Surface acidities and catalytic activities of acid-activated clays

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Abstract

Two commercially available acid-activated montmorillonite clay catalysts, K5 and K10, have been characterised by ammonia adsorption microcalorimetry at 150 °C. The adsorption capacities and molar enthalpies of adsorption have been interpreted in terms of the concentration and strength of surface acid sites. Clays exchanged with Al^{3+}, Fe^{3+} and Na^+ have been examined. Catalytic activities have also been measured, in liquid phase reactions in swelling and non-swelling solvents, and in reactions catalysed by Bronsted and by Lewis acid sites. The relationships between ammonia adsorption characteristics and catalytic activities have been determined. It has been shown that anhydrous ammonia is able to access all acid sites on the clay surface, including those in the residual clay interlayer regions which would normally only be accessible in the presence of a swelling solvent. Ammonia adsorption on clays exchanged with Fe^{3+}, where Lewis acidity is maximised, is more extensive and with a higher molar enthalpy of adsorption than on clays maximised for Bronsted acidity. It is concluded that ammonia can be satisfactorily used as a probe of surface acidity when Bronsted acidity dominates but, if there is significant Lewis acidity, ammonia adsorption data is difficult to interpret.
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1. Introduction

Acid-activated clays are efficient and relatively inexpensive solid acid catalysts for liquid phase processes. They possess comparatively strong acid sites (H_0 typically quoted in the range -5.6 to -8.2 [1]) and their part-amorphous nature provides mesoporosity over a wide range of pore sizes. Despite the discovery of many new inorganic mesoporous molecular sieves on which solid acids can be based, activated clays remain one of the most important and widely used classes of mesoporous solid acid catalyst available to industry [2].

They are usually based on swelling, montmorillonite clays. The acid treatment process firstly renders the surface of the clay acidic. It also strips metal ions from the clay lattice, partially delaminating the clay. This increases the external surface area of the clay and introduces permanent mesoporosity. In the resultant material, acid sites can be thought of as being on two types of surface. The first are ex-

ternal, readily accessible surfaces which have been opened up by the delamination process. The second are surfaces in residual laminar regions of the clay. Acid sites in these laminar regions are only accessible in the presence of a solvent capable of swelling the clay. In designing acid-activated clay catalysts for specific reactions it is necessary to take into account the dependence of acid site accessibility on reaction medium or solvent.

Another feature of acid activated clays which influences catalytic properties is that they are not stable in the H^+-exchanged form. Autotransformation results in the gradual dissolution of metal ions, mainly Al^{3+}, from the lattice which take the place of H^+ ions in cation exchange sites [3]. Bronsted acidity then arises through the hydrolysis of water in the hydration sphere of these Al^{3+} cations. For this reason, acid strength generally shows a very sensitive dependence on the water content of the clay and the level of hydration of the cation [4]. Lewis acidity is also associated with the exchangeable cations, and dominates when water is largely removed [4]. The strength of Lewis acid sites can be increased by changing the exchangeable cation. Many workers have shown that clays exchanged with Fe^{3+} cations exhibit some of the strongest Lewis acid sites [4–7].

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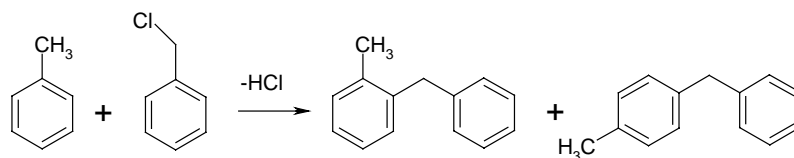
Scheme 1. Toluene alkylation.
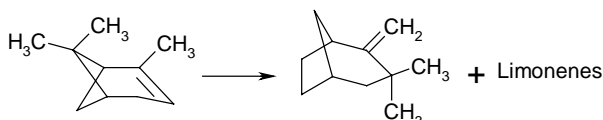
Scheme 2. α-Pinene isomerisation to camphene.
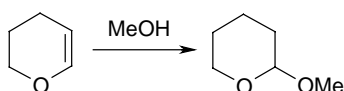
Scheme 3. Methoxylation of 3,4 dihydropyran.

These variables mean that it is more difficult to characterise acid-activated clays in a way that is meaningful for predicting catalytic activities than many other solid acid catalysts. The objective of this work has been to investigate the link between surface acidities of typical acid-activated clays, measured by ammonia base adsorption microcalorimetry, and the catalytic activities of the same materials in solvents of varying swelling capacities and in reactions requiring both Bronsted and Lewis acid sites for catalysis. Three model test reactions have been employed.

The first is the Friedel–Crafts alkylation of toluene with benzyl chloride [8]. This reaction is catalysed most effectively by a Lewis acid catalyst. By carrying the reaction out in excess toluene, the mono-alkylated products predominate, and the toluene provides a non-swelling medium in which the clay catalyst operates (Scheme 1).

The second reaction is the proton catalysed rearrangement of α-pinene to camphene and other products [9]. The driving force in the reaction is the relief of ring strain in the starting material. The first step is the protonation of the double bond in α-pinene and it is an example of a Bronsted-acid catalysed reaction in a non-polar, non-swelling medium (Scheme 2).

The third reaction is the methoxylation of 3,4-dihydropyran with methanol [9]. This reaction is Bronsted acid catalysed through protonation of the methanol hydroxyl group. By carrying out the reaction in an excess of methanol, the clay catalysts operate in the swollen, expanded state (Scheme 3).

2. Experimental

2.1. Catalysts

The commercially available K-montmorillonites (Süd-Chemie AG) are derived from the Bavarian montmorillonite Tonsil 13 through varying levels of acid activation.

This study is based on two clays from this series, K5 and K10, kindly provided by Süd-Chemie. They were used in the Al^{3+} form, and K10 was also examined following ion exchange with Fe^{3+} and Na^+.

Cation exchange of the clays was carried out by preparing a 1% suspension of the parent clay in a $1.5\,mol\,dm^{-3}$ solution of the desired cation (as the nitrate or chloride), and stirring overnight. On settling, the supernatant solution was discarded and the exchange process repeated. The ion-exchanged material was filtered and washed free of electrolyte with deionised water, and dried in air.

2.2. Characterisation

Cation exchange capacities (CEC) and elemental compositions were provided by Süd-Chemie AG. The BET surface areas were obtained from nitrogen adsorption data at 77 K. Clays were activated for 2 h at 150 °C under a vacuum of 10^{-5} Torr prior to adsorption. The pore size distributions were calculated using the BJH method applied to the nitrogen desorption data. Powder X-ray diffraction patterns were obtained using Cu Kα radiation ($\lambda = 0.154\,nm$), recording from $2\theta = 2$ to $50°$.

2.3. Acidity measurements

A commercially available Tian-Calvet type differential microcalorimeter (Setaram C80) was used to measure the heats of adsorption of ammonia. The gas was introduced to the catalyst using a volumetric gas handling system. Catalyst samples (40 mg dry weight) were conditioned in the calorimeter sample cell at 150 °C under dynamic vacuum for 2 h. Ammonia adsorption was carried out at 150 °C. Because ammonia adsorption equilibrium is established relatively slowly on clay catalysts, data for progressive coverage of ammonia was collected by carrying out a number (typically 15–20) of separate experiments, with ammonia doses varying from 0.05 to 50 μmol. In each case enthalpy measurements were combined with adsorption data to determine the average molar enthalpy of ammonia adsorption over the coverage established. The data for each of the experiments was then combined to generate the results shown below.

2.4. Catalytic activity

Three liquid phase test reactions were used. All chemicals were of Analar purity, and were dried over 4A molecular sieve before use. In each case reaction progress was

monitored at 5 min intervals with GC, and initial rates determined. Reactions were performed in stirred batch reactors under dry air. Stirrer speeds were established to ensure that reaction rates were not under diffusion control.

(a) Alkylation of toluene with benzyl chloride [8]: the catalyst was activated at 250 °C in a furnace under forced air for 1 h. A mixture of 0.10 mol toluene, 0.0050 mol benzyl chloride and 0.0010 mol tetradecane internal standard was added to 250 mg activated catalyst. The experiments were performed at 85 °C.

(b) Rearrangement of α-pinene [9]: the catalyst was activated at 150 °C for 1 h. A reagent/internal standard mixture containing 0.060 mol α-pinene and 0.010 mol of decane was added to 200 mg activated catalyst. Reaction temperature was 97 °C.

(c) Addition of methanol to 3,4-dihydropyran [9], the catalyst was activated at 150 °C. A mixture containing 0.010 mol of dihydropyran and 0.30 mol of methanol was added to 200 mg catalyst. Reaction temperature was 7 °C.

3. Results

3.1. Catalyst characterisation

Elemental analysis [10] of the clays in their as-received state (Table 1) shows that K5 contains significantly more metal ions than K10, consistent with K10 having received the more extensive acid activation. The higher cation exchange capacity of K5 (Table 1) is also consistent with this. Powder X-ray diffraction traces (not shown) exhibit broad 0 0 1 reflections at around 2θ of 5.8°, corresponding to a c-axis spacing of 1.52 nm. The intensity of these reflections is an indicator of the degree of laminar structure retained by the clay. For K5 this intensity is something like half that seen for a typical untreated montmorillonite, and for K10 it is closer to a quarter. Surface areas by nitrogen adsorption (Table 1) show an increase from K5 to K10. Note that these represent the accessible surface in the unswollen state of the clay and are, again, consistent with increasing delamination on going from K5 to K10.

The nitrogen adsorption/desorption isotherms and pore size distribution profiles (Fig. 1) show equivalent trends. A sharp feature appears for both clays at a pore diameter of about 4 nm. It is larger for K5 than K10. This feature is an artefact found with clay minerals, thought to be due to the rapid expulsion of nitrogen from the clay on rearrangement

of clay layers at a certain overpressure of nitrogen, and is an indicator of the degree of laminar structure in the clay [11]. The overall distributions of pore volumes show a very broad band of pore sizes, with K10 exhibiting a much greater volume in permanent pores of diameters over 2 nm than K5 (Table 1). This confirms the idea that K10 has a much greater amorphous, mesoporous content than K5, which is much closer in structure to the parent clay.

3.2. Acidities

The K5 was examined only in its Al^{3+} form, whereas K10 was studied in the Al^{3+}, Fe^{3+} and Na^+ forms. The plots shown in Fig. 2 illustrate how the ammonia adsorption calorimetric data was collected. As described above, for each clay, successive experiments were performed in which progressively larger doses of ammonia were introduced to the sample. For K5, the resultant adsorption isotherm is shown in (a). The enthalpies of adsorption for each dose were measured and the cumulative enthalpy is plotted against ammonia surface coverage in (b). The gradient of this line is the differential or molar enthalpy of ammonia adsorption.

The data shown in Fig. 2b, and the equivalent data for the other clays, has been interpreted as follows to obtain the comparative values for the strengths and concentrations of surface acid sites shown in Table 2. It is based on the assumptions that (1) when ammonia is adsorbed on acid sites the molar enthalpy of adsorption is a comparative measure of the strength of these sites, and (2) only one ammonia molecule can adsorb on a Bronsted acid site, forming the NH_4^+ ion.

Firstly, the average molar enthalpy of adsorption over the first $0.05 \, mmol \, g^{-1}$ coverage is given, taken as the gradient of the best fit straight line through points up to this value. On the basis that the strongest sites are populated first (which is likely to be at least partially correct [12]) this value represents the strongest five or ten per cent of acid sites. The second figure is the average molar enthalpy of adsorption over the first $0.15 \, mmol \, g^{-1}$ coverage, being more representative of the overall acid site strength.

Finally, the surface coverage is determined at which the molar enthalpy of adsorption falls to $80 \, kJ \, mol^{-1}$. This is taken as the point at which all the genuinely acidic sites are saturated with ammonia, and therefore corresponds to the concentration of acid sites on the surface of the clay. This threshold has been chosen on the basis that adsorption of ammonia on solids with no significant surface acidity, amorphous silica gels for example, leads to molar adsorption

Table 1
Partial elemental analyses, BET surface areas by N_2 adsorption, pore volumes and cation exchange capacities for Al^{3+}-K5 and Al^{3+}-K10

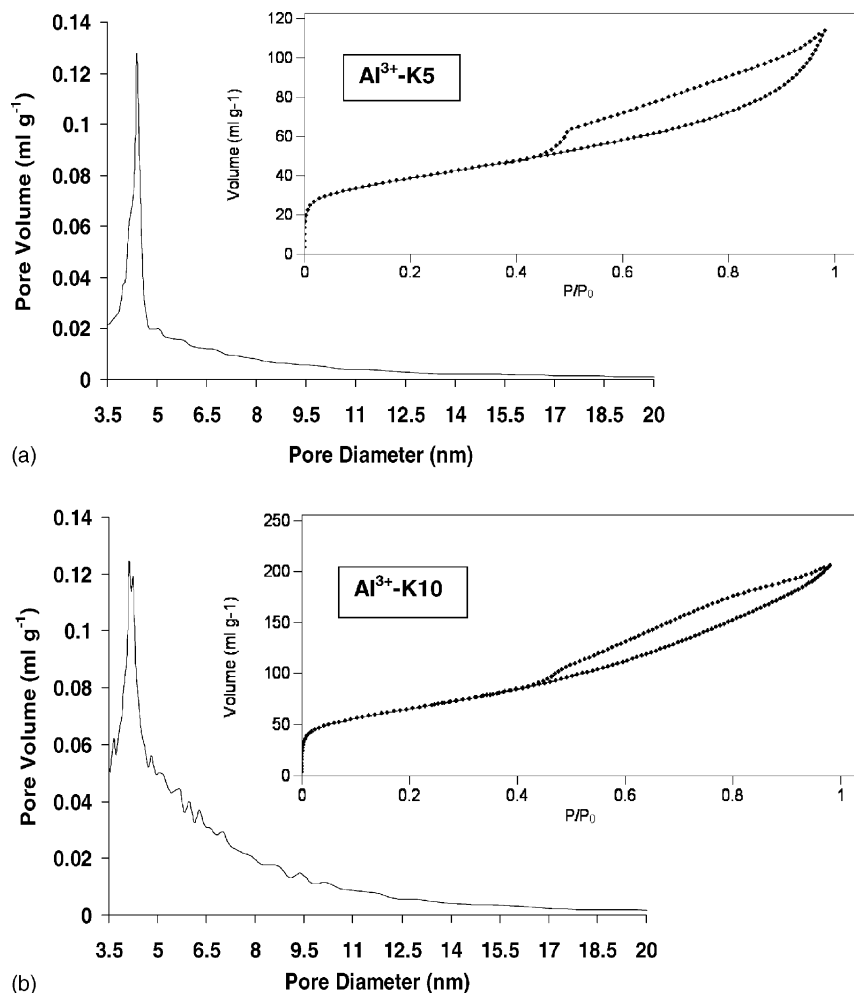| Catalyst	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	Surface area $(m^2 \, g^{-1})$ (± 10)	Pore volume (diameter >2 nm) $(cm^3 \, g^{-1})$ (± 0.05)	Cation exchange capacity (meq. g^{-1})
Al^{3+}-K5	65.0	19.0	4.8	2.4	137	0.148	0.55
Al^{3+}-K10	73.0	14.0	2.7	1.1	234	0.293	0.30

Fig. 1. Nitrogen adsorption/desorption isotherms at 77 K and pore size distributions (from desorption using the BJH method) for Al^{3+}-K5 and Al^{3+}-K10.

enthalpies of around this value [13]. Note, that for Al^{3+}-K5 this point is reached at a coverage of 0.5 mmol g^{-1}. Examination of Fig. 2a shows that this value compares with a coverage of approximately 0.6 mmol g^{-1} at which the plateau is detected in the adsorption isotherm, and (from Table 1) a cation exchange capacity for the clay of 0.55 mmol g^{-1}. These observations all support the idea that saturation of acid sites does indeed correspond reasonably closely to the point where the molar enthalpy of adsorption falls below 80 kJ mol^{-1}.

Based on the acidity data in Table 2, a comparison between the Al^{3+} forms of K5 and K10 shows that both clays exhibit concentrations of acid sites (based on ammonia adsorption) similar to their cation exchange capacities, with the higher concentration of sites on K5. In terms of acid strength, it is possible that Al^{3+}-K10 exhibits slightly stronger sites than Al^{3+}-K5, but the difference between the two is probably within experimental error.

The Na^+-K10 shows a very much lower concentration of acid sites and a lower acid strength than Al^{3+}-K10. The Fe^{3+}-K10, in contrast, exhibits both a higher apparent concentration of acid sites than Al^{3+}-K10, and a higher overall acid strength.

3.3. Catalytic activity

Activities are reported in terms of the initial rates of the model reactions (Table 3). The Na^+-K10 shows undetectable activity in two reactions and low activity in the toluene benzylation. This, together with the low acidity data for Na^+-K10 described above, suggests that acidity and activity are mainly associated with the exchangeable cations on the clay surface.

A comparison between Al^{3+}-K10 and Al^{3+}-K5 illustrates the effect of the degree of acid activation on the catalytic activities of the clays. The more delaminated clay K10 is the more active in the benzylation reaction (by a factor of about six) and in the rearrangement of α-pinene (by about three). Both of these reactions are in non-swelling solvents. In contrast, in the dihydropyran methoxylation reaction, carried out in the swelling solvent methanol, the K10 is less active, by a factor of about a half. This ordering can be explained in terms
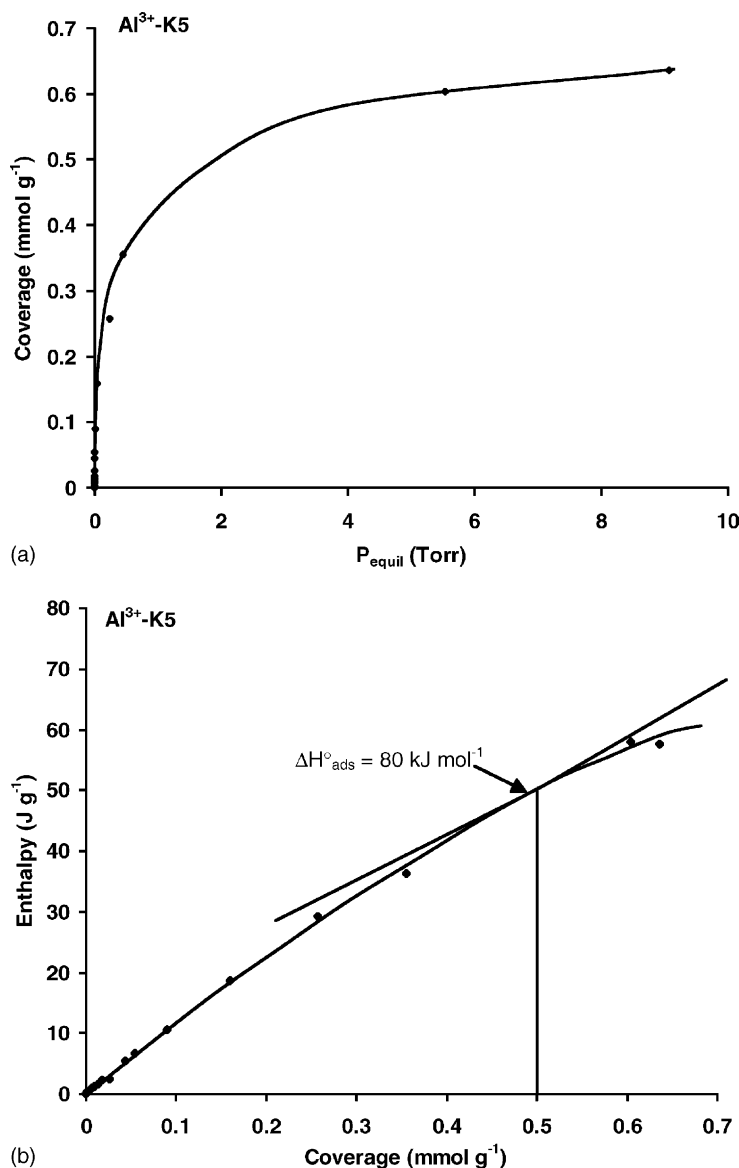
Fig. 2. (a) Ammonia adsorption isotherm for Al^{3+}-K5, recorded at 150 °C, (b) cumulative ammonia adsorption enthalpy recorded as a function of surface coverage, as described in the text.

of the relative concentrations of acid sites on external surfaces and on surfaces in the residual interlayer regions of the clay. The more extensively delaminated K10 exhibits more external sites than K5 and is more active in the non-swelling

Table 2
Surface acidity data, based on ammonia adsorption at 150 °C

Catalyst	ΔH^0_{ads} (kJ mol^{-1}), up to coverage 0.05 mmol g^{-1} (± 15 kJ mol^{-1})	ΔH^0_{ads} (kJ mol^{-1}), up to coverage 0.15 mmol g^{-1} (± 15 kJ mol^{-1})	Acid site concentration (mmol g^{-1}), in terms of adsorbed NH$_3$ (± 0.05 mmol g^{-1})
Al^{3+}-K5	123	117	0.50
Al^{3+}-K10	140	127	0.30
Fe^{3+}-K10	160	137	0.57
Na^+-K10	120	97	0.13

solvents. However, the less extensively treated K5 has a greater total concentration of acid sites, but full access to these sites is only possible in the presence of a swelling solvent like methanol, hence its higher activity in this solvent.

The effect of exchangeable cation can be seen by comparing Fe^{3+}-K10 and Al^{3+}-K10 in the three reactions. In the toluene benzylation reaction the Fe^{3+} exchanged clay is almost twice as active as the Al^{3+} clay, whereas in the rearrangement of α-pinene the order is reversed with the Al^{3+} clay showing over ten times the activity of the Fe^{3+} clay. The former reaction is generally assumed to be catalysed by Lewis acid sites, and the latter by Bronsted acid sites. The ordering of activities is consistent with Fe^{3+} exchange ions providing superior Lewis acid strength (under anhydrous conditions), and Al^{3+} ions generating higher Bronsted acid strength (under conditions of limited hydration).

Table 3
Catalytic activity data. Initial rates for the three test reactions, normalised for 1 g catalyst. Reaction temperatures are given

Catalyst	Toluene/benzyl chloride alkylation (s^{-1}) (85 °C) (±0.5)	α-Pinene isomerisation $(10^{-2}\,s^{-1})$ (97 °C) (±0.5)	Dihydropyran methoxylation $(10^{-3}\,s^{-1})$ (7 °C) (±0.5)
Al^{3+}-K5	6.5	6.2	21.5
Al^{3+}-K10	39.6	19.9	8.8
Fe^{3+}-K10	64.5	1.4	8.1
Na^{+}-K10	7.4	<0.1	<0.1

The Al^{3+} and Fe^{3+} forms of the clay show similar activities in the methoxylation of dihydropyran. Although this may seem inconsistent with the order of activities for the α-pinene rearrangement (both reactions are Bronsted acid catalysed) the solvent for the dihydropyran methoxylation reaction is methanol, which will fully solvate the Al^{3+} and Fe^{3+} exchange ions. The Bronsted acidity associated with these cations is very sensitive to their level of hydration (or solvation by a protic solvent like methanol) and maximum Bronsted acid strength requires controlled and very limited hydration conditions. Therefore, in the presence of excess methanol, it is likely that the acid strength will be attenuated, as the polarisation of co-ordinated solvent molecules by the cations which gives rise to H^{+} release is effectively diluted. This would lead to much reduced, and also similar, acid strengths for both Fe^{3+} and Al^{3+} exchanged clays, explaining why the activities of the two clays in this solvent are similar. Because the methoxylation of dihydropyran is a relatively facile reaction, the fact that the clays are, in effect, relatively inactive catalysts may be substantially disguised.

4. Discussion

The objective of this work has been to assess how acidity measured by ammonia adsorption reflects acid catalytic activities of acid-activated clays in swelling and non-swelling solvents, and in Bronsted and Lewis acid catalysed reactions. On the issue of acid site accessibility and the relative importance of acid sites on external and interlayer surfaces, our catalytic data confirms previous observations [9] that only external sites are active in non-swelling solvents but in swelling solvents all acid sites are accessible for reaction. In relating this to ammonia adsorption measurements, we anticipated that, on dry clays, anhydrous ammonia would only probe external acid sites and that acid sites in the residual interlayer regions of the clay would be inaccessible. Surprisingly, this does not appear to be the case. In fact, the concentrations of acid sites probed by ammonia on both Al^{3+}-K10 and Al^{3+}-K5 appear to be very close to the cation exchange capacities of the clays, suggesting that all acid sites are accessible to the ammonia probe.

In a related study, Flessner et al. studied ammonia adsorption by the K-series catalysts [14]. These workers measured the capacity for chemisorption in a slightly different way to us however, adsorbing at 80 °C and distinguishing between chemi- and physisorbed (or irreversibly and reversibly bound) ammonia through a two cycle, adsorption-desorption-adsorption process, measuring coverage at an equilibrium pressure of 36 Torr. They reported rather lower acid site concentrations than us (K5–0.27 meq. g^{-1}; K10–0.20 meq. g^{-1}) but the crucial fact that they, like us, detected more acid sites on K5 than on K10 is entirely consistent with our finding that ammonia is able to probe interlayer acid sites as well as those on the external surfaces.

It therefore appears that ammonia, even at very low pressures, can penetrate the supposedly collapsed interlayer regions of the clay catalyst and react at surface acid sites. How this access is achieved is unclear. One possibility is that the exchangeable cations (Al^{3+} in this case) provide some form of limited pillaring between clay layers [15]. It is also conceivable that ammonia itself is able to swell the clay enough to allow access. A combination of these two mechanisms may also be responsible. The idea that some of the ammonia adsorbed by the clays has to overcome an additional energy barrier in the process of expanding the layered regions of the clay may be supported by the differences in the molar enthalpies of ammonia adsorption measured for Al^{3+}-K10 and Al^{3+}-K5 (Table 2). A slightly higher value was recorded for K10, and this would be consistent with this clay having a larger proportion of its acid sites on readily accessible external surfaces than K5 which retains more laminar structure and so a higher proportion of acid sites in the interlayers.

The second issue is the extent to which ammonia adsorption depends on the nature of the exchangeable cation in the clay, and the nature of the acid site, whether Bronsted or Lewis. Firstly, the relatively low acidity and activity of Na^{+}-K10 confirm that the exchangeable cations are mainly responsible for both acidity and activity. However, Na^{+}-K10 does show some activity in the Lewis acid catalysed Friedel–Crafts reaction, and this suggests that those non-exchangeable acid sites that do exist on the clay surface are predominantly Lewis acidic. These sites would be defect sites on the clay surface and other co-ordinatively unsaturated edge sites in the lattice, and it is quite reasonable to suppose that they would be electron deficient, and therefore behave as Lewis acids. Concentrating on clays exchanged with acidic cations, a comparison between Al^{3+}-K10 (activated at 150 °C) and Fe^{3+}-K10 (activated at 250 °C) can be effectively regarded as a direct comparison between a Bronsted acid and a Lewis acid catalyst. Previous work on clays exchanged with these cations and activated at these temperatures [4–7], together with the catalytic data reported here, bear this out as described earlier.

Ammonia adsorption evidently occurs on both ions. The extent of ammonia chemisorption on Al^{3+} exchanged clays equates to the cation exchange capacity of the clay and is

equivalent to one ammonia molecule per cationic charge. This means that each hydrated Al^{3+} ion is equivalent to three Bronsted acid sites. Ammonia adsorption on Fe^{3+} exchanged clays is more extensive and exceeds the cation exchange capacity, with almost six ammonia molecules adsorbing per Fe^{3+} ion. Note, however that the Fe^{3+} exchanged clay was activated at a higher temperature than the Al^{3+} clay to maximise Lewis acidity, and it is presumably anhydrous or close to it. Ammonia adsorption is therefore most likely by direct coordination to the metal ion, and it does not seem unreasonable that six ammonia molecules could coordinate each Fe^{3+} ion in this way.

Also, the molar enthalpy of ammonia adsorption is higher for Fe^{3+}-K10 than for Al^{3+}-K10. Other workers have observed higher enthalpies of adsorption for ammonia on Lewis acid sites than on Bronsted sites [16–19]. Indeed, the relatively strong binding of ammonia to Lewis acid sites has often been cited as a reason why ammonia is a relatively poor basic probe molecule in the study of surface acidity, at least in cases where Bronsted acidity is the major interest [20].

5. Conclusion

The measurement of ammonia adsorption and the associated enthalpy of adsorption on acid-activated clays certainly provides information valuable in predicting catalytic activity. Interpretation of adsorption data, however, must take account of the rather surprising fact that ammonia is able to access interlayer regions of the acid-activated clays, certainly at 150 °C. The acidic surface probed by ammonia is therefore closer to that exposed in a swelling solvent than in a non-swelling solvent. It is also necessary to take into account the sensitivity of ammonia to Lewis acid sites. Adsorption can be more extensive than expected on such sites, and with higher adsorption enthalpies. This means that ammonia adsorption data can be used for comparative purposes if Bronsted acidity is dominant, but if a significant and perhaps unknown concentration of Lewis acid sites may be present, then ammonia adsorption data cannot be used with confidence to predict catalytic properties. In such cases, other methods that are more selective for Bronsted acid sites might be used. An example might be the use of temperature programmed surface reactions, such as the dehydration of primary alcohols or the deamination of primary amines [21,22].

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