THERMOGRAVIMETRIC AND INFRARED STUDY OF THE DESORPTION OF BUTYLAMINE, CYCLOHEXYLAMINE AND PYRIDINE FROM NI- AND CO-EXCHANGED MONTMORILLONITE

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ABSTRACT: The acidity of Ni\textsuperscript{2+} - and Co\textsuperscript{2+}-exchanged montmorillonite has been probed using the diagnostic bases n-butylamine, cyclohexylamine and pyridine. Derivative thermograms for the desorption of pyridine from Ni\textsuperscript{2+} - and Co\textsuperscript{2+}-exchanged montmorillonite exhibited strong maxima at 40°, 90° and 360°C, together with a weak maximum near 170°C. The desorption maximum at 360°C is usually attributed to desorption of base from Bronsted acid sites. However, IR spectra of pyridine adsorbed on Ni\textsuperscript{2+} - and Co\textsuperscript{2+}-exchanged montmorillonite, at 250°C, were dominated by intense bands near 1450 and 1607 cm\textsuperscript{-1} which are diagnostic of Lewis-bound pyridine. Consequently, the desorption maximum at 360°C must, in this instance, be attributed to desorption of pyridine from Lewis acid centres. Other bases, including cyclohexylamine and butylamine, also desorb at temperatures which have previously been attributed to the desorption of protonated base. Ni\textsuperscript{2+} - and Co\textsuperscript{2+}-exchanged clay contained predominatly Lewis acid or electron accepting sites, which is in marked contrast to the behaviour of trivalent cation exchanged clays.

It is now well established that trivalent cation-exchanged clays are effective catalysts for a range of synthetic organic reactions and that, for applications where the clay is required to act as a solid source of protons, Al\textsuperscript{3+}-exchanged clays exhibit the most activity (Adams, 1987; Ballantine, 1986; Thomas, 1982). However, Ballantine et al. (1984, 1985) reported that Ni\textsuperscript{2+} - and Co\textsuperscript{2+}-exchanged smectites exhibited up to 80% of the activity of the Al\textsuperscript{3+} counterpart, for both the esterification of hex-1-ene with acetic acid and the formation of dicyclohexylamine from cyclohexylamine with the concomitant elimination of ammonia, respectively. Conversely, Adams et al. (1982) found that the divalent transition metal cation-exchanged forms were ineffective for the formation of methyltertiarybutylether from isobutene and methanol, although a very small quantity of t-butanol was formed, indicating that some protonation of isobutene did occur. In addition, Co\textsuperscript{2+}-exchanged montmorillonite formed small amounts of 2,2'-dihexylether when refluxed in 1-hexene (Adams et al., 1979).

More recently, the ability of transition metal cation-exchanged clays to catalyse Diels-Alder cycloadditions at room temperature, probably via one electron transfer, has been noted (Adams et al., 1987). Again, whilst Ni\textsuperscript{2+} - and Co\textsuperscript{2+}-exchanged Tonsil 13 clays are not as effective as the Cu\textsuperscript{2+}-exchanged form, they are able to reduce the endo : exo ratio of the product from 19:1 in the uncatalysed reaction to =6:1. Given that the exo product is less bulky than the endo species, this probably reflects the restrictions imposed on the transition state by the confines of the interlamellar environment. Finally, Adams & Gabbutt (1990)
have studied the interaction of organic photochromic compounds with variously exchanged smectites because the reversible colour changes which can be induced are potentially useful in data storage and labelling applications. Their investigations have revealed that the Z to E isomerization of the reactant fulgide is an acid catalysed process which is very sensitive to the presence of even low levels of polar compounds and that, once again, Ni$^{2+}$- and Co$^{2+}$-exchanged clays, whilst exhibiting some activity, are not as effective for this process as the trivalent cation exchanged forms.

It is, therefore, timely to consider the acidity of the Ni$^{2+}$- and Co$^{2+}$-exchanged forms of montmorillonite to obtain an understanding of how these exchange forms can be so effective for the esterification of hex-1-ene and the formation of dicyclohexylamine but relatively inactive for the formation of methyltertiarybutylether and the Z to E isomerization of the fulgide. To this end the desorption of several bases (pyridine, butylamine and cyclohexylamine) from Ni$^{2+}$- and Co$^{2+}$-exchanged montmorillonite has been studied and compared with the much more catalytically active Al$^{3+}$-exchanged form. Moreover, a limited study of the desorption of di-n-butylamine and dicyclohexylamine is included because of the ability of Ni$^{2+}$- and Co$^{2+}$-clays to catalyse their formation from the diagnostic bases butylamine and cyclohexylamine, respectively.

**EXPERIMENTAL**

Homoionic samples of the <2 μm fraction of a Wyoming montmorillonite (supplied by Volclay Ltd., Wallasey, Cheshire) were prepared by immersing the clay in a 0.3 M solution of the appropriate salt for 24 h. Excess salt was removed by successive washing and centrifugation steps. Chemical analysis of the Na-exchanged form produced results consistent with a layer formula of (Si$_{3.9}$Al$_{0.1}$)(Al$_{1.33}$Fe$_{0.88}$Mg$_{0.59}$)O$_{10}$(OH)$_{2}$ and a cation exchange capacity (CEC) of 68 ± 2 mEq/100 g of clay. Self-supporting clay films (~2 mg cm$^{-2}$) for infrared (IR) analysis were prepared by evaporation of a dilute aqueous slurry on a polyethylene backing which was subsequently removed.

The samples for both thermal analysis and IR spectroscopy were air-dried (20°C, r.h. ~60%) prior to exposure to reagent grade pyridine, n-butylamine or cyclohexylamine vapour for periods in excess of 48 h. IR spectra were recorded at room temperature and pressure, then after 1 h at 50, 100, 150, 200 and 250°C using an evacuable variable temperature cell with a maximum operating temperature of 250°C. The spectrometer used was a Perkin-Elmer model 783 equipped with a PE3600 data station.

Thermograms and their first derivative were recorded on a Mettler TG50 thermobalance equipped with a TC10A processor. Samples (~7-0 mg, <45 μm grain size) were transferred directly out of the solvent vapour to the thermobalance and the desorption traces recorded at various heating rates under a flow rate for dry N$_2$ purge gas of 25 cm$^3$ min$^{-1}$.

**RESULTS AND DISCUSSION**

Figure 1 shows that the profiles for the desorption of pyridine from Al$^{3+}$-, Ni$^{2+}$- and Co$^{2+}$-exchanged montmorillonite were quite different below 300°C. The shaded portions of the desorption thermograms for the Ni$^{2+}$- and Co$^{2+}$-exchanged forms represent pyridine which is removed by treatment in flowing N$_2$ purge gas at 25°C and is thus attributed to physisorbed pyridine. The Ni$^{2+}$- and Co$^{2+}$-exchanged forms underwent a weight loss of 25% up to 300°C, subsequent to nitrogen pretreatment, whilst the Al$^{3+}$-form lost only 12%.
The derivative thermograms for the desorption of pyridine from the Ni\(^{2+}\)- and Al\(^{3+}\)-exchanged forms have been described before (Breen et al., 1987). With the aid of corroborative IR evidence, peaks II and III, in the derivative thermogram for the desorption of pyridine from Al\(^{3+}\)-montmorillonite, have been shown to correspond to the desorption of pyridine from Lewis and Bronsted acid centres, respectively, whereas peak I indicates the desorption of physisorbed base. The Ni\(^{2+}\)- and Co\(^{2+}\)-exchanged forms exhibited a desorption maximum in the vicinity of peak III, which in the absence of further evidence may indicate the presence of protonated pyridine. The Ni\(^{2+}\)- and Co\(^{2+}\)-exchanged forms exhibited two further desorption maxima near 90 and 170°C, labelled IIa and IIb, respectively, although the IIb peak for the Ni\(^{2+}\)-form was quite small.

Figure 2b presents IR spectra of the air-dried Ni\(^{2+}\)-montmorillonite following exposure to pyridine and subsequent evacuation at increasing temperatures. The sample fresh from pyridine vapour exhibited absorption bands which, following Ward (1968), were assigned to physisorbed pyridine (1435 and 1445 cm\(^{-1}\)), hydrogen-bonded pyridine (753, 1435 and 1590 cm\(^{-1}\)), Lewis-bound pyridine (1452, 1486, 1578, 1590 and 1606 cm\(^{-1}\)) and the pyridinium cation (1486, 1540 and 1635 cm\(^{-1}\)). Degassing at the IR beam temperature of 35°C resulted in significant reductions in the intensity of the 753, 1435, 1445 and 1590 cm\(^{-1}\) bands, together with a sharpening of a band at 760 cm\(^{-1}\). Subsequent to heating at 50°C, the IR spectrum of pyridine-treated Ni\(^{2+}\)-exchanged montmorillonite (bottom spectrum, Fig. 2b) retained some evidence of the large amount of physisorbed pyridine originally present, but by 100°C the peaks at 1435 and 1455 cm\(^{-1}\) had all but disappeared. A weak band at 1540 cm\(^{-1}\), attributed to Bronsted-bound pyridine, was clearly resolved at 50°C but
Fig. 2. The effect of evacuation temperature on the IR spectra of pyridine sorbed on (a) Co$^{2+}$- and (b) Ni$^{2+}$-montmorillonite. Temperatures from bottom to top are 50°C, 100°C, 200°C and 250°C, respectively.
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became indistinct as the temperature was raised to 250°C, and was hard to discern in the presence of strong peaks at 1452, 1485 and 1606 cm$^{-1}$ attributed to Lewis-bound pyridine. In contrast, the pyridine treated Co$^{2+}$-form (Fig. 2a) exhibited a much broader envelope of peaks in the 1560–1605 cm$^{-1}$ region which, even at 250°C, exhibited resolved maxima at 1590 and 1605 cm$^{-1}$. These differences in the IR spectra correlate well with the relative intensities of the maxima denoted IIb in the derivative thermograms for the desorption of pyridine from Ni$^{2+}$- and Co$^{2+}$-exchanged montmorillonite (Fig. 1). Moreover, the presence of an unresolved shoulder centred at 1535 cm$^{-1}$ suggested the presence of some Bronsted-bound pyridine at 250°C in the Co$^{2+}$-form. However, the truly striking feature of these IR spectra was the overall dominance of bands associated with Lewis-bound pyridine, in marked contrast to the results of almost identical studies on Al$^{3+}$-, Fe$^{3+}$- and Cr$^{3+}$- exchanged montmorillonite (Breen et al., 1987) in which all three cation exchanged forms exhibited well resolved, intense, Bronsted-bound pyridine bands at 1540 cm$^{-1}$. Clearly, the major type of acid site in the Co$^{2+}$- and Ni$^{2+}$-exchanged montmorillonite is of electron accepting or Lewis acid character.

Velghe et al. (1977) studied the coordination of water to Ni$^{2+}$ in the interlayer space of Camp Berteau montmorillonite and found that their data indicated Ni(H$_2$O)$_6^{2+}$ in octahedral coordination in agreement with the X-ray photoelectron spectroscopy results of Koppelmann & Dillard (1977). Following evacuation of this hydrated sample at 140°C, Velghe et al. (1977) found that part of the Ni$^{2+}$ was present as a tetrahedral complex, formed with three oxygens of the hexagonal rings in the tetrahedral sheets and one residual water molecule. The other Ni$^{2+}$ ions were completely dehydrated and coordinated only to the three surface oxygens of the tetrahedral sheet. Moreover, Calvet & Prost (1971) reported that a Ni$^{2+}$ ion is small enough to migrate into the clay layer much as Li$^+$ does in the Hofmann-Klemen effect (Hofmann & Klemen, 1950) and an ion needs to shed its water molecules to do this. It is thus not surprising that the Ni$^{2+}$ and Co$^{2+}$ ions in these studies were readily dehydrated to give pyridine molecules which were directly coordinated to the bare cation.

The derivative thermograms for the desorption of the diagnostic bases pyridine, cyclohexylamine and n-butylamine from Co$^{2+}$-exchanged montmorillonite are presented in Fig. 3, together with those for dicyclohexylamine and di-n-butylamine. The maxima at 330°C and 420°C in the desorption thermograms for cyclohexylamine and n-butylamine from Al$^{3+}$-montmorillonite have been taken to indicate protonated base (Ballantine et al., 1987; Breen et al., 1987) by analogy with the behaviour seen with pyridine. The difference in the desorption temperatures for these bases, which have very similar pK$_b$s, was attributed to the fact that cyclohexylamine is a secondary base. Indeed the desorption of tertiary butylamine from the Bronsted sites in Al$^{3+}$-exchanged montmorillonite occurred at the even lower temperature of 250°C, thus confirming the trend (Deane, 1987). In the current context it must be assumed that these bases are desorbing from Lewis sites on the Ni$^{2+}$- and Co$^{2+}$-exchanged clay. It is also worthwhile to note that the temperatures for the desorption maxima, in the 250–400°C range, of di-n-butylamine coincided with those for n-butylamine, whilst that for dicyclohexylamine could explain the high temperature shoulder on the desorption maximum for cyclohexylamine. Consequently, it may not be possible to allow for small conversions to the di-n-amine in the desorption experiment.

Having determined that the diagnostic bases desorbed at similar temperatures from both Lewis and Bronsted sites, an attempt was made to ascertain whether the activation energy for desorption, if it could be determined, from the different sites was also similar. It is
possible to derive activation energies for thermally induced desorption by determining how the temperature at which the desorption maximum occurs, $T_m$, varies with heating rate, $\beta$ (Gasser, 1987). For a first order desorption process the relevant equation is:

$$2 \ln T_m - \ln \beta = \frac{\Delta E}{RT_m} + \ln \frac{\Delta E}{RA}$$

where $\Delta E$ is the activation energy for the desorption process, $R$ is the universal gas constant and $A$ is the pre-exponential factor in the Arrhenius equation. Consequently, a plot of $(2 \ln T_m - \ln \beta)$ versus $1/T$ yields a slope of $\Delta E/R$ and an intercept of $\Delta E/RA$. The requirement that $\beta$ must be varied over two orders of magnitude was satisfied by employing heating rates from 0.5 to 50°C min$^{-1}$. Fig. 4, which uses the desorption of pyridine from Co$^{2+}$-montmorillonite as an example, illustrates that the shifts in peak temperature were significant and discernible, whereas Fig. 5 shows the fit of a selection of data (derived from similar families of desorption profiles) to the equation outlined above. Clearly the data fit this formulation. There was a significant, though small, difference between the activation energies, $\Delta E$, derived from the cyclohexylamine (190 ± 10 kJ mol$^{-1}$), pyridine (140 ± 10 kJ mol$^{-1}$) $n$-butylamine (120 ± 10 kJ mol$^{-1}$), dicyclohexylamine (140 ± 10 kJ mol$^{-1}$)
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Fig. 4. The effect of heating rate, $\beta$ (in °C min$^{-1}$), on the profiles for the thermal desorption of pyridine from Co$^{2+}$-exchanged montmorillonite.

Fig. 5. Plots of $(2 \ln T_m - \ln \beta)$ vs. $1/T$ for the desorption of the diagnostic bases (△) pyridine, (□) $n$-butylamine, (◇) di-$n$-butylamine, (○) cyclohexylamine and (◇) dicyclohexylamine from Al$^{3+}$- (open symbols) and Co$^{2+}$-montmorillonite (closed symbols).
and di-n-butylamine (120 ± 10 kJ mol⁻¹) data but these values were independent of the exchange cation, and consequently the type of acid site also. Similar activation energy values were derived using data for the desorption of pyridine from Ni²⁺- and Co²⁺-exchanged montmorillonite using a Stanton Redcroft TG750 thermobalance, which thus eliminates the possibility that the variation of $T_m$ with $\beta$, and hence the derived value of $\Delta E$, was an instrumental artifact. However, given that the relative basicities of cyclohexylamine and $n$-butylamine are very similar, it is difficult to reconcile the differences in activation energies with the strengths of the bonds between the adsorbed base and the acid site. Hence, the differences may possibly reflect either the potential barrier associated with passage of the desorbed base out of (i) the interlayer, or (ii) interparticulate space. However, it should be noted that the grain size of <45 μm was chosen and used to minimize the diffusional limitations described by Tronconi & Forzatti (1985), and considered by Deane (1987).

The desorption maximum at 330°C in the derivative thermogram for the desorption of cyclohexylamine from Al³⁺- and H⁺-montmorillonite has been used to quantify the number of Bronsted sites present on these clays, in mmol H⁺ (g clay)⁻¹, and these values have correlated well with the experimentally determined catalytic activity (Ballantine et al., 1987; Breen, 1991). In order to compare the acidities of the Al³⁺-, Ni²⁺- and Co²⁺-exchanged clays used, it was decided to express both the Lewis and the Bronsted

![Graph](image)

**FIG. 6.** (a) Profiles for the thermal desorption of cyclohexylamine from montmorillonite samples containing increasing amounts of Ni²⁺. The figures on the curves indicate the number of cation exchange equivalents in the initial exchange solution. (b) Acidity of Ni²⁺-montmorillonite, expressed as mmol cyclohexylamine (g clay 250°C)⁻¹, as a function of the number of cation-exchange equivalents in the initial exchange solution.
acidities in terms of mmol cyclohexylamine desorbed (g clay at 250°C)\(^{-1}\). The temperature 250°C was chosen so that the different amounts of physisorbed and low-temperature Lewis sites in the various exchange forms did not affect the final value. This approach yielded acidity values for Al\(^{3+}\), Co\(^{2+}\) and Ni\(^{2+}\)-montmorillonite, measured at \(\beta = 200\)°C min\(^{-1}\), of 0.59, 0.63 and 0.78 mmol cyclohexylamine desorbed (g clay at 250°C)\(^{-1}\). Furthermore, the evolution of Lewis acid sites on Ni\(^{2+}\)-montmorillonite was determined, at the same heating rate, as a function of Ni\(^{2+}\) loading on the clay by varying the number of cation exchange equivalents of Ni\(^{2+}\) in the exchange solution. Analysis of the supernatant solution by solution spectrophotometry showed that all the Ni\(^{2+}\) was adsorbed until the CEC was saturated, after which the excess Ni\(^{2+}\) was quantitatively detected. The samples prepared in this way were washed, air-dried and exposed to cyclohexylamine vapour. The resulting derivative thermograms are shown in Fig. 6a and the acidity value determined from them plotted as a function of Ni\(^{2+}\) content of the initial exchange solution in Fig. 6b. The Lewis acidity increases as the Ni\(^{2+}\) loading increases, clearly showing that the Ni\(^{2+}\) ions are the seat of this acidity.

**CONCLUSIONS**

These investigations show that the Ni\(^{2+}\) and Co\(^{2+}\)-exchanged montmorillonites exhibit predominantly Lewis acid character which increases with Ni\(^{2+}\), and presumably Co\(^{2+}\), loading on the clay. This is in marked contrast to the predominantly Bronsted character shown by trivalent cation-exchanged clays. The desorption of the diagnostic bases used in this study occurred from both Lewis and Bronsted sites at temperatures and with activation energies characteristic of the base but independent of the exchange cation. Consequently, caution should be exercised when attributing the desorption of the bases at temperatures in excess of 250°C solely to the desorption from Bronsted acid centres, unless corroborated by IR studies.

**REFERENCES**


