Catalysis Letters 45 (1997) 35–40

Brønsted and Lewis acid catalysis with ion-exchanged clays

D.R. Brown * and C.N. Rhodes ‡

Catalysis Research Unit, School of Applied Sciences, Leeds Metropolitan University, Leeds LS1 3HE, UK
E-mail: d.r.brown@lmu.ac.uk

Received 18 October 1996; accepted 18 February 1997

An acid-treated montmorillonite clay has been ion-exchanged with Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Na^+. The catalytic activities of these materials have been measured in the Brønsted acid catalysed rearrangement of α-pinene to camphene, and the Lewis acid catalysed rearrangement of camphene hydrochloride to isobornyl chloride, following thermal activation at temperatures from 75 to 350°C. The surface acidities of the ion-exchanged clays have been measured using a microcalorimetric method involving ammonia adsorption, and through the infrared spectra of adsorbed pyridine. The results show that maximum Brønsted acidity is generated on thermal activation at approximately 150°C and maximum Lewis acidity at 250–300°C. A good correlation has been found between the surface acidities and the catalytic activities of the ion-exchanged clays in both reactions. A significant result is the relatively low surface Lewis acid strength of Al^{3+}-exchanged clays, for which a possible explanation is proposed.

Keywords: clay, acid-activated clay, acid-treated clay, montmorillonite, catalysis, solid acid, Lewis acid, Brønsted acid, ion-exchange

1. Introduction

Clay minerals, particularly montmorillonites, have been widely used as acid catalysts [1–3]. The exchangeable cations in these materials play a key role in controlling surface acidity and catalytic activity. The method by which Brønsted acidity is developed in these materials is relatively well established [2,3]. However, the source of Lewis acidity, and its dependence on exchange ion and state of hydration, are less well understood. In the reported work two simple test reactions, catalysed by Brønsted and Lewis acids respectively, are used to study the relationship between Brønsted acid and Lewis acid catalytic activities, and their dependence on thermal activation, in a range of ion-exchanged clays. These results are compared with direct study of surface acidity using calorimetric measurements of ammonia adsorption and the infrared spectra of adsorbed pyridine.

1.1. Surface acidity in acid-treated clays

There are many examples of Brønsted acid catalysed reactions carried out with montmorillonite catalysts [2–4]. The majority of these have used commercially available acid-treated montmorillonites. These materials are partially delaminated and exhibit higher surface areas than the parent clays. Although, initially, H^+ ions occupy exchange sites in acid-treated montmorillonites, the H^+ forms of the clays are unstable and they rapidly convert predominantly to the Al^{3+} forms as these and other lattice metal ions migrate from lattice to exchange sites [5]. The ability of Al^{3+} ions in exchange sites to polarise coordinated water molecules is enhanced by the adjacent hydrophilic clay surface and, under appropriate hydration conditions, these clays show Brønsted acid strengths almost as high as those of the original H^+ clays [6]. For this reason, most acid-activated clay catalysts are used without further ion exchange, relying on the acidity of the Al^{3+} centres for catalysis. Because of the way in which protons are generated in these materials however, the Brønsted acidity is very sensitive to water content and acid-treated montmorillonite catalysts are usually thermally activated within a relatively narrow temperature range typically around 150°C.

There have been a number of studies of the effect of exchange ion on Brønsted acid catalytic activity [7–9]. For the majority of reactions of this type the dependence of activity on exchange ions is similar, with Al^{3+} providing the highest activity and other ions with lower charge/radius such as Fe^{3+} and Zn^{2+} being less active, and cations such as Na^+ and Ca^{2+} being inactive.

Lewis acid catalysis using clays has been studied on a smaller number of reactions, mainly simple Friedel–Crafts alkylations using alkyl halides [10] and acylations using acyl halides [11], and some Diels–Alder reactions [12–14]. However, a consistent pattern of catalytic activities has emerged from these studies. Firstly, Lewis acid sites are generated at higher thermal activation temperatures than Brønsted acid sites. Secondly, the order of exchange ions in terms of catalytic activity is different to that in Brønsted acid catalysed reactions. The most significant difference is that Fe^{3+}-exchanged clays invariably show higher activities than Al^{3+}-exchanged clays

---

* To whom correspondence should be addressed.

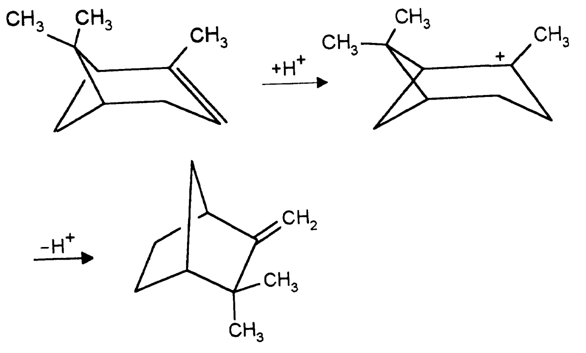
‡ Current address: Department of Chemistry, University of York, York YO1 5DD, UK.

[9–12] in Lewis acid catalysed reactions. The reason for this is not clear. However, recent work by Cseri et al. [9] on alkylation of aromatics with benzyl chloride, has suggested that the enhanced activity of Fe^{3+}-exchanged clays may be associated with an additional catalytic mechanism. The first step in this proposed mechanism is the homolytic fission of the benzyl chloride, producing a benzyl radical and a chlorine atom. The benzyl radical is immediately oxidised by Fe^{3+} to the carbocation, which attacks the aromatic in the usual way. The Fe^{2+} ion produced in this process reacts with the chlorine atom, regenerating Fe^{3+} and the chloride ion. As a result, these workers have suggested that a requirement for high activity in a Lewis acid catalysed reaction may be the presence of a *reducible* exchange cation.

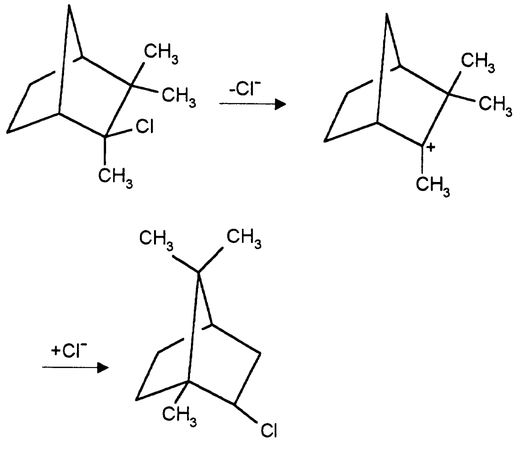
1.2. Test reactions

The following liquid phase reactions have been used. Important features are that they are simple and only single products are formed. The reactants in the two reactions are of similar size so steric factors associated with the active sites on the catalysts are likely to be similar. Both reactions are relatively facile, involving quite stable carbocation intermediates. Neither reaction requires nor produces water, which could affect the strength of acid sites on clay surfaces and could hydrate Lewis acid centres converting them to Brønsted acid centres.

Brønsted acid catalysed reaction: The first step in the relatively facile rearrangement of α-pinene to camphene is the protonation of the less substituted end of the double bond in α-pinene. The resulting carbocation then rearranges by the migration of one of the ring bonds to the positive carbon. The driving force for the reaction is the relief of ring strain in the intermediate carbocation.



Lewis acid catalysed reaction: The rearrangement of camphene hydrochloride to isobornyl chloride is a facile Lewis acid catalysed reaction. It proceeds via abstraction of a chloride ion by a Lewis acid to produce a tertiary carbocation. Steric hindrance drives rearrangement of the carbocation, which then recovers the chloride ion from the catalyst.



2. Experimental

The clay used throughout was Fulcat 40, an acid-treated montmorillonite supplied by Laporte Industries. This material is based on the high-iron montmorillonite from Clophill, Surrey. Details of both the parent clay and Fulcat 40 appear in table 1.

Samples of Fulcat were ion-exchanged with Al^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+} and Na^{+}, by stirring 1% suspensions of the clay in 1.5 mol dm^{-3} solutions of the metal chlorides or nitrates overnight. In each case the clay was then separated from the solution and treated with fresh salt solution for the same time. The suspensions were then centrifuged and the resulting clays thoroughly washed, and dried at room temperature. Previous workers have shown that ion-exchange with each of these metal ions into montmorillonites and acid-treated montmorillonites is essentially complete when the ions are applied at this concentration and under these conditions [9,15,16].

For catalytic testing the clays were thermally activated under dry air for 1 h at specified temperatures. For

Table 1
Properties of Clophill montmorillonite and Fulcat 40 acid-treated montmorillonite

Analysis (%)	Clophill montmorillonite	Fulcat 40 acid-treated montmorillonite
SiO_2	58.3	66.9
Al_2O_3	14.9	8.1
Fe_2O_3	9.4	5.0
TiO_2	0.8	1.0
MgO	4.2	1.4
CaO	2.5	2.6
Na_2O	0.2	0.9
K_2O	0.7	0.4
surface area ($m^2 g^{-1}$)	106	322
cation exchange capacity (mequiv $100g^{-1}$)	89	52

all reactions reagents were of Analar grade and were dried over molecular sieve or redistilled before use.

For the first reaction 50 mg activated catalyst were added under dry air to 0.06 mol α-pinene held at 80°C. No additional solvent was used. The mixture was continuously stirred. Product yields were measured at 20 min intervals with GC [17].

For the second reaction camphene hydrochloride was freshly prepared, since it is not commercially available and tends to decompose on storage. Hydrogen chloride was bubbled through a 1% camphene solution in hexane at 0°C. The white camphene hydrochloride precipitate was separated, washed in cold ethanol, dried and stored in a desiccator. The product was identified with NMR and its purity established with GC.

The reaction was carried out in the same way as above, using 250 mg catalyst and 0.01 mol camphene hydrochloride in 0.1 mol cyclohexane, and a reaction temperature of 0°C. Product yields were measured at 10 min intervals with GC.

Surface acidity measurements by ammonia adsorption were made using a modified Stanton Redcroft 625 combined thermobalance/differential scanning calorimeter, described fully elsewhere [18]. The principle of this method is that the sample is thermally activated in situ under flowing helium. The temperature is then set at a suitable level to permit chemisorption of ammonia on the catalyst surface but prevent physisorption. Experience has shown that 150°C is suitable. A controlled series of ammonia pulses is then introduced into the helium stream. Sample weight and enthalpy changes are monitored as ammonia is adsorbed and, assuming one ammonia molecule is adsorbed on each acid site, these are interpreted in terms of the abundance of acid sites on the catalyst surface and their average strength, expressed as enthalpies of adsorption of ammonia.

Infrared spectra were recorded in transmission mode on self-supporting wafers of the catalysts. These were mounted in a gas cell, thermally activated under vacuum at appropriate temperatures for 1 h, and then exposed to pyridine vapour at 150°C overnight. Excess pyridine was pumped away and spectra recorded on an FTIR spectrophotometer.

3. Results and discussion

The activities of each of the exchanged Fulcats towards the Brønsted and Lewis acid catalysed reactions as a function of thermal activation temperature are shown in figure 1. The activities of the Na^+-exchanged clays are not shown because they were too low to measure for both reactions at all thermal activation temperatures. This observation means that the catalytically active sites in these materials must be the exchangeable cations. Even though there may be Lewis, and possibly Brønsted, acid sites elsewhere on the clay, these are not sufficiently abundant or acidic to impart activity, even towards these relatively facile reactions.

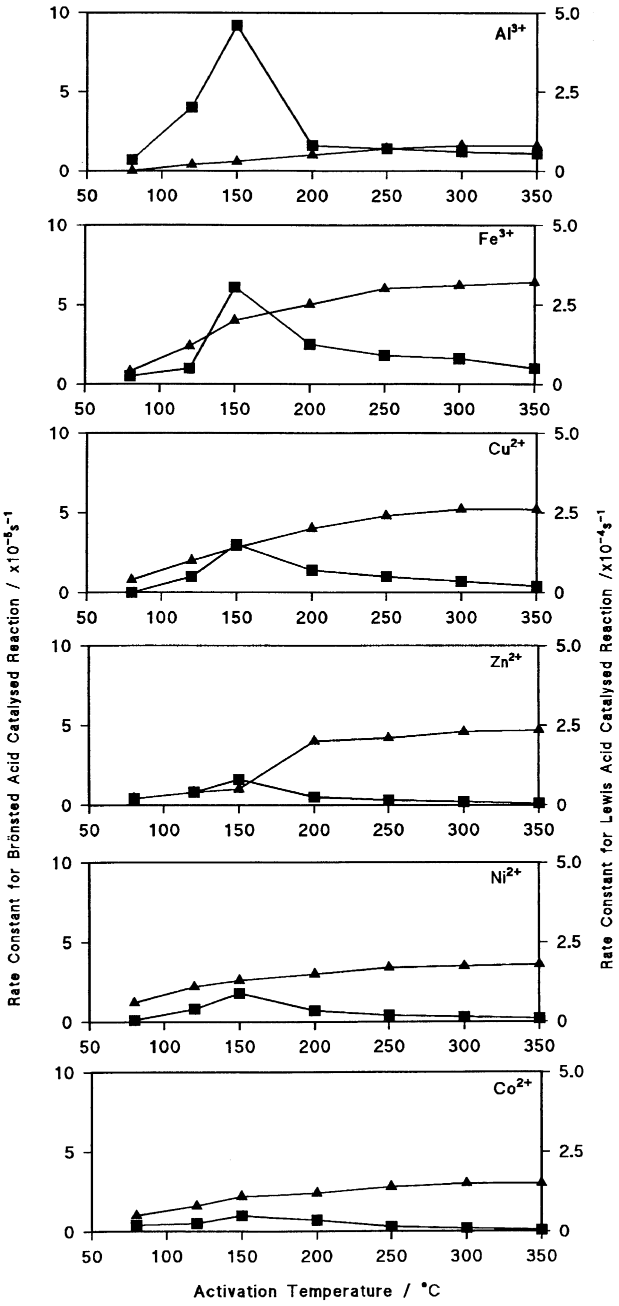


Figure 1. The dependence of catalytic activity on thermal activation temperature, in the Brønsted acid catalysed rearrangement of α-pinene (■), and the Lewis acid catalysed rearrangement of camphene hydrochloride (▲), for Fulcat 40 acid-treated montmorillonite, exchanged with Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}.

It can be seen from figure 1 that the Brønsted acid catalytic activities (α-pinene rearrangement) for all exchange ions reaches a maximum after thermal activation at 150°C, with very low activities below 100°C and above 200 °C. This implies that the critical water content of the clay which allows maximum polarisation by the cation, and hence proton formation, is similar for the six exchange cations.

The Brønsted acid catalytic activities are shown in order for the ion-exchanged Fulcats in figure 2a. The order of activities is broadly in line with the accepted charge-to-radius ratios for the various metal ions, and therefore reflects the abilities of the cations to polarise coordinated water molecules.

Returning to figure 1, the activities towards the Lewis acid catalysed reaction in most cases increases as the thermal activation temperature rises above 150°C. The behaviour of Al^{3+}-, Fe^{3+}-, Cu^{2+}- and Zn^{2+}-exchanged Fulcat suggests that Lewis acidity increases as Brønsted acidity falls, and this is consistent with a model in which the exchange ions become Lewis acidic as the directly coordinated water is driven off. Clays exchanged with Ni^{2+} and Co^{2+} show a less obvious conversion of Brønsted to Lewis acid activity and show higher Lewis acid activity at low thermal activation temperatures than might be expected based on this model. These two exchange ions appear to behave as Lewis acids even when they are still hydrated.

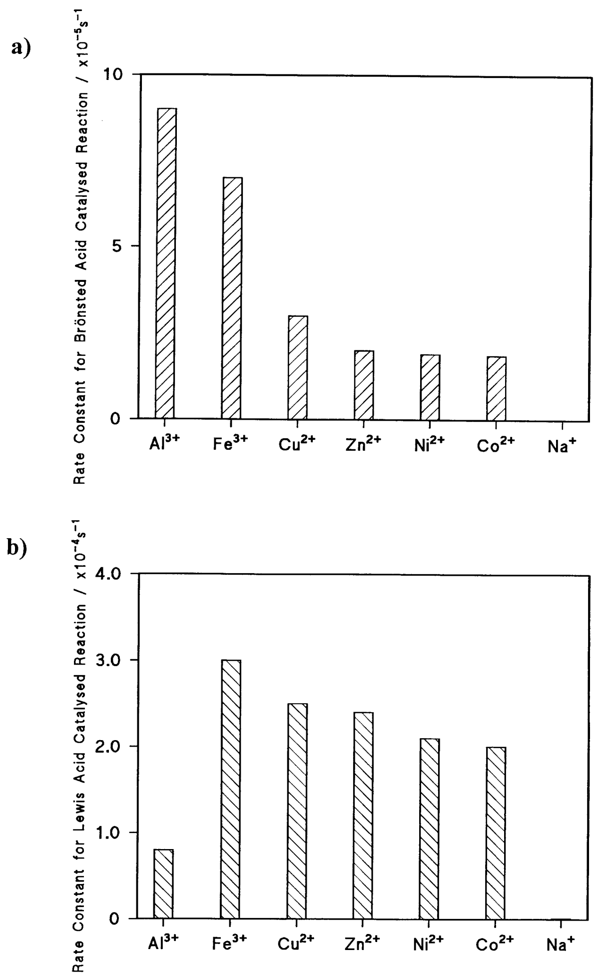


Figure 2. Catalytic activities of ion-exchanged Fulcat 40 in (a) the Brønsted acid catalysed rearrangement of α-pinene following activation at 150°C and (b) the Lewis acid catalysed rearrangement of camphene hydrochloride following activation at 250°C.

For each of the ion-exchanged clays, the maximum activity in the Lewis acid catalysed reaction is reached by 250–300°C. Although not shown, thermal activation at higher temperature, up to 500°C, has little further effect. The activities of the clays following 250°C activation are shown in figure 2b. The main difference between the Brønsted and Lewis activity series is the relatively low activity of Al^{3+}-exchanged clay in the Lewis catalysed reaction.

The infrared spectra of adsorbed pyridine on the Al^{3+}-, Fe^{3+}- and Ni^{2+}-exchanged clays, following activation at 150 and 250°C, are shown in figure 3. Bands are observed at 1540, 1490 and 1440–1460 cm^{-1} for clays activated at 150°C. Clays activated at 250°C show bands at 1490 and 1455–1460 cm^{-1} only.

Hydrogen-bonded pyridine, which typically absorbs at 1440 and 1490 cm^{-1}, may be contributing in these regions of the spectrum [19]. However, spectra (not shown) of pyridine adsorbed on clays exchanged with non-acidic cations like Na^+ and degassed at similar temperatures, exhibited only weak bands in these regions after 150°C activation, and no absorption in these regions after 250°C activation. We conclude therefore that the bands seen in figure 3 are predominantly due to pyridine adsorbed on surface acid sites [20,21].

The 1540–1550 cm^{-1} band is assigned to the pyridinium ion, formed when pyridine associates with a Brønsted acid site. The band at 1455–1460 cm^{-1} is assigned to pyridine coordinated to surface Lewis acid

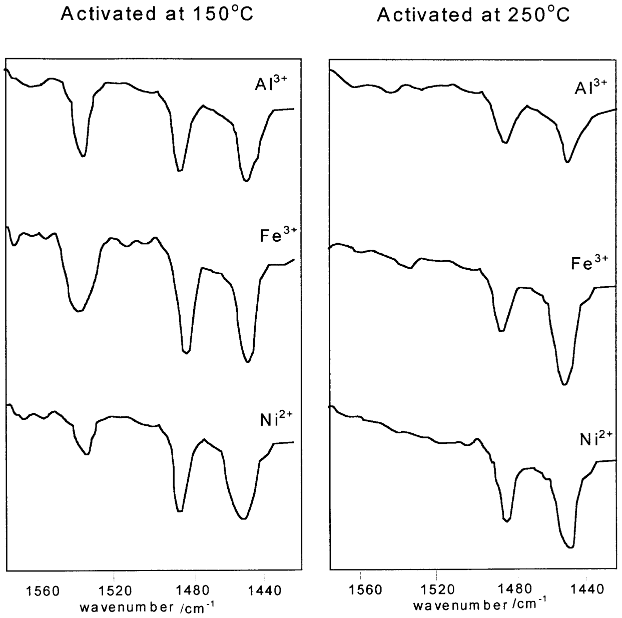


Figure 3. Transmission infrared spectra of pyridine adsorbed on Al^{3+}, Fe^{3+}- and Ni^{2+}-exchanged Fulcat 40, following activation of the catalysts at 150°C and 250°C. In each case catalysts were exposed to pyridine vapour overnight at 150°C

sites. The band at 1490 cm^{-1} is assigned to a combination of pyridine on Lewis and Brønsted acid sites.

The spectra in figure 3 for all three catalysts following 150°C activation show both types of acid site, although it is difficult to assess the precise intensities of the bands associated with Lewis acid sites because of overlap from hydrogen-bonded pyridine. The Ni^{2+}-exchanged clay shows relatively few Brønsted acid sites compared to the other two. High-temperature activation effectively removes Brønsted acid sites from all three clays, leaving only surface Lewis acid centres.

In principle, the positions of the Lewis acid bands in the 1455–1460 cm^{-1} region can be related to the strength of the Lewis acid centres, and we hoped to be able to compare the three ion-exchanged clays on this basis. However, even after 250°C activation these bands are very broad, suggesting that each clay exhibits a wide range of acid site strengths, and the precise positions of the maxima, which are in fact very similar at 1455 cm^{-1} (Al^{3+}), 1458 cm^{-1} (Fe^{3+}) and 1456 cm^{-1} (Ni^{2+}), probably have relatively little significance in terms of overall acid strength and catalytic activities.

Despite the difficulty of obtaining quantitative information from the spectra, these results are broadly consistent with the relative catalytic activities of the three clays in the Lewis and Brønsted acid catalysed reactions. One of the important things that the infrared data shows is that high temperature activation yields *only* Lewis acidity on all three catalysts. This means that the calorimetric data taken after high-temperature activation reflects the catalytic Lewis acid sites only, and therefore provides quantitative data on the abundance and strength of Lewis acid sites, with which the catalytic activities in the camphene hydrochloride reaction can be compared.

This calorimetric surface acidity data, based on ammonia adsorption, is shown in table 2. It shows that, after 250°C activation, the abundance of surface (Lewis) acid sites follows the order Al^{3+} $>$ Fe^{3+} $>$ Ni^{2+}, whereas the acid strength follows the reverse order Ni^{2+} $>$ Fe^{3+} $>$ Al^{3+}, with the Al^{3+}-exchanged clay being significantly weaker than the first two. If this result is compared with the relative catalytic activities of the clays towards the Lewis acid catalysed conversion of camphene hydrochloride to isobornyl chloride, it seems that the anomalously low catalytic activity of the Al^{3+} clay is probably due to the relative weakness of the surface Lewis acid sites on this catalyst. In contrast, the Ni^{2+}- and Fe^{3+}-exchanged clays both exhibit stronger Lewis acidity, and significantly higher catalytic activities.

Table 2
Surface acidity data for ion-exchanged Fulcat 40 acid-treated montmorillonite, determined by ammonia adsorption

Exchangeable cation	Activation temperature (°C)	Number of acid sites (mmol g^{-1}) (±0.05)	Acid site strength (kJ mol^{-1}) (±5)
Al^{3+}	150	0.50	120
	200	0.21	80
	250	0.20	75
	300	0.20	73
Fe^{3+}	150	0.30	90
	200	0.24	100
	250	0.22	101
	300	0.21	103
Ni^{2+}	150	0.20	87
	200	0.15	101
	250	0.14	105
	300	0.14	110

It is worth returning to the Brønsted acid catalysed rearrangement of α-pinene to examine the relationship between activity and Brønsted acid strength. This is not quite straightforward because calorimetric acidity measurements after activation at 150°C give combined Brønsted and Lewis acidities. Nevertheless, the data in table 2 show very clearly that the Al^{3+} clay has both the strongest and the most abundant acid sites after this lower temperature activation, and this is almost certainly a reflection of the surface Brønsted acidity on this catalyst. The activity in the Brønsted acid catalysed reaction of the Al^{3+} clay is the highest of the group. Looking at the three ion-exchanged clays for which calorimetric data has been collected, there seems to be a reasonable correlation between surface acidity after 150°C activation and Brønsted acid catalytic activity.

Overall therefore, we conclude that the catalytic activities of ion-exchanged clays, in both Brønsted and Lewis acid catalysed reactions, reflect quite closely the surface acidities of the clays. The trend shown in Brønsted acidity (on activation at 150°C) is predictable, and can be explained in terms of the abilities of the cations in the clay to polarise coordinating water molecules and hence generate protons. The way in which Lewis acidity (250°C activation) varies with exchangeable cation is similar, except that Al^{3+}-exchanged clays exhibit relatively low acid strengths (and catalytic activities). It is difficult to see an obvious explanation for this. A possibility is that, compared with the other cations studied, the Al^{3+} ion may behave as a very hard acid on a clay surface. Its low catalytic activity may reflect its incompatibility with the soft Cl^{-} base, and its low apparent Lewis acid strength as measured by ammonia adsorption may also be a consequence of the incompatibility between the hard Al^{3+} acid and the softer base. This could be tested using reactions where alternative Lewis bases are involved. Ideally a harder base should be employed, but the choice is limited, so we are currently working with analogous reactions where the Lewis acid catalyst has to abstract bromide and iodide ions, on the basis that the effect on relative activities will be magnified if the hardness of the Lewis acid is an important factor.

Another feature of note is that the Ni^{2+}- and Co^{2+}-exchanged clays exhibit Lewis acid catalytic activity even after low-temperature activation, and possibly, if the lines in figure 1 are extrapolated, under ambient conditions. This observation is consistent with a detailed study of the infrared spectra of adsorbed pyridine on ion-exchanged clays by Breen [22], who showed that Co^{2+}- and Ni^{2+}-exchanged clays tend to exhibit greater Lewis acidity than clays exchanged with trivalent metal ions under mild activation conditions. Given that the Lewis acid catalytic activity of these clays has to be associated with the exchange ions, the implication of this is that Co^{2+} and Ni^{2+} ions on clay surfaces retain vacant coordination sites enabling them to coordinate Lewis bases, even when the clays exhibit relatively high water contents.

An objective of this work was to investigate the possibility of the radical/redox mechanism described above contributing to the overall rate of Lewis acid catalysed reactions where the clay catalyst is exchanged with a reducible cation [9]. The results clearly show that it is not necessary to invoke such an additional mechanism, since the trend in catalytic activities is satisfactorily explained in terms of the surface acidities of the ion-exchanged clays, for both reducible and non-reducible cations. In further support of this view is the observation that clays exchanged with Zn^{2+}, as an example of a non-reducible cation, do not show anomalously low activity in Lewis acid catalysed reactions. Indeed, the relative activity of Zn^{2+}-exchanged clay compared to Cu^{2+}-, Ni^{2+}- and Co^{2+}-exchanged clays is virtually the same in Brønsted and Lewis acid catalysed reactions.

Acknowledgement

Laporte Industries Ltd (Laporte Absorbents) are gratefully acknowledged for funding a postdoctoral fellowship for CNR.

References

[1] L.B. Ryland, M.W. Tamele and J.N. Wilson, in: *Cracking Catalysts*, Catalysis, Vol. VII, ed. P.H. Emmitt (Reinhold, New York, 1960).

[2] J.H. Purnell, Catal. Lett. 5 (1990) 203.

[3] M. Balogh and P. Laszlo, *Organic Chemistry using Clays* (Springer, New York 1993).

[4] J.A. Ballantine, in: *Solid Supports and Catalysts in Organic Synthesis*, ed. K. Smith (Horwood, Chichester, 1992) p. 100.

[5] C.N. Rhodes and D.R. Brown, J. Chem. Soc. Faraday 91 (1995) 1031.

[6] M. Frenkel, Clays Clay Miner. 22 (1974) 435.

[7] J. Tateiwa, H. Horiuchi, K. Hashimoto, T. Yamauchi and S. Uemura, J. Org. Chem. 59 (1994) 5901.

[8] C. Cativiela, J.I. Garcia, M. Garcia-Matres, J.A. Mayoral, F. Figueras, J.M. Fraile, T. Cseri and B. Chiche, Appl. Catal. A 123 (1995) 273.

[9] T. Cseri, S. Bekassy, F. Figueras and S. Rizner, J. Mol. Catal. A 98 (1995) 101.

[10] P. Laszlo and A. Mathy, Helv. Chim. Acta 70 (1987) 577.

[11] A. Cornelis, A. Gerstmans, P. Laszlo, A. Mathy and I. Zieba, Catal. Lett. 6 (1990) 103.

[12] J.M. Adams, S. Dyer, K. Martin, W.A. Matear and R.W. McCabe, J. Chem. Soc. Perkin I (1994) 761.

[13] A. Cornelis and P. Laszlo, Synlett. (1994) 155.

[14] P. Laszlo and H. Moison, Chem. Lett. (1989) 1031.

[15] J.H. Purnell and Lu Yun, Catal. Lett. 18 (1993) 235.

[16] C.N. Rhodes and D.R. Brown, Clay Miner. 29 (1994) 799.

[17] C.N. Rhodes and D.R. Brown, Catal. Lett. 24 (1994) 285.

[18] D.R. Brown and C.N. Rhodes, Thermochim. Acta (1997), in press.

[19] S.A. Bagshaw and R.P. Cooney, Chem. Mater. 5 (1993) 1101.

[20] E.P. Parry, J. Catal. 2 (1963) 371.

[21] M. Lefrancois and G. Malbois, J. Catal. 20 (1971) 350.

[22] C. Breen, Clay Miner. 26 (1991) 487.