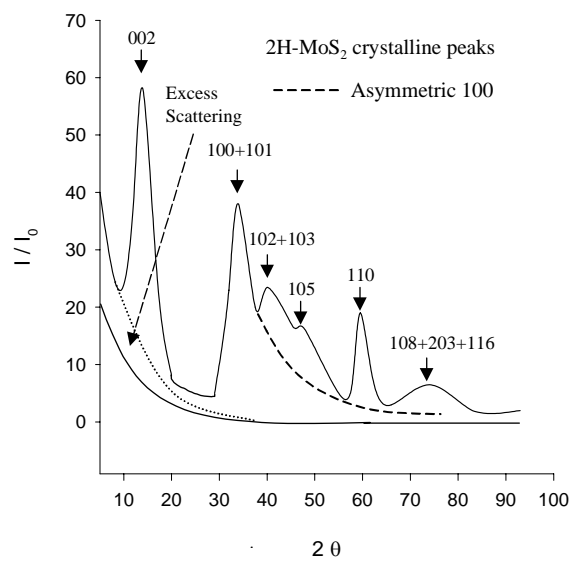


Figure 5

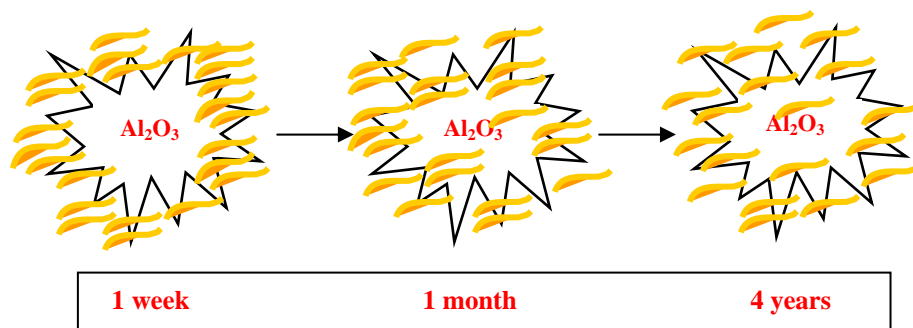


Figure 6

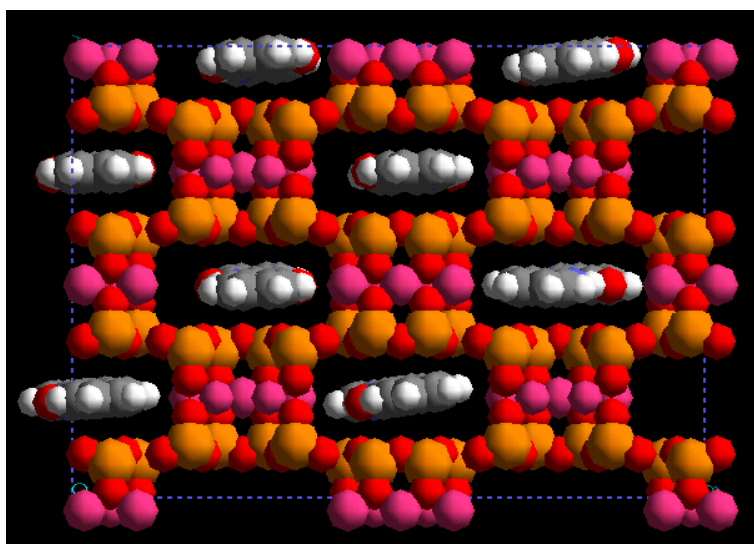
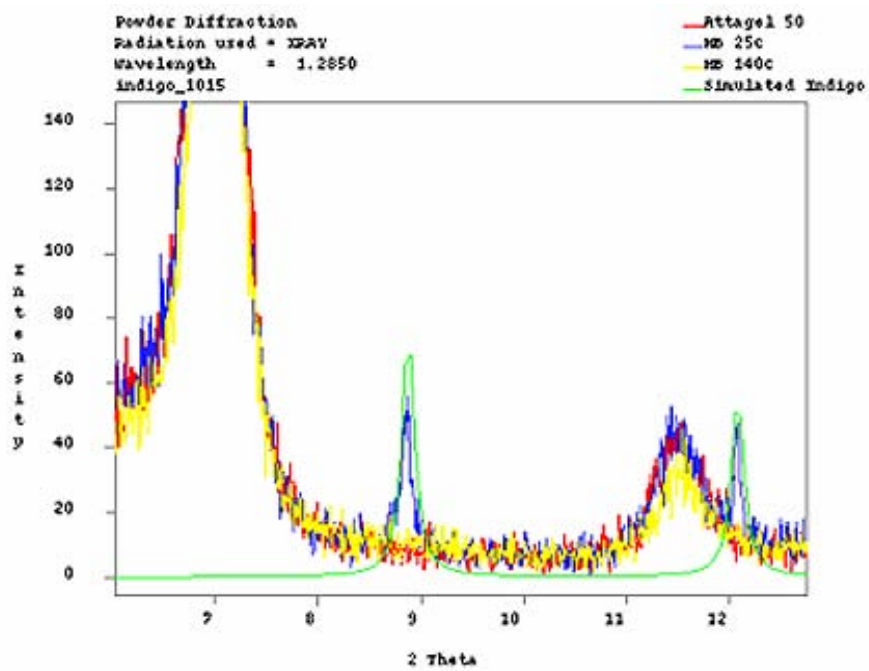


Figure 7



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