A Study Of The Interaction Of Thioindigo Dye, With Several Inorganic Host Materials

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A STUDY OF THE INTERACTION OF THIOINDIGO DYE, WITH
SEVERAL INORGANIC HOST MATERIALS

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Für meinen Dennis
A STUDY OF THE INTERACTION OF THIOINDIGO DYE, WITH
SEVERAL INORGANIC HOST MATERIALS

by

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ABSTRACT

Maya Blue has been the focus of numerous studies and is believed to be a mixture of palygorskite clay and indigo dye. Several derivatives of this pigment have been developed with intriguing properties. For instance, the dye thioindigo reacts with the palygorskite clay to exhibit a broad range of colors from red to blue under UV-Vis excitation. Based on FT-Raman and computer simulation, previous work performed in our group could relate indigo and thioindigo interaction to the aluminum sites in the framework.

The work performed with other inorganic host materials such as, layer structures and zeolites have displayed reversible acid indicator properties, similar to the ones observed in concentrated sulfuric acid. Spectroscopic analyses and computer modeling of the above mentioned interactions have been evaluated. Results obtained by these techniques showed that in dehydrated materials a disturbance of thioindigo C=O at 1655 cm\(^{-1}\) to lower frequencies occurs, due to the C=O---Lewis acid sites (LAS) interaction. In the presence of water, a smaller C=O shift due to C=O---HO(H)LAS was observed. Moreover, displacement of the 001 plane in some layer materials confirmed the effect of water on the color changes displayed by UV-Vis spectroscopy.

Based on these premises, it was concluded that weak electron donor-acceptor interactions took place between thioindigo functional groups (electron donors) and LAS of the aluminum silicate framework (electron acceptor). LAS (extra-framework aluminum and exchangeable cations) high hydration enthalpy made them extremely susceptible to
water molecules (electron donors); generating a hydrogen bond between the two sites. The reversibility of these chromatic hybrid materials could have potential applications as water sensors and charge transfer photosensitizers in nanocrystalline TiO$_2$-based solar cells.
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CHAPTER 1

INTRODUCTION

1.1 Background

Natural dyes have been widely used after their discovery in 2600 B.C. The method of synthesis is through the fermentation and extraction from roots and leaves of different plants and insects. By the end of the nineteenth century, synthetic production of these organic dyes substituted the natural dye extraction from inexpensive starting materials. Adolf von Baeyer, among others, was at the forefront of this work. Today, dyes are synthesized in large quantities through large-scale industrial processes, based upon the original synthetic pathways. A problem with these organic dyes is their gradual degradation; one major step towards the solution of this problem was discovered by chance in America (Figure 1).

Figure 1 Mural from Bonampak, Palenque (Classic period, 200 B.C. - 900 A.C.)


Mayans, at the peak of their civilization (250 - 900 A.C.), extracted indigo dye from the leaves of indigofera suffruticosa. This Mesoamerican pigment became what is known today as Maya Blue; it has been the focus of numerous studies and is a mixture of indigo and palygorskite/sepiolite clays.

Palygorskite and Sepiolite belong to a phyllosilicate group, which are naturally occurring hydrated magnesium silicates with varying compositions based on the region. Palygorskite has been found to be the main component in Maya Blue pigment. The second component, indigo, is a common organic dye with the chemical formula $\text{C}_{16}\text{H}_{10}\text{N}_{2}\text{O}_{2}$. Several theories have been proposed that seek to explain the shades and longevity of the blue pigments. G. Chiari et al. have proposed that indigo resides in the surface grooves (half channels) of palygorskite, since zeolitic water is still inside the channels at 100°C, which they get from their interpretation of their thermogravimetric analysis. The binding of indigo is possibly explained by hydrogen bonding with the structural water or hydroxyl groups in the clay. Using thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR) and textural analysis techniques, B. Hubbard et al. proposed that indigo molecules, via the carbonyl and amine moieties, are anchored in the entrance of the channels through hydrogen bonds with silanol groups. A. Domenech et al. proposed that varying amounts of dehydroindigo, the oxidized form of indigo, in the mixture, causes the different shades of blue observed in samples of Maya Blue. L.A. Polette-Niewold et al. proposed that oxidation of indigo to
dehydroindigo does occur during the production of the pigment and the chemical interaction between the carbonyl oxygen of the dehydroindigo binds to the surface $\text{Al}^{3+}$ in the Si-O lattice. This is a plausible explanation of the observed phenomena.

Several derivatives of the Maya Blue pigment have been developed and more intriguing properties have been found. For instance, the dye thioindigo reacts with palygorskite clay to exhibit a broad range of colors from red to purple under thermal treatment and UV excitation. In the case of sepiolite, color change is not as drastic, and for faujasite synthetic zeolites, color change is reversible.

The immobilization of thioindigo on SiO$_2$, Al$_2$O$_3$ and bentonite was first recorded by G.M. Schwab et al.$^{15}$ where color changes from red to blue were detected. Conversely, H.D. Breuer et al.$^{16}$ observed photoisomerization from $\text{trans}$ to $\text{cis}$ of thioindigo molecule and an energetically stable $\text{cis}$- thioindigo was preferentially absorbed on the Al$_2$O$_3$ surface rather than the $\text{trans}$ counterpart. Using tetrachloro derivatives of thioindigo, D. Reinen et al.$^{17}$ reported similar changes in color and suggested different hydrogen bonding patterns of thioindigo with palygorskite as the basis for the different colors. This team also reported that thioindigo derivatives bound to palygorskite are weaker than indigo. Analogous results were obtained by R. Hoppe et al.,$^{18}$ where bathochromic shifts under visible excitation inducing a surface reaction of thioindigo with a zeolite (faujasite structure) were observed. Concluding silanol interaction could be responsible for this behavior, but no reversible color change was detected.
1.2 Research Objectives

The issue addressed in this paper was the nature of the interaction between inorganic host materials and a small dye molecule such as thioindigo. The root of this is the clay’s organic interaction in Maya pigments, but the scope of this paper includes other materials. In addition, the organic molecular interaction with a concentrated acid was also described.

Several characterization techniques such as, wide range X-ray fluorescence spectrometry, diffuse reflectance and transmission ultraviolet-visible spectroscopy, electron dispersive X-ray analysis, Fourier transformed infrared spectroscopy, magic angle nuclear magnetic resonance and X-ray diffraction were used to examine the samples. Moreover, computer simulation helped enormously to draw further conclusions observed experimentally.
CHAPTER 2
METHODOLOGY

2.1 Materials Sampling

Thioindigo dye was obtained from TCI America Inc. and was used as received.

Inorganic host materials were obtained from several providers and a complete list of information is listed in Appendix A. All materials were used as received.

A number of inorganic salts for cationic exchange such as, KCl (Fischer Scientific), CaCl₂ (EM Science), Al₂(SO₄)₃ (Sigma-Aldrich), NH₄Cl (J.T. Baker) and NaNO₃ (Fischer Scientific) were used as received.

Solvents such as: Ethanol reagent grade (Sigma-Aldrich), 98.7% sulfuric acid (EM Science) and HCl (Sigma-Aldrich) were used without further purification. Pyridine (Sigma-Aldrich) was dried overnight with KOH (Sigma-Aldrich) and purified by distillation under N₂ gas.¹⁹
2.2 Sample Preparation

2.2.1 Thioindigo

Thioindigo was reported by Brode et al.\textsuperscript{20} to present bathochromic shifts around 666nm when in contact with a concentrated solution of sulfuric acid. This reaction was reproduced with \( \sim 1 \) mg of thioindigo added to 2 mL of 98.7\% sulfuric acid in a beaker. The blue greenish solution was stirred and measured under UV-Vis spectroscopy.

2.2.2 Inorganic Host Materials

A number of inorganic materials used in these experiments were synthesized by Penn State University or pretreated at UTEP before mixed with thioindigo. The following section describes the procedures used which were: synthetic route for swelling micas, neutral templating route for mesoporous zeolites, cationic exchange zeolites and high temperature treatment. Additionally, the surface acidity evaluation was performed.

\textit{Synthetic Route for Swelling Micas}

YN6 and YN8 synthetic swelling micas and mesoporous zeolites (MS-1, MAS-1 and MA-1) were prepared by Penn State University using the following methodology: YN6 and YN8 were synthesized by mixing in a stoichiometric ratio sodium fluoride, silicic acid and aluminum chloride. Once homogenized the mixture was placed in a platinum crucible and heated at 1123K for five hours, then it was cooled down to room
temperature and washed several times with deionized water using centrifugation. The white powder was dried prior to being used as a host with thioindigo.\textsuperscript{21}

\textit{Neutral Templating Route for Mesoporous Zeolites}

Mesoporous zeolites of silica (MS-1), alumina (MAS-1) and aluminosilicate (1:1 Si:Al atomic ratio) were synthesized by tetraethoxysilane, Al isopropoxide, and a mixture of tetraethoxysilane and Al isopropoxide, respectively, using a neutral templating route. This route entailed the addition of 1 mol of alkoxide to a solution of 0.27 moles of dodecylamine, 9.09 moles of ethanol and 29.6 moles of deionized water under vigorous stirring for thirty minutes and kept aside at room temperature for thirty-five hours. After this time the sample was transferred to a glass plate and air dried. The neutral template was heated at 773K for four hours in order to remove the organic matter.\textsuperscript{22}

\textit{Cationic Exchange Zeolite}

One cation exchange mordenite was prepared from synthetic zeolite CBV21A (Si/Al = 9.5). The method involved 5 g of sample two times washed with 250 mL of 0.2 M solution [KCl, CaCl\textsubscript{2}, Al\textsubscript{2} (SO\textsubscript{4})\textsubscript{3}, NH\textsubscript{4}Cl, NaNO\textsubscript{3}, and HCl ] containing the desired cation at 373K for 1 hour. All solutions were prepared with ultra pure water to avoid contamination by other cations. The slurry solution was then filtered in a fluorocarbon filter membrane (Chemplast, Inc.), washed several times and centrifuged at 1000 rpm
(International centrifuge, model CM). The slurry solution was then dried at 413K in a tube furnace (Lindberg/Blue M) with an electronic thermocouple (Omega Engineering DP900) and the powder collected.\textsuperscript{23} Moreover, hydrogen cation exchange was also performed through a different procedure where an NH\textsubscript{4}\textsuperscript{+}-MOR sample was calcined in an air stream at 873K for three hours.\textsuperscript{24}

\textbf{High Temperature Treatment}

In order to reduce the pore size of the crystal structure, zeolon\textsuperscript{®} and palygorskite were exposed to 1223K and 823K, respectively, for a time period of fifteen hours.

\textbf{Surface Acidity Evaluation}

Inorganic materials were treated with pyridine following the sample preparation by C. Ravindra Reddy \textit{et al.}\textsuperscript{25} where a fast pyridine evaluation was performed. Samples (~50 mg each) were set to dry at 413K for one hour before pyridine adsorption. This thermal treatment allowed a closer evaluation of the framework Brønsted acids, instead of the hydration protons that could give similar vibration in FTIR. After thermal treatment, samples were set in a crucible individually with 0.2 - 0.5 mL of pyridine. The crucible was then placed in a tubular furnace at 413K for one hour to remove physisorbed pyridine. After this time samples were left inside a desiccator for further FTIR analysis.
2.2.3 Inorganic Host Materials Treated with Thioindigo

6 wt. % thioindigo was added to 94 wt. % inorganic host materials (including pretreated samples) in a glass mortar and finely ground until a homogenous mixture was obtained. The mixture was placed in a ceramic crucible and heated in a tube furnace at 413K for nine hours. Evaluation of stability was performed by soxhlet ethanol extraction with cellulose thimbles. High hydration environment was fabricated with a glass desiccator and water instead of desiccant.

2.3 Instrumentation

2.3.1 Wide Range X-Ray Fluorescence Spectrometry (WD-XRF)

Minerals were analyzed using a WD-XRF Axios Panalytical spectrophotometer by an external company (SGS Mineral Services Analytical). Sample preparation required the formation of a homogenous glass disk by the fusion of 0.2 g to 0.5 g of a clay powder sample, with 7 g of lithium tetraborate/ lithium metaborate (50/50). The loss on ignition (LOI) at 1000°C was gravimetrically determined separately. The LOI was included in the calculations.
2.3.2 Diffuse Reflectance Ultraviolet-Visible Spectroscopy

Diffuse reflectivity measurements were recorded using a Shimadzu 3101 spectrophotometer with a 50 cm integrating sphere or Ulbricht sphere (a sphere with a fully reflective inner surface) and BaSO$_4$ as a standard for 100% reflectance. Reflectance values were acquired from 200 to 800 nm, which were then converted to absorption using the Kubelka-Munk method.

2.3.3 Transmission Ultraviolet-Visible Spectroscopy

Liquid UV-Vis spectra were recorded with a Varian Cary 50 Conc. spectrophotometer using a 1.00 cm fused quartz absorption cell over the entire wavelength range (200 - 800 nm).

2.3.4 Fourier Transformed Infrared Spectroscopy (FTIR)

FTIR measurements were carried out with two different experimental setups. The first setup was a Bruker IFS 66v spectrometer equipped with a DTGS detector and a potassium bromide beamsplitter. The samples for the IR studies were prepared in the form of pellets by embedding the pigments in a polycrystalline potassium bromide matrix. An accumulation of 256 scans was performed for each spectrum from 400 to 4000 cm$^{-1}$. The data were normalized at each frequency to a vacuum throughout spectrum.
The second equipment was a Thermo Nicolet Nexus 470 FTIR spectrometer. Samples were embedded in mineral oil and smeared between two sodium chloride windows and supported by a metallic sample holder. The spectrum was recorded from 400 to 4000 cm\(^{-1}\) with an accumulation of 60 scans.

### 2.3.5 X-ray Powder Diffraction

Starting materials were characterized by a Scintag XDS 2000 seal tube diffractometer with a copper K\(\alpha\) source. Calcium carbonate and quartz were used as internal standards. Experimental parameters involved diffraction angles between 5 - 50 degrees, a step size 0.02 degrees per sec. and a time scan of 1.5 sec. Braggs Law (\(\lambda = 2dsin\theta\)) was used to compute the spacing. Characterization was performed by comparison of XRD results with reported patterns from the inorganic crystallographic database.

### 2.3.6 Electron Dispersive X-ray Analysis (EDAX)

Chemical analysis was performed in a Hitachi S-4800 high performance scanning electron microscope at 20 kV voltage in high resolution mode with carbon plates for sample loading and an EDAX detector. Gold sputtering for 120 seconds was carried out for all samples tested to improve conductivity. Sensitivity of this technique is 1000 ppm (0.1 wt.%), with a lateral and depth spatial resolution approximately 1 \(\mu m\).\(^{26}\)
2.3.7 Magic Angle Nuclear Magnetic Resonance (MAS-NMR)

$^{27}$Al MAS-NMR spectra were obtained at 94.7 MHz using a 360 MHz Tecmag NMR system, equipped with a 5 mm Doty SuperSonic probe. The operating conditions of the spectrometer were: a pulse width of 1.1 μsec; the solution for a 90 degree pulse of 6.5 μsec, a solid 45 degree pulse of (I = 5/2); the pulse length was 15 degrees and the delay was 0.3 seconds; number of transients was 2000 or higher, and a spinning speed in the range of 8.2 to 10 kHz. Chemical shifts were measured relative to 1 M aqueous Al nitrate solution.

2.3.8 Computer Simulation

We have chosen a semi-empirical calculation method called ZINDO (Zerners Intermediate Neglect of Differential Overlap)$^{27}$ through the CERIUS$^2$ modeling platform, to perform excited states calculations and geometry optimization. Moreover, the adsorption of thioindigo molecule into a 3D inorganic framework was performed by a Monte Carlo method with a similar platform. A newer version of this platform called Materials Studio (MS) was also used to performed similar calculations for some other systems. In this case, the semi-empirical molecular orbital application was called VAMP$^{28}$. This application was carried out using a Hamiltonian of neglect of diatomic differential overlap (NDDO) for best results. NDDO is a basic approximation for neglecting less important integrals.$^{29}$
3.1 Thioindigo Dye

Thioindigo belongs to a group of derivatives with structurally related compounds usually formed of two nuclei (heterocyclic or homocyclic), united by a double bond and conjugated by both sides with a carbonyl group. The chromophoric center responsible for the color in these dyes is mainly the electronic excitation of the $\pi-\pi^*$ transition. In the case of thioindigo, two carbonyl and sulfur moieties are present in the chromophoric center of the molecule. Thioindigo molecule proportions are 15.17 Å (length), 7.42 Å (width) and 3.4 Å (thickness) (see Figure 2).

Figure 2 Trans-Thioindigo molecule (the most stable conformation). C= gray, H= white, S= yellow, and O= red. [Materials Studio v4.0].
Thioindigo forms dark red crystals by sublimation at 563K with a structural formula $C_{16}H_{10}S_{2}O_{2}$. It crystallizes in a monoclinic arrangement elongated in the a-axis, with a space group of $P2_1/n$ and cell parameters $a = 3.981(3)$, $b = 20.65(2)$, $c = 7.930(7)\text{Å}$, $\beta = 98.84(5)^\circ$ (see Figure 3).33

![Thioindigo crystal structure](image)

Figure 3 Thioindigo crystal structure [Materials Studio v4.0].

Thioindigo can be obtained by three different procedures. (1) Oxidation of benzo[b]thiophene-3-ol(thioindoxyl) II, or its carboxylic acid by ferricyanide, sulphur, or by nitro-substituted arenesulphonic acids (III) (Figure 4). (2) Condensation of thioindoxyl with its 2,2-dibromo derivative or with phenylliminothioisatin. (3) Reaction with thiosalyscyclic acid with 1,2-dichloroethene followed by dehydration with chlorosulphonic acid.30
Figure 4 Synthesis of thioindigo by oxidation [Image courtesy of M. Saunsbury, et al.].

Trans-thioindigo is found to be a stable isomer in the solid state and is believed to be mostly due to the electrostatic charges on the slightly negative and positive charges of oxygen and sulfur atoms, preventing isomerization.\(^{34}\)

In solution, the electrostatic forces mentioned previously are lost, and thioindigo, for example, in benzene is found to change from \textit{trans} red-purple (\(\lambda_{\text{max}} \approx 545\) nm) to \textit{cis} orange-yellow (Figure 5) (\(\lambda_{\text{max}} \approx 485\) nm) for a short period when exposed to visible light.\(^{30,35}\) In the eighties, a vast amount of research was performed using thioindigo, mainly to pursue alternative photochromic materials suitable for electronic applications. However, its use in the liquid state made it difficult to handle. Accordingly, research focused in the immobilization of thioindigo in different solids such as Al\(_2\)O\(_3\), SiO\(_2\), etc. G.M. Wyman \textit{et al.}\(^{36}\) successfully separated the red-purple solution (\textit{trans}) and the orange-yellow solution (\textit{cis}) isomers in a silica gel column when thioindigo/benzene was
irradiated ($\lambda_{\text{max}} > 520 \text{ nm}$) for 20 min. Moreover, the same authors also reported thioindigo bathochromic shifts up to 666 nm when reacted with concentrated sulfuric acid.\textsuperscript{20}

![Thioindigo isomers](image)

**Figure 5** Representing the four forms at which the isomers could exist in solution. No double bond present [Image courtesy of G.M. Wyman, *et al.*,\textsuperscript{36}]

*Molecular Orbitals of Thioindigo*

In order to better understand color changes occurring in these systems, the HOMO (Highest Occupy Molecular Orbital)-LUMO (Lowest Unoccupied Molecular Orbital) excitations have to be looked at closely. This energy difference is what defines color in molecules, and is easily affected by molecular isomerization, conjugation, electron donating substituents and more. As mentioned before, *cis*- thioindigo isomer in benzene has been reported to occur at higher energies ($\lambda_{\text{max}} = 470 \text{ nm}$), displaying a red-orange color.
Using TD-DFT (Time Dependent - Density Functional Theory), Jacquemin et al.\textsuperscript{35} identified the full $\pi$ orbital (HOMO) on the sulfur and the central C=C bond, whereas the empty $\pi^*$ orbital (LUMO) was centered on the single C-C bonds and oxygen atoms. Based on the electron-donating substitution of the HOMO and LUMO of some aluminum complexes, Chai et al.\textsuperscript{37} observed by UV-Vis spectroscopy, the raise of LUMO energy leading to a blue (hypsochromic) shift in the emission. On the other hand, the raise of HOMO energy resulted in a red (bathochromic) shift. Location of HOMO and LUMO for thioindigo (Figure 6), given by ZINDO, are in agreement with the information previously reported by Fabian et al.\textsuperscript{38}

\textbf{Figure 6} (a) Highest Occupied Molecular Orbital (HOMO) location on the sulfur and C=C bond of thioindigo. (b)Lowest Unoccupied Molecular Orbital (LUMO) location on C-C single bond and oxygen bond of thioindigo [Cerius$^2$ accelrys software].
3.2 Inorganic Host Materials

3.2.1 Natural Occurring Clay Minerals

**Palygorskite and Sepiolite Clays**

Clays are naturally occurring minerals with varying compositions. Palygorskite with a general formula, \((R^{2+},R^{3+})_5(Si,R^{3+})_8O_{20}(OH_2)_4M^{n+}(H_2O)_4\) with cation substitution \(Ca^{2+}, Mg^{2+}, Fe^{2+}(R^{2+}), Al^{3+}, Fe^{3+}(R^{3+})\), and sepiolite \([R^{2+},R^{3+}, R^{2+}, R^{3+})_8(H_2O)_4(OH)_{4}(Si,Al)_{10}O_{30}\).\(^{39}\) exhibit a fibrous structure-like ribbons where silicon atoms coordinate tetrahedrally with basal oxygens forming pyroxene chains periodically inverted. At the same time, and in order to balance the oxygen negative charge, apical oxygens bind to aluminum atoms forming non-continuous octahedral chains.\(^{40}\)

Palygorskite is a mixture of two polymorphs, one with monoclinic unit cell, space group \(C2/m\), cell parameters \(a = 13.24\), \(b = 17.89\), \(c = 5.21\) Å and an orthorhombic unit cell with a space group \(P2_1/b2/m2/n\) and cell parameters \(a = 12.762\), \(b = 17.882\), \(c = 5.249\) Å. Conversely, sepiolite is orthorhombic, with a space group \(P2_1/n2/c2/n\) and cell parameters \(a = 14.66\), \(b = 26.71\), \(c = 5.26\) Å.\(^{41}\)
Palygorskite and sepiolite are built of two types of discontinued polyhedral building blocks, one octahedral sheet is bonded between two tetrahedral sheets on each side, forming micro-channels throughout the structure,\textsuperscript{13} with tunnel measurements along the yz axis of 6.4 x 3.7 Å for palygorskite, and 10.7 x 3.7 Å for sepiolite.\textsuperscript{42} Correspondingly, palygorskite and sepiolite contain three forms of water in their structure: zeolitic water, coordinated water and structural which is water, coordinated at two positions to the magnesium/aluminum ion in the crystal lattice (see Figure 7). The difference in channel size between the two clays allows the storage of 5 zeolitic waters for palygorskite,\textsuperscript{13} and 8 zeolitic waters for sepiolite, per formula unit.

Thermal analysis of palygorskite by G. Chiari \textit{et al.}\textsuperscript{43} reported the reversible process up to 623K. At 393K, 6.3% weight loss is detected for free pore water and surface water. Over the range 393-573K and with 4% weight loss, zeolitic water is removed. Below 603K hydroxyl groups are still unmodified, and at higher temperatures structural water is removed.\textsuperscript{44}

\textbf{Figure 7} (left) Palygorskite unit cell, visualization on 001 plane. (right) Block unit representation showing dimension of channels [Image courtesy of the Coastal and Marine Geology Program].\textsuperscript{45}
Sepiolite thermal analysis by U. Shuali et al.\textsuperscript{46} reported a 18.6\% weight loss in a range of temperatures between 298 and 513K, together with an endothermic peak at 413K, which is characteristic of absorbed water and some zeolitic water as well. At 623-773K several sepiolites show two endothermic peaks and 5.3\% weight loss in TG is detected; this was related to a change in the bonding energy of bound water, due to the formation of a stable new phase of sepiolite anhydrite (\(\text{Mg}_8\text{Si}_{12}\text{O}_{30}\text{(OH)}_4\)) at 623K.\textsuperscript{47}

\textbf{Figure 8} (right) Sepiolite orthorhombic unit cell.(left) Schematic 001 plane representation of the cross-section of a sepiolite fiber [Image courtesy of Coastal and Marine Geology Program].\textsuperscript{45}

Using FTIR and elemental chemical analysis Serna et al.\textsuperscript{48} helped to elucidate the distribution of metals inside the structure bonded to coordinated (bonded) water and structural water (hydroxyl groups). In general, palygorskite clay contains Mg\textsuperscript{2+} located in the external octahedral sites bound to 2 structural waters (M3 position). Moreover, Al\textsuperscript{3+} and Fe\textsuperscript{3+} are found in the inner octahedral sites, bound to 2 hydroxyl groups when a high concentration of Fe\textsuperscript{3+} is found (M2 position) This arrangement is called dioctahedral, where two trivalent cations (2R\textsuperscript{3+}) are occupying two of the three octahedral sites available. \textsuperscript{40}
In the case of sepiolite, Mg\(^{2+}\) cations are reported in the inner octahedral sites, forming an trioctahedral arrangement,\(^{49}\) where three divalent cations (3R\(^{2+}\)) occupy the three octahedral sites available (M3 and M1 positions).

**Figure 9** Octahedral ribbon for palygorskite [Image courtesy of Suarez et al.\(^{44}\)].
Neutral Layer Clays (Charge almost zero)

Most clays that belong to this group present dioctahedral or trioctahedral character. Talc belongs to this group and would be tested in this research. Its main characteristic is the zero charge imbalances due to low aluminum substitution in its layers; therefore, no cations are present between the interlayer and no hydration takes place. This gives talc the slippery and dry property. 40

Low Charge Swelling Minerals: Smectites (Charge between 0.7 to 0.2)

This group of minerals with a 10 Å layer structure and an excess charge of 0.7 to 0.2 allow hydrated cations between the layers. This characteristic causes the layers to expand from a monohydrated state (one water layer around the cation) of d spacing 12.5 Å to 15.2 Å for a trihydrated state (three water layers around the cation). The maximum expansion smectite clays can handle are 17 Å, when measured with ethylene glycol. Clay minerals that belong to this group are montmorillonite clays, among others. 40
**Montmorillonite Clays**

Montmorillonite is a clay mineral with expandable layers, with continual polyhedral sheets, consisting primarily of one octahedral between two tetrahedral sheets (2:1 minerals). The octahedral sheets contain varied hexa-coordinate ions, forming dioctahedral and trioctahedral arrangements. As in most of the aluminosilicates, substitution of aluminum in the silicon tetrahedral sites is observed, generating negative charges between the layers, this charge is neutralized by the proximity of exchangeable cations in the layers (Figure 11).

*Figure 11* Montmorillonite structure displaying building units of tetrahedral and octahedral sheets [Materials Studio v4.0].
**High Charge Mica Group (Charge almost 1)**

Charge imbalance in this group is from 0.8 to 1, normally for dioctahedral substitution. Due to the high charge imbalance the cation in the interlayer is strongly bound, usually potassium is the cation present in this type of mineral, due to its high polarizability these clays typically do not expand.\(^{40}\) However, recent research in synthetic micas, have manipulated these properties by inserting other cations less polarizable such as sodium, and giving mica the property to expand.\(^{21}\)

**Low Charge Synthetic Swelling Micas**

Low charge synthetic micas derived from the reduction of the high interlayer charge by hydroxylation (oxygen from tetrahedral sites replaced by OH), or by silification (Al\(^{3+}\) in tetrahedral sites substituted by Si\(^{4+}\)). In addition, a less polarizing cation such as sodium improves mica swelling with polar solvents.\(^{50}\) In this research two low charge swelling micas (YN6 and YN8) prepared by Dr. Komarneni and his group were tested. In YN6 (Na\(^{0.125}\) Al\(^{0.125}\) Si\(^{7.875}\) Mg\(^{6}\) O\(^{20}\) F\(^{4}\)) and YN8 (Na\(^{0.5}\) Al\(^{0.5}\) Si\(^{7.5}\) Mg\(^{6}\) O\(^{20}\) F\(^{7}\)) fluorine anion was used to lower the high charge of the mica clays instead of OH.\(^{21}\)
3.2.2 Synthetic Aluminosilicates

Zeolites are crystalline aluminosilicates with a general formula, $M_{x/n}[(AlO_2)_{x}(SiO_2)_{y}]\cdot mH_2O$, where cations (M) balance the negative charge created in the framework. In general, these crystalline minerals consist of building blocks of $[SiO_4^{4-}]$ and $[AlO_5^{5-}]$, tetrahedrally coordinated and corner sharing. The substitution of Si(IV) by Al(III) in the tetrahedral sites creates an electrical imbalance in the $[AlO_5^{5-}]$ building block; hence, to preserve the neutral charge, exchangeable cations are held within the zeolite.\(^{51}\)

Differences in topology help to classify the structural variety found in zeolites. Simple Secondary Building Units (SBU) were chosen by W.M. Meier \(^{52}\) to explain in a simple way the complicated structures of zeolites. SBU are the smallest number of building units (Figure 12) from which zeolites are mostly formed; for example, in the case of modernite, the framework can be made only by 5-1 units. For some other zeolites more than one SBU is involved; for example, faujasite with four SBU of 4-,6-, 8- rings and 6-6 hexagonal prisms, and Linde zeolite A, with 4-,6-,8- and 4-4 cubic units.

Ring size in the structure is defined by the amount of tetrahedrals sharing corners. Six tetrahedral groups form a hexagon where twenty four form a truncated octahedron shape, called a sodalite unit or β-cage.\(^{53}\)

Three zeolite groups will be discussed in this research, such as: faujasite (FAU), Linde Type A (LTA) and mordenite (MOR).
Figure 12 Meier’s secondary building units of zeolite frameworks [Image courtesy of J.V. Smith\textsuperscript{51}].
**Faujasite (FAU)**

Faujasite is the proper name given to the natural occurring mineral with a cubic unit cell, cell parameters $a = 27.4\text{Å}$ and space group $Fd\overline{3}m$.\textsuperscript{40} Zeolite falling into this category have a similar framework such as X and Y. However, in the case of Linde Type A (LTA), some variations in the crystal structure are found. For zeolite X and Y, the unit cell consists of sodalite units linked to hexagonal prisms (6-6 SBU, see (Figure 12). The tetrahedral array of this structure encloses a large supercage ($\alpha$-cage) which is entered through a twelve-ring window (Figure 13).\textsuperscript{53}

![Visualization of Faujasite framework](image)

**Figure 13** Visualization of Faujasite framework in (left) tetrahedral arrangement, and (right) secondary building units of sodalite and hexagonal prism linked together [Image courtesy of G. Bergerhoff et al.\textsuperscript{54}].
Linde Type A (LTA)

Linde Type A is a member of the faujasite group; however, there are small differences that characterize this zeolite. LTA crystallizes in a cubic arrangement with cell parameters $a = 11.9\text{Å}$, and space group $Pm3-m$. In the framework, sodalite units are modified to the 4-ring found in the truncated octahedron at the corner of the unit cell and replaced by a 4-4 secondary building unit, forming a center cage with a shape of a truncated cuboctahedron with twelve 4-rings, eight 6-rings and six 8-rings. These cages are connected in three directions by windows of 8-ring (Figure 14).

Figure 14 Visualization of LTA framework in (left) tetrahedral arrangement, and (right) secondary building units of sodalite and cubes linked together [Image courtesy of T.B. Reed et al.].
Modernite

Modernite is orthorhombic, cell parameters of $a = 18.1$, $b = 20.5$ and $c = 7.5\text{Å}$, and space group $Cmcm$. The framework of modernite is composed of horizontal 4-rings and tilted 5-rings sharing an edge. Together these units form a 12-ring in interconnected zig-zag channels made up of 5-, 6-, 8-rings. Pairs of 5-rings connected to other 5 rings form vertical strips of high rigidity. These strips can be arranged in different ways to form other members of the modernite group.\(^{51}\)

*Figure 15* Visualization of MOR framework in (left) tetrahedral arrangement, and (right) secondary building units of 4 different secondary building units linked together [Image courtesy of W.M. Meier].\(^{56}\)
3.2.3 Charge Imbalance Substitution in Inorganic Host Materials

As indicated by B. Velde⁴⁰ there are four types of substitutions that can create charge imbalance in natural occurring clays: constant ionic site occupation, interlayer substitution, non-stoichiometric substitution and di and trioctahedral substitution.

Constant ionic occupation is created by the substitution of silicon in the tetrahedral sites by aluminum. This substitution is then compensated by another substitution in the octahedral site, thus leaving a electrostatic balance in the clay. Figure 16 illustrates this situation.

Interlayer substitution refers to the charge imbalance originated in either tetrahedral or octahedral site of the clay, this extra charge is compensated by the introduction of an external ion which neutralizes the charge. Figure 16 illustrates this situation.

![Figure 16](left) Substitution of ions of different charge. (right) Interlayer cation compensation charge imbalance originated in 2:1 [Image courtesy of B.Velde⁴⁰].
Non-stoichiometric, dioctahedral and trioctahedral substitution is a major subdivision among clay minerals defining the composition and therefore their origin. The main characteristic of this substitution is that its changes exclusively take place in octahedral sites of the structure. Substitution of 3 $R^{2+}$ cations (called trioctahedral) to complete an overall charge of +6, or substitution of 2 $R^{3+}$ cations (called dioctahedral) leaving an octahedral site empty.$^{40}$ Figure 17 illustrates this situation.

![Figure 17](image)

**Figure 17** Trioctahedral and dioctahedral substitution exclusively in octahedral sites.

Now that the origin of the negative charge in the framework has been explained, interlayer substitution will be reviewed more closely in this section since this effect is responsible for the cations detected in most of the materials evaluated.


**Exchangeable Cations in Inorganic Host Materials**

In accordance with B. Velde\(^{40}\), cations are fixed in two different sites in clay minerals: surface and interlayers (montmorillonites) or channels - cages (palygorskite - sepiolite and synthetic zeolites), as indicated in Figure 18 where absorbed and adsorbed cations are displayed.

![Figure 18](image.png)

**Figure 18** Location of cations in internal layers (absorbed) and surface of layersilicate clay mineral (adsorbed) [Image courtesy of B. Velde\(^{40}\)].

### Polarizing Power of the Cations

Polarizing power is influenced by the charge and the ionic radius of the cation. To quantify this effect a function called ionic potential (\(\phi\)) is widely used and is defined as:

\[
\phi = \frac{z^+}{r}
\]

Equation 1

where \(z^+\) is the charge of the cation and \(r\) its radius. Table 1 displays a variety of cations properties.
Table 1 Main cation properties

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>r (nm)*</th>
<th>(nm⁻¹)</th>
<th>ΔH_{hydration} (KJ/mol)</th>
<th>pka</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>0.143</td>
<td>6.99</td>
<td>-</td>
<td>9.25</td>
<td>57,58</td>
</tr>
<tr>
<td>H⁺</td>
<td>~</td>
<td>~</td>
<td>-1075</td>
<td>-</td>
<td>59</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.0588</td>
<td>17.0</td>
<td>-515</td>
<td>13.6</td>
<td>60,61,58</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.100</td>
<td>10.5</td>
<td>-405</td>
<td>14.2</td>
<td>59,60,58</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.153</td>
<td>7.00</td>
<td>-321</td>
<td>14.5</td>
<td>59,60,58</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.1000</td>
<td>20.0</td>
<td>-1592</td>
<td>12.8</td>
<td>59,60,58</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.0645</td>
<td>31.0</td>
<td>-1922</td>
<td>11.4</td>
<td>59,60,58</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>0.0313</td>
<td>64.0</td>
<td>-2487</td>
<td>6.2</td>
<td>59,60,58</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.0500</td>
<td>60.0</td>
<td>-4613</td>
<td>5.14</td>
<td>60,62,63</td>
</tr>
<tr>
<td>B³⁺</td>
<td>0.0200</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>59,64</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>0.0400</td>
<td>100</td>
<td>-</td>
<td>9.66</td>
<td>60,62,63</td>
</tr>
</tbody>
</table>

* value calculated from

In this data it is clear that the charge to ionic radius ratio enhances the ionic potential and therefore the covalent character. An example of this covalent character is the melting points of two oxides such as, Al₂O₃ and MgO, where Al₂O₃ presents lower melting point due to its higher covalent character.⁵⁹

Cations have a large tendency to hydrate accordingly to their ionic radius and charge, as observed by Latimer⁶⁵, with low electronegative elements. Latimer's equation relates these variables as follow;⁵⁹

\[
\Delta H_{hyd} = \frac{-60.900z^2}{(r + 50)}
\]

Equation 2

where \( z \) is the charge of the cation and \( r \) its radius in picometers. According to G. Wulfberg⁵⁹ electronegativity increases the hydration energy of the cation of similar ionic potential, which suggest there is not only an electrostatic attraction between the metal and negative charge of the water molecule but a covalent character in the bond, where
an unshared electron pair of the water molecules is shared with the ion, as illustrated in Figure 19.

![Figure 19](image_url) Hydrolysis of a hydrated cation [Image courtesy of G. Wulfsberg].

The process of hydration is well known to be a Lewis acid - base process where metal ions act as Lewis acids and water molecules as Lewis bases. The O-H bond then polarizes and becomes acidic. This behavior was detected by C. Ravindra Reddy et al. in cation exchanged montmorillonite clay, where adsorbed pyridine (weak base) reacted with the O-H water surrounding the cations to form pyridinium at room temperature. Moreover, the water interaction with a high ionic potential cation such as aluminum increased the strength of the electron withdrawing observed in the esterification of succinic acid.
3.2.4 Brønsted and Lewis Acids Sites

The acidity of natural and synthetic aluminosilicates is an important reactivity factor for catalytic materials and sorbent applications.\textsuperscript{67} This acidity results from the presence of surface groups such as siloxanes, silanols, aluminols, Al-O, and Mg-O, usually found at the edges of the alumino-magnesium silicate framework.\textsuperscript{68}

In order to differentiate between both acid sites present in aluminosilicates, both terminologies have been used in the catalysis field. Brønsted acids refer to the hydrogen ion attracted to the negatively charge oxygen, which is attached to aluminum and silicon atoms (Figure 20-top), and Lewis acids refers to the active aluminum site, when H\textsubscript{2}O has been removed (Figure 20-bottom).

\begin{center}
\textbf{Brønsted Acid}
\end{center}

\begin{center}
\textbf{Lewis Acid}
\end{center}

\textbf{Figure 20} (Top) Brønsted acid site (H\textsuperscript{+}) in a tetrahedral site,(bottom) Lewis acid hydrated.
However, this classification is slightly obsolete when evaluating an inorganic material, mostly because it is not including other acidic species also present in the host, such as cations. As mentioned before these cations also have presented a Lewis acid character.  

Elemental analysis normally describes the surface Si/Al ratio, which portrays acid sites density; however, this type of analysis can not distinguish between aluminum incorporated in the framework, as cation aluminum, or aluminum oxide, this being an important factor to determine catalytic activity. Therefore, different spectroscopic techniques such as FTIR and MAS-NMR have been used for qualitative and quantitative characterization of active acid sites.  

The activity and strength studies for sepiolite and palygorskite by U. Shuali et al. revealed the presence of more Brønsted than Lewis acids at 423K by the decomposition products of cumene. The strength of the active sites was determined by FTIR vibration modes of pyridine, triphenylpyridine and n-butylamine adsorbed in the clays. Weak-medium surface Brønsted acid sites were detected at room temperature until 373K. The interaction was mainly due to the hydrogen bonding between nitrogen (proton acceptor) and hydrogen (proton donor) from zeolitic water and bound water. At higher temperatures (623K) and after the loss of water, Lewis acids sites were detected by the binding of nitrogen to aluminum and magnesium. Similar strength experiments for zeolite NaY by F. Mauge et al. revealed the absence of certain representative vibration modes of Brønsted (1655 and 1620 cm\(^{-1}\)) and Lewis (1610 cm\(^{-1}\)) active sites.
Pyridine adsorption by L. Pinard et al.\textsuperscript{71} confirmed this statement by the absence of pyridinium ions in the Brønsted sites (1455 cm\(^{-1}\)), and pyridine coordinated at Lewis sites (1545 cm\(^{-1}\)).
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Chemical Analysis by Wide Range X-Ray Fluorescence Spectrometry (WD-XRF).

The complete elemental chemical analysis for all natural occurring clay minerals and synthetic aluminosilicates is shown in Appendix A.

4.2 Physical Properties

4.2.1 Inorganic Host Materials Treated with Thioindigo

A display of different shades of color were observed when 0.5 mol % thioindigo interacted with different inorganic hosts before thermal treatment (Figure 21).
Figure 21 Pure thioindigo color and samples prepared with 0.5 mol % thioindigo in different host materials before thermal treatment.
A variety of color changes were noticed in samples thermally treated at 413K for nine hours (Figure 22).

**Figure 22** Colors observed in pure thioindigo and 0.5 mol %thioindigo in different host materials heated at 413K for nine hours.
High moisture effect was also observed in some of the thermally heated samples, as seen in Figure 23.

**Figure 23** High moisture effect in thioindigo and 0.5 mol %thioindigo in different host materials at 413K for nine hours.
Water content in sepiolite and montmorillonite clays was noticed to color change the unheated dye composite with time. Evaporation of loosely bound water from Lewis acid sites (LAS) could be responsible for this behavior; therefore leaving the tightly bound water – LAS to interact with C=O, this effect was displayed as a purple color in the samples.

![Figure 24 Example of color change of 0.5 mol %thioindigo in Bentolite L® UNHEATED when exposed to three different levels of moisture.](image)

Palygorskite, bentolite L®, Ca-MMT (Wyoming Deposit) and Valfor CP300-35® mixed with 0.5 mol % thioindigo exhibited blue color change when exposed to vacuum for more than 3 hrs. Nevertheless, the blue color observed in these samples was not stable once the vacuum was removed, exhibiting a purple color. This purple color could be related to hydrogen bonding between the C=O and the H₂O surrounding the active sites. Moreover, the color change observed in this experiment seemed to be associated to surface active sites easily approach by moisture. In the case of palygorskite, temperature seemed to play an important role as a driving force to locate thioindigo in active sites less susceptible to moisture. Conversely, the amount and the type of cations present in the inorganic materials, and a more open type of structure, were two factors in the fast hydration of the mixture.
4.3 Diffusive Reflectance Ultraviolet-Visible Spectroscopy

4.3.1 Thioindigo

The decomposition of the diffuse reflectance UV-Vis spectra was better evaluated using multiple Voight bands by peak fit v4.11 software. These bands revealed that thioindigo absorption band best fitted with two main $\pi-\pi^*$ transitions bands at 504 nm ($A = 0.7$) and 578 nm ($A = 0.6$) in the visible region (see Figure B.1). However, these values seemed to vary in the references reviewed.\textsuperscript{72} On the other hand, it is known that diffuse reflectance UV-Vis spectrophotometers have poor reproducibility depending on (a) limitations in method and apparatus, (b) variations in the surface treatment and (c) differences in extrapolations used in the Kramers-Kronig dispersion relation.\textsuperscript{73} In conclusion, these values reported were specific for thioindigo from TCI America and the spectrophotometer used for this specific analysis (see Chapter 2, Section 2.3.1).
4.3.2 Inorganic Host Materials Treated with Thioindigo

**Palygorskite - Thioindigo Interaction**

Thioindigo reacts with palygorskite to exhibit a non-reversible broad range of colors, from red-pink to purple-blue. Palygorskite a natural occurring clay with a Si/Al ratio = 5.68 was mixed with 0.5 mol % thioindigo and heated at 413K for nine hours. This mixture displayed a bathochromic shift to a bright purple-blue color identified by peak fit v4.11 software as four main absorption bands 468 nm (A = 0.09), 570 nm (A = 0.46), 568 nm (A = 0.72) and 629 nm (A = 0.48) in the visible region (see Figure B.3). The thermally treated palygorskite mixture, was the most stable of all mixtures tested, when exposed to a slight hydration displayed a small reduction in absorbance values 468 nm (A = 0.08), 565 nm (A = 0.41), 568 nm (A = 0.67) and 628 nm (A = 0.48) was observed (see Figure B.4); conversely, palygorskite mixture upon prolonged evacuation, displayed a bright blue color; however, once the sample was removed from evacuation, a purple color was observed. UV-Vis spectra of the dull purple color revealed no change in wavelength with a reduction in absorbance values 466 nm (A = 0.065), 569 nm (A = 0.32), 568 nm (A = 0.66) and 625 nm (A = 0.34) (see Figure B.5).
Figure 25 (Top) Color variation of palygorskite / 0.5 mol % thioindigo unheated and heated at 413K for nine hours, hydrated after heat treatment and hydrated after exposure to vacuum. (Bottom) Diffuse Reflectance UV-Vis spectra of the above mentioned samples and thioindigo starting material.
A pretreated palygorskite at 833K mixed with 0.5 mol % thioindigo and heated at 413K for nine hours displayed a red color with two main absorbance bands at 512 nm ($A = 0.36$) and 571 nm ($A = 0.69$) (see Figure B.85). This red color was not stable after washing with ethanol soxhlet extraction. On the other hand, palygorskite blue color was demonstrated to be stable in ethanol soxhlet extraction.\textsuperscript{74}

\textbf{Figure 26} Comparison of (a) pretreated palygorskite (833K for 16h) / 0.5 mol % thioindigo heated at 413K for nine hours, and (b) palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours.
**Sepiolite-Thioindigo Interaction**

Sepiolite, a natural occurring clay with a Si/Al ratio = 15 mixed with 0.5 mol % thioindigo exhibited a magenta color shade with two main absorption bands at 526 nm (A = 0.80) and 584 nm (A = 0.75) when thermally treated (see Figure B.7). The slight hydration of sepiolite displayed a reduction in the absorbance of the two bands at 526 nm (A = 0.65) and 570 nm (A = 0.54) and the appearance of a new band at 610 nm (A = 0.52) (see Figure B.8). This new band was responsible for the color change magenta to purple exhibited in sepiolite. This bright purple color was also observed in the unheated mixture after some time exposed to air. Further hydration of either sample reduced absorbance to lower values similar to the unheated sample. The behavior of these samples after time was very puzzling. In the case of the heated sample color change from magenta to purple could be explained as the LAS hydration, forming a thin hydration sphere around them. For the unheated sample color change (light pink to purple), a possible reason could be the dehydration of the excess water in the LAS due to the dry climate of El Paso, thus leaving only a thin water layer between thioindigo and the LAS displayed as a purple color.
Figure 27 (Top) Color variation of sepiolite / 0.5 mol % thioindigo unheated and heated at 413K for nine hours, hydrated after heat treatment and hydrated after exposure to vacuum. (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Montmorillonite clays – Thioindigo Interaction

Ca$^{2+}$-MMT (Bentolite L$^\circ$ and Texas deposit) and Na$^+$-MMT (Wyoming and Kunipia deposit) displayed reversible color changes when exposed to different levels of moisture.

Figure 28 Effect of moisture in montmorillonite clays.
Figure 29  (Top) Color variations of (Ca$^{2+}$-MMT) bentolite L° / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 30 (Top) Color variations of Ca$^{2+}$-MMT (Texas deposit) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 31 (Top) Color variations of Na⁺-MMT (Wyoming deposit) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 32 (Top) Color variations of Na⁺-MMT (Kunipia deposit) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Neutral layer clays (Talc) – Thioindigo Interaction

Figure 33 (Top) Color variations of Talc / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
**Synthetic Swelling Micas (YN6, YN8 and Na-Ts)- Thioindigo Interaction**

No major color change was observed with YN6 Si/Al = 63 and YN8 Si/Al = 15, however, the presence of the 579 nm band was more predominant than the 505 nm band (see Figure B.22).

![Figure 34](image)

Figure 34 (Top) Color variations of YN6 / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 35 (Top) Color variations of YN8 / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
In the case of Na-Ts Si/Al = 608 a similar effect is observed, however the color was observed to be more red than for YN6 and YN8.

Figure 36 (Top) Color variations of Na-Ts / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Synthetic Zeolites, Faujasite (FAU)

Faujasite (FAU) synthetic zeolites with a range of Si/Al ratio from 2 to 4, when mixed with 0.5 mol % thioindigo, also revealed reversible color changes related to water absorption. Additionally, cation substitution was detected to have an effect in the color shades obtained after thermal treatment (Figure 37).

Figure 37 Reversible color changes in presence of water of 0.5 mol % thioindigo in Na⁺-FAU (NaY), Na⁺,Ca²⁺-FAU (13X), NH₄⁺-FAU (LZY-62) and H⁺-FAU heated at 413K for nine hours.
Figure 38 (Top) Color variations of Valfor CP300-35\textsuperscript{®} (H\textsuperscript{+}-FAU) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 39 (Top) Color variations of LZY-62 (NH₄⁺-FAU) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 40 (Top) Color variations of 13X (Na⁺,Ca²⁺-FAU) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
**Figure 41** (Top) Color variations of NaY (Na⁺-FAU) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Synthetic Zeolites, Linde Type A (LTA)

4A and 5A Linde Type A zeolites (LTA) with a Si/Al ratio = 1.00, exhibited a bright pink color when mixed with thioindigo and no further color changes were perceived with temperature. This behavior could be explained by the small dimensions of the pore cages (4.2 Å) in comparison with thioindigo molecule proportions (15.17 Å (length), 7.42 Å (width) and 3.4 Å (thickness)\textsuperscript{32}, thus not allowing the entrance of the dye inside the cages and therefore no major interaction took place. In addition the predominance of the 577 nm band was also observed (see Figure B.30 and B.32).
Figure 42 (Top) Color variations of 4A (Na⁺-FAU) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 43 (Top) Color variations of 5A (Na⁺-FAU) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
**Synthetic Zeolite, Mordenite (MOR)**

Zeolon®, a mordenite type zeolite with a Si/Al ratio = 2.5, was noticed to have more stability towards moisture than other zeolites tested; the main reason could be its cylindrical pore shape similar to palygorskite shape. Due to the low amount of zeolon® available and the item was no longer available; two other mordenites were tested for further analysis. Nevertheless, zeolon® exhibited two broad bands at 573 nm (A = 0.51) and 676 nm (A = 0.33) (see Figure B.43). The intensity of these bands was lower than expected; however, this could be due to an aged sample instead of a freshly prepared sample.
Figure 44  (Top) Color variations of Zeolon® (Na⁺-MOR) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
CBV21A (NH₄⁺-MOR) Si/Al ratio = 9.5 and CBV10A (Na⁺-MOR) Si/Al ratio = 4.0 mixed with 0.5 % mol thioindigo displayed different colors, however when similar cations were present in the framework analogous colors were observed. Si/Al ratio difference between these two mordenites did not play a significant role in the colors observed, however when compared to zeolon® (Na⁺-MOR) Si/Al = 7.3, the difference was more drastic, since zeolon® exhibited a darker color.

Figure 45 Color changes of samples prepared with 0.5 mol % thioindigo in CBV10A (Na⁺-MOR), CBV21A (Na⁺-MOR) and Zeolon® (Na⁺-MOR) with different Si/Al ratios.
Figure 46  (Top) Color variations of CBV10A (Na⁺-MOR) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
**Figure 47** (Top) Color variations of CBV21A (Na⁺-MOR) / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Mesoporous Zeolites

Mesoporous zeolites such as, aluminum silicates, aluminum oxide and silicon oxide displayed different colors shades when in contact with thioindigo. Samples behaved differently when heated: Aluminum oxide exhibited a bright pink color with two bands at 552 nm (A = 0.45) and 678 nm (A = 0.05) with no changes when hydrated (see Figure B.80). In the case of silicon oxide and aluminum, silicon (1:1) a bright magenta with three bands at 502 nm (A = 0.38), 554 nm (A = 0.66) and 604 nm (A = 0.38) and for the later a bright red color with three bands at 507 nm (A = 0.40), 548 nm (A = 0.57) and 587 nm (A = 0.35) were observed (see Figure B.82 and B.84).
Figure 48 (Top) Color variations of MA-1 / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 49  (Top) Color variations of MS-1 / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
Figure 50  (Top) Color variations of MAS-1 / 0.5 mol % thioindigo unheated, dehydrated at 413K for nine hours and hydrated after heat treatment (Bottom) UV-Vis spectra of the above mentioned samples and thioindigo starting material.
4.3.3 Sulfuric Acid Treated with Thioindigo

A bright blue-green color was displayed when thioindigo reacted with concentrated sulfuric acid (98.7%). The UV-Vis spectra of the blue-greenish solution with a concentration of $4.4 \times 10^{-5}$ M (taken from measurements by Brode et al.\textsuperscript{20}) revealed 7 bands separated in two broad peaks from 425 nm ($A = 0.40$) to 439 nm ($A = 0.41$) and 582 nm ($A = 0.31$) to 700 nm ($A = 0.20$) (see Figure B.87). In addition a large absorption was also observed in the ultraviolet region with an extinction coefficient ($\varepsilon$) value of 17,647 L mol$^{-1}$ based on measurements by Brode et al.\textsuperscript{20} The bright blue-greenish color was noted to change to red suspended particles when small amount of water was added to the solution, eventually the red suspended particles precipitated after some time. Nevertheless a UV-Vis of this reddish solution was obtained at 529 nm ($A = 0.03$) and 587 nm ($A = 0.01$). UV-Vis spectrum illustrated in Figure 51 was normalized for better visualization.
Figure 51 (Top) Color change of thioindigo with concentrated sulfuric acid. (Bottom) UV-Vis spectra of (a) concentrated sulfuric acid reaction with thioindigo and (b) concentrated sulfuric acid reaction with thioindigo after water addition.
4.3.4 Cation Exchanged Mordenite Treated with Thioindigo

Exchanged mordenites, (K⁺, Na⁺, Ca²⁺, NH₄⁺, H⁺, Al³⁺-MOR) combined with 0.5 mol % thioindigo at 413K for nine hours, displayed a variety of color changes depending on the exchanged cation, as shown in Figure 52.

**Figure 52** (Top) Color changes observed in heated samples of CBV21A (MOR) exchanged with different cations (K⁺, Na⁺, Ca²⁺, NH₄⁺, Al³⁺ and H⁺) and mixed with 0.5 mol% thioindigo. (Bottom) UV-Vis Spectra of the above mentioned samples.
Bathochromic shifts in the mixtures were observed after heat treatment at 413K for nine hours according to the cation. Exchanged cations with higher acidic strength such as aluminum and hydrogen ($\phi = 60.0 \text{ nm}^{-1}$ and $\phi > 60.0 \text{ nm}^{-1}$) were observed to present higher bathochromic shifts when compared to other cations with lower strength such as potassium ($\phi = 7.0 \text{ nm}^{-1}$).

**Water Effect in Exchanged Mordenites (K$^+$, Na$^+$, Ca$^{2+}$, NH$_4^+$, H$^+$, Al$^{3+}$-MOR)**

The absorption of water in most zeolites is one of the main applications among others. However, thioindigo color in this research has made the water absorption more visible than in raw zeolites. Thioindigo contact with the exchanged zeolites, such as faujasite and mordenite, displayed a variety of different color changes when heated. However, these colors were susceptible to hydration as shown in Figure 53.

![Figure 53](image)

**Figure 53** Color changes observed in 0.5 mol % thioindigo in exchanged zeolites unheated, dehydrated at 413K for nine hours and hydrated.
UV-Vis spectra of hydrated exchange mordenites (K⁺, Na⁺, Ca²⁺, NH₄⁺, H⁺, Al³⁺-MOR) exhibited a reduction in absorbance and hypsochromic shifts.

Figure 54  (Top) Color changes observed in 0.5 mol % thioindigo in K⁺-MOR unheated (21AK+dye Unheated), dehydrated at 413K for nine hours (21AK+dye Dehydrated) and hydrated (21AK+dye Hydrated). (Bottom) UV-Vis spectra of the above mentioned samples.
Figure 55 UV-Vis spectra of color change observed during hydration of 0.5 mol % thioindigo in Na⁺-MOR (21ANa+dye Hydrated). Hydrated sample was compared with heated mixture at 413K for nine hours (21ANa+dye Dehydrated) and unheated mixture (21ANa+dye Unheated).
**Figure 56** UV-Vis spectra of color change observed during hydration of 0.5 mol % thioindigo in Ca²⁺MOR (21ACa²⁺+dye Hydrated). Hydrated sample was compared with heated mixture at 413K for nine hours (21ACa²⁺+dye Dehydrated) and unheated mixture (21ACa²⁺+dye Unheated).
Figure 57 UV-Vis spectra of color change observed during hydration of 0.5 mol % thioindigo in NH₄⁺MOR (21ANH₄⁺+dye Hydrated). Hydrated sample was compared with heated mixture at 413K for nine hours (21ANH₄⁺+dye Dehydrated) and unheated mixture (21ANH₄⁺+dye Unheated).
**Figure 58** UV-Vis spectra of color change observed during hydration of 0.5 mol % thioindigo in Al³⁺-MOR (21AAI+dye Hydrated). Hydrated sample was compared with heated mixture at 413K for nine hours (21AAI+dye Dehydrated) and unheated mixture (21AAI+dye Unheated).
Figure 59  UV-Vis spectra of color change observed during hydration of 0.5 mol % thioindigo in H⁺-MOR (21AH+dye Hydrated). Hydrated sample was compared with heated mixture at 413K for nine hours (21AH+dye Dehydrated) and unheated mixture (21AH+dye Unheated).
4.4 Structural Analysis by Fourier-Transform Infrared Spectroscopy

4.4.1 Inorganic Host Materials

Palygorskite and Sepiolite

The position of the bands, identified in the FTIR spectra of the palygorskite sample, showed the existence of dioctahedral coordination, which was clearly noticed by the absence of the 3Mg-OH vibration (M3 and M1 positions) at 3680 cm$^{-1}$. Magnesium presence is found in the trioctahedral ends (M3 position) attached to coordinated water; however, M1 position is an empty occupancy. Stretching and bending vibrations of the Al-Al-OH vibration (M2 position) at 3620 and 913 cm$^{-1}$ was detected, and that corresponding to Al-Fe$^{3+}$-OH (M2 position) at 3589 and 863 cm$^{-1}$ was identified as well. Data for the structural characterization of this clay was in accordance to the studies of M. Suarez et al.\textsuperscript{44} for several palygorskite clays from different regions around the world. Structural arrangement is illustrated in Figure 9.

Sepiolite, on the other hand, revealed an intense peak in the 3Mg-OH (M3 and M1 positions) at 3680 cm$^{-1}$ and (M1 position) Mg-OH bending mode in the 649 cm$^{-1}$ region, thus trioctahedral coordination is believed to be present. In addition, another sharp vibration in the Fe-Al-Mg-OH was detected at 693 cm$^{-1}$.\textsuperscript{44}
Figure 60 Trioctahedral arrangement for sepiolite clay [Image courtesy of Suarez et al.].

Impurities such as quartz and calcite were also visible in the spectrum correlating with the X-ray diffraction pattern (see Figure 98).
Figure 61 FTIR spectra for palygorskite and sepiolite clays with KBr support.

Table 2 Observed vibrational assignments for palygorskite and sepiolite clays.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic Water</td>
<td>3270(sh), δ-3383(w), v-1621(w)</td>
<td>44,75,76</td>
</tr>
<tr>
<td></td>
<td>3240(sh), δ-3383(w), v-1619(sh), v-1621(w)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>Mg-OH₂</td>
<td>δ-3550(w), v-1656(s), δ-3550(m), v-1656(s)</td>
<td>44,75,76, 48</td>
</tr>
<tr>
<td>Al-Fe³⁺-OH</td>
<td>δ-3589(m) NA</td>
<td>44,75,76</td>
</tr>
<tr>
<td>Loosely bound H₂O</td>
<td>1697(w)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>Hydroxyl or hydrate water</td>
<td>1377(m)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>v-1192(w), 500 region (vs)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>2Al-OH</td>
<td>δ-3620(m), δ-913(sh)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>3Mg-OH</td>
<td>δ-3686(s), 638(w)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>Si-O quartz (impurity)</td>
<td>778(sh)</td>
<td>77</td>
</tr>
<tr>
<td>CaCO₃ (impurity)</td>
<td>1425(m)</td>
<td>77</td>
</tr>
<tr>
<td>Si-O-Al</td>
<td>512(vs)</td>
<td>44</td>
</tr>
<tr>
<td>Si-O</td>
<td>v-1033(vs), 981(vs)</td>
<td>44,75,76</td>
</tr>
<tr>
<td>Fe,Al,Mg-OH</td>
<td>693(m), δ-863(sh)</td>
<td>44,75,76</td>
</tr>
</tbody>
</table>

(vs): very strong, (s): strong, (m): medium, (w): weak, (sh): shoulder
(v): bending, (δ): stretching
NA: Not Available
Low Charge Swelling Natural Occurring Clays (Smectite Group)

FTIR spectra of Na+-montmorillonite clays (Na+-MMT) [Kunipia and Wyoming deposits] and Ca²⁺-montmorillonite clays (Ca²⁺-MMT) [Bentolite L® and Texas deposit] revealed the absence of 3Mg-OH 3686 cm⁻¹ vibration mode indicative of no trioctahedral arrangement. Thus, these clays mostly have dioctahedral character due the presence of 2R³⁺-OH (R= Al³⁺ or Fe²⁺) at 3630 cm⁻¹ and the presence of Si-O-Fe²⁺ at 468 cm⁻¹.⁴⁴ The charge imbalance in these type of clays is mostly originated by divalent substitution in the octahedral sites as mentioned before in chapter 3, section 3.1.0. This occupancy was also confirmed by ²⁷Al-NMR. In addition, we may be tempted to assign vibrations similar to palygorskite and sepiolite; however, attention needs to be paid to changes in the water vibration, such as 1643 cm⁻¹ in Na⁺-MMT and 1638 cm⁻¹ in Ca²⁺-MMT. This vibration has been mentioned by H.W. van der Marel et al.⁷⁸ to be resistant up to 853K; therefore, it was assigned to hydroxyl groups instead of zeolitic water as in palygorskite and sepiolite.

Figure 62 Dioctahedral arrangement in Na⁺ and Ca²⁺- Montmorillonite clays
The presence of quartz and calcite impurities in Na\textsuperscript{+}-MMT clays and primarily quartz in Ca\textsuperscript{2+}-MMT clays were also observed. These impurities were confirmed by X-ray diffraction. However, in some cases as in Kunipia deposit, the concentration of impurities in the sample probably was lower than 5\% (xrd detection limit) since the characteristic peaks in the 2 theta (26 - 29 degrees) region were not detected (see Figure 99).
Figure 63 FTIR spectra for Na⁺-montmorillonite clays in KBr support.

Table 3 Observed vibrational assignments for Na⁺-montmorillonite clays.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm⁻¹)</th>
<th>Ref.</th>
<th>Mode</th>
<th>Frequency (cm⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic H₂O</td>
<td>δ-3439(s), 3258(sh)</td>
<td>44,76</td>
<td>2Al-OH</td>
<td>δ-3630(m), δ-915(m)</td>
<td>44</td>
</tr>
<tr>
<td>Loosely Bound H₂O</td>
<td>1706(w)</td>
<td></td>
<td>1706(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-O-H deformation vibration</td>
<td>1643(m)</td>
<td>78</td>
<td>H-O-H deformation vibration</td>
<td>1643(m)</td>
<td>78</td>
</tr>
<tr>
<td>Hydrate H₂O</td>
<td>1368</td>
<td>77</td>
<td>Hydrate H₂O</td>
<td>1368</td>
<td>77</td>
</tr>
<tr>
<td>Si-O</td>
<td>1116(vs), v-1032(vs)</td>
<td>75,77</td>
<td>Si-O</td>
<td>1116(vs), v-1032(vs)</td>
<td>75,77</td>
</tr>
<tr>
<td>CaCO₃ (impurity)</td>
<td>1429(sh), δ-849(m), 879 (sh)</td>
<td>77</td>
<td>CaCO₃ (impurity)</td>
<td>1429(sh), δ-849(sh), 879(w)</td>
<td>77</td>
</tr>
<tr>
<td>Si-O quartz (impurity)</td>
<td>804(m)</td>
<td>77</td>
<td>Si-O quartz (impurity)</td>
<td>804(w)</td>
<td>77</td>
</tr>
<tr>
<td>Al-O</td>
<td>δ-629(w)</td>
<td>79</td>
<td>Al-O</td>
<td>δ-629(w)</td>
<td>79</td>
</tr>
<tr>
<td>Si-O-Mg</td>
<td>δ-525(vs)</td>
<td>79</td>
<td>Si-O-Mg</td>
<td>δ-525(vs)</td>
<td>79</td>
</tr>
<tr>
<td>Si-O-Fe</td>
<td>δ-468(vs)</td>
<td>79</td>
<td>Si-O-Fe</td>
<td>δ-468(vs)</td>
<td>79</td>
</tr>
</tbody>
</table>

(vs): very strong, (s): strong, (m): medium, (w): weak, (sh): shoulder
(v): bending, (δ): stretching
NA = Not available
Figure 64 FTIR spectra for Ca$^{2+}$-montmorillonite clays in KBr support.

Table 4 Observed vibrational assignments for Ca$^{2+}$-montmorillonite clays.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Ca-MMT (Texas)</th>
<th>Ca-MMT (Bentolite L$^\circ$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic H$_2$O</td>
<td>δ-3439(m)</td>
<td>δ-3439(m)</td>
<td></td>
<td>76,79</td>
</tr>
<tr>
<td>2Al-OH</td>
<td>δ-3627(m), δ-920(m)</td>
<td>δ-3627(m), δ-920(m)</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>Loosely bound H$_2$O</td>
<td>1699(w)</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-O-H deformation vibration</td>
<td>1638(m)</td>
<td>1638(m)</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>Hydrate H$_2$O</td>
<td>1368(m)</td>
<td>1368(m)</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>Si-O</td>
<td>v-1038(vs),1100(vs)</td>
<td>v-1038(vs),1100(vs)</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>Mg-Al-Fe-OH</td>
<td>δ-850(m)</td>
<td>δ-850(m)</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>Si-O quartz (impurity)</td>
<td>763</td>
<td>763</td>
<td></td>
<td>77</td>
</tr>
<tr>
<td>Al-O</td>
<td>629(w)</td>
<td>629(w)</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>Si-O-Mg</td>
<td>v-523(vs)</td>
<td>v-523(vs)</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>Si-O-Fe</td>
<td>v-468(vs)</td>
<td>v-468(vs)</td>
<td></td>
<td>79</td>
</tr>
</tbody>
</table>

(vs): very strong, (s): strong, (m): medium, (w): weak, (sh): shoulder
(v): bending, (δ): stretching
NA = Not Available
FT-IR spectra of synthetic fluorinated Na⁺-micas (YN6, YN8 and sodium trisilisic [Na-Ts]) showed the absence of bridging acidic OH groups in the 3000 cm⁻¹ region, mostly due to the fluorine presence in the mineral formation. Therefore, most of the vibration modes present were in the low frequency region. FTIR measurements were in accordance with S. Sharma et al.²¹ in which hydrated mica displayed a strong water deformation at 1636 cm⁻¹ and symmetric water stretching at 3453 cm⁻¹. Si-O-Al deformation band was found near 624 cm⁻¹, Si-O-Al bending along with Mg-OH at 698 cm⁻¹, Si-O-Al in plane at 794 cm⁻¹, and a band due to Si-O at 1101, 996 and 895 cm⁻¹. These values are summarized in Table 5.
Figure 65 FTIR spectra for three low charge synthetic micas (YN6, YN8 and Na-Ts) in KBr support.

Table 5 Observed vibrational assignments for three low charge fluorinated micas.

<table>
<thead>
<tr>
<th>Mode</th>
<th>YN6</th>
<th>YN8</th>
<th>Na-Ts</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic H₂O</td>
<td>δ-3453(w)</td>
<td>δ-3453(w)</td>
<td>δ-3453(w)</td>
<td>79</td>
</tr>
<tr>
<td>Loosely bound H₂O</td>
<td>1706(w)</td>
<td>1706(w)</td>
<td>NA</td>
<td>79</td>
</tr>
<tr>
<td>H-O-H</td>
<td>δ-1636(m)</td>
<td>δ-1636(m)</td>
<td>δ-1636(m)</td>
<td>79</td>
</tr>
<tr>
<td>Hydrated Water</td>
<td>1364(sh)</td>
<td>1364(sh)</td>
<td>NA</td>
<td>75</td>
</tr>
<tr>
<td>Si-O</td>
<td>v-1101(vs),996(vs),895(vs)</td>
<td>v-1101(vs),996(vs),895(vs)</td>
<td>v-1101(vs),996(vs),895(vs)</td>
<td>75</td>
</tr>
<tr>
<td>Si-O-Al</td>
<td>v-794(m)</td>
<td>v-794(m)</td>
<td>v-794(m), δ-753(sh)</td>
<td>79</td>
</tr>
<tr>
<td>Mg-OH</td>
<td>698(w)</td>
<td>698(w)</td>
<td>698(m)</td>
<td>79</td>
</tr>
<tr>
<td>Si-O-Al</td>
<td>v- 624(m)</td>
<td>v- 624(m)</td>
<td>v-621(m)</td>
<td>44</td>
</tr>
<tr>
<td>Si-O</td>
<td>474(vs)</td>
<td>474(vs)</td>
<td>474(vs)</td>
<td>79</td>
</tr>
</tbody>
</table>


NA: Not Available
**Synthetic Zeolites (LTA, FAU, and MOR)**

FTIR of synthetic zeolites revealed the presence of water by the $\delta$(OH) at 1635 cm$^{-1}$ and a broad band around 3400 cm$^{-1}$. The absence of $\nu$(OH) in the ~3660 and ~3550 cm$^{-1}$ range indicates the deficiency of hydroxyl groups in the supercage and sodalite cages, confirming the pure cation. However, the large amount of zeolitic water generally covers these vibrations only visible when heated or under prolonged vacuum.$^{80}$

Different cations were present in the zeolites evaluated, therefore some differences in 3400 region and 1400 cm$^{-1}$ were observed.
Figure 66 FTIR spectra of several faujasite sieves with different cations (KBr support): Valfor CP300-35 (H⁺-FAU), LZY-62 (NH₄⁺-FAU), NaY (Na⁺-FAU), 13X (Ca²⁺,Na⁺-FAU).

Table 6 Observed vibrational assignments for several faujasite synthetic zeolites.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm⁻¹)</th>
<th>NaY</th>
<th>Valfor CP300-35</th>
<th>LZY-62</th>
<th>13X</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic H₂O</td>
<td>δ-3441(s)</td>
<td>δ-3431(s)</td>
<td>δ-3441(s)</td>
<td>δ-3441(s)</td>
<td></td>
<td>79,</td>
</tr>
<tr>
<td>NH₄⁺*</td>
<td>NA</td>
<td>NA</td>
<td></td>
<td>1207(m),</td>
<td>1139(vs),</td>
<td>81,82</td>
</tr>
<tr>
<td>Loose bound H₂O</td>
<td>1705(w)</td>
<td>NA</td>
<td>1705(sh)</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-O-H vibration</td>
<td>δ-1643(m)</td>
<td>δ-1643(m)</td>
<td>δ-1643(m)</td>
<td>δ-1643(m)</td>
<td></td>
<td>76,78</td>
</tr>
<tr>
<td>Hydrate H₂O</td>
<td>NA</td>
<td>NA</td>
<td>1385</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asymmetrical stretch*</td>
<td>1139(vs), v-1006(vs)</td>
<td>1207(m), 1180<a href="sh">3</a>, 1075(vs)</td>
<td>1139(vs), v-1006(vs)</td>
<td>1139(vs), 1092(vs), 1010(vs)</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>Symmetrical stretch**</td>
<td>v-790(w)</td>
<td>v-790(w), 829(m)</td>
<td>v-790(w)</td>
<td>NA</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Symmetrical stretch*</td>
<td>713(w)</td>
<td>792<a href="sh">2</a>, 678<a href="sh">1</a></td>
<td>713(w)</td>
<td>674(w)</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Double ring**</td>
<td>575(w)</td>
<td>609(w)</td>
<td>575(w)</td>
<td>566(w)</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Tetrahedral cation -O bend*</td>
<td>506(sh), 462(m)</td>
<td>527(sh),462(m)</td>
<td>506(sh),462(m)</td>
<td>462(m)</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Pore opening**</td>
<td>385(w)</td>
<td>402(m)</td>
<td>385(w)</td>
<td>363(w)</td>
<td></td>
<td>83</td>
</tr>
</tbody>
</table>

(vs): very strong, (s): strong, (m): medium, (w): weak, (sh): shoulder
(ν): bending, (δ): stretching
NA: Not Available
*Internal tetrahedral
**External linkages
Figure 67 FTIR spectra of several mordenite synthetic zeolites with different cations (KBr support): Zeolon® (Na⁺-MOR), CBV21A (NH₄⁺-MOR), CBV10A (Na⁺-MOR).

Table 7 Observed vibrational assignments for mordenite synthetic zeolites.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Zeolon®</th>
<th>CBV21A</th>
<th>CBV10A</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supercages-OH</td>
<td>3617(sh)</td>
<td>NA</td>
<td>3617(sh)</td>
<td>83</td>
</tr>
<tr>
<td>Zeolitic H₂O</td>
<td>δ-3462(s)</td>
<td>δ-3462(s)</td>
<td>3-3462(s)</td>
<td>75</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>NA</td>
<td>δ-3150(sh), 1452(w), v-1402(m)</td>
<td>NA</td>
<td>81,82</td>
</tr>
<tr>
<td>Loosely bound H₂O</td>
<td>1711(w)</td>
<td>1711(w)</td>
<td>1711(w)</td>
<td>79</td>
</tr>
<tr>
<td>H-O-H vibration</td>
<td>1636(m)</td>
<td>1636(m)</td>
<td>1636(m)</td>
<td></td>
</tr>
<tr>
<td>hydrate H₂O</td>
<td>NA</td>
<td>1372(sh)</td>
<td>1372(sh)</td>
<td></td>
</tr>
<tr>
<td>Asymmetrical stretch*</td>
<td>1218(vs), v-1067(vs)</td>
<td>1218(vs), v-1084(vs)</td>
<td>1218(vs), v-1084(vs)</td>
<td>83</td>
</tr>
<tr>
<td>Symmetrical stretch**</td>
<td>908(w), 808(w), 750(m)</td>
<td>908(w), 808(w), 750(m)</td>
<td>908(w), 808(w), 750(m)</td>
<td>83</td>
</tr>
<tr>
<td>Double ring**</td>
<td>628(w), 582(w), 557(w)</td>
<td>628(w), 582(w), 557(w)</td>
<td>628(w), 582(w), 557(w)</td>
<td>83</td>
</tr>
<tr>
<td>Tetrahedral cation -O bend*</td>
<td>461(m), 422(sh)</td>
<td>461(m), 422(sh)</td>
<td>461(m), 422(sh)</td>
<td>83</td>
</tr>
</tbody>
</table>

(vs): very strong, (s): strong, (m): medium, (w): weak, (sh): shoulder
(v): bending, (δ): stretching
NA: Not Available
*Internal tetrahedral linkages
**External linkages
Figure 68 FTIR spectra of several LTA synthetic zeolites with different concentrations of sodium cation (KBr support): 4A (0.6 moles Na⁺-LTA), 5A (0.2 moles Na⁺-LTA).

Table 8 Observed vibrational assignments for LTA synthetic zeolites.

<table>
<thead>
<tr>
<th>Mode</th>
<th>4A</th>
<th>5A</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic H₂O</td>
<td>δ-3414(s)</td>
<td>δ-3414(s)</td>
<td>79,76</td>
</tr>
<tr>
<td>H-O-H deformation vibration</td>
<td>1633(m)</td>
<td>1633(m)</td>
<td>76</td>
</tr>
<tr>
<td>Hydrate H₂O</td>
<td>1366(sh)</td>
<td>1477(w), 1420(sh), 1362(sh)</td>
<td>78</td>
</tr>
<tr>
<td>Asymmetrical stretch*</td>
<td>ν-958(vs)</td>
<td>ν-1007(vs)</td>
<td>83</td>
</tr>
<tr>
<td>Symmetrical stretch*</td>
<td>665(w), 554(vs)</td>
<td>745(w), 709(w), 665(w), 554(vs)</td>
<td>83</td>
</tr>
<tr>
<td>Tetrahedral cation -O bend*</td>
<td>466(m)</td>
<td>466(m)</td>
<td>83</td>
</tr>
<tr>
<td>Pore opening*</td>
<td>377(m)</td>
<td>377(m)</td>
<td>83</td>
</tr>
</tbody>
</table>

(vs):very strong, (s):strong, (m):medium, (w):weak, (sh):shoulder
(v)bending, (δ)stretching  NA= Not Available
*Internal tetrahedral
** External linkages
4.4.2 Surface Acidity by Pyridine Adsorption

Pyridine (C₅H₅N) is a weak base used extensively in catalysis to evaluate the acidity of zeolites and clays. In this work the FTIR spectra of simulated pyridine was performed by Gaussian 3.0, and compared with reported data.

Figure 69 FTIR spectra of simulated pyridine by Gaussian 3.0.
Table 9 Fundamental frequencies (cm$^{-1}$) in pyridine.

<table>
<thead>
<tr>
<th>Vibration No.</th>
<th>Symmetry</th>
<th>Form of Vibration</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>$B_1$</td>
<td>$\nu$-C-H</td>
<td>3129(w)</td>
<td>87</td>
</tr>
<tr>
<td>14</td>
<td>$B_1$</td>
<td>$\nu$-C-H</td>
<td>3102(m)</td>
<td>85</td>
</tr>
<tr>
<td>2,13</td>
<td>$A_1$</td>
<td>$\nu$-C-H</td>
<td>3049(m)</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Overtones/combination</td>
<td>1700(m)</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Overtones/combination</td>
<td>1660(w)</td>
<td>87</td>
</tr>
<tr>
<td>8a</td>
<td>$A_1$</td>
<td>C-C, CCH</td>
<td>1600(m)</td>
<td>86</td>
</tr>
<tr>
<td>19b</td>
<td>$B_1$</td>
<td>C-C, CCH</td>
<td>1552(w)</td>
<td>86</td>
</tr>
<tr>
<td>14</td>
<td>$B_1$</td>
<td>$\nu$-C-C</td>
<td>1340(w)</td>
<td>86</td>
</tr>
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</tr>
<tr>
<td>1</td>
<td>$A_1$</td>
<td>C-H</td>
<td>971(vs)</td>
<td>86</td>
</tr>
<tr>
<td>10b</td>
<td>$B_2$</td>
<td>C-H</td>
<td>859(m)</td>
<td>86</td>
</tr>
<tr>
<td>11</td>
<td>$B_2$</td>
<td>C-H</td>
<td>692(w)</td>
<td>85</td>
</tr>
</tbody>
</table>

(vs): very strong, (s): strong, (m): medium, (w): weak, (sh): shoulder

($\nu$): bending, ($\delta$): stretching
**Palygorskite and Sepiolite**

FTIR spectra of pyridine adsorption at 413K revealed the presence of pyridine – Lewis Acid sites at 1447 cm\(^{-1}\) for palygorskite and 1445 cm\(^{-1}\) and 1596 cm\(^{-1}\) for sepiolite.

The origin of a Lewis acid in palygorskite (Si/Al = 5.68) could be primarily from extra-framework aluminum cations since the high concentration of potassium could not have any important effect due to its low acidity in comparison to aluminum.

![FTIR spectra comparison](image)

**Figure 70** FTIR comparison of palygorskite raw material [Palygorskite Raw] and pyridine adsorption on palygorskite [Paly-PY] (KBR support).
In the case of sepiolite, two vibration modes of pyridinium-Lewis acids sites were detected by FTIR spectroscopy. Sepiolite (Si/Al = 15) contained a high concentration of Ca$^{2+}$ to compensate the negative charge created by the aluminum substitution; therefore, the Lewis acid sites present in the FTIR spectra could be related to Ca$^{2+}$ or Al$^{3+}$ cations.

**Figure 71** FTIR comparison of sepiolite raw material [Sepiolite Raw] and pyridine adsorption on sepiolite [Sepio-PY] (KBR support).
Montomorillonite Clays

$\text{Ca}^{2+}$-MMT

FTIR of pyridine adsorption of both $\text{Ca}^{2+}$-MMT clays (Bentolite L® Si/Al = 4.08 and Texas deposit Si/Al = 3.52) revealed the presence of Brønsted and Lewis acid sites. Brønsted acid sites were assigned to the protons from the framework and Lewis acid sites to the extra-framework aluminum.

![FTIR comparison of bentolite raw material [Bentolite L® Raw] and pyridine adsorption on bentolite [Bentolite L® -PY] (KBR support).](image)

**Figure 72** FTIR comparison of bentolite raw material [Bentolite L® Raw] and pyridine adsorption on bentolite [Bentolite L® -PY] (KBR support).
Figure 73 FTIR comparison of Ca\(^{2+}\)-MMT raw material [Ca-MMT Raw] and pyridine adsorption on Ca\(^{2+}\)-MMT [Ca-MMT-PY] (KBR support).

**Na\(^{+}\)-MMT**

FTIR of pyridine adsorption of both Na\(^{+}\)-MMT clays (Wyoming deposit, Si/Al = 2.8 and Kunipia deposit, Si/Al = 2.4) revealed a small amount of Lewis acid sites in Wyoming deposit and no Lewis acid sites in Kunipia deposit. This could be explained by the WD-XRF cation concentration in the samples. Na\(^{+}\)-MMT (Wyoming deposit) presented almost an equal amount of calcium when compared to sodium, which could be responsible for the small bands corresponding to the Lewis acid sites. On the other hand, a larger concentration of sodium was detected in Na\(^{+}\)-MMT (Kunipia deposit).
where no Lewis acids were observed. The color changes observed in both samples under UV-Vs spectroscopy agreed with the poor withdrawing effect of the cations present in both samples, as observed in cation exchanged modernites.

Figure 74 FTIR comparison of Na⁺-MMT (Wyoming deposit) raw material [Na-MMT(W) Raw] and pyridine adsorption [Na-MMT(W) -PY] (KBR support).
Figure 75 FTIR comparison of Na⁺-MMT (Kunipia deposit) raw material [Na-MMT(K) Raw] and pyridine adsorption [Na-MMT(K) -PY] (KBR support).
**Synthetic zeolite, Faujasite (FAU)**

FTIR pyridine adsorption spectra for Valfor CP300-35 (H⁺-MOR) displayed a large amount of Brønsted and Lewis acids, in accordance with the acidic characteristic of this zeolite.

![FTIR comparison](image)

**Figure 76** FTIR comparison of Valfor CP300-35 (H⁺-MOR) raw material [Valfor CP300-35Raw] and pyridine adsorption [Valfor CP300-35-PY] (KBR support).
Synthetic Zeolite, Mordenite (MOR)

Three mordenites were evaluated by this method: CBV21A (NH$_4^+$ and Na$^+$-MOR) and zeolon® (Na$^+$-MOR).

FTIR spectra of CBV21A (NH$_4^+$-MOR) Si/Al = 9.5 revealed the presence of Brønsted acids by the pyridinium vibration at 681, 755, 1490, and 1546 cm$^{-1}$ in accordance to Serratosa et al.$^{89}$ The presence of these vibrations could be explained by the acidic character of NH$_4^+$ cation present in the zeolite, rather than OH vibrations present in the framework. The unshared pair of electrons of pyridine acted as Lewis base when in contact with the empty orbital of the acidic proton from NH$_4^+$, thus producing pyridinium.

$$C_5H_5N + NH_4^+ \rightarrow C_5H_5NH^+ + NH_3$$

The effect of the acidic proton was an important factor in the color change observed in thioindigo; however, due to a poor electronegative neighboring atom such as nitrogen, this proton was not as acidic and therefore could not withdraw electrons as strongly as, for example, other protons attach to an oxygen atom.
Figure 77 FTIR spectra of pyridine adsorption in CBV21A [NH$_4^+$-MOR] (KBr support).

On the other hand, FTIR pyridine adsorption spectra of the Na$^+$-MOR (cation exchanged form of CBV21A [NH$_4^+$-MOR]) revealed the absence of almost all the Brønsted acids previously seen in the NH$_4^+$-MOR. Thus, the previous hypothesis was confirmed in this experiment where the origin of the Brønsted acids in NH$_4^+$-MOR was related primarily to the acidic proton of NH$_4^+$ rather than the framework. The Lewis acid present in the framework could be related to some residual extraframework aluminum; however, due to the low concentration of aluminum (Si/Al = 9.5) this may not be enough to display a drastic color change.
Figure 78 FTIR spectra of pyridine adsorption in CBV21A [Na⁺-MOR] (KBr support).

FTIR spectra of Zeolon® (Na⁺-MOR) with a Si/Al = 7.31 revealed a large concentration of Brønsted acids in the framework. The large aluminum substitution in the framework correlates with these findings, where sodium cations and Brønsted acids neutralized this imbalance charge; however, due to the large amount of sodium, color change is only purple instead of blue, which would be the case when a high concentration of protons were available.
**Figure 79** FTIR spectra of pyridine adsorption in Zeolon® (Na⁺-MOR) with KBr support.
4.4.3 Inorganic Host Materials Treated with Thioindigo

Palygorskite - Thioindigo Interaction

Palygorskite interaction with thioindigo unheated revealed the carbonyl vibration mode at 1655 cm\(^{-1}\) in agreement with thioindigo C=O vibration reported by Tatsch et al.\(^90\) However, a downshift of this vibration mode to 1628 cm\(^{-1}\) was observed when the sample was heated at 413K for nine hours. This could be tentatively assigned to C=O stretching mode of thioindigo, with a possible downshifting from 1656 cm\(^{-1}\), due to dye-clay interaction. This behavior has also been detected in indigo/palygorskite mixtures.\(^91\)

The origin of the vibration mode at 1697 cm\(^{-1}\) in Figure 80 was not well understood, mostly because sometimes it would not disappear even under heating conditions. Therefore a change of support from KBr to mineral oil was pursued. FTIR spectra showed the absence of this vibration mode when the sample was immersed in mineral oil. Hence, this vibration mode could be related to the hygroscopic KBr support, nevertheless KBr water vibration mode was at 1638 cm\(^{-1}\). The higher frequency of the water vibration could be correlated to the clay loosely bound water from the KBr support. The use of mineral oil avoided this misleading vibration mode, and also was able to capture the mixtures in their highest excitation state, as shown later in this section.
Figure 80 FTIR spectra of palygorskite raw material, thioindigo raw material, 0.5 mol % thioindigo/palygorskite mixture heated (paly+dye H), and unheated (paly+dye UN). All of the above mentioned samples mixed with KBr as support.
Figure 81 FTIR spectra of palygorskite raw material, thioindigo raw material, 0.5 mol % thioindigo/palygorskite mixture heated [paly+dye D (blue)], unheated [paly+dye UN (pink)] and vacuum [paly+dye UN vacuum (purple)]. Mineral oil as support.
**Sepiolite - Thioindigo Interaction**

In the case of sepiolite, 0.5 mol % thioindigo/sepiolite heated at 413K for nine hours displayed a magenta color at 1625 cm\(^{-1}\) vibration mode related to C=O-LAS, this peak was also assigned to the downshift of thioindigo free C=O at 1655 cm\(^{-1}\). The disappearance of the 1655, 3270, and 3411 cm\(^{-1}\) water vibration modes of sepiolite related this interaction to the direct binding to LAS in the absence of water. Moreover, the downshift of the structural water (Mg-OH\(_2\)) from 3566 to 3543 cm\(^{-1}\) and hydroxyl groups (Mg-OH) from 3686 to 3677 cm\(^{-1}\), could be an indicative of a less interaction of these sites with the zeolitic water. This displacement was also observed by E. Mendelovici\(^92\) where the 3590 cm\(^{-1}\) peak shifted to 3570 cm\(^{-1}\) on heating. Moreover, this hypothesis is confirmed in Figure 82, where the heated mixture was left to hydrate outside the desiccator (deep purple color), displaying the shift of 3000 cm\(^{-1}\) region peaks to their original positions, additionally the 1625 cm\(^{-1}\) vibration mode was shifted back slightly to higher frequencies at 1631 cm\(^{-1}\). These changes could be related to the less interaction of thioindigo C=O with the active sites due to the hydration of the site C=O---H(OH)-LAS).
Figure 82 FTIR spectra of sepiolite raw material, thioindigo raw material, 0.5 mol % thioindigo/sepiolite mixture heated (sepio+dye D magenta) unheated (sepio+dye UN pink) and heated mixture hydrated (sepio+dye D purple). Mineral oil as support.
Ca$^{2+}$-MMT – Thioindigo Interaction

The FT-IR spectra of Ca$^{2+}$-MMT (Bentolite L® and Texas deposit) mixed with 0.5 mol % thioindigo and heated at 413K for nine hours shows no free C=O peak at 1655 cm$^{-1}$, and a C=O--LAS in 1632 cm$^{-1}$. This behavior is similar to palygorskite/thioindigo mixtures when heated or exposed to vacuum. Solids exposed to lower pressure exhibited water removal from the Lewis active sites (LAS), leaving direct interaction of the carbonyl group to the LAS. However, the blue color observed was not stable when exposed to moisture from the air (desiccator samples displayed no color change). Besides the open layer structure typical of montmorillonite clays, the susceptibility of Ca$^{2+}$ cation to hydration due to its characteristic high hydration energy ($\Delta H_{\text{hyd}} = -1592$ KJ/mol) were two important factors in the instability of the color.
Figure 83 FTIR spectra of bentolite L\textsuperscript{®} raw material, thioindigo raw material, 0.5 mol % thioindigo/bentolite L\textsuperscript{®} mixture heated (bentolite L + dye D blue) and unheated (bentolite L+dye UN purple). Mineral oil as support.
Figure 84 FTIR spectra of Ca-MMT (Texas deposit) raw material, thioindigo raw material, 0.5 mol % thioindigo/ Ca-MMT mixture heated (Ca-MMT + dye D blue) and unheated (Ca-MMT+dye UN purple). Mineral oil as support.
**Na⁺-MMT- Thioindigo Interaction**

For Na-MMT samples (Wyoming and Kunipia deposits), the FT-IR spectra shows a weak free C=O peak at 1655 cm⁻¹ and no water vibration at 1638 cm⁻¹.

![FTIR spectra](image)

**Figure 85** FTIR spectra of Na⁺-MMT (Wyoming deposit) raw material, thioindigo raw material, 0.5 mol % thioindigo/ Na⁺-MMT mixture heated (Na-MMT + dye D purple) and unheated (Na-MMT+dye UN purple). Mineral oil as support.
Figure 86 FTIR spectra of Na-MMT (Kunipia deposit) raw material, thioindigo raw material, 0.5 mol % thioindigo/ Na-MMT mixture heated (Na-MMT +dye D purple) and unheated (Na-MMT+dye UN purple). Mineral oil as support.
FTIR spectra of NaY (Si/Al = 2.5) revealed the displacement of C=O (1655 cm⁻¹) vibration mode to lower frequencies when 0.5 mol % thioindigo / zeolite unheated (NaY+dye UN pink) was exposed to thermal treatment at 413K for nine hours (NaY+dye D purple). Re-appearance of free C=O at 1655 cm⁻¹ was detected when NaY+dye D purple was left to rehydrate (data not shown in Figure 87).
As mentioned before, no Brønsted or Lewis acids were reported in zeolite NaY; therefore, color change from pink to purple of thioindigo-NaY mixture is considered to take place through sodium (a weak Lewis acid) interaction with carbonyl group (C=O---Na⁺). The high aluminum substitution (Si/Al = 2.5) indicated a large amount of sodium to compensate the negative charge in the framework; therefore, this zeolite had poor stability when exposed to moisture due to the high hydration energy of sodium ion (ΔH_{hyd} = -405 KJ/mol). A similar effect was noticed by Yoon et al. with immobilized complexes inside NaY zeolite and moisture exposure.

**Valfor CP300-35 (H⁺-FAU) - Thioindigo Interaction**

Pyridine adsorption revealed a high concentration of Brønsted and small amount of Lewis acids in the zeolite (see Figure 76); moreover, the downshift of thioindigo C=O to 1643 cm⁻¹ could indicate a possible interaction (C=O---H⁺), mainly due to the strong acidity of hydrogen ion. High aluminum substitution (Si/Al = 4.00) indicated a large amount of protons to compensate the negative charge in the framework; therefore, this zeolite had poor stability when exposed to moisture due to the high hydration energy of hydrogen ion. A similar effect was noticed by Yoon et al. with immobilized complexes inside NaY zeolite and moisture exposure.
Figure 88 FTIR spectra of Valfor CP300-35 raw material, thioindigo raw material, 0.5 mol % thioindigo/Valfor mixture heated (Valfor +dye D purple), and hydrated (Valfor +dye UN pink). Mineral oil as support.
Na⁺- MOR (Zeolon®) – Thioindigo Interaction

FTIR spectra of zeolon® revealed no disturbance in thioindigo C=O vibration mode at 1655 cm⁻¹. The band at 3631 cm⁻¹ corresponding to stretching OH mode showed a slight displacement to higher frequencies related to the removal of zeolitic water, since rehydration reversed this shift.
Figure 89 FTIR spectra of Zeolon® raw material, thioindigo raw material, 0.5 mol % thioindigo/Zeolon® mixture heated (Zeolon® + dye D purple), and hydrated (Zeolon® + dye UN pink). Mineral oil as support.
4.4.4 Cation Exchange Zeolite Treated with Thioindigo

FTIR spectra of exchanged mordenite (CBV21A) revealed a carbonyl shift to higher frequencies when heated. Water stretching vibration mode corresponding to zeolitic water, was observed to disappear after heat treatment. Moreover, a downshift of the bending water vibration mode at 1630 cm\(^{-1}\) was also observed. This behavior has been previously observed by Mendelovici et al.\(^{92}\)
Figure 90 FTIR spectra of starting materials thioindigo and K⁺-MOR (21AK Raw) and 0.5 mol % thioindigo mixture with K⁺-MOR heated at 413K for nine hours (21AK+dye dehydrated) and unheated (21AK+dye Unheated) with Mineral Oil as support.
Figure 91 FTIR spectra of starting materials thioindigo and Ca$^{2+}$-MOR (21ACa Raw) and 0.5 mol % thioindigo mixture with Ca$^{2+}$-MOR heated at 413K for nine hours (21ACa+dye dehydrated) and unheated (21ACa+dye unheated) with Mineral Oil as support.
Figure 92 FTIR spectra of starting materials thioindigo and Na⁺-MOR (21ANa Raw) and 0.5 mol % thioindigo mixture with Na²⁺-MOR heated at 413K for nine hours (21ANa+dye dehydrated) and unheated (21ANa+dye unheated) with Mineral Oil as support.
**Figure 93** FTIR spectra of starting materials thioindigo and NH$_4^+$-MOR (21ANH4 Raw) and 0.5 mol % thioindigo mixture with NH$_4^+$-MOR heated at 413K for nine hours (21ANH4+dye dehydrated) and unheated (21ANH4+dye unheated) with Mineral Oil as support.
Figure 94 FTIR spectra of starting materials thioindigo and Al$^{3+}$-MOR (21AAl Raw) and 0.5 mol % thioindigo mixture with Al$^{3+}$-MOR heated at 413K for nine hours (21AAl+dye dehydrated) and unheated (21AAl+dye unheated) with Mineral Oil as support.
Figure 95 FTIR spectra of starting materials thioindigo and H⁺-MOR (21AH Raw) and 0.5 mol % thioindigo mixture with H⁺-MOR heated at 413K for nine hours (21AH+dye dehydrated) and unheated (21AH+dye unheated) with Mineral Oil as support.
4.5 Structural Analysis by X-ray Powder Diffraction

4.5.1 Thioindigo

X-ray powder diffraction of thioindigo was in agreement with the simulated triclinic unit cell, space group \(P\bar{1}\), investigated by H. von Eller\textsuperscript{94} and built with Materials Studio v4.0 software. Thioindigo experimental reflections were slightly off the simulated structure. Lattice parameters adjustment should be performed in order to fit the simulated structure better to the experimental values.

Figure 96 XRD pattern comparison of (a) thioindigo raw material, (b) thioindigo - triclinic simulated by Materials Studio v4.0 software.
4.5.2 Inorganic Host Materials

Palygorskite and Sepiolite

Palygorskite crystallizes in a mixture of two polymorphs (orthorhombic and monoclinic unit cell), confirmed by the reflections of its diffraction pattern. Moreover, trigonal \( \alpha \)-quartz was identified as an impurity. In the case of sepiolite, a monoclinic unit cell was identified. Impurities such as trigonal calcite and \( \alpha \)-quartz were observed. These impurities were confirmed by FTIR. (see Figure 61).

![XRD pattern comparison](image)

**Figure 97** XRD pattern comparison of (a) palygorskite raw material, (b) palygorskite-orthorhombic (c) palygorskite -monoclinic and (d) \( \alpha \)-quartz-trigonal. [Simulation of palygorskite and quartz unit cells by Cerius² accelrys software].
Figure 98 XRD pattern comparison of (a) sepiolite raw material, (b) α-quartz-trigonal, (c) calcite-trigonal, (d) sepiolite - monoclinic. [Simulation of sepiolite, quartz and calcite unit cells by Materials Studio v4.0 software].
Montmorillonite clays belong to the smectite group, which are characteristic of low framework charge and expandable or swelling layers. X-ray powder diffraction of these clays was of poor quality and reflections other than the basal were diffused. The basal reflection 001, corresponding to the most intense band, was identified in the four montmorillonite clays tested; however, d spacing values for this reflection was slightly higher for Ca-MMT than for Na-MMT. This behavior is probably in relation to the degree of hydration of the interlayer cations. Sodium with a $\Delta H_{\text{hyd}} = -405 \text{ KJ/mol}$ and a large ionic radius ($r = 0.1 \text{ nm}$) generally requires one molecule of water to hydrate; calcium ($\Delta H_{\text{hyd}} = -1592 \text{ KJ/mol}$), with a smaller ionic radius ($r = 0.05 \text{ nm}$), requires two water molecules to hydrate. Consequently, Ca$^{2+}$-MMT would display larger d spacing values than Na$^{+}$-MMT. This behavior was observed in the samples tested as shown in Table 10. In the case of Wyoming deposit and based on the chemical analysis (appendix A) the larger d spacing value, when compared with Kunipia deposit, could be related to an equal amount of calcium in the interlayer. Therefore, Wyoming deposit could be considered a Na$^{+}$, Ca$^{2+}$-MMT clay.

Table 10 D spacing values for the studied montmorillonite clays.

<table>
<thead>
<tr>
<th>SPECIMEN:</th>
<th>Ca$^{2+}$-MMT</th>
<th>Na$^{+}$,Ca$^{2+}$-MMT</th>
<th>Na$^{+}$-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bentolite L®</td>
<td>Texas deposit</td>
<td>Wyoming deposit</td>
</tr>
<tr>
<td>Na moles*</td>
<td>-</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>Ca moles*</td>
<td>0.027</td>
<td>0.027</td>
<td>1.19</td>
</tr>
<tr>
<td>d spacing (Å)</td>
<td>13.3</td>
<td>13.6</td>
<td>11.1</td>
</tr>
</tbody>
</table>

*Values calculated from XRF measurements, appendix A.
Consistent with J. Thorez et al.\textsuperscript{95}, other reflections also observed in these montmorillonite clays were 8.5 Å (002), 5.7 Å (003), 4.2 Å (004), and 3.4 Å (005), as seen in Figure 99. However, some discrepancies were found for the 003 reflection which, in some references, has been reported to appear around 4.0 Å.\textsuperscript{21} Moreover, some impurities were identified in all samples such as \(\alpha\)-quartz, calcite and mica\textsuperscript{95}. In the case of Kunipia deposit, no mica was identified; however, calcite and quartz were determined by FTIR, perhaps the levels were lower than 5% (XRD detection limit), and thus could not be detected by XRD.

The dioctahedral and trioctahedral character of montmorillonite clays is easily observed by the reflection 1.57 Å (060). Unfortunately, the experiments were only measured up to 50 degrees in the two theta scale; however, using FTIR, this characteristic could be confirmed.
Figure 99 Powder X-ray diffraction pattern of (a) Na⁺-MMT (Kunipia deposit) raw material, (b) Na⁺-MMT (Wyoming deposit) raw material, (c) Ca²⁺-MMT (Texas deposit) raw material, and (d) Ca²⁺-MMT (bentonite L®).
**Low Charge Synthetic Swelling Clays (Mica group)**

X-ray powder diffraction for swelling Na⁺ micas (YN6, YN8 and Sodium Trisilisic [Na-Ts]) displayed a strong symmetrical 001 reflection with d spacing values around 11 and 12.5 Å (as shown in Figure 100). These values were higher than the ones usually found in non-swelling natural micas (10 Å). The larger d-spacing was related to the introduction of a sodium cation instead of the potassium usually found in natural micas framework. Table 11 shows a comparison between concentration of ions and d-spacing of the Na⁺-Micas tested. D-spacing values are in agreement for YN6 and YN8, where at larger concentration of sodium, more displacement was observed. However, in the case of Na-Ts this effect was not observed.

A small 002 reflection was found in YN6 but not in YN8 and Na-Ts; this reflection is related to the dioctahedral character of the structure,⁹⁵ i.e. the substitution of trivalent atom in the octahedral sites. The absence of this reflection therefore is indicative of the trioctahedral character. This is also in agreement with the infrared spectrum of these samples (see Figure 65).

**Table 11** d spacing values for the studied mica clays.

<table>
<thead>
<tr>
<th>SPECIMEN: Na⁺-Mica</th>
<th>YN6</th>
<th>NaTs</th>
<th>YN8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na moles*</td>
<td>0.125</td>
<td>0.225</td>
<td>0.5</td>
</tr>
<tr>
<td>d spacing (Å)</td>
<td>12.3</td>
<td>11.6</td>
<td>12.5</td>
</tr>
</tbody>
</table>

* Values calculated from XRF measurements, appendix A.
Figure 100 Powder X-ray diffraction pattern of (a) YN6 raw material, (b) YN8 raw material, and (c) Sodium Trisilic (Na-Ts) raw material.
Neutral Synthetic Talc

X-ray diffraction of Talc was identified by the index reflections reported by J. Thorez.\textsuperscript{95} None of the crystallographic data available in the Inorganic Crystal Structure Database (ICSD) or Materials Studio v4.0 software gave a close match to these reflections.

\textbf{Figure 101} Powder X-ray diffraction pattern of Talc raw material.
Synthetic Zeolites (LTA, FAU and MOR)

Linde Type A (LTA)

X-ray powder diffraction of Linde Type A synthetic zeolites corresponded to a cubic unit cell and space group $F\ 4/m\ -3\ 2/c$. This crystal structure was in agreement with the LTA framework identified and available in Materials Studio v4.0 software.

Figure 102 Powder X-ray diffraction pattern of (a) [Na⁺-LTA] 4A Raw material, (b) [Na⁺-LTA] 5A Raw material (c) LTA framework by Materials Studio v4.0 software.
**Faujasite (FAU)**

X-ray powder diffraction of faujasite synthetic zeolites corresponded to a cubic unit cell and space group $F2/D -3$. This crystal structure was in agreement with the faujasite framework measured and available in Materials Studio v4.0 software. Slight displacement of d-spacing values was observed for $H^+$-FAU. This could be due to the proton present in the structure. The new cell parameters were not measured.

![Figure 103](image)

**Figure 103** Powder X-ray diffraction pattern of (a) $[H^+\text{-FAU}]$ Vallfor CP300-35© Raw material, (b) $[Na^+\text{-FAU}]$ NaY Raw material (c) $[NH_4^+\text{-FAU}]$ LZY-62 Raw material, (d) $[Na^+,Ca^{2+}\text{-FAU}]$ 13X Raw material and (e) FAU framework by Materials Studio v4.0 software.
**Mordenite (MOR)**

X-ray powder diffraction of mordenite synthetic zeolites corresponded to an orthorhombic unit cell and space group $C 2/m 2/c 21/m$. This crystal structure was in agreement with the mordenite framework measured and available in Materials Studio v4.0 software.

![Powder X-ray diffraction pattern](image)

**Figure 104** Powder X-ray diffraction pattern of (a) $[\text{Na}^+\text{-MOR}]$ CBV10A Raw material, (b) $[\text{NH}_4^+\text{-MOR}]$ CBV21A Raw material (c) $[\text{Na}^+\text{-MOR}]$ Zeolon® Raw material and (e) MOR framework by Materials Studio v4.0 software. (Calcite-standard).
Mesoporous Zeolites

X-ray powder diffraction of three mesoporous zeolites (MA-1, MAS-1 and MS-1) displayed broad and diffuse reflections indicative of a poorly crystalline structure, characteristic of sol-gel products before exposed to higher temperatures.

Figure 105 Powder X-ray diffraction pattern of (a) MS-1 Raw material, (b) MA-1 Raw material (c) MAS-1 Raw material.
4.5.3 Thermally Treated Inorganic Host Materials

**CBV21A (NH$_4^+$-MOR)**

The procedure to prepare H$^+$-MOR requested the calcination of NH$_4^+$-MOR at 873K for three hours. An X-ray diffraction pattern of the calcined sample was performed in order to corroborate no changes in the crystal structure. The X-ray powder diffraction of the H$^+$-MOR displayed no major structural changes as shown in Figure 106.

![Figure 106](image.png)

**Figure 106** Powder X-ray diffraction pattern of (a) [NH$_4^+$-MOR] CBV21A Raw material, (b) [H$^+$-MOR] CBV21A (c) MOR framework by Materials Studio v4.0 software.
After thermal treatment at 1223K for sixteen hours zeolon® lost partially its crystal arrangement displayed by a broad diffuse peak. Only two reflection bands were resistant to this treatment.

Figure 107 Powder X-ray diffraction pattern of (a) Zeolon® 1223K 16h, (b) Zeolon® Raw material.
**Palygorskite**

Disappearance of the 001 reflection corresponding to the pore channel of palygorskite structure was observed to disappear after thermal treatment at 833K for sixteen hours. This experiment was also performed with in-situ thermal X-ray powder diffraction by D. Williams,\textsuperscript{74} where the reduction of the peak was monitored with time and temperature.

![Figure 108: Powder X-ray diffraction pattern of (a) Palygorskite heated at 823K for sixteen hours. (b) Palygorskite raw material (c) trigonal $\alpha$-Quartz simulated by Materials Studio v4.0. software.](image-url)
4.5.4 Inorganic Host Materials Treated with Thioindigo

**Palygorskite and Sepiolite**

Mixtures of palygorskite and sepiolite with 0.5 mol % thioindigo displayed almost no thioindigo reflection bands in the unheated mixture and none in the heated sample or dehydrated at 413K for nine hours.

![Figure 109 X-ray powder diffraction of (a) palygorskite + dye dehydrated [blue], (b) palygorskite + dye unheated [magenta], (c) palygorskite raw material and (d) thioindigo raw material.](image)

**Figure 109** X-ray powder diffraction of (a) palygorskite + dye dehydrated [blue], (b) palygorskite + dye unheated [magenta], (c) palygorskite raw material and (d) thioindigo raw material.
Figure 110 X-ray powder diffraction of (a) sepiolite + dye dehydrated [purple], (b) sepiolite + dye unheated [magenta], (c) sepiolite raw material and (d) thioindigo raw material.
As mentioned in chapter 4.1, mixtures with 0.5 % mol thioindigo presented color changes when exposed to different levels of humidity. This behavior was also confirmed by the displacement to higher d-spacing values in the hydrated samples, and to lower d-spacing values for dehydrated samples. Moreover, purple samples indicative of a dehydrated state showed similar or less d-spacing values when compared to the raw material. The intercalation of thioindigo in the interlayer of the clays could be a feasible option based on the thioindigo molecules size (15.17 Å (length), 7.42 Å (width) and 3.4 Å (thickness)\textsuperscript{32} and the clay interlayer dimensions (10 Å when dehydrated\textsuperscript{61}). The displacement of d-spacing values and color changes in the layer materials could be an indication of a possible horizontal intercalation of the thioindigo molecules in the interlayer of the clays, therefore originating zero d-spacing changes when in contact with each other. This effect has also been observed for indigo carmine inserted in layer double hydroxides.\textsuperscript{97}
Figure 11. Powder X-ray diffraction pattern of (a) thioindigo, (b) bentolite L\textsuperscript{®} + dye dehydrated [purple], (c) [Ca\textsuperscript{2+}-MMT] bentolite L\textsuperscript{®} raw material, and (d) bentolite L\textsuperscript{®} + dye hydrated [red].

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Figure 112 Powder X-ray diffraction pattern of (a) thioindigo, (b) Ca$^{2+}$-MMT + dye dehydrated [purple], (c) Ca$^{2+}$-MMT (Texas) raw material, and (d) Ca$^{2+}$-MMT + dye hydrated [red].
Figure 113 Powder X-ray diffraction pattern of (a) thioindigo, (b) Na⁺-MMT + dye dehydrated [purple], (c) Na⁺-MMT (Wyoming) raw material, and (d) Na⁺-MMT + dye hydrated [red].
Figure 114 Powder X-ray diffraction pattern of (a) thioindigo, (b) Na\(^+\)-MMT + dye dehydrated [purple], (c) Na\(^+\)-MMT + dye hydrated [red], (d) Na\(^+\)-MMT (Kunipia) raw material.
Low Charge Synthetic Swelling Clays (Mica group)-Thioindigo Interaction

X-ray powder diffraction of YN6 and YN8 displayed no change in the basal reflection (001) when thioindigo was incorporated in the mixture; moreover, thioindigo main reflections were still present after thermal treatment at 413K for nine hours. This could indicate a zero intercalation in the interlayer of the Na-Mica.

Figure 115 Powder X-ray diffraction pattern of (a) thioindigo, (b) YN8 +dye dehydrated [pink] and (c) [Na⁺-LTA] YN8 raw material.
Figure 116 Powder X-ray diffraction pattern of (a) thioindigo, (b) YN6 +dye dehydrated [pink] and (c) [Na⁺-Mica] YN6 raw material.
4.6 Chemical Analysis by Energy Dispersive Analysis (EDAX)

*Cation Exchange of Mordenite*

The cation exchange in CBV21A-NH$_4^+$ was carried out and confirmed by Energy Dispersive X-Ray Analysis.

Energy Dispersive X-Ray Analysis showed the presence of the cations exchange in the solution. In some cases, the temperature had an effect in the concentration of silicon of the zeolite, lowering the Si/Al ratio.

**Table 12** Summary of Chemical Analysis for CBV21A exchanged with different cations by EDAX.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>wt. %</th>
<th>Si/Al</th>
<th>Si/Al XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV21A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>40.05</td>
<td>5.11</td>
<td>47.3</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>39.41</td>
<td>5.18</td>
<td>52.47</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>42.62</td>
<td>4.78</td>
<td>47.43</td>
</tr>
<tr>
<td>$^*$NH$_4^+$</td>
<td>40.59</td>
<td>5.21</td>
<td>54.2</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>40.23</td>
<td>7.36</td>
<td>52.41</td>
</tr>
<tr>
<td>H$^+$</td>
<td>44.16</td>
<td>5.33</td>
<td>50.51</td>
</tr>
</tbody>
</table>

* As received from Zeolyst International
Figure 117 Sodium cation exchanged in Na$^+$-MOR.
**Figure 118** Calcium cation exchange for Ca\(^{2+}\) [MOR].

**Figure 119** Potassium cation exchanged in K\(^+\)-MOR.
Figure 120 Aluminum cation exchanged in $\text{Al}^{3+}$-MOR.

Figure 121 Hydrogen cation exchanged in $\text{H}^+$-MOR.
4.7 Magic Angle Nuclear Magnetic Resonance

Palygorskite and sepiolite

$^{27}\text{Al}$ NMR spectra for untreated palygorskite revealed two main resonances at 3.92 ppm (100% peak area) and 66.6 ppm (9.5% peak area) representing octahedral and tetrahedral Al respectively. This is consistent with previous results of Al coordination in palygorskites.$^{67}$

On the other hand, untreated sepiolite showed two main resonances at 54.67 ppm (100% peak area) and 3.43 ppm (30.8% peak area) for tetrahedral and octahedral Al, respectively. This is in agreement with previous results of Al coordination in sepiolites.$^{87}$

Figure 122 $^{27}\text{Al}$ magic angle spinning-nuclear magnetic resonance of (a) palygorskite and (b) sepiolite.
Montmorillonite Clays

Ca$^{2+}$-MMT (Bentolite L $^\circledR$) showed two main resonances at -0.63 ppm (100% peak area) and 52.2 ppm (9.75 % peak area) representing octahedral and tetrahedral Al, respectively (see Figure 123[a]). In the case of Ca$^{2+}$-MMT (Texas deposit) two main resonances at 0.90 ppm (100% peak area) and 53.1 ppm (9.56 % peak area) representing octahedral and tetrahedral Al were observed (see Figure 123[b]). This is in accordance with previous results of Al coordination in Ca$^{2+}$-MMT.$^{98}$

Figure 123 $^{27}$Al magic angle spinning-nuclear magnetic resonance of (a) Ca$^{2+}$-MMT (Bentolite L $^\circledR$) and (b) Ca$^{2+}$-MMT (Texas deposit).
Na⁺-MMT (Kunipia deposit) showed two main resonances at 1.08 ppm (100% peak area) and 68.5 ppm (7.74% peak area) representing octahedral and tetrahedral Al, respectively (see Figure 124[a]). In the case of Na⁺-MMT (Wyoming deposit) two main resonances at -0.14 ppm (100% peak area) and 58.5 ppm (9.75% peak area) representing octahedral and tetrahedral Al were observed (see Figure 124[b]). This is consistent with previous results of Al coordination in Na⁺-MMT.99

Figure 124 $^{27}$Al magic angle spinning-nuclear magnetic resonance of (a) Na⁺-MMT (Kunipia deposit) and (b) Na⁺-MMT (Wyoming deposit).
Table 13 NMR resonances of several natural occurring clay minerals.

<table>
<thead>
<tr>
<th>Clay Mineral</th>
<th>Octahedral</th>
<th>Tetrahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palygorskite</td>
<td>100</td>
<td>9.5</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>30.8</td>
<td>100</td>
</tr>
<tr>
<td>CaMMT (Bentonite L®)</td>
<td>100</td>
<td>9.8</td>
</tr>
<tr>
<td>CaMMT (Texas)</td>
<td>100</td>
<td>9.6</td>
</tr>
<tr>
<td>NaMMT (Wyoming)</td>
<td>100</td>
<td>27.3</td>
</tr>
<tr>
<td>NaMMT (Kunipia)</td>
<td>100</td>
<td>7.8</td>
</tr>
</tbody>
</table>

**Palygorskite-Thioindigo Interaction**

In this analysis two concentrations of thioindigo were studied: 0.5 mol % and 1 mol % thioindigo.

In the case of palygorskite / 1 mol % thioindigo after thermal treatment at 413K, slight changes in the peak areas of the tetrahedrally coordinated Al resonance were observed. However, more evident change with 0.5 mol % dye content was noted, as can be seen in Figure 125. Since the amount of tetrahedrally coordinated Al is very low in palygorskite, it is difficult to conclude any changes to the tetrahedral coordination of Al in the dye treated palygorskite samples. The accuracy of NMR measurements in the presence of metal atoms such as iron, is known to be reduced by its magnetic properties and therefore a lack of resolution in the spectra was observed.
Figure 125 $^{27}$Al magic angle spinning-nuclear magnetic resonance of (a) palygorskite from MinTech; (b) palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours; (c) palygorskite/1 mol %thioindigo heated at 413K for nine hours.

**Sepiolite-Thioindigo**

After treatment with thioindigo dye at 413K, the peak areas of octahedrally coordinated Al resonance increased with an increase in dye content as can be seen in Figure 126. The peak areas of octahedrally coordinated Al are 30.8, 43.6 and 62.9 in untreated sepiolite, sepiolite treated with 0.5 mol % thioindigo and sepiolite treated with 1 mol % thioindigo, respectively. Thus it appears that the dye changes the coordination of some tetrahedral Al to octahedral Al.
In order to prove these coordination changes were due to thioindigo addition, and no other factors, samples before heating were tested. A significant change was observed with and without heating as seen in Figure 127. This process is most likely to be unlinked to the organic additive.
Figure 127 $^{27}$Al magic angle spinning-nuclear magnetic resonance of (a) sepiolite (Pansil) from Tolsa; (b) Sepiolite dehydrated at 413K for nine hours
4.8 DFT Method for Calculation of Optical Spectra

The interaction of thioindigo with ammonium and hydrogen exchanged cations in an aluminum silicate framework was performed by MS (Materials Studio) modeling software. Two non-periodic superstructure fragments of an aluminum silicate tetrahedral framework with different cations substituted were modeled and optimized representing the active sites in the zeolite cavity. One thioindigo molecule was then located close to the two framework fragments, with two cations sites in the structure. The final interaction was again optimized and the optical spectra calculated with a semiempirical molecular orbital application called VAMP.\textsuperscript{100} VAMP application was carried out with a Hamiltonian of neglect of diatomic differential overlap (NDDO) for best results.

\textsuperscript{NH}_4^+ \text{ zeolite / thioindigo simulated interaction displayed a bathochromic shift under UV-Vis spectroscopy similar to the experimental values. Similar bathochromic shift was also observed with hydrogen cation. This simulation confirmed the effect of the cations in the electron withdrawing from thioindigo molecules when exposed to an acidic framework. However, the broadness of the peak was not as precise and more work in this area should be performed in other to acquire closer fittings to the experimental values and the rest of the cations tested in this research.
Figure 128 Ammonium cation interaction with one thioindigo molecule.

Figure 129 UV-Vis spectra simulated and experimental for 0.5 mol % thioindigo in $\text{NH}_4^+$-MOR.
Figure 130 Hydrogen interaction with one thioindigo molecule.

Figure 131 UV-Vis spectra simulated and experimental for 0.5 mol % thioindigo in H⁺-MOR.
A reversible thioindigo excited state was obtained when immersed in some inorganic host materials after thermal treatment and upon moisture uptake. This excited state is related to a charge transfer of electron donor-acceptor complexes taking place with thioindigo C=O groups and Lewis acid sites (LAS). These acid sites were available in the materials tested. Charge transfer interactions (C=O---LAS) were confirmed by the increment in absorbance in most samples after thermal treatment or prolonged evacuation. Moreover, FTIR thioindigo C=O perturbation due to LAS polarizing effect was also observed. Similar complexes have been observed in dimmers of chlorophyll C=O group and magnesium metal.\textsuperscript{101}

In general, there were three different LAS available depending on the nature of the inorganic host: (a) Proton acids, (b) Exchangeable cations\textsuperscript{40,102} and (c) Extra-framework aluminum originated by the disruption of the framework.\textsuperscript{103,104} In this work, different available LAS in the framework engendered color changes when in contact with thioindigo. The crystal structure of the inorganic host materials also played a significant role in the selectivity of the organic molecule; moreover, exchangeable cations were crucial for the moisture uptake in these materials.
LAS hydration was proved to reduce the absorbance of most samples; this effect could be explained as being mainly due to a highly polarized thin layer of water molecules absorbed around LAS. Blockage of the LAS could have interrupted direct interaction (C=O—-[LAS]) and only allowed hydrogen bonding interaction (C=O—H(HO)[LAS]) as revealed by FTIR (Chapter 4, section 4.3.3). Further hydration showed the presence of free thioindigo C=O vibration mode perhaps due to the higher concentration of water molecules, thus it was less polarized due to larger distance from LAS.

**Natural Occurring Clay Minerals**

**Palygorskite and Sepiolite**

Palygorskite and sepiolite presented different color hues when in contact with thioindigo. This could be explained by the ratio of Al(VI) [aluminum occupancy in octahedral sites] and Al(IV) [aluminum occupancy in tetrahedral sites] available in both clays; however, 10% occupancy of Al(IV) seemed to be the ideal substitution for the blue color change to happen. The comparison with other clays, such as Ca^{2+} montmorillonites, confirmed this hypothesis. The iron concentration did not show any tendency in the samples evaluated.
Table 14 NMR spectra and color changes observed in several natural occurring clay minerals.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cation (moles)</th>
<th>Fe (moles)</th>
<th>Al(VI) (moles)</th>
<th>Al(IV) (moles)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palygorskite</td>
<td>K</td>
<td>0.067</td>
<td>0.15</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td>Ca, Na</td>
<td>0.008</td>
<td>0.019</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td>CaMMT (Bentolite L®)</td>
<td>Ca</td>
<td>0.011</td>
<td>0.24</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>CaMMT (Texas)</td>
<td>Ca</td>
<td>0.024</td>
<td>0.27</td>
<td>0.029</td>
<td></td>
</tr>
<tr>
<td>NaMMT (Wyoming)</td>
<td>Ca, Na</td>
<td>0.058</td>
<td>0.26</td>
<td>0.099</td>
<td></td>
</tr>
<tr>
<td>NaMMT (Kunapia)</td>
<td>Na</td>
<td>0.029</td>
<td>0.37</td>
<td>0.031</td>
<td></td>
</tr>
</tbody>
</table>

*Calculations based on WD-XRF chemical analysis (Table A.4)
Table 15 Cation content in natural occurring clay minerals.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Na (moles)</th>
<th>Ca (moles)</th>
<th>K (moles)</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palygorskite</td>
<td>0.003</td>
<td>0.005</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Bentolite L®</td>
<td>0.007</td>
<td>0.03</td>
<td>0.002</td>
<td>0.04</td>
</tr>
<tr>
<td>CaMMT (Texas)</td>
<td>0.01</td>
<td>0.03</td>
<td>0.004</td>
<td>0.04</td>
</tr>
<tr>
<td>NaMMT (Wyoming)</td>
<td>0.05</td>
<td>0.03</td>
<td>0.012</td>
<td>0.09</td>
</tr>
<tr>
<td>NaMMT (Kunipia)</td>
<td>0.1</td>
<td>0.008</td>
<td>0.002</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In the case of palygorskite and sepiolite, FTIR spectra of pyridine adsorbed in these clays revealed vibration modes at 1445 cm\(^{-1}\) and 1445, 1596 cm\(^{-1}\), respectively. These vibration modes were characteristic of LAS-pyridine interaction.\(^{106}\) Nevertheless, this technique does not distinguish the cation responsible for this vibration; however the intensity of aluminum has been reported to be more intense than any other cation.\(^{51}\) In the case of palygorskite, the cation in higher concentration was potassium (0.02 moles K), which is known to be highly polarized by the framework\(^{61}\) and not very acidic (\(\phi = 7\) nm\(^{-1}\)); thus this metal could not be responsible for this band. A more acidic metal also available in the surface of the framework is aluminum (\(\phi = 60\) nm\(^{-1}\)) and could be accountable for the LAS-pyridine band in palygorskite, in agreement with the simulation previously done by L.A. Polette et al.\(^{11}\) However, in the case of sepiolite, the LAS-pyridine could also be related to the calcium or sodium larger concentration and relatively strong ionic potential (\(\phi_{\text{Ca}} = 20\) nm\(^{-1}\) and \(\phi_{\text{Na}} = 10.5\) nm\(^{-1}\)).
Figure 132 (Left) Lewis Acid Site (LAS) present in palygorskite. (Right) Lewis Acid Site (LAS) present in sepiolite.

The effect of temperature seemed to be a crucial factor for the stability of palygorskite – thioindigo interaction; the thermal energy given to the system at 413K appeared to be enough to drive thioindigo to further places in the structure where thioindigo bulky molecules could block the entrance of the channels for further hydration of the mixture. Besides temperature, moisture uptake due to a larger concentration of high energy hydration cations was another important factor in the stability of the mixture.

Sepiolite, with a larger channel size than palygorskite, managed to display bathochromic shifts only under slight hydration but not while heated. This behavior could be explained by the hydration of the LAS, where a thin layer of water surrounding the LAS, in a C=O---H(HO)LAS interaction with an acidic hydrogen; therefore a bathochromic shift was observed.

Furthermore, higher hydration loses strength by the distance of the water molecules from LAS, displayed as a hypsochromic shift to the original unheated sample and lower absorption.
Figure 133 Schematic representation of possible explanation for color changes in sepiolite.

Montmorillonite Clays

Ca\textsuperscript{2+}-MMT

Ca\textsuperscript{2+}-montmorillonite clays (Bentolite L\textsuperscript{®} and Texas deposit) behaved similarly to palygorskite when exposed to thioindigo; a bluer color was obtained under UV-Vis spectroscopy. This color could be explained by the presence of aluminum-LAS and Brønsted acids in these clays. Brønsted acid sites and Lewis acids were confirmed by FTIR pyridine adsorption.
Figure 134 Acid Sites present in Ca$^{2+}$-Montmorillonite clays (Ca$^{2+}$-MMT).

The high concentration of calcium (1.1 wt.%) could have been overtaken by the acidic strength of aluminum ($\phi = 60.0$ nm$^{-1}$) and hydrogen, therefore displaying a more intense blue (C=O---Al and C=O---H). However, a FT-Raman analysis of these samples could help us draw more conclusions regarding the stress observed in the entire molecule. Color reversibility could be due to the high hydration energy of calcium ($\Delta H_{\text{hyd}}$ = -1,592 KJ / mol$^{-1}$) which was found in high concentration in these clays.
In addition, in these types of clays similar color changes were observed as in sepiolite, where after some time the unheated sample dehydrated due to the dry atmosphere in the region. Therefore, thioindigo molecules were drawn closer to the LAS, displaying a purple color and further dehydration displayed an intense blue. This behavior could be explained in a similar way as in sepiolite interaction shown in Figure 133.
On the other hand, Na\(^+\)-montmorillonite clays (Wyoming and Kunipia deposits) exhibited only a slight bathochromic shift (purple color) when exposed to thermal treatment. FTIR of pyridine adsorption of these clays revealed no Brønsted acids and low aluminum-LAS (see Figure 74), thus the only available Lewis acids to withdraw thioindigo C=O electrons could be the large amount of sodium cations.

Due to the weak Lewis acid character of sodium (\(\phi = 10 \text{ nm}^{-1}\)), color change (purple) was not as drastic as the purple-blue observed in aluminum (\(\phi = 60 \text{ nm}^{-1}\)). This effect was confirmed by the cation exchanged in mordenite (Na\(^+\)-MOR) where sodium presented only a slight bathochromic shift. Other inorganic host materials with similar behavior were Zeolon\textsuperscript{®} (Na\(^+\)-MOR) and NaY (Na\(^+\)-FAU). Color reversibility in these, Na\(^+\)-MMT clays and zeolites, was obtained during hydration mostly due to the high hydration energy of sodium (\(\Delta H_{\text{hyd}} = -405 \text{ KJ / mol}^{-1}\)).\textsuperscript{61}
Figure 137  (Top) Schematic representations of tetrahedral sites in Na⁺-MMT structure. Interaction with Na⁺-LAS. (Bottom) Hydrated sites of C=O---H(HO)Na⁺-LAS interaction.
**Synthetic Zeolites**

**Cation Exchange**

As mentioned before, cations and protons acted as LAS in some of the inorganic host materials tested.

![Lewis Acid](image)

**Figure 138** Acid Sites present in silicon-aluminum tetrahedral framework of synthetic zeolite.

Cation exchange $H^+$, $K^+$, $Na^+$, $NH_4^+$, $Ca^{2+}$, and $Al^{3+}$ in mordenite synthetic zeolite ($M^{n+}$-MOR) demonstrated that a charge to radius ratio (ionic potential) of the cations increased the bathochromic shift of thioindigo when immersed in mordenite. In other words, HOMO-LUMO higher energy states were reached. Ionic potential is known to increase the strength of the electron shift when interacting with electron donor elements.\(^{66}\) This was well demonstrated in this experiment where the cation strength was observed to decrease in order of exchange of ions $H^+ > Al^{3+} > Ca^{2+} > Na^+ > NH_4^+ > K^+$-MOR (see Table 16).
**Table 16** Color changes related to exchangeable cation.

<table>
<thead>
<tr>
<th>Metal  [M (^{n+})]</th>
<th>Charge ([z^+])</th>
<th>Ionic Radius (nm) ([r])</th>
<th>Ionic Potential ((1/\text{nm})^{106}) ([\phi])</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(^+)</td>
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<td>H(^+)</td>
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\(^*\) Ionic radius calculated from ionic potential  
\(^**\) Value from ref.[107]  
\(^***\) Calculated from ref.[107]
Based on the ionic potential values, NH$_4^+$ displayed a larger bathochromic shift than expected. This could be explained by the proton acidity of the cation when attached to an electronegative neighboring atom. However, the shift was not as strong as the one observed in H$^+$, since oxygen from the framework presented larger electronegativity as displayed in Figure 139.

Figure 139  (a) Brønsted acid sites and (b) Ammonium exchange in silicon-aluminum tetrahedral framework.

This effect was also demonstrated by computer simulation (see Figure 129 and Figure 131) where structural models matched the experimental UV-Vis spectra. In addition, the acidic strength of the O-H bond was also tested in a solution where 100% sulfuric acid reacted with thioindigo to produce a bright blue-green color which was susceptible to humidity.
Figure 140 (Top) Schematic representation of tetrahedral sites in synthetic zeolites. Interaction with H⁺-LAS. (Bottom) Hydrated sites of C=O---H(OH)H⁺-LAS interaction.
Figure 141 (Top) Schematic representation of tetrahedral sites in synthetic zeolites. Interaction with NH₄⁺-LAS. (Bottom) Hydrated sites of C=O---H(HO) NH₄⁺-LAS interaction.
Influence of Channel Dimension in Zeolites

Surface interaction in zeolites appeared to be minimal; zeolites with channel size smaller than the size of thioindigo [15.17 Å (length), 7.42 Å (width) and 3.4 Å (thickness)\textsuperscript{32}] displayed no color changes. This effect was also confirmed by Monte Carlo sorption simulation\textsuperscript{108} of the absorbed thioindigo molecules in three types of zeolites: faujasite (FAU) [11.7 molecules per unit cell], mordenite (MOR) [1 molecule per unit cell] and Linde type A (LTA) [0 molecules per unit cell], where FAU (channel size 7.4 Å\textsuperscript{53}) was able to accommodate more molecules than MOR (channel size 17.5 Å [length] x 6.5 Å [width]) and LTA (channel size 4.2 Å\textsuperscript{53}). Moreover, the destruction of the channel in Zeolon\textsuperscript{®} (Na\textsuperscript{+}-MOR) at 950°C did not display the characteristic purple obtained originally.

Figure 142 (Left) Mordenite (MOR) unit Cell with 1 molecule of thioindigo inserted in the channels. (Right) Linde Type A (LTA) unite cell with 0 molecules of thioindigo inserted in the channels by Monte Carlo Simulation [Cerius\textsuperscript{2}-Software].
Figure 143 Faujasite (FAU) unit cell with 11.7 molecules of thioindigo inserted in the channels by Monte Carlo Simulation [Cerius² Software].
CHAPTER 6
INDUSTRIAL APPLICATION

6.1 Introduction

Hybrid materials color reversibility was observed to be water sensitive; therefore, a potential application could be their use as humidity sensors. A Water sensor, such as Co(II) chloride, is one of the main chemicals used in order to identify humidity in air tight compartments. The chemistry involved is the hydration of the salt to form $\text{Co(H}_2\text{O)}_6^{2+}$. This salt is normally added to silica gel and used as indicator.\textsuperscript{109} Nevertheless, hybrid materials chemistry is different since it is more related to the aluminum silicate framework acidity, thus withdrawing electrons from the organic molecule; however, the output is the same, i.e. color change when exposed to humidity. The use of clays is extensive and if this could have color changes depending on humidity, could be a beneficial point. A patent would be filed to limit the dissemination of this specific processing.

On the other hand, two materials with these reversible properties were tested in polyethylene resin in order to evaluate if the pigment would still go into reversible changes when immersed in a different matrix.
6.2 Experimental

Polyethylene resin RSN-001-01 was used as received. Reversible hybrid materials: Bentolite / 0.5 mol % thioindigo and Valfor CP300-35 / 0.5 % mol thioindigo heated at 413K for nine hours were used after thermal treatment.

40 g of polyethylene resin was treated with 0.4 g of reversible hybrid material and mixed inside a plastic container until a homogeneous cover on the polyethylene pellets was observed. These samples were then placed in a bench-top injection molding machine (Galmob, Inc, Model A-100) at 477K for 1 minute.

In order to obtain color changes previously observed in the hybrid material, the new composite was placed inside a furnace at 413K for 1 hour.

6.3 Results and Discussion

Chromatic samples were obtained after injection molding. However, no reversible color changes were observed (see Figure 144). Samples placed inside the furnace at 413K for 1 hour, displayed no color change. The absence of reversibility could be related to the matrix not allowing the free hydration and dehydration of the hybrid material, therefore no color change is observed.
**Figure 144** Injection molding samples (left) Valfor CP300-35 (H\(^+\)-MMT) / 0.5 % thioindigo and (right) Bentolite L (Ca\(^{2+}\)-MMT) / 0.5 mol % thioindigo.

### 6.4 Conclusions

The use of this reversible hybrid material is exclusive to open systems, due to the major effect water molecules have on the color reversibility.
REFERENCES


7 A von Baeyer, Berichte der Deutschen Chemischen Gesellschaft, 1900, 33 (3), Supplement.


45. Coastal and Marine Geology Program, Report number 01-041.


65 W. M. Latimer, K. S. Pitzer, C. M. Slansky, J. Chem. Phys. 1989, 7, 108. The original equation given by Latimer has been updated by Roger Todd to fit the more modern thermodynamic data and radii.


74 D. Williams, Masters Thesis, Durham University, 2008.


<table>
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<tr>
<th>Clay Type</th>
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<th>% LOI*</th>
<th>% V2O5</th>
<th>% Cr2O3</th>
<th>% MnO</th>
<th>% P2O5</th>
<th>% TiO2</th>
<th>% K2O</th>
<th>% Na2O</th>
<th>% CaO</th>
<th>% MgO</th>
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*LOI = Loss of Ignition

Table A. 1 WD-XRF chemical analysis clays and synthetic aluminosilicates used in this study.
Table A. 2
WD-XRF Chemical analysis of synthetic zeolites used in this study.

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<th>%Cr2O3</th>
<th>%MnO</th>
<th>%P2O5</th>
<th>%TiO2</th>
<th>%K2O</th>
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*LOI = Loss of Ignition

**Table A. 3** WD-XRF Chemical analysis of synthetic zeolites used in this study.

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*LOI= Loss on Ignition
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Table A.4: List of natural occurring clay minerals used in this research. Chemical formula derived from WD-XRF measurements, pore size and general structure based on literature.
Table A. 5 List of synthetic zeolites used in this research. Chemical formula derived from WDXRF measurements, pore size and general structure based on literature.

H

H+

Na

Na

Na

Na

NH4

Na

Cation

1

100% Si

3.99

0.987

0.989

1.26

2.48

2.50

7.31

Si/Al

7.4

4.2

4.2

7.4

7.4

7.4

6.5 X 7.0

Pore Size
(Å)

FAU

LTA

LTA

FAU

FAU

FAU

MOR

Structure

S.Komarneni

S.Komarneni

S.Komarneni

US5320773

O.Cairon

R.M.Barrer

O.Cairon

L.Smart

X.Qiao

R.M.Barrer

Ref.

PSU*

PSU*

PSU*

PQ corp.

Alfa Aesar

Alfa Aesar

Alfa Aesar

Alfa Aesar

Unknown

Norton Co.

Provider

ZEOLON®
LZY-62
NaY
13X
4A
5A
VALFOR®
CP300-35

Si 1.23 Al 0.308 O 2.92 H2O 0.553

Si 0.604 Al 0.612 Na 0.212 O 2.43 H2O 0.806

Si 0.557 Al 0.563 Na 0.558 O 2.24 H2O 1.16

Si 0.657 Al 0.520 Na 0.506 O 2.35 H2O 1.02

Si 0.815 Al 0.329 Na 0.335 O 2.30 H2O 1.35

Si 0.852 Al 0.341 O 2.26 H2O 1.65

Si 1.25 Al 0.171 Na 0.020 O 2.77 H2O 0.894

Chemical Formula

MS-1

H

100%Al

Specimen

MAS-1

H

Synthetic Zeolites

MA-1
(i.s.) interlayer spacing
*PSU: Synthesized by Penn State University

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Table A.6: List of synthetic swelling micas used in this research. Chemical formula derived from WD-XRF measurements, pore size and general structure based on literature.

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<td>100</td>
<td>PSU*</td>
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<td>0.50</td>
<td>10 (i.s.)</td>
<td>180</td>
<td>PSU*</td>
</tr>
<tr>
<td>Topy</td>
<td>Na 0.5 Al 0.5 Si 10.0 Mg 7.5 O 20 F 7</td>
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<td>0.50</td>
<td>10 (i.s.)</td>
<td>180</td>
<td>PSU*</td>
</tr>
</tbody>
</table>

*PSU: Synthesized by Penn State University

Sodium tetrasilic Mica
APPENDIX B

STARTING MATERIALS AND SOLID SYNTHESIS

THIOINDIGO

C:\Documents and Settings\Ale\Desktop\thioindigo.xls

**Figure B.1** Peak fit of thioindigo.

**Table B.1** Peak fit statistics of thioindigo.

Description: C:\Documents and Settings\Ale\Desktop\thioindigo.xls
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\thioindigo\thioindigopeakfit.txt

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<th>Measured Values</th>
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</thead>
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</tr>
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</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
</tr>
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<td>4</td>
</tr>
<tr>
<td>5</td>
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<tr>
<th>Peak</th>
<th>Type</th>
<th>Anlytc Area</th>
<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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<td>13.4527459</td>
<td>8.81699403</td>
<td>13.3063493</td>
<td>8.7336015</td>
<td>264.222627</td>
<td>718.009543</td>
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<tr>
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<td>6.11553254</td>
<td>4.00814929</td>
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<td>4.01210141</td>
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<td>8.47889082</td>
<td>5.55710561</td>
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<td>352.457981</td>
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<td>264.222627</td>
<td>718.009543</td>
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208
PALYGORSKITE

paly6\%thioUnfresh - C:\COLOR\Data\ALE\pennstate\07.01.08UV\paly6\%thioUn

Figure B. 2 Peak fit of Palygorskite / 0.5 mol % thioindigo unheated.

Table B. 2 Peak fit statistics of Palygorskite / 0.5 mol % thioindigo unheated.

Description: paly6\%thioUnfresh - smooth - C:\COLOR\Data\ALE\pennstate\07.01.08UV\paly6\%thioUn
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\palygorskite\paly6\%thiouunfreshpeakfit.txt

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<th>Asym10</th>
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<tbody>
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<td></td>
<td></td>
<td></td>
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<td>0.15211084</td>
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<tr>
<td>4</td>
<td>Voigt Area</td>
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<td>85.8824648</td>
<td>1.00000002</td>
<td>171.911636</td>
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Total | 87.0718100 | 100.000000 | 87.0375263 | 100.000000 |

---

209
Paly6%thio Dehydrated C:\COLOR\Data\ALE\pennstate\07.02.08U
Pk=Voigt Area  8 Peaks
$R^2=0.999702$  $SE=0.00753644$  $F=80446.2$

**Figure B. 3** Peak fit of Palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours.

**Table B. 3** Peak fit statistics of Palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: Paly6%thio140C9hsuperfresh07.02 - smooth - C:\COLOR\Data\ALE\pennstate\07.02.08U
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\palygorskite\paly6%thio140c9hsuperfresh07.02-peakfit.txt

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<th>Asym10</th>
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<td>87.04</td>
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<th>% Area</th>
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<th>Moment2</th>
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<td>2.0588</td>
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</table>

210
Figure B. 4 Peak fit of Palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 4 Peak fit statistics of Palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: Paly6%thio1409hnofreshswati - smooth - C:\COLOR\Data\ALE\pennstate\07.01.08\Paly
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\palygorskite\paly6%thio1409hnofreshswatipeakfit.txt

Figure B. 5 Peak fit of Palygorskite / 0.5 mol % thioindigo unheated / exposed to vacuum.

Table B. 5 Peak fit statistics of Palygorskite / 0.5 mol % thioindigo unheated / exposed to vacuum.

Description: C6UNvacuum - RawData - C:\COLOR\Data\ALE\pennstate\10.13.08UV\C6UNvacuum.spc
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\palygorskite\c6unvacuumpeakfit.txt

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<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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**SEPIOLITE**

sep6%thioUnfresh - smooth - C:\COLOR\Data\ALE\pennstate\07.01.08UV\sep6%thioUnfr

![Peak fit of Sepiolite / 0.5 mol % thioindigo unheated.](image)

**Figure B. 6** Peak fit of Sepiolite / 0.5 mol % thioindigo unheated.

**Table B. 6** Peak fit statistics of Sepiolite / 0.5 mol % thioindigo unheated.

Description: sep6%thioUnfresh - smooth - C:\COLOR\Data\ALE\pennstate\07.01.08UV\sep6%thioUnfr
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\sepiolite\sep6%thiounfreshpeakfit.txt

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<th>Asym50</th>
<th>FW Base (nm)</th>
<th>Asym10</th>
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<th>Anlytc Area</th>
<th>% Area</th>
<th>Int Area (nm)</th>
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<th>Centroid (nm)</th>
<th>Moment2</th>
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213
Table B. 7 Peak fit statistics of Sepiolite / 0.5 mol % thioindigo heated at 413K for nine hours.

<table>
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<tr>
<th>Peak</th>
<th>Type</th>
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<th>Center</th>
<th>FWHM</th>
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<th>FW Base</th>
<th>Asym10</th>
<th>Centroid</th>
<th>Moment2</th>
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Total   | 221.759657  | 100.000000  | 219.155097   | 100.000000  |

Figure B. 7 Peak fit of Sepiolite / 0.5 mol % thioindigo heated at 413K for nine hours.
Figure B. 8 Peak fit of Sepiolite / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 8 Peak fit statistics of Sepiolite / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

<table>
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<th>Measured Values</th>
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<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
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MONTMORILLONITE CLAYS

BENTOLITE L ®

bentolite-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\bentolite-thio 6% UN
Pk=Voigt Area 5 Peaks
r^2=0.999105  SE=0.00824718  F=21218.2

Figure B. 9 Peak fit of Bentolite L ® / 0.5 mol % thioindigo unheated.

Table B. 9 Peak fit statistics of Bentolite L ® / 0.5 mol % thioindigo unheated.

Description: bentolite-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\bentolite-thio 6% UN
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\bentolite\bentolite-thio 6% unpeakfit.txt

Measured Values

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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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Peak | Type     | Anlytc Area | % Area | Int Area | % Area | Centroid | Moment2 |
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Table B. 10 Peak fit statistics of Bentolite L® / 0.5 mol % thioindigo heated at 413K for nine hours.

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<th>Type</th>
<th>Anlytc Area</th>
<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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</table>
**Figure B. 11** Peak fit of Bentolite L\(^©\) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

**Table B. 11** Peak fit statistics of Bentolite L\(^©\) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: bentoliteL+dyered - RawData - C:\COLOR\Data\ALE\pennstate\11.25.08XRD\BentoliteL
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\bentolite\bentolite+dyeredpeakfit.txt

### Measured Values

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<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
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<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
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Total 123.082367 100.000000 122.477989 100.000000
Ca-MMT (Texas)

Ca-Mont. texas-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\Ca-Mont. texas-
Pk=Voigt Area 5 Peaks
\( r^2=0.999117 \) \( SE=0.00794833 \) \( F=21500.2 \)

![Graph](image)

**Figure B. 12** Peak fit of Ca-MMT (Texas) / 0.5 mol % thioindigo unheated.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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<td>0.99999996</td>
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**Table B. 12** Peak fit statistics of Ca-MMT (Texas) / 0.5 mol % thioindigo unheated.

Description: Ca-Mont. texas-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\Ca-Mont. texas-
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\ca-mmt wyoming\ca-mont. texas-thio 6%
unpeakfit.txt

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</table>
**Figure B. 13** Peak fit of Ca-MMT (Texas) / 0.5 mol % thioindigo heated at 413K for nine hours.

**Table B. 13** Peak fit statistics of Ca-MMT (Texas) / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: Ca-Mont.+dye - Ca-Mont.+dye smooth - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH B
X Variable: Wavelength (nm)
Y Variable: Absorbance
File Source: c:documents and settings\ale\desktop\thesis final\peak fit\ca-mmt wyoming\ca-mont.+dye\peakfit\ca-mont.+dye\new runs with b\peak fit\ca-mmt wyoming\ca-mont.+dyenofreshpeakfit.txt

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Figure B. 14 Peak fit of Ca-MMT (Texas) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 14 Peak fit statistics of Ca-MMT (Texas) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: NaMMT+dyered - RawData - C:\COLOR\Data\ALE\pennstate\11.25.08XRD\CaMMT+dyered.sp
X Variable: Wavelength nm.
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Na-MMT (Kunipia)

Na-Mont.Kunipia-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\Na-Mont.Kunipia

Table B. 15 Peak fit statistics of Na-MMT (Kunipia) / 0.5 mol % thioindigo unheated.

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Total        | 113.851824 | 100.000000 | 113.656163 | 100.000000

Figure B. 15 Peak fit of Na-MMT (Kunipia) / 0.5 mol % thioindigo unheated.

Table B. 15 Peak fit statistics of Na-MMT (Kunipia) / 0.5 mol % thioindigo unheated.

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X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\kunipia\na-mont.kunipia-thio 6% unpeakfit.txt

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Figure B. 16 Peak fit of Na-MMT (Kunipia) / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 16 Peak fit statistics of Na-MMT (Kunipia) / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: Kunipia Na-Mont - Kunipia Na-Mont - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH Ba
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\kunipia\kunipia na-montpeakfit.txt

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Figure B. 17 Peak fit of Na-MMT (Kunipia) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 17 Peak fit statistics of Na-MMT (Kunipia) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

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<th>FWHM</th>
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Total 120.894524 100.000000 120.798290 100.000000
Na-MMT (Wyoming)

Na-Mont. Wyoming-thio 6% - UN - C:\COLOR\Data\ALE\pennstate\Na-Mont. Wyoming
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<th>% Area</th>
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<th>Moment2</th>
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Figure B. 18 Peak fit of Na-MMT (Wyoming) / 0.5 mol % thioindigo unheated.

Table B. 18 Peak fit statistics of Na-MMT (Wyoming) / 0.5 mol % thioindigo unheated.

Description: Na-Mont. Wyoming-thio 6% - smooth - C:\COLOR\Data\ALE\pennstate\Na-Mont. Wyoming
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\n-mmt wyoming\na-mont. wyoming-thio 6% unpeakfit.txt

Measured Values
Na-Mont+dye Dehydrated- C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH Ba
Pk=Gauss Amp 5 Peaks
$\chi^2=0.999078$  SE=0.007295  F=45369.7

Figure B. 19 Peak fit of Na-MMT (Wyoming) / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 19 Peak fit statistics of Na-MMT (Wyoming) / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: Na-Mont.+dye - Na-Mont+dye smooth - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH Ba
X Variable: Wavelength (nm)
Y Variable: Absorbance
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\n-mmt wyoming\na-mont.+dyebaselinepeakfit.txt

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<th>% Area</th>
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<td>15.3377024</td>
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<td>43.5582387</td>
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<td>635.535406</td>
<td>2987.52318</td>
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Total 163.581763 100.000000 162.968969 100.000000
Figure B. 20 Peak fit of Na-MMT (Wyoming) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 20 Peak fit statistics of Na-MMT (Wyoming) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: NaMMT+dyered - RawData - C:\COLOR\Data\ALE\pennstate\11.25.08XRD\NaMMT+dyered.sp
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\n-mmt wyoming\nammt+dyeredpeakfit.txt

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Figure B. 21 Peak fit of YN6 / 0.5 mol % thioindigo unheated.

Table B. 21 Peak fit statistics of YN6 / 0.5 mol % thioindigo unheated.

Description: YN6-6%THIOUN - YN6-6%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\YN6-6%THIOUN.sp

X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\yn6\yn6-6%thiounpeakfit.txt

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<th>FWHM</th>
<th>Asym50</th>
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<th>Asym10</th>
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<td>0.12648480</td>
<td>342.973091</td>
<td>58.6222113</td>
<td>0.99999989</td>
<td>117.344563</td>
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<td>505.812173</td>
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<td>1.00000000</td>
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<td>543.645919</td>
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Peak     | Type          | Anlytc Area | % Area | Int Area | % Area | Centroid | Moment2 |
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Table B. 22 Peak fit statistics of YN6 / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: YN6 - YN6 SMOOTH - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\YN6.spc
X Variable: Wavelength (nm)
Y Variable: Absorbance
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\yn6\yn6peakfit.txt

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Total         | 97.4874110 | 100.000000 | 97.4819556 | 100.000000 |
Figure B. 23 Peak fit of YN8 / 0.5 mol % thioindigo unheated.

Table B. 23 Peak fit statistics of YN8 / 0.5 mol % thioindigo unheated.

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<th>Int Area</th>
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Total 95.2618072 100.000000 95.2618063 100.000000
Figure B. 24 Peak fit of YN8 / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 24 Peak fit statistics of YN8 / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: YN8 - YN8 SMOOTH - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\YN8.spc
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\yn8\yn8peakfit.txt

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Total         96.1601180   100.000000   95.5425487   100.000000

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<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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Na-Ts

Na-Ts6%THIOUN - Na-Ts6%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\Na-Ts6%THIOUN.

**Figure B. 25** Peak fit of Na-Ts / 0.5 mol % thioindigo unheated.

**Table B. 25** Peak fit statistics of Na-Ts / 0.5 mol % thioindigo unheated.

Description: Na-Ts6%THIOUN - Na-Ts6%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\Na-Ts6%THIOUN.
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\na-ts\na-ts6%thiounpeakfit.txt

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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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<th>% Area</th>
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Na-TS+dye - Na-TS+dye dehydrated C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\N

\( r^2 = 0.998511 \)  \( \text{SE} = 0.00770479 \)  \( F = 18490.5 \)

### Figure B. 26
Peak fit of Na-Ts / 0.5 mol % thioindigo heated at 413K for nine hours.

### Table B. 26
Peak fit statistics of Na-Ts / 0.5 mol % thioindigo heated at 413K for nine hours.

**Description:** Na-TS+dye - Na-TS+dye smooth - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\N

**X Variable:** Wavelength (nm)

**Y Variable:** Absorbance

**File Source:** c:\documents and settings\ale\desktop\thesis final\peak fit\na-ts\na-ts+dyebaselinepeakfit.txt

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<th>Asym50</th>
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<th>% Area</th>
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233
Talc

**Figure B. 27** Peak fit of Talc / 0.5 mol % thioindigo unheated.

**Table B. 27** Peak fit statistics of Talc / 0.5 mol % thioindigo unheated.

Description: TALC-6%THIOUN - RawData - C: \ COLOR \ Data \ ALE \ pennstate \ 09.02.08 \ TALC-6%THIOUN.spc

X Variable: Wavelength nm.

File Source: C:\documents and settings\ale\desktop\thesis final\peak fit\talc\talc-6%thiouenpeakfit.txt
Figure B. 28 Peak fit of Talc / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 28 Peak fit statistics of Talc / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: Talc-6%thio140C9hrs - RawData - C:\COLOR\Data\ALE\pennstate\09.03.08UV\Talc-6%th
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\talc\talc-6%thio140c9hrspeakfit.txt

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<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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235
Zeolite 4A

4A-6\%THIOUN - 4A-6\%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\4A-6\%THIOUN.spc

\textbf{Figure B. 29} Peak fit of 4A / 0.5 mol \% thioindigo unheated.

\textbf{Table B. 29} Peak fit statistics of 4A / 0.5 mol \% thioindigo unheated.

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<th>Type</th>
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<th>FWHM</th>
<th>Asym50</th>
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<th>Asym10</th>
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<th>Int Area</th>
<th>% Area</th>
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<th>Moment2</th>
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| Total |               | 99.4585807     | 100.000000 | 99.4015788 | 100.000000 | 169.208565 | 100.000000 |
Figure B. 30 Peak fit of 4A / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 30 Peak fit statistics of 4A / 0.5 mol % thioindigo heated at 413K for nine hours.

Measured Values

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<th>FWHM</th>
<th>Asym50</th>
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<th>Int Area</th>
<th>% Area</th>
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Zeolite 5A

5A-6\%THIOUN - 5A-6\%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\5A-6\%THIOUN.spc

Figure B. 31 Peak fit of 5A / 0.5 mol % thioindigo unheated.

Table B. 31 Peak fit statistics of 5A / 0.5 mol % thioindigo unheated.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Voigt Area</td>
<td>0.06807938</td>
<td>308.970255</td>
<td>64.9160157</td>
<td>1.00000001</td>
<td>129.942923</td>
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</tr>
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<td>Voigt Area</td>
<td>0.07496297</td>
<td>356.166582</td>
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<td>92.4716087</td>
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</tr>
<tr>
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<tr>
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<td>575.883305</td>
<td>79.0907400</td>
<td>0.99999986</td>
<td>159.955984</td>
<td>0.99999992</td>
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Peak | Type          | Anlytc Area     | % Area | Int Area     | % Area | Centroid     | Moment2     |
<table>
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<td>6.09425403</td>
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<td>759.470769</td>
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<td>38.0573434</td>
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<td>38.0574330</td>
<td>505.071673</td>
<td>1496.99356</td>
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<td>6.75722903</td>
<td>5.21593289</td>
<td>6.75724493</td>
<td>525.167026</td>
<td>576.491015</td>
</tr>
<tr>
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<td>Voigt Area</td>
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<td>44.3154037</td>
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<td>44.3155079</td>
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<td>1151.55315</td>
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Total |                | 77.1904114      | 100.000000 | 77.1902298 | 100.000000 |
Figure B. 32 Peak fit of 5A / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 32 Peak fit statistics of 5A / 0.5 mol % thioindigo heated at 413K for nine hours.
Figure B. 33 Peak fit of NaY / 0.5 mol % thioindigo unheated.

Table B. 33 Peak fit statistics of NaY / 0.5 mol % thioindigo unheated.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
</tr>
</thead>
<tbody>
<tr>
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<td>234.712165</td>
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<td>70.3963860</td>
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<tr>
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<td>118.096397</td>
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<td>103.388933</td>
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<tr>
<td>4</td>
<td>Voigt Area</td>
<td>0.47282556</td>
<td>519.479229</td>
<td>86.1429326</td>
<td>1.00000000</td>
<td>197.614714</td>
<td>1.00000005</td>
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<tr>
<td>5</td>
<td>Voigt Area</td>
<td>0.35007399</td>
<td>576.327046</td>
<td>65.0052662</td>
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Peak   Anlytc Area | % Area | Int Area | % Area | Centroid | Moment2 |
<table>
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</thead>
<tbody>
<tr>
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<tr>
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<td>Voigt Area</td>
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<td>5.00489308</td>
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<tr>
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<td>Voigt Area</td>
<td>5.61674389</td>
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<td>28.0889368</td>
<td>31.1146763</td>
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<td>31.2580382</td>
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Total | 90.2755232 | 100.000000 | 87.4167148 | 100.000000 |
**Table B. 34** Peak fit statistics of NaY / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: NaY6%thio140C9hfresh - smooth - C:\COLOR\Data\ALE\pennstate\07.01.08\NaY6%thio14
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\nay\nay+6%thio1409hfreshpeakfit.txt

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<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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<tbody>
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<td>349.048884</td>
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<td>536.379094</td>
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<th>Type</th>
<th>Anlytc Area</th>
<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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<td>3.09893406</td>
<td>6.14281625</td>
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<td>3.77122428</td>
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<td>76.28592103</td>
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<td>535.883227</td>
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<td>2343.66764</td>
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Total | 207.299247  | 100.000000  | 204.606736  | 100.000000  |

**Figure B. 34** Peak fit of NaY / 0.5 mol % thioindigo heated at 413K for nine hours.
Figure B. 35 Peak fit of NaY / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 35 Peak fit statistics of NaY / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Measured Values

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
</tr>
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<td>Voigt</td>
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<td>3</td>
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<td>0.23196982</td>
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<tr>
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<td>515.761700</td>
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<tr>
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<td>0.999999</td>
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Total         129.640451   100.000000   127.523601   100.000000
Figure B. 36 Peak fit of 13X / 0.5 mol % thioindigo unheated.

Table B. 36 Peak fit statistics of 13X / 0.5 mol % thioindigo unheated.

Description: 13x6%THIOUN - 13x6%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\13x6%THIOUN.spc

X Variable: Wavelength nm.

File Source: c:\documents and settings\ale\desktop\thesis final\peakfit\13x\13x6%thiounpeakfit.txt

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<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
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</table>

Peak | Type      | Anlytc Area | % Area | Int Area | % Area | Centroid | Moment2 |
<table>
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<th></th>
<th></th>
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<th></th>
<th></th>
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<tbody>
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<td>4.53633897</td>
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<td>24.3577929</td>
<td>32.7774526</td>
<td>581.254334</td>
<td>1103.25019</td>
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Total | 74.3127430 | 100.000000 | 74.312647 | 100.000000 |
Figure B. 37 Peak fit of 13X / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 37 Peak fit statistics of 13X / 0.5 mol % thioindigo heated at 413K for nine hours.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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<th>Type</th>
<th>Anlytc Area</th>
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<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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</thead>
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<td>30.7713169</td>
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Total 179.507008 100.000000 179.397459 100.000000
Figure B. 38 Peak fit of 13X / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 38 Peak fit statistics of 13X / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.
Zeolites LZY62

Figure B. 39 Peak fit of LZY62 / 0.5 mol % thioindigo unheated.

Table B. 39 Peak fit statistics of LZY62 / 0.5 mol % thioindigo unheated.

Measured Values

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
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Total |          | 108.624881  | 100.000000   | 91.1307758 | 100.000000|

% Area, Int Area, % Area, Centroid, Moment2:

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File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\lzy-62\lzy-62-6%thiounpeakfit.txt
Figure B. 40 Peak fit of LZY62 / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 40 Peak fit statistics of LZY62 / 0.5 mol % thioindigo heated at 413K for nine hours.

Measured Values

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Figure B. 41 Peak fit of LZY62 / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 41 Peak fit statistics of LZY62 / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: ZeoliteLZY-62 - ZeoliteLZY-62 - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\ X Variable: Wavelength (nm)
Y Variable: Absorbance
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Total 82.6671935 100.000000 77.5358965 100.000000
Zeolites Zeolon®

Zeolon-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\Zeolon-thio 6% UN.spc
Pk=Voigt Area 4 Peaks
\( r^2=0.999241 \) \( SE=0.00483516 \) \( F=31604.4 \)

Table B. 42 Peak fit statistics of Zeolon® / 0.5 mol % thioindigo unheated.

Description: Zeolon-thio 6% UN - smooth - C:\COLOR\Data\ALE\pennstate\Zeolon-thio 6% UN.spc
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\zeolon\zeolon-thio 6% unpeakfit.txt

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Total       | -           | 83.8096402    | 100.000000   | 83.7970258   | 100.000000   |

Figure B. 42 Peak fit of Zeolon® / 0.5 mol % thioindigo unheated.

Table B. 42 Peak fit statistics of Zeolon® / 0.5 mol % thioindigo unheated.
Table B. 43 Peak fit statistics of Zeolon® / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: Storage 045540 PM - zeolon smooth - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH Ba
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\zeolon\zeolonpeakfit.txt

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Figure B. 44 Peak fit of Zeolon® / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 44 Peak fit statistics of Zeolon® / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: zeolonH-6%thio 140C 9hrs - RawData - C:\COLOR\Data\ALE\pennstate\09.11.08UV\zeol
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\zeolon\zeolonh-6%thio 140c 9hrsnofreshpeakfit.txt

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Zeolite CBV21A

Figure B. 45 Peak fit of CBV21A / NH₄ / 0.5 mol % thioindigo unheated.

Table B. 45 Peak fit statistics of CBV21A / NH₄ / 0.5 mol % thioindigo unheated.

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Figure B. 46 Peak fit of CBV21A / NH₄ / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 46 Peak fit statistics of CBV21A / NH₄ / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: CBV21A6%thioH1409h - smooth - C:\COLOR\Data\ALE\pennstate\06.05.08\CBV21A6%thioH
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Total | 169.229358| 100.000000| 169.228421| 100.000000|
Figure B. 47 Peak fit of CBV21A / NH$_4$ / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 47 Peak fit statistics of CBV21A / NH$_4$ / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: CBV21ANH4-6%thio1409hno-fresh - smooth - C:\COLOR\Data\ALE\pennstate\06.21.08UV\  
X Variable: Wavelength nm.  
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21anh4\cbv21anh4-6%thio1409hno-freshpeakfit.txt

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21A-Al6%thio UN - RawData - C:\COLOR\Data\ALE\pennstate\10.20.08UV\21A-Al6%thio

PK=Voigt Area  3 Peaks

$\chi^2=0.99748$  $SE=0.00853535$  $F=52371.8$

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**Figure B. 48** Peak fit of CBV21A / Al / 0.5 mol % thioindigo unheated.

**Table B. 48** Peak fit statistics of CBV21A / Al / 0.5 mol % thioindigo unheated.
Figure B. 49 Peak fit of CBV21A / Al / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 49 Peak fit statistics of CBV21A / Al / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: 21A-Al6%thio H - RawData - C:\COLOR\Data\ALE\pennstate\10.20.08UV\21A-Al6%thio H
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21a-al\21a-al6%thio hpeakfit.txt

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21A-Al1weekoutsidedesiccator - RawData - C:\COLOR\Data\ALE\pennstate\10.30.08UV\ 
Pk=Voigt Area  7 Peaks 
\( r^2 = 0.998668 \)  \( SE = 0.00754647 \)  \( F = 42083.6 \)

Figure B. 50 Peak fit of CBV21A / Al / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 50 Peak fit statistics of CBV21A / Al / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: 21A-Al1weekoutsidedesiccator - RawData - C:\COLOR\Data\ALE\pennstate\10.30.08UV\ 
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21a-al\21a-al1weekoutsidedesiccator-bluepeakfit.txt

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Total | 135.961266 | 100.000000 | 133.281481 | 100.000000

Figure B. 51 Peak fit of CBV21A / Al / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated for 1 week.

Table B. 51 Peak fit statistics of CBV21A / Al / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated for 1 week.

Description: 21A-Al1weekoutsidedesiccator-purplechange - RawData - C:\COLOR\Data\ALE\pennstat
X Variable: or-purple.spc
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21a-al\21a-al1weekoutsidedesiccator-purplepeakfit.txt

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Total: 121.522381 100.000000 118.984147 100.000000
Figure B. 52 Peak fit of CBV21A / Ca / 0.5 mol % thioindigo unheated.

Table B. 52 Peak fit statistics of CBV21A / Ca / 0.5 mol % thioindigo unheated.

Description: 21ACa-6%thioUNpink(outside desiccator) - RawData - C:\COLOR\Data\ALE\pennstate\1
X Variable: iccator).spc
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21aca\21aca-6%thiounpink(outside desiccator)peakfit.txt

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<th>Type</th>
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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Voigt Area</td>
<td>0.05360005</td>
<td>321.757918</td>
<td>72.952666</td>
<td>1.000000</td>
<td>146.260487</td>
<td>1.000000</td>
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<tr>
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<td>0.32175512</td>
<td>520.065472</td>
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<td>0.999999</td>
<td>203.610972</td>
<td>1.000000</td>
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<tr>
<td>3</td>
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<td>0.25881710</td>
<td>585.449635</td>
<td>93.952666</td>
<td>1.000000</td>
<td>188.362724</td>
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</tr>
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</table>

Total Amplitude | 64.9896452 | 100.000000 |
Total FWHM     | 321.866564 | 993.442089 |
Total Centroid | 321.866654 | 993.442089 |

Peak | Type     | Anlytc Area | % Area | Int Area | % Area | Centroid | Moment2 |
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<td>993.442089</td>
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<td>34.8691330</td>
<td>53.6533673</td>
<td>34.8458031</td>
<td>53.6539856</td>
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<td>1904.07599</td>
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<tr>
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<td>39.9262260</td>
<td>25.9304038</td>
<td>39.9264585</td>
<td>585.392969</td>
<td>1633.59037</td>
</tr>
</tbody>
</table>
Figure B. 53 Peak fit of CBV21A / Ca / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 53 Peak fit statistics of CBV21A / Ca / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: 21A-Ca H fresh - RawData - C:\COLOR\Data\ALE\pennstate\10.20.08UV\21A-Ca H fresh
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21aca\21a-ca h freshpeakfit.txt

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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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</thead>
<tbody>
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<td>1</td>
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<td>0.21077794</td>
<td>301.186267</td>
<td>61.4687607</td>
<td>1.000000000</td>
<td>124.378727</td>
<td>1.000000000</td>
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<tr>
<td>2</td>
<td>Voigt Area</td>
<td>0.18736514</td>
<td>341.306179</td>
<td>56.4199354</td>
<td>1.000000000</td>
<td>114.162701</td>
<td>1.000000000</td>
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<tr>
<td>3</td>
<td>Voigt Area</td>
<td>0.20624323</td>
<td>482.474604</td>
<td>58.3261411</td>
<td>1.000000000</td>
<td>118.019806</td>
<td>1.000000000</td>
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<td>4</td>
<td>Voigt Area</td>
<td>0.54330286</td>
<td>528.944931</td>
<td>72.5787837</td>
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<td>146.859260</td>
<td>1.000000000</td>
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<td>0.57138126</td>
<td>593.477038</td>
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<tr>
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<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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<td>9.23880885</td>
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<td>761.117631</td>
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<td>100.000000</td>
<td>151.057648</td>
<td>100.000000</td>
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</table>
**Figure B. 54** Peak fit of CBV21A / Ca / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

**Table B. 54** Peak fit statistics of CBV21A / Ca / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: 21A-Ca1weekoutsidedesiccator - RawData - C:\COLOR\Data\ALE\pennstate\10.30.08UV\X Variable: Wavelength nm.

File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21aca\21aca1weekoutsidedesiccatorpeakfit.txt

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<th>FWHM</th>
<th>Asym50</th>
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<th>Asym10</th>
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</thead>
<tbody>
<tr>
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<td>61.5739445</td>
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<td>1.00000000</td>
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<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
</tr>
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<tbody>
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<td>40.9328190</td>
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</table>
Peak fit of CBV21A / K / 0.5 mol % thioindigo unheated.

Table B. 55 Peak fit statistics of CBV21A / K / 0.5 mol % thioindigo unheated.

<table>
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<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
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<th>FWHM</th>
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<td>93.2923942</td>
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<td>186.744153</td>
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Total          |                       | 103.216445| 100.000000| 102.385062| 100.000000|
Figure B. 56 Peak fit of CBV21A / K / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 56 Peak fit statistics of CBV21A / K / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: 21A-K H fresh - RawData - C:\COLOR\Data\ALE\penstate\10.20.08UV\21A-K H fresh.s
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ak\21a-k h freshpeakfit.txt
Figure B. 57 Peak fit of CBV21A / K / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 57 Peak fit statistics of CBV21A / K / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: 21AK-6%thioHbrightpink(outside desiccator) - RawData - C:\COLOR\Data\ALE\pennsta
X Variable: side desiccator).spc
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ak\21ak-6%thiohbrightpink(outside desiccator)peakfit.txt

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<th>Asym50</th>
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<th>% Area</th>
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<td>12.4920582</td>
<td>10.945762</td>
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<td>100.000000</td>
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</table>
Figure B. 58 Peak fit of CBV21A / Na / 0.5 mol % thioindigo unheated.

Table B. 58 Peak fit statistics of CBV21A / Na / 0.5 mol % thioindigo unheated.

Measured Values

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<tr>
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<th>Type</th>
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<th>FWHM</th>
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<th>Asym10</th>
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</table>

![Graph showing peak fit of CBV21A / Na / 0.5 mol % thioindigo unheated.](image-url)
Table B. 59 Peak fit statistics of CBV21A / Na / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: 21A-Na H fresh - RawData - C:\COLOR\Data\ALE\pennstate\10.20.08UV\File 081020 03
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ana\21a-na h fresh peakfit.txt

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<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
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<th>% Area</th>
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<th>Moment2</th>
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Figure B. 59 Peak fit of CBV21A / Na / 0.5 mol % thioindigo heated at 413K for nine hours.
Figure B. 60 Peak fit of CBV21A / Na / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 60 Peak fit statistics of CBV21A / Na / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: 21A-Na1weekoutsidedessicant - RawData - C:\COLOR\Data\ALE\pennstate\10.30.08UV\2
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ana\21-a-
na1weekoutsidedessicatorpeakfit.txt

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<th>Asym10</th>
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Measured Values

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<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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Total | 140.277680    | 100.000000    | 138.197259 | 100.000000 |
Figure B. 61 Peak fit of CBV21A / H / 0.5 mol % thioindigo unheated.

Table B. 61 Peak fit statistics of CBV21A / H / 0.5 mol % thioindigo unheated.

Description: CBV21AH6%THIOUN - SMOOTH - C:\COLOR\Data\ALE\pennstate\06.12.08IR\CBV21AH6%THIOU
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ah\cbv21ah6%thiounpeakfit.txt

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<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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Peak | Type          | Anlytc Area   | % Area | Int Area    | % Area | Centroid | Moment2 |
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Total |              | 76.1621743    | 100.000000 | 75.0926113 | 100.000000 | 591.757666 | 2686.46178 |
Figure B. 62 Peak fit of CBV21A / H / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 62 Peak fit statistics of CBV21A / H / 0.5 mol % thioindigo heated at 413K for nine hours.

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Total 112.525177 100.000000 107.144053 100.000000
Figure B. 63 Peak fit of CBV21A / H / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 63 Peak fit statistics of CBV21A / H / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: C:\Documents and Settings\Ale\Desktop\Peak Fit\CBV21AH+6%thioHnofresh.xls
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ah\cbv21ah6%thio-h-nofreshpeakfit.txt

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Peak | Type          | Anlytc Area   | % Area       | Int Area     | % Area      | Centroid    | Moment2    |
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Total | 148.522152 | 100.000000 | 148.335081 | 100.000000 |
Figure B. 64 Peak fit of CBV21A / H(HCL) / 0.5 mol % thioindigo unheated.

Table B. 64 Peak fit statistics of CBV21A / H(HCL) / 0.5 mol % thioindigo unheated.

| Description: 21AHCl0.2M100Ctwice+6%thioUN - RawData - C:\COLOR\Data\ALE\pennstate\10.10.08UV\ |
| X Variable: Wavelength nm. |
| File Source: c:\documents and settings\ale\desktop\thesis final\peakfit\21ahcl\21ahcl0.2m100ctwice+6%thiounpeakfit.txt |

Measured Values

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Total | 115.806295 | 100.000000 | 113.424891 | 100.000000 |
Figure B. 65 Peak fit of CBV21A / H(HCL) / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 65 Peak fit statistics of CBV21A / H(HCL) / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: 21AHCl0.2M100Ctwice+6%thioHblue - RawData - C:\COLOR\Data\ALE\pennstate\10.10.08
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\21ahcl\21ahcl0.2m100ctwice+6%thiohbluepeakfit.txt

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Total 182.710503 100.000000 178.550385 100.000000
Figure B. 66 Peak fit of CBV21A / H(HCL) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 66 Peak fit statistics of CBV21A / H(HCL) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

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**Measured Values**

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Zeolite CBV10A

CBV10AH6%THIOUN - SMOOTH - C:\COLOR\Data\ALE\pennstate\06.13.08\CBV10AH6%THIOUN.

Table B. 67 Peak fit statistics of CBV10A / H / 0.5 mol % thioindigo unheated.

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Figure B. 67 Peak fit of CBV10A / H / 0.5 mol % thioindigo unheated.

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File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\10ah\cbv10ah6%thiounpeakfit.txt
Figure B. 68 Peak fit of CBV10A / H / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 68 Peak fit statistics of CBV10A / H / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: CBV10AH-6%THIOH140C9H - SMOOTH - C:\COLOR\Data\ALE\pennstate\06.14.08\CBV10AH-6%
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\10ah\cbv10ah-6%thioh140c9hpeakfit.txt
Figure B. 69 Peak fit of CBV10A / H / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 69 Peak fit statistics of CBV10A / H / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

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File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\10ah\cbv10ah-6%thioh140c9hno-freshpeakfit.txt

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Table B. 70 Peak fit statistics of CBV10A / H(HCl) / 0.5 mol % thioindigo unheated.

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Figure B. 71 Peak fit of CBV10A / H(HCl) / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 71 Peak fit statistics of CBV10A / H(HCl) / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: 10AHCl0.2M100Ctwice+6%thioH - RawData - C:\COLOR\Data\ALE\pennstate\10.10.08UV\1
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak
fit\10ahch\10ahcl0.2m100ctwice+6%thiohbluepeakfit.txt

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Figure B. 72 Peak fit of CBV10A / H(HCl) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Table B. 72 Peak fit statistics of CBV10A / H(HCl) / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: 10AHCI0.2M100Ctwice+6%thiopurple - RawData - C:\COLOR\Data\ALE\pennstate\10.10.0
X Variable: pc
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak
fit\10ahcl\10ahcl0.2m100ctwice+6%thiopurplepeakfit.txt

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Peak | Type          | Anlytc Area    | % Area         | Int Area       | % Area         | Centroid      | Moment2      |
| 1    | Voigt Area    | 2.26301251     | 1.52953482     | 1.21173761     | 0.82528352    | 210.046678   | 56.002255    |
| 2    | Voigt Area    | 0.22830785     | 0.15430971     | 0.22830785     | 0.15549464    | 283.214901   | 34.088254    |
| 3    | Voigt Area    | 16.5697904     | 11.1926262     | 16.5691183     | 11.2848030    | 324.863002   | 100.000000   |
| 4    | Voigt Area    | 0.08390474     | 0.05670990     | 0.08390474     | 0.05714537    | 417.628949   | 18.178666    |
| 6    | Voigt Area    | 66.2605701     | 44.7844847     | 66.2605700     | 45.1283807    | 566.653779   | 1463.63649   |
| 7    | Voigt Area    | 48.8858709     | 33.0411968     | 48.8103480     | 33.2434805    | 663.608880   | 2086.40244   |

Total | 147.954298 | 100.000000 | 146.826828 | 100.000000
Table B. 73 Peak fit statistics of CBV10A / NH$_4$ / 0.5 mol % thioindigo unheated.

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Total         75.5360488   100.000000   75.5336712   100.000000

Figure B. 73 Peak fit of CBV10A / NH$_4$ / 0.5 mol % thioindigo unheated.
Figure B. 74 Peak fit of CBV10A / NH₄ / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 74 Peak fit statistics of CBV10A / NH₄ / 0.5 mol % thioindigo heated at 413K for nine hours.

<table>
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**Figure B. 75** Peak fit of CBV10A / NH₄ / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

**Table B. 75** Peak fit statistics of CBV10A / NH₄ / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

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<th><strong>% Area</strong></th>
<th><strong>Centroid</strong></th>
<th><strong>Moment2</strong></th>
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Figure B. 76 Peak fit of CBV10A / Na / 0.5 mol % thioindigo unheated.

Table B. 76 Peak fit statistics of CBV10A / Na / 0.5 mol % thioindigo unheated.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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Peak | Type           | Anlytc Area | % Area | Int Area | % Area | Centroid | Moment2 |
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Figure B. 77 Peak fit of CBV10A / Na / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 77 Peak fit statistics of CBV10A / Na / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: CBV10A6%thioH1409h - smooth - C:\COLOR\Data\ALE\pennstate\06.05.08\CBV10A6%thioH
X Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\10ana\cbv10a6%thioh1409hpeakfit.txt

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<tr>
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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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</thead>
<tbody>
<tr>
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<table>
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<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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<td>15.3411104</td>
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<td>15.3411636</td>
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Total 177.184218 100.000000 177.183489 100.000000
**Figure B. 78** Peak fit of CBV10A / Na / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

**Table B. 78** Peak fit statistics of CBV10A / Na / 0.5 mol % thioindigo heated at 413K for nine hours / hydrated.

Description: CBV10ANa-6%thio1409hnofresh - smooth - C:\COLOR\Data\ALE\pennstate\06.21.08UV\CB

X Variable: Wavelength nm.

File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\10ana\cbv10ana-6%thio1409hnofreshpeakfit.txt

### Measured Values

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<th>Type</th>
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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
</tr>
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<th>% Area</th>
<th>% Area</th>
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<td>76.9030777</td>
<td>76.9030777</td>
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</table>

Total | 100.000000 | 100.000000 | 2895.82680 |
Figure B. 79 Peak fit of MA-1 / 0.5 mol % thioindigo unheated.

Table B. 79 Peak fit statistics of MA-1 / 0.5 mol % thioindigo unheated.

Description: MA1-6%thioUN - MA1-6%thioUNsmooth - C:\COLOR\Data\ALE\pennstate\MA1-6%thioUN.spc
X Variable: Wavelength nm.
File Source: c:documents and settings\ale\desktop\thesis final\peak fit\ma-1\ma1-6%thiouneakfit.txt

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<th>Asym50</th>
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<th>Asym10</th>
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<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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286
MA-1+dye - MA-1+dye sDEHYDRATED\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\MA-
Pk=Voigt Area 6 Peaks

\(r^2=0.996405\)
\(\text{SE}=0.00752998\)
\(F=8962.57\)

233.66
323.59
389.81
592.02
678.14

Figure B. 80 Peak fit of MA-1 / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 80 Peak fit statistics of MA-1 / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: MA-1+dye - MA-1+dye smooth - C:\COLOR\Data\ALE\pennstate\NEW RUNS WITH BaSo4\MA-
X Variable: Wavelength (nm)
Y Variable: Absorbance
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\ma-1\ma-1+dyepeakfit.txt

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<th>Asym50</th>
<th>FW Base</th>
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</table>
Figure B. 81 Peak fit of MS-1 / 0.5 mol % thiondigo unheated.

Table B. 81 Peak fit statistics of MS-1 / 0.5 mol % thiondigo unheated.

Description: MS1-6%THIOUN - MS1-6%THIOUNsmooth - C:\COLOR\Data\ALE\pennstate\MS1-6%THIOUN.spc

X Variable: Wavelength nm.

File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\ms-1\ms1-6%thionpeakfit.txt

Measured Values

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<tr>
<th>Peak</th>
<th>Type</th>
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<th>Center</th>
<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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<tbody>
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<th>Int Area</th>
<th>% Area</th>
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<th>Moment2</th>
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<td>589.498279</td>
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Total 109.251174 100.000000 109.251171 100.000000
Figure B. 82 Peak fit of MS-1 / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 82 Peak fit statistics of MS-1 / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: MS1-6%thio1409hfreshfiucha - MS1-6%thio1409hfreshfiucha - C:\COLOR\Data\ALE\penn
X Variable: iucha.spc
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\ms-1\ms1-6%thio1409hfreshfiuchapeakfit.txt

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<tr>
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<th>% Area</th>
<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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Figure B. 83 Peak fit of MAS-1 / 0.5 mol % thioindigo unheated.

Table B. 83 Peak fit statistics of MAS-1 / 0.5 mol % thioindigo unheated.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
<th>Center</th>
<th>FWHM</th>
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<th>Asym10</th>
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<td>Voigt Area</td>
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<td>550.403542</td>
<td>101.734739</td>
<td>1.000000000</td>
<td>203.643264</td>
<td>1.00000000</td>
</tr>
<tr>
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<td>Voigt Area</td>
<td>0.30507173</td>
<td>586.531369</td>
<td>72.7111663</td>
<td>1.000000001</td>
<td>145.546540</td>
<td>1.00000000</td>
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</table>

Total         126.270108   100.000000   126.269432   100.000000
Figure B. 84 Peak fit of MAS-1 / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 84 Peak fit statistics of MAS-1 / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: MAS1-6%thio1409hfreshredlila - MAS1-6%thio1409hfreshredlila - C:\COLOR\Data\ALE\X Variable: reshredlila.spc
Y Variable: Wavelength nm.
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\mas-1\mas1-6%thio1409hfreshredlilapeakfit.txt

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<th>FWHM</th>
<th>Asym50</th>
<th>FW Base</th>
<th>Asym10</th>
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<td>224.086054</td>
<td>0.99999996</td>
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<tr>
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<td>Voigt Area</td>
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<td>586.575529</td>
<td>83.4757654</td>
<td>0.99999996</td>
<td>167.212003</td>
<td>0.99999996</td>
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</table>

Total |           | 165.643701 | 100.000000 | 165.591831 | 100.000000 |
Pretreated Palygorskite at 833K

Palygorskite (pre-treated 833K) + dye pretreated
Pk = Voigt Area  12 Peaks
r^2 = 0.998754  SE = 0.0093677  F = 12556

Figure B. 85 Peak fit of pretreated palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours.

Table B. 85 Peak fit statistics of pretreated palygorskite / 0.5 mol % thioindigo heated at 413K for nine hours.

Description: C:\Documents and Settings\Ale\Desktop\THESIS FINAL\Peak Fit\Palygorskite\paly550
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\palygorskite\paly550peakfit.txt

Measured Values

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<th>FWHM</th>
<th>Asym50</th>
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<th>Int Area</th>
<th>% Area</th>
<th>Centroid</th>
<th>Moment2</th>
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Table B. 86 Peak fit statistics of pretreated palygorskite / 0.5 mol % thioindigo unheated.

Description: C:\Documents and Settings\Ale\Desktop\THESIS FINAL\Peak Fit\Palygorskite\paly550
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\palygorskite\paly550unpeakfit.txt

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</table>

Figure B. 86 Peak fit of pretreated palygorskite / 0.5 mol % thioindigo unheated.
LIQUID INTERACTION

THIOINDIGO- 98.7% SULFURIC ACID

Table B. 87 Peak fit statistics of thioindigo in concentrated sulfuric acid.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Type</th>
<th>Amplitude</th>
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<th>FW Base</th>
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Figure B. 87 Peak fit of thioindigo in concentrated sulfuric acid.

Table B. 87 Peak fit statistics of thioindigo in concentrated sulfuric acid.

Description: C:\Documents and Settings\Ale\Desktop\09.12.08UV Varian\thioH2SO4-18N.txt
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\thioindigo-h2so4\thioh2so4- 0.18npeakfit.txt
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<th>Moment2</th>
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**Figure B. 88** Peak fit of thioindigo interaction with concentrated sulfuric acid, after water addition.

**Table B. 88** Peak fit statistics of thioindigo interaction with concentrated sulfuric acid, after water addition.

Description: C:\Documents and Settings\Ale\Desktop\09.12.08UV Varian\ThioH2SO4-0.18N.txt
File Source: c:\documents and settings\ale\desktop\thesis final\peak fit\thioindigo-h2so4\thioh2so4- 0.18npeakfit.txt

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**Total** 6.57352405 100.000000 5.49101566 100.000000
CURRICULUM VITAE

Alejandra Ramirez earned her Bachelor of Science degree in Chemistry from the Universidad Autonoma de Nuevo Leon in 1995. She received her Master of Science degree in Materials Science and Engineering in 2000 from the University Autonoma de Nuevo Leon. In 2008 she will graduate from the PhD of Materials Science and Engineering program at the University of Texas at El Paso (UTEP). Alejandra Ramirez was the recipient of a study abroad scholarship from the UTEP International Office to perform research in Berlin, Germany at the Hahn- Meitner Institute. While pursuing her degree, she worked as a research associate and teaching assistant for the department of Materials Science and Engineering. In addition, as part of her academic training, she had the opportunity to teach Chemistry at El Paso Community College. Alejandra Ramirez has presented her research at international conferences and workshops such as the 2008 Pan American Advanced Studies Institute. Her dissertation entitled, “A Study of the Interaction of Thioindigo Dye, with Several Inorganic Host Materials”, was supervised by Dr. Russell Chianelli and Dr. Pannell. After graduation, she will pursue her academic career with a postdoctoral position overseas at the Helmholtz-Zentrum Berlin für Materialien und Energie in Germany.