The Effect of Acid Treatment on the Activity of Clay Supports for ZnCl₂ Alkylation Catalysts

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Acid treatment of Ca^{2+} montmorillonite has been shown to increase significantly its effectiveness as a support for $ZnCl_2$ Friedel–Crafts alkylation catalysts; optimum treatment conditions have been established and evidence is reported for a synergistic interaction between absorbed salt and acid-activated clay.

The smectite clays have shown only limited potential as industrial catalysts since acid bentonites were replaced as petroleum cracking catalysts.[1] Even chemically modified clays containing thermally stable pillaring cations have not realised their early promise. However, smectite clays have been shown to be very effective supports for a number of transition metal salt catalysts,[2–4] conferring additional activity on the salt as well as offering advantages in terms of ease of handling. A good example of these supported catalysts is $ZnCl_2$ supported on the acid-treated montmorillonite Fluka K10. This material has been shown by Clark et al.[2] to be an extremely effective Friedel–Crafts alkylation catalyst. In marked contrast to this

material, $ZnCl_2$ supported on montmorillonite which has had no acid treatment shows extremely low Friedel–Crafts activity. It is the object of this work to investigate the effect of acid treatment of montmorillonite on the activity of these supported catalysts, in an attempt to identify the structural features in the treated clay which are important in conferring activity as catalyst supports.

For these studies, a naturally occurring Ca^{2+} montmorillonite (Carmargo White, kindly provided by Volclay Ltd.) was used as supplied. The clay was subjected to acid activation by boiling a 2% suspension in 30% H_2SO_4 solution. Samples were taken after various activation times, washed thoroughly and dried. The Brunauer–Emmett–Teller (BET) surface areas of the clays were measured by N_2 adsorption at 77 K after degassing at 120 °C. (The surface area measured in this way does not include the internal surfaces of the clay, but these

Table 1 Dependence of rate of reaction on acid treatment time of clay support[a]

Acid treatment time[b]	Yield (%)[c]
0 min	2
1 min	7
5 min	50
15 min	52
4 h	70
8 h	86
20 h	92
42 h	74

[a] Catalyst prepared as 2 mmol $ZnCl_2$ (g clay)$^{-1}$, activated at 150 °C for 1 h, 0.25 g of catalyst added to 0.2 mol of benzene and 0.01 mol of benzyl chloride. [b] 2% suspension of clay in boiling 30% H_2SO_4. [c] Yield of diphenylmethane after 30 min reaction time.
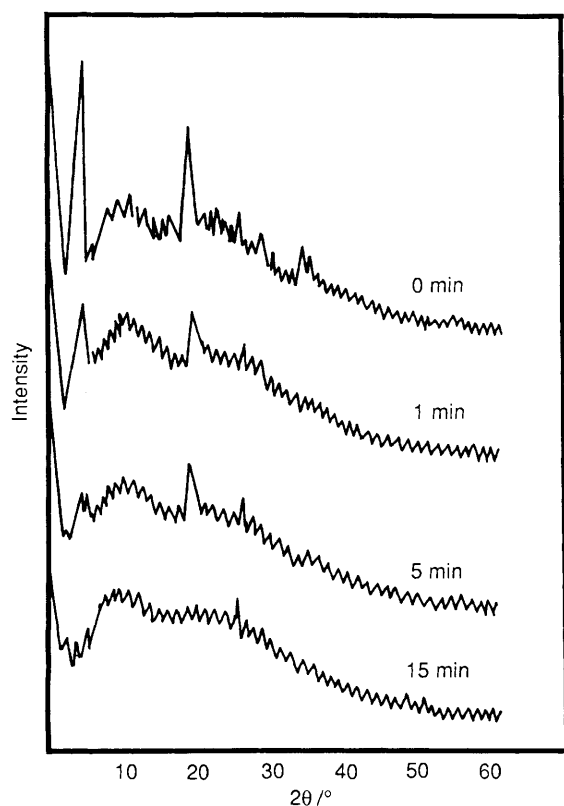

Fig. 1 X-Ray diffraction patterns for montmorillonite Carmargo White after various treatment times with boiling 30% H_2SO_4. Cu–Kα radiation was used, λ = 154 pm. Acid treatment for longer than 15 min caused no further significant changes in the clay diffraction pattern. The peak at ca. 28° is thought to be due to cristobalite impurity.

surfaces would be largely inaccessible in the non-polar medium used in these experiments). The cation exchange capacities (CECs) were determined by Methylene Blue adsorption. Powder X-ray diffraction patterns were recorded on partially orientated films deposited from aqueous suspension.

Catalysts were prepared by evaporating to dryness a suspension of clay in methanolic $ZnCl_2$ solution. A range of salt loadings were prepared. BET surface areas were measured on the catalysts. Thermal analyses (DSC) were also performed.

Catalysts were activated at 150 °C under N_2 for 1 h, and their catalytic activities were measured using the same reaction as used by Clark et al.,[2] between benzyl chloride and benzene. This is a convenient screening reaction since a dominant product, diphenylmethane, is formed, and reactant and product concentrations are easily measured. The mixture was stirred at room temperature and the % conversion of benzyl chloride recorded after various reaction times.

Table 1 shows the dependence of activity of the supported $ZnCl_2$ catalyst on acid treatment time, using a salt loading of 2.0 mmol g^{-1} clay. Even short treatment times result in profound increases in activity. The X-ray diffraction patterns (Fig. 1) show a pronounced decrease in the characteristic smectite 001 and higher order reflections after similarly short treatment times, suggesting that the rise in activity is related to the breakdown of the laminar structure of the clay.

Optimum activity for the clay support is achieved after 20 h treatment. By this stage the X-ray pattern shows little crystallinity. However, further reaction between the acid and the clay is possible as shown by the gentle decrease in activity exhibited by clays subjected to longer acid treatments.

It appears that the optimum state of the clay lies between the laminar, ordered smectite structure and the amorphous silica which is the ultimate product of prolonged treatment. Neither the surface area of the clay nor the CEC (Table 2) shows changes which correlate with the activity of the supported catalysts. Although the surface area does increase on acid treatment, it does not do so in proportion to the increase in catalytic activity. Further evidence suggesting that surface area alone is not an important factor controlling activity is provided by the high-surface-area synthetic Laponites (BET surface area ca. 250 m² g^{-1}), which have been shown by the authors to exhibit activities as catalyst supports only marginally higher than those of untreated natural montmorillonites and hectorites (BET surface areas ca. 70–100 m² g^{-1}).

Fig. 2(a) shows the effect of $ZnCl_2$ loading on catalytic activity, using an acid-treated clay. The activity is at a maximum at 2.0 mmol g^{-1} clay, decreasing quite rapidly at loadings above 4 mmol g^{-1}. The surface areas of the salt–clay catalysts, also shown in Fig. 2, decrease with increasing loading, falling rapidly to less than 5 m² g^{-1} at salt loadings

Table 2 Dependence of BET surface area and cation exchange capacity (CEC) of montmorillonite on acid treatment time

Acid treatment time[a]	BET surface area[b]/m² g^{-1}	CEC[c]/mequiv. per 100 g
0 min	67	120
1 min	121	90
5 min	279	84
15 min	330	72
4 h	226	45
8 h	160	34
20 h	130	22
42 h	94	11

[a] 2% suspension of clay in boiling 30% H_2SO_4. [b] BET surface area by N_2 adsorption at 77 K. [c] CEC measured by Methylene Blue adsorption (R. H. S. Robertson and R. M. Ward, J. Pharm Pharmacol., 1951, 3, 27).
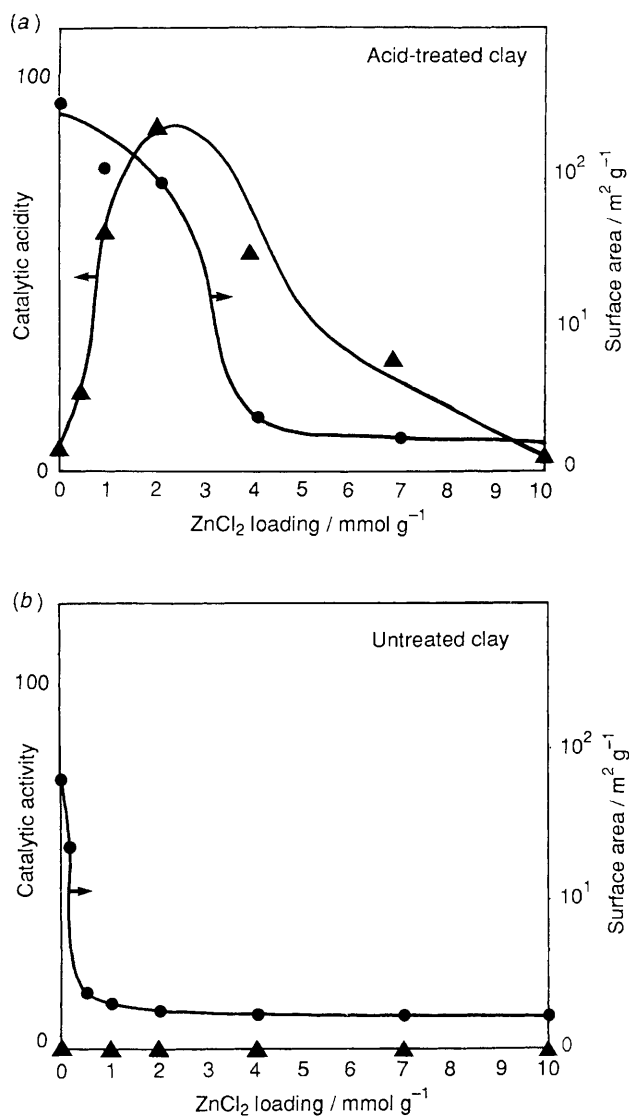
Fig. 2 The dependence of a catalytic activity (▲) and surface area (●) on salt loading for $ZnCl_2$/montmorillonite catalysts, using (a) acid-treated (8 h) montmorillonite, and (b) untreated montmorillonite. Catalytic activity is reported in terms of % conversion of benzyl chloride after 30 min reaction.
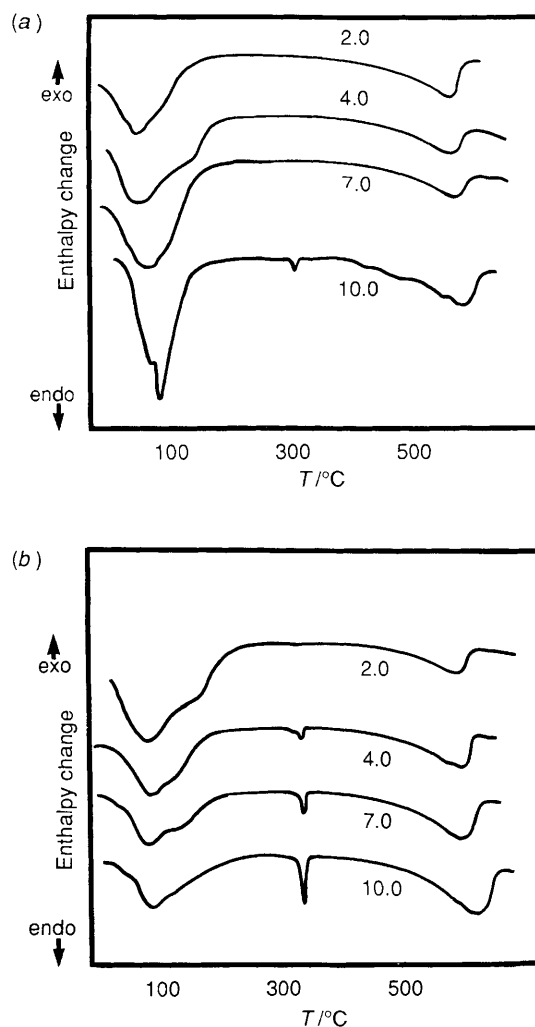

Fig. 3 The dependence of differential scanning calorimetry (DSC) curves on salt loading for $ZnCl_2$/montmorillonite, using (a) acid-treated (8 h) clay, and (b) untreated clay. Numbers on curves refer to salt loadings in mmol g^{-1} clay.

above 4 mmol g^{-1}. Furthermore, the DSC data for this series [Fig. 3(a)] show that the characteristic endotherm at ca. 310 °C, associated with fusion of crystalline $ZnCl_2$, only appears at loadings of 10 mmol g^{-1} and above. Together, these observations suggest that, up to a critical loading of between 4 and 10 mmol g^{-1}, $ZnCl_2$ interacts with the clay such that it does not exhibit the properties of the bulk salt. In this form the salt is catalytically active. Above this loading bulk salt appears, which seems to aggregate the small $ZnCl_2$–clay particles, dramatically reducing their surface areas and rendering them inactive.

The extent to which Zn^{2+} ions occupying cation exchange sites on the clay surface are responsible for the catalytic activity of these materials may be judged from the fact that optimum activity is achieved at a $ZnCl_2$ loading corresponding to a Zn^{2+} concentration over ten times the CEC of the clay. Clark et al.[2] have shown that fully Zn^{2+} exchanged montmorillonite K10, while exhibiting much higher catalytic activity than the Na^+ and Ca^{2+} exchanged clay, is a very much less active alkylation catalyst than $ZnCl_2$–K10. Our results support the view that the adsorbed salt is crucial to achieving optimum activity.

The behaviour of $ZnCl_2$ adsorbed on untreated clay is different [Fig. 2(b)]. The activities of these catalysts are insignificant at all salt loadings. Consistent with the absence of activity is the observation that these materials exhibit very low surface areas even at very low $ZnCl_2$ loadings, suggesting bulk salt behaviour throughout the range, or at least down to very low salt loadings. Furthermore, the 310 °C endotherm is observed down to 4 mmol g^{-1} [Fig. 3(b)], considerably lower than for the $ZnCl_2$ on treated clays, again suggesting the presence of bulk $ZnCl_2$ even at low salt loadings. (The absence of peaks at lower loadings may be due to the very small quantities of salt in the samples.)

The catalytic activities of these materials appear to depend upon a synergistic interaction between $ZnCl_2$ and the clay surface. Only acid-treated clays take part in this interaction and there is a well defined limit to the amount of $ZnCl_2$ which can adsorb effectively.

It is clear that the key to understanding the nature of the active sites in these supported salt catalysts lies in the structure of the acid-treated clay. Relatively little is known about the structural changes that occur within clays on acid treatment. Previous workers[5,6] have suggested that even quite mild acid treatment of montmorillonite results in significant dissolution of Al from the octahedral lattice layers. Models have been suggested in which partial dissolution of octahedral lattice Al is accompanied by the conversion of a fraction of the remaining Al to tetrahedral coordination.[5] However, [27]Al and

^{29}Si NMR data on $ZnCl_2/K10$ catalysts recently reported by Laszlo[4] suggest that the acid treatment to which K10 has been subjected has not perturbed the octahedral Al lattice layer significantly. He reports evidence for interaction between Zn^{2+} ions in surface-exchange sites and tetrahedral lattice Si atoms, but no evidence for interaction between Zn^{2+} and octahedral Al atoms. The surprising implication of these results is that the lattice structure of acid-treated K10 is not very different from that of the parent untreated montmoril-lonite. In contrast, the limited structural evidence from X-ray data reported here strongly suggests that the development of effective clay catalyst supports through acid treatment is associated with major structural changes.

In order to study more fully the effect of acid treatment on clay structure and on clay–salt interactions, it is clearly necessary to monitor structural changes in the clay and the salt–clay mixture associated with *progressive* acid treatment of the clay. Work in this group is currently directed towards this objective.

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