CHEMICAL AND STRUCTURAL PROPERTIES OF CLAY MINERALS MODIFIED BY INORGANIC AND ORGANIC MATERIAL

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ABSTRACT: Modification of clay minerals by exchange, intercalation, calcination and imbibition of organics followed by their polymerization and carbonization was studied. The surface properties of the clays were investigated by inverse gas chromatography at infinite dilution employing alkanes and alkenes as probes; the structural properties were measured directly by X-ray diffraction and inferred from the results of high pressure hydrogen adsorption. Calcination of pillared smectites prior to polymerization and carbonization of organic material in the interlayer space leads to a microporous “activated carbon” that demonstrates unique properties as an adsorbent for hydrogen, significantly different from clays that have not been calcined.

Design principles whereby the structural and chemical properties of suitable precursors are exploited to create new materials can be designated molecular engineering. This conceptual idea has seen repeated applications in recent years. For example, in the area of microelectronics the biochip offers the potential of constructing, by building up from individual molecules, electronic devices, thus offering alternatives to the silicon based technological strategy of shrinking large structures to meet the demands of very large scale integration.

Such microporous materials as zeolites and clay minerals have many applications in the industrial sector. They can be used as catalyst carriers (Pinnavaia, 1983), catalysts themselves (Diddams et al., 1984; Kikutchi et al., 1985), molecular sieves, and sorbents (Zyla & Bandosz, 1987). Unfortunately, their design and construction protocol is poorly understood in relation to their end use. The molecular engineering of such materials is an attractive approach and one of the objectives of the study outlined in this paper is to provide such a molecular engineering strategy.

The intercalation of smectites with hydroxy-metal polycations is a method of mineral modification developed in the late 1970s (Brindley & Sempels, 1977; Brindley & Yamanaka, 1979). The method involves the introduction of large metal polycations into the interlayer spaces of clay minerals using ion exchange from aqueous solutions. The polycations act as “pillars” supporting the layers and in addition make the structure rigid after calcination. After heat treatment the hydroxycation “pillars” are converted into oxide “pillars” (Occelli & Tindwa, 1983). The intercalated smectite is characterized by large

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specific surface area, developed porous structure and high surface acidity (Lahav et al., 1978; Vaughan et al., 1979; Occelli & Tindwa, 1983; Brindley & Yamanaka, 1979).

Based on the idea of Pekala & Hopper (1987), Sonobe et al. (1990) prepared microporous carbon using the Na form of montmorillonite as a matrix. After imbibition and processing furfuryl alcohol and polyvinyl acetate, they obtained a homogeneous carbon with a spacing of 0.337 nm. The properties of smectites depend on the manner of modification of the initial mineral, and on the heat treatment of the resulting product. As an extension to the earlier work of Sonobe et al. (1990), we used the intercalated form of smectite modified in different ways as a starting matrix to obtain microporous carbon in the interlayer spaces of the clay mineral. The interlayer spacing of smectite intercalated by hydroxyaluminium oligocations is quite different from the Na form of this mineral: it has a value of 1.92 nm with a microporous volume of ~90 mm$^3$/g and surface area of 400 m$^2$/g (Brindley & Yamanaka, 1979; Zyla & Bandosz, 1987). By saturating this material with furfuryl alcohol followed by polymerization and then carbonization of the interlayer compound, we have obtained new adsorbents whose chemical and physical properties were investigated using X-ray diffraction (XRD) and inverse gas chromatography. Finally, the adsorption properties of these molecularly engineered carbons were evaluated on the basis of their high pressure adsorption of hydrogen.

**MATERIALS AND METHODS**

*Materials*

The smectite fractions of particle diameter $<2~\mu$m were separated by sedimentation from a water suspension of bentonite from Wyoming. The sedimentate was mixed with 1 M NaCl to obtain the initial material (Na-form of smectite) which was then subjected to ion exchange with hydroxyaluminium cations. The solution of hydroxyaluminium oligocations was prepared by dropping NaOH into AlCl$_3$ solution and stirring the mixture to prevent local precipitation of Al(OH)$_3$ at room temperature; the size of oligocations was controlled by the amount of NaOH used, whereby solutions with the OH/Al ratio of ~2.5 are obtained (Vaughan et al., 1979). The solution prepared in this way was mixed directly, without ageing, with the water suspension of smectite, and the modification product was washed with distilled water until the reaction to chloride ions was negative. The sample was then dried in a water bath and heated at 673 K for 10 h. These three steps resulted in samples which are designated as NaS (sodium form), ISA (hydroxyaluminium smectite), ISAH (hydroxyaluminium smectite after heat treatment) according to their modification.

Smectite-furfuryl alcohol complexes were prepared as follows. Dry Na-smectite, ISA, and ISAH were added to 20% solution of furfuryl alcohol (FA) in benzene, and the mixture was stirred in a N$_2$ atmosphere for three days at room temperature. The samples were then washed with pure benzene to remove FA adsorbed on the outer surface of smectite. The polymerization of furfuryl alcohol between the layers was carried out by heating the samples under N$_2$ flow at 353 K for 24 h and then at 423 K for 6 h (Sonobe et al., 1990). The samples of minerals with polymer in the interlayer space were heat treated at 973 K for 3 h under N$_2$ flow in order to carry out the carbonization reaction. The symbols “P” and “C” were added to NaS, ISA and ISAH to designate samples after the polymerization and carbonization processes.
Methods

**X-ray analysis.** Oriented clay mounts were made by settling a suspension of smectite on to a glass slide. All clay mounts were dried at room temperature, heat-treated clay mounts were rehydrated after calcination at humidity <50%. X-ray diffractograms were produced with a Philips PW1729 diffractometer using filtered Cu-Kα radiation. Relative humidity during measurement was <50%.

**Inverse gas chromatography.** The surface properties of modified clay minerals were measured by means of inverse gas chromatography. A brief description of this method and the relevant parameters determined from analysis of the data are presented below.

The parameters which characterize gas-solid interactions are derived from the net retention volumes, $V_N$, of molecular probes injected into the stream of the carrier gas flowing through the chromatographic column filled with the solid to be investigated. The net retention volume is calculated from the measured net retention time, $t_N$, which is the difference between retention times of a probe and a non-adsorbing gas used as a reference,

$$V_N = jFt_N$$

(1)

where $F$ is the flow rate and $j$ is the James-Martin (Conder & Young, 1979) compressibility factor which is dependent on the pressure drop along the chromatographic column.

The net retention volume is directly related to the standard free energy of adsorption at infinite dilution (Kiselev & Yashin, 1969).

$$\Delta G^o = -RT \ln \frac{V_N}{Sm} + C$$

(2)

where $R$ and $T$ are the gas constant and temperature, $m$ and $S$ are mass and specific surface area of the adsorbent, and $C$ is a constant related to the standard states of gas and adsorbed phases. Values of $\Delta G^o$ obtained under the conditions of infinite dilution are dependent on the interaction of probe molecules with the surface only; interactions between adsorbed molecules are neglected.

In this work, alkanes and alkenes were used to assess dispersive, and specific gas-solid interactions. It is well known from the chromatographic literature (Kiselev & Yashin, 1969) that the logarithms of $V_N$ for $n$-alkanes vary linearly with their number of carbon atoms, therefore the quantity, $\Delta G^o_{CH_2}$, which is defined as the difference in the $\Delta G^o$ of two subsequent $n$-alkanes, represents the free energy of adsorption of a CH$_2$ group. This quantity is not related to any particular alkane molecule, and due to its incremental character is not dependent on the choice of the reference state. Dorris & Gray (1980) proposed the method in which $\Delta G^o_{CH_2}$ is used to calculate the dispersive component of the surface free energy, $\gamma^D_s$

$$\gamma^D_s = \frac{(\Delta G^o_{CH_2})^2}{4\gamma_{CH_2}A^2}$$

(3)

where $A$ is the surface area occupied by 1 mole of CH$_2$ groups and $\gamma_{CH_2}$ is the surface energy of polyethylene.

Unsaturated and aromatic hydrocarbons have been used to study specific interactions with different surfaces in terms of the enthalpy of adsorption (Barrer, 1978; Belyakova et al., 1970). Sidqi et al. (1989) proposed a comparison of $\Delta G^o$ values of $n$-alkenes and $n$-alkanes to study the effect of the $\pi$ bond interactions with electron acceptor sites on the surface. The specific interaction parameter, $\varepsilon_\pi$, is defined by the equation
Based on the well known electronic structure of alkanes and alkenes, this parameter can be taken as a measure of the specific (electron acceptor) interaction capacity of the surface.

The chromatographic experiments were performed with an ANTEK 3000 gas chromatograph equipped with a flame ionization detector. The stainless steel columns 2.17 mm in diameter and 50 cm long were used; the appropriate particle granulation (0.2-0.4 mm) was obtained by grinding the dried material and sieving. It was impossible to fill the column with the NaSP sample because it was soft and waxy and therefore it was excluded from the chromatographic experiments. Helium was used as a carrier gas with a flow rate of ~30 cm³/min. The samples were conditioned at 473 K in the chromatographic column under helium gas flow for 15 h prior to the measurements. The alkanes and alkenes used for injections were HPLC grade (Aldrich Chemical Co.). A 50 µl Hamilton syringe was used for injection of very small volumes of gaseous solutes. The experiments were performed in the range of temperature 423-623 K. Under these conditions all chromatographic peaks were symmetrical and retention times did not depend on the amount injected (Henry's law region). Retention volumes were corrected for the gas compressibility. The error of the measurement of retention time was 5% and the temperature was stabilized with an accuracy ±0.1 K.

Hydrogen sorption. The high-pressure hydrogen adsorption measurements were performed with a Cahn 1000 microbalance using the procedures described in detail by Agarwal & Schwarz (1988). Before sorption experiments, samples were heated and evacuated to 10⁻⁷ atm at 393 K until no further weight loss of the sample took place; this procedure ensured removal of preadsorbed gases and physically adsorbed water. The isotherms were obtained at a temperature of 77 K, each isotherm comprising 10 to 20 data points up to 20 atm. Selected pressures were tested for reversibility in adsorption, and in all cases the isotherms were reversible indicating that adsorption equilibrium was achieved. Buoyancy corrections were applied for the sample holder, the sample, and the adsorbed phase. Selected replicate runs were carried out; the reproducibility of the adsorption isotherms was within 2%.

RESULTS AND DISCUSSION

The modification of clay minerals by intercalation, calcination, polymerization, and carbonization caused significant changes in their properties. After the NaS sample was intercalated with hydroxyaluminium complexes, an increase of ~0.4 nm in d₀₀₁ was observed (Table 1), due to the introduction of large oligocations between the silicate layers (Occelli & Tindwa, 1983). The interlayer spaces in Table 1 were calculated assuming the thickness of the silicate layer to be 0.98 nm. During heating at 673 K, the interlayer oligocations were transformed to aluminium oxide pillars (Occelli & Tindwa, 1983) resulting in a small decrease in d₀₀₁ compared to the unheated sample.

After saturation by furfuryl alcohol and polymerization an increase of ~0.3 nm in d₀₀₁ distances was observed for NaSP and ISAP. Only the ISAHP sample showed no significant change in d₀₀₁ (increase of ~0.08 nm). The fact that the ISAHP sample does not swell suggests that the rigid structure obtained is caused not only by holding the layers by pillars but also by the cross-linked structure of this material.

After carbonization all samples had the same value for d₀₀₁ (1.4 nm). The carbonized
Properties of modified clays

Table 1. X-ray results (see text).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_{001} ) nm</th>
<th>Interlayer space nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaS</td>
<td>1.24 ± 0.01</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>ISA</td>
<td>1.70 ± 0.01</td>
<td>0.72 ± 0.01</td>
</tr>
<tr>
<td>ISAH</td>
<td>1.60 ± 0.01</td>
<td>0.62 ± 0.01</td>
</tr>
<tr>
<td>NaSP</td>
<td>1.55 ± 0.01</td>
<td>0.57 ± 0.01</td>
</tr>
<tr>
<td>ISAP</td>
<td>1.96 ± 0.01</td>
<td>0.98 ± 0.01</td>
</tr>
<tr>
<td>ISAHP</td>
<td>1.68 ± 0.01</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td>NaSC</td>
<td>1.41 ± 0.02</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>ISAC</td>
<td>1.40 ± 0.02</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td>ISAHC</td>
<td>1.45 ± 0.02</td>
<td>0.47 ± 0.02</td>
</tr>
</tbody>
</table>

NaS sample showed an increase in interlayer spacing compared to the fresh NaS sample but a net decrease compared to its polymerized counterpart. The ISAC and ISAHC also showed decreases in \( d_{001} \) when compared to their polymerized counterparts. The carbonization step was carried out at 973 K. At this temperature, regardless of the content of the interlayer material, the spacing decreased. Presumably the thermal stability of the matrix determines the structure.

The gas chromatographic results are obtained from retention volumes of alkanes and alkenes. The variation in these quantities with the number of carbon atoms is presented in Fig. 1 which illustrates the principles of the method. The values for alkenes are higher than the values for corresponding alkanes due to their specific interaction with electron acceptor surface sites (Lewis acidic sites). The parameter \( \varepsilon_{\text{a}} \) defined by eqn. (4) is adopted as a measure of the contribution of the specific interaction with electron acceptor surface sites (Jagiello et al., 1992). The values of this parameter presented in Table 2 were obtained from butane and butene results except for ISAP and ISAHP samples. Butane and butene probes were chosen to minimize any experimental artifacts due to possible cracking effects which

![Graph showing dependence of \( \Delta G \) of alkane and alkene adsorption vs. number of carbon atoms](image)
TABLE 2. Inverse gas chromatography results at 423 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter of specific interactions $\varepsilon_r$ (butane/butene) kJ/mol</th>
<th>Parameter of dispersive interactions $\Delta G_{CH_4}$ kJ/mol</th>
<th>Dispersive component of surface energy $\gamma_p$ mJ/m$^2$</th>
<th>Specific retention volume of hexane $V_H/m^3/g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaS</td>
<td>5.03</td>
<td>4.76</td>
<td>155</td>
<td>21</td>
</tr>
<tr>
<td>ISA</td>
<td>4.22</td>
<td>5.09</td>
<td>177</td>
<td>263</td>
</tr>
<tr>
<td>ISAH</td>
<td>3.05</td>
<td>4.74</td>
<td>153</td>
<td>68</td>
</tr>
<tr>
<td>ISAP</td>
<td>0.60*</td>
<td>2.92</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>ISAHP</td>
<td>1.17*</td>
<td>2.42</td>
<td>37</td>
<td>1.5</td>
</tr>
<tr>
<td>NaSC</td>
<td>3.01</td>
<td>6.06</td>
<td>232</td>
<td>—</td>
</tr>
<tr>
<td>ISAC</td>
<td>3.15</td>
<td>5.12</td>
<td>166</td>
<td>97</td>
</tr>
<tr>
<td>ISAHC</td>
<td>3.05</td>
<td>4.40</td>
<td>122</td>
<td>29</td>
</tr>
</tbody>
</table>

* From heptane/heptene.

may occur for longer hydrocarbons in contact with acidic surfaces. Heptane and heptene were chosen for ISAP and ISAHP samples as the retention times of butane and butene were too short to detect. The fact that parallel alkane and alkene lines were obtained (Fig. 2) and no cracking effect was observed for these samples justifies the use of this alkane/alkene pair to calculate $\varepsilon_r$.

The $\varepsilon_r$ parameter, according to its definition (eqn. 4), is sensitive to the electrostatic field distribution on the surface, especially that arising from electron acceptor sites. The value of this parameter is dependent on the average density of these sites as well as on their strength. Contribution of positive charge to the effective electrostatic field may be due to either Bronsted or Lewis acid sites. For the complex structures of the materials used, it would, in general, be difficult to establish which may have the stronger effect on specific interactions with alkene $\pi$ electrons. However, two factors do enable a hypothesis to be suggested.

![Fig. 2. Dependence of $\Delta G$ of alkane (——) and alkene (-----) adsorption vs. number of carbon atoms measured for hydroxyaluminium smectite (□, ■), hydroxyaluminium/polyfurfuryl alcohol smectite (○, ●) and hydroxyaluminium/polyfurfuryl alcohol smectite after carbonization (▲, △) at 383 K.](image)
Firstly, water molecules interact with Lewis acids and transform them into Bronsted acids whose acidity is associated with labile protons. Secondly, it is known from the analysis of ethane and ethylene adsorption on zeolites (Bezus et al., 1971) that the energy of specific interaction increases with decreasing radius of the exchange cation. This suggests that we should expect higher $\varepsilon_\pi$ values for Bronsted acid sites because they are related to the presence of H$^+$ cations whereas Lewis sites are related to metal cations.

From our results (Table 2) it can be seen that the samples which were not heat treated and contain Bronsted acidity (NaS, ISA) have, indeed, the highest $\varepsilon_\pi$ values (5.03, 4.22 kJ/mol). The difference in $\varepsilon_\pi$ values could be attributed to the difference in their surface chemical composition. For the calcined ISAH sample, $\varepsilon_\pi$ decreases to 3.05 kJ/mol. In light of the above hypothesis this can be explained by the transformation of Bronsted to Lewis acidity due to water removal. Small $\varepsilon_\pi$ values for ISAP and ISAHP, we propose, are the result of saturation and hence covering of the entire mineral surface by the PFA polymer. Interlayer spaces as well as silicate layers have their active acidic centres blocked by this material. For all samples, carbonization results in $\varepsilon_\pi$ values nearly equal to the value of $\varepsilon_\pi$ which characterizes the ISAH sample. This indicates that the surface of the mineral is now accessible for the molecular probes and that the effective acidity of these other materials is equivalent to the ISAH sample. This is consistent with the fact that during carbonization at 973 K, the water bound in the mineral structure would be removed, and thus only Lewis centres would be present.

Results for $\gamma_s^D$ and $\Delta G_{CH_4}$ show that these values, which represent dispersive (non-specific) components of the surface free energy, are affected by the modification processes. The values for the first three initial mineral samples are similar, suggesting that the internal and external surface of smectite are very similar as regards non-specific interactions. After introducing the PFA into the interlayer spaces a significant decrease in $\Delta G_{CH_4}$ ($\gamma_s^D$) was observed. These results are similar to the results of Papirer et al. (1989), obtained on silica grafted by different organic compounds, who reported that $\gamma_s^D$ was ~40 mJ/m$^2$, a two fold decrease when compared to the initial silica. For our samples, values of $\gamma_s^D$ and $\Delta G_{CH_4}$ for the initial mineral were much higher because of the influence of the microporous structure which exists between the silicate layers. Fine microporous structures increase the energy of adsorption (Carrott & Sing, 1987; Everett & Powl, 1976). After polymerization of the interlayer material, the $\Delta G_{CH_4}$ values are similar to the values obtained by Papirer et al. (1989) on “organic surfaces”. If we assume that all pores are filled by polymer, then the silicate layers surface would be similar to the materials investigated by Papirer et al. (1989).

After carbonization, a large value for $\Delta G_{CH_4}$ was observed for NaSC. This result is not fully understood and interpretation is further confounded because its counterpart (NaSP) could not be studied. For ISAC and ISAHC, $\Delta G_{CH_4}$ values are almost the same as before modification. This suggests that the non-specific interaction of the probe with the silicate layer is the major contribution to this quantity. The difference seen in values of $\gamma_s^D$ are magnified due to its dependence on the square of $\Delta G_{CH_4}$ (see eqn. 3).

A significant increase in the amount of hydrogen adsorbed for the ISAHC sample is observed compared to the relatively small sorption capacity of H$_2$ on the ISAC sample (Fig. 3). Since both samples have their interlayer space “filled” with carbonized polymer and their silicate layer surface properties are similar ($\varepsilon_\pi$ values are the same), the difference in adsorption capacity is attributed to differences in the microstructure of the carbonized materials. Two factors could contribute, the first being chemical in origin, and the second structural. Bronsted acidity of the ISA sample can cause some chemical reactions like
polymerization of furfuryl alcohol during the construction of the ISAC sample. On the other hand, the structure of the ISHC sample is more rigid due to pillaring. Differences in compression of the smectite matrix are likely to lead to differences in the pore structure of the carbonized polymer. The H₂ adsorption results suggest that a preferred microporosity is developed in ISAHC compared to ISAC.

The modification process changes the measured specific retention volumes, \( V_N/m \), of hexane calculated per gram of adsorbent (Table 2). The effect of intercalation of Na-smectite is reflected by an increase in the specific retention volume of ISA by more than an order of magnitude compared to the untreated smectite. As the surface energy, \( \gamma^P \), is practically constant for the initial samples, it can be assumed that Henry's constant is also unchanged. This implies that, according to eqn. (3), \( V_N/m \) is proportional to the specific surface area of adsorbent. The \( V_N/m \) values can not provide a value for the surface area, but only enable estimation of the trend as a result of modification. The intercalated sample after heat treatment (ISAH) has a lower surface area, probably due to a decrease in the \( d_{001} \) value. The surface area of samples with polymer in the interlayer spaces is very small, and although they have similar \( \gamma^P \) values, the retention volumes indicate the lack of internal surface; the interlayer spaces in these samples are filled with PFA. After carbonization, the surface energy, \( \gamma^D \), is different for all samples, hence it is difficult to estimate changes of surface area based on the specific retention volume of hexane, \( V_N/m \). For ISAC, with a value of \( \gamma^D \) similar to that of ISA before polymerization and carbonization, a significant decrease in surface area is observed. It was argued earlier that changes in microporosity of the carbonized polymer resulted in significant differences in H₂ adsorption capacity. The decrease in surface area of the ISAC sample compared to the ISA sample is consistent with changes in microstructure, and hence hydrogen adsorption characteristics.

**CONCLUSIONS**

The parameters determined from inverse gas chromatography and the results of XRD and hydrogen sorption studies have been used to study the effects of inorganic and organic modification of clay minerals. These parameters enabled changes in structural and chemical
Properties of modified clays

properties to be followed during the modification of Na-smectite as the result of the following steps: intercalation with hydroxyaluminium cations, impregnation with polyfurfuryl alcohol, and carbonization of organic material. It was found that the final products retain some of the other properties of the initial mineral such as high effective acidity. The adsorption properties of these products depend on the modification method of the precursor, e.g. hydrogen adsorption amounts are higher when the mineral structure is rigid due to heat treatment of the intercalated sample.

Our objective was to establish preparation procedures that would allow us to engineer molecularly inorganic-carbon containing materials based on a given smectite precursor. We find that there is a strong inter-relationship between the properties of the inorganic templates and properties of the final products.

REFERENCES


