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The roles of Brønsted and Lewis surface acid sites in acid-treated montmorillonite supported $ZnCl_2$ alkylation catalysts

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The catalyst known as "clayzic" ($ZnCl_2$ supported on acid-treated montmorillonite) exhibits both Brønsted and Lewis surface acidities. The relative catalytic activities of these two types of acid site have been determined in a range of reactions, by comparing the activities of clayzic with those of related catalysts which exhibit only one type of surface acidity. Acid-treated montmorillonite has been used as the Brønsted acid catalyst in this comparison, and $ZnCl_2$ supported on a mesoporous silica has been used as the Lewis acid catalyst. The results confirm that the relative activities of the two types of acid site depend on both the nature of the reaction and the polarity of the reaction medium. They will be of value in optimising the choice of support and the $ZnCl_2$ loading in clayzic-type catalysts for specific reactions.

Keywords: clay; montmorillonite; acid treatment; acid activation; supported catalysts; $ZnCl_2$; clayzic; alkylation; surface acidity

1. Introduction

Recently we, and others, have been studying the role of acid-treated clays as catalyst supports, particularly for $ZnCl_2$ Friedel-Crafts alkylation catalyst [1–8]. In most of the reported work the commercially available acid-treated montmorillonite K10 has been used as a support for $ZnCl_2$. This catalyst/support system, known as "clayzic", shows very much higher activity in many Lewis acid catalysed reactions than $ZnCl_2$ used alone, and it is regarded as important in the development of replacement catalysts for traditional homogeneous Friedel-Crafts catalysts such as $AlCl_3$ and H_2SO_4, which are presenting increasingly serious disposal problems for users.

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Clayzic is typically dehydrated at 100–200°C before use. An attractive feature of clayzic activated in this way is that it exhibits both Lewis acidity (from $ZnCl_2$) and Brønsted acidity (from the acid-treated clay support). The objective of this study is to measure the catalytic activities of these sites in a number of reactions, and to identify the factors which govern the relative importance of the two types of acid sites under varying reaction conditions. To achieve this we have compared clayzic with $ZnCl_2$ supported on a mesoporous silica [2] ("silizic") as a source of Lewis acid sites only, and with the acid montmorillonite K10 used alone, as a source of Brønsted acid sites only.

In related work Clark and coworkers have compared the activities of the acid montmorillonite K10 and clayzic [5], as a way of assessing the contribution to the activity of clayzic made by the support. This study differed from ours in that neither clayzic nor K10 was thermally activated before use, with the result that catalytic activities were relatively low, and quantitative comparison with our work, in which all catalysts were thermally activated before use, cannot easily be made. However, the observation made by Clark that the Brønsted acid sites on the clay support can be significant contributors to the overall activity of clayzic, even in aromatic alkylation with alkyl halides, supports our view that further efforts to quantify the relative contributions of the two types of acid site are worthwhile.

Three test reactions have been used in the characterisation of these catalysts. The first is the benzylation of benzene, or toluene, with benzyl chloride, forming diphenylmethane, or (4- and 2-methylphenyl)phenylmethane. This reaction has been widely used in the development of clayzic [1–5], and the activity of clayzic is extremely high. It is generally accepted that the active centre for this reaction is the Lewis acid $ZnCl_2$ itself.

The second reaction is a similar benzylation reaction with benzyl chloride, but using anisole as the substrate, forming (4- and 2-methoxyphenyl)phenylmethane. This reaction is normally very much more facile than the reaction with benzene. However, using clayzic, the reaction has been shown by Clark [5] and by Laszlo [6] to be surprisingly slow. This observation is consistent with the general observation that the activity of clayzic is low when reactants or products are very polar, and it is generally believed that the Lewis acid sites in clayzic are mainly in regions of strong electrostatic fields, and polar molecules tend to adsorb strongly in these environments, effectively blocking these sites and hindering catalysis [5–8].

The third reaction is the benzylation of toluene using benzyl alcohol, forming (4- and 2-methylphenyl)phenylmethane. This reaction is very much less facile than the equivalent reaction using benzyl chloride, and clayzic is known to be much less active towards alkylation with the alcohol than with the chloride [8]. However, the reaction is included because it is most likely catalysed by Brønsted acid much more effectively than by Lewis acid, since carbocation formation would be expected to rapidly follow protonation of the alcohol through loss of the good leaving group, water.

2. Experimental

The acid-treated montmorillonite K10 was supplied by Sud-Chemie. The mesoporous silica used was EP12, supplied by Crosfield Catalysts. Other chemicals were of Analar grade and were obtained from Aldrich. All organic compounds were distilled prior to use. Pyrex glass vessels were used throughout for catalyst preparation, activation and testing.

Deposition of $ZnCl_2$ on K10 and on silica was from methanolic solution as previously described [2]. Catalyst loadings of 1.0 mmol g^{-1} support were used throughout. In all cases catalysts were activated at 150°C for 1 h under dry air or N_2 before use.

For each reaction 0.5 g catalyst, or supported catalyst, was used with 0.4 mol substrate (benzene, toluene or anisole) and 0.02 mol alkylating reagent (benzyl chloride or benzyl alcohol). No additional solvents were used.

For reactions between benzyl chloride and benzene, and benzyl chloride and anisole, reactant conversion and product yields were measured at several reaction times using gas chromatography, with *n*-hexadecane internal standard. Pseudo first-order rate constants were determined from plots of log (100 – %conversion of limiting reagent) vs. time. Typically the reaction times used gave conversions of 5% to 75%. Using this range, non-linearities due to deviations from pseudo first-order kinetics were undetected above random experimental error, and rate constants were determined from straight lines of best fit. The reactions were carried out at various temperatures between 20 and 70°C, and Arrhenius plots constructed.

For the reaction between benzyl chloride and toluene, data was collected at a single temperature of 25°C. For the reaction between benzyl alcohol and toluene, a single temperature of 110°C was used.

Infrared spectra of adsorbed pyridine were recorded in transmission mode, using pellets of catalyst. Pellets of clayzic were difficult to prepare and, where necessary, small additions of silica were made to the pellets to increase their strengths. (Measurements made on silica alone verified that this did not affect the IR spectrum of adsorbed pyridine.) The pellets were mounted in a heatable gas cell, connected to a vacuum line. Samples were activated at 150°C under vacuum for 1 h and then exposed to pyridine vapour for a further hour at the same temperature. Excess pyridine was pumped off at 150°C, and the gas cell disconnected from the line and transferred to a Philips PU9800 FTIR spectrophotometer for measurement. Spectra were recorded at a resolution of 4 cm^{-1} and typically using 1000 scans.

3. Results and discussion

3.1. ADSORBED PYRIDINE INFRARED SPECTRA

Surface Brønsted and Lewis acid sites can be differentiated through the infrared spectrum of adsorbed pyridine, which shows well resolved, characteristic bands for pyridine adsorbed on the two types of acid site [9]. The infrared spectra of thermally activated clayzic and silizic with adsorbed pyridine are shown in fig. 1. The bands associated with pyridine coordinated to Lewis acid sites at 1452 and 1490 cm^{-1} are relatively intense in both spectra. The band at 1544 cm^{-1}, characteristic of the pyridinium ion formed when pyridine interacts with a Brønsted acid site, is virtually absent in the silizic spectrum but is intense in the clayzic spectrum. A second band associated with the pyridinium ion at 1490 cm^{-1} overlaps the band due to pyridine coordinated to a Lewis acid site at the same frequency. This combined band has a much higher relative intensity in the clayzic spectrum than in the silizic spectrum, consistent with the presence of both Lewis acid and Brønsted acid bound pyridine on clayzic, but only Lewis acid bound pyridine on silizic.

Although this data is not quantitative, the relative intensities of the bands at 1452, 1490 and 1544 cm^{-1} suggest that Brønsted and Lewis acid sites are present on clayzic in comparable abundances, but on silizic surface acid sites are essentially all of the Lewis type. A similar infrared study of pyridine adsorbed on activated

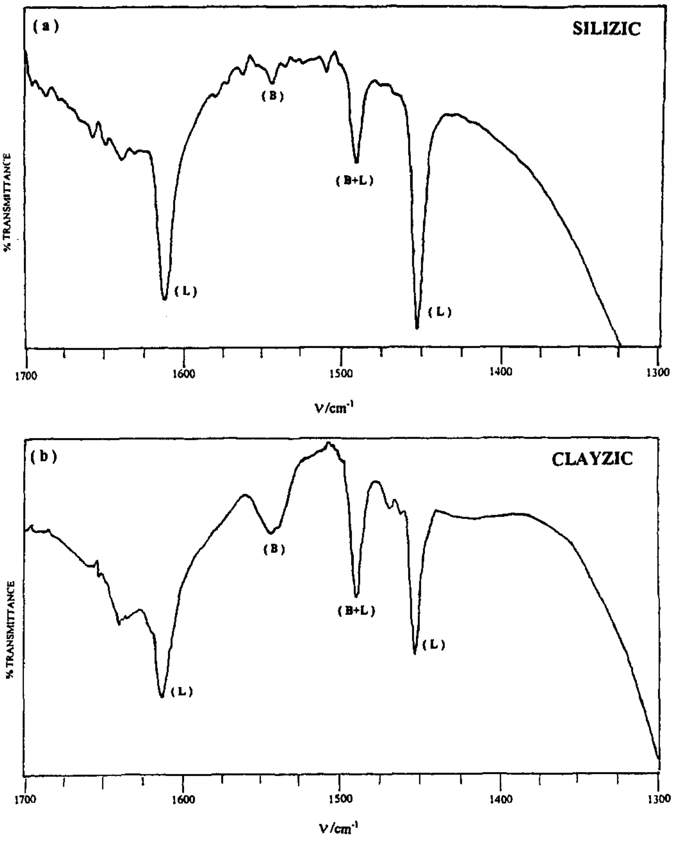

Fig. 1. Transmission infrared spectra of self-supporting wafers of (a) clayzic and (b) silizic, following activation under vacuum at 150°C, exposure to pyridine vapour at the same temperature, and re-evacuation.

K10 by Clark has confirmed that Lewis acid sites are absent on this acid-treated montmorillonite, and surface acidity is essentially all of the Brønsted type [4].

3.2. BENZENE/BENZYL CHLORIDE

The Arrhenius plots for the alkylation of benzene with benzyl chloride, using clayzic and silizic, are shown in fig. 2. A single very low rate constant is also shown for K10 at 345 K.

The low activity of K10 suggests that the reaction is not significantly catalysed by surface Brønsted acid sites. The much higher activities of the other two catalysts and the similarity in their activation energies support this view, and suggest that the active sites on clayzic and silizic are associated with adsorbed $ZnCl_2$.

A possible explanation for the larger pre-exponential factor for silizic than for clayzic is that a larger number of active sites are available on the former catalyst. This would be consistent with our previous work, which indicates that the enhanced activity which $ZnCl_2$ exhibits when it is adsorbed on acid clays or silicas is due specifically to $ZnCl_2$ which has been adsorbed into mesopores of diameters 10–20 nm on the support. Silica EP12 exhibits a very narrow pore size distribution with a large pore volume almost entirely within this range, whereas K10 has a very much broader distribution with a much lower pore volume in the important size range. It

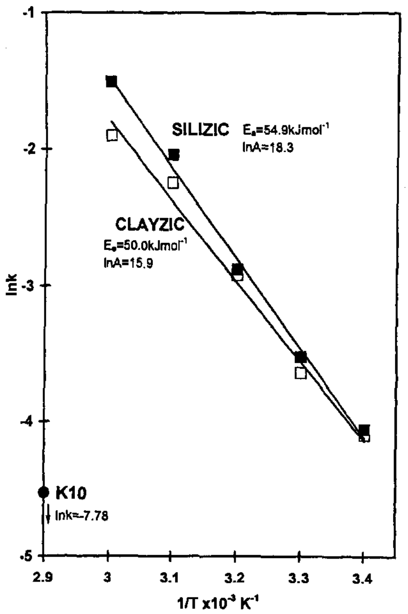

Fig. 2. Arrhenius plots for the alkylation of benzene with benzyl chloride, catalysed by clayzic (□) and silizic (■). A single data point for the acid-treated clay catalyst K10 is also shown (●). Note that the 95% confidence limits associated with E_{act} are estimated to be ± 5 kJ mol^{-1}, and $\ln A \pm 1.5$.

is therefore quite possible that a greater proportion of the $ZnCl_2$ is adsorbed in an active form on the silica than on the acid-treated clay.

3.3. ANISOLE/BENZYL CHLORIDE

The equivalent Arrhenius plots for the alkylation of anisole with benzyl chloride are shown in fig. 3. Reaction rates are generally higher with anisole than with benzene. K10 shows the largest increase, with anisole reacting over a hundred times faster than benzene. The corresponding increase for clayzic is very much less. Silizic shows slightly higher activity towards anisole than benzene at high temperatures but actually shows lower activity towards anisole at low temperatures.

The relatively high activity of K10 for anisole alkylation with benzyl chloride suggests that surface Brønsted acidity is considerably more catalytically active in this reaction than in the analogous alkylation of benzene. However, the observation that clayzic is more active than K10 means that the Lewis acid sites on clayzic must still make a significant contribution to the overall activity of the catalyst in this reaction. But the relatively low activity of silizic suggests that surface Lewis acidity *alone* is not as effective as the combination of Lewis and Brønsted acidity exhibited by clayzic.

The relatively low activity of Lewis acid sites towards anisole alkylation compared to benzene alkylation supports the idea that anisole coordinates to Lewis

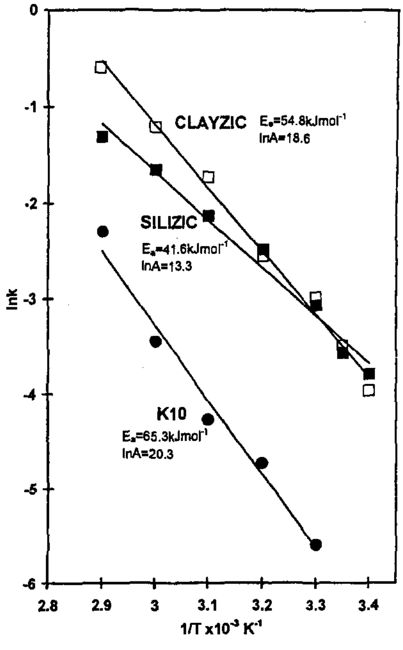

Fig. 3. Arrhenius plots for the alkylation of anisole with benzyl chloride using clayzic (□), silizic (■) and K10 (●). Confidence limits are as in fig. 2.

acid sites, blocking them for reaction. If this is the case, the modified rate constant for silizic, which exhibits essentially only Lewis acidity, would be of the form:

$$k = k_L/(1 + b[\text{anisole}])\,, \tag{1}$$

where k_L is the rate constant for the surface Lewis acid sites in the absence of anisole and b is the adsorption coefficient for anisole on Lewis acid sites. The linearity of the Arrhenius plot for this system suggests that the temperature dependence of b is small compared to the experimental errors in determining rate constants.

A comparison between the Arrhenius plots for silizic (Lewis only) in the anisole reaction (fig. 3) and the benzene reaction (fig. 2) shows a much lower activation energy for anisole. This is expected, and it confirms that the rate determining step for the Lewis acid catalysed process is not simply the generation of a carbocation from benzyl chloride but is a concerted process in which the bond to the substrate forms as the C–Cl bond weakens through coordination to the Lewis acid.

The large difference between the pre-exponential factors for the anisole and the benzene reactions on silizic reflects the reduced numbers of available Lewis acid sites in the presence of anisole. Based on their relative values it appears that only a very small percentage of the Lewis acid sites are available for reaction when anisole is present.

Turning now to the Arrhenius plot for K10 in the alkylation of anisole, the activity is many times higher than in the benzene reaction. This difference is expected, based upon the relative reactivities of benzene and anisole, and strongly suggests that Brønsted acid sites, unlike Lewis sites, are not blocked by anisole.

Comparing the Arrhenius plot for K10 with that of silizic shows directly the difference between a Brønsted acid catalyst and a Lewis acid catalyst in the presence of anisole. Silizic exhibits a much lower activation energy, suggesting that the reaction is still more facile in the presence of Lewis acid than Brønsted acid catalyst, but K10 shows a very much larger pre-exponential factor, suggesting that the active Brønsted sites on K10 are much more abundant than the active Lewis sites on silizic.

Finally, clayzic can be thought of as having properties of both silizic (Lewis acidity) and K10 (Brønsted acidity). Both types of acid site in clayzic show significant activity for the alkylation of anisole with benzyl chloride.

The Arrhenius plot for clayzic relative to the other two catalysts can be rationalised if the rate constant is assumed to be the sum of a rate constant k_L for the Lewis sites ($ZnCl_2$), and a rate constant k_B for the Brønsted sites (on the accessible acid-treated clay support),

$$k = k_L + k_B\,, \tag{2}$$

$$k = A_L e^{-E(L)/RT} + A_B e^{-E(B)/RT}\,. \tag{3}$$

In principle, A_L and $E(L)$ could be estimated from the silizic kinetic data, and A_B

and $E(\mathrm{B})$ from the K10 data, provided that corrections were applied for the generally lower activity of $ZnCl_2$ on clayzic than on silizic (see fig. 2) and the reduction in Brønsted acidity of K10 when it is partially covered with $ZnCl_2$. Although it is possible to predict rate constants for clayzic using this model which, within experimental errors, agree with the experimental rate constants, the inevitably very large uncertainties in the predicted rate constants make meaningful comparisons difficult. However, the model does allow us to confidently describe clayzic as a combination of a large number of Brønsted acid sites of relatively low activity (like those on K10) acting in concert with a small number of more active Lewis acid sites arising from that fraction of the adsorbed $ZnCl_2$ which is not coordinatively blocked by anisole.

3.4. TOLUENE ALKYLATION WITH BENZYL CHLORIDE AND BENZYL ALCOHOL

Table 1 shows single point %conversions of the limiting reagents in the alkylation of toluene with benzyl chloride and in the same alkylation with benzyl alcohol, using the three catalysts. Based on these data the order of catalyst activities with benzyl chloride is as expected for a reaction catalysed predominantly by surface Lewis acidity. Silizic is the most active catalyst, followed by clayzic and K10. In contrast, the alkylation reaction with benzyl alcohol is catalysed most effectively by the Brønsted acid K10, followed by clayzic, and silizic is essentially inactive.

These results suggest that the alkylation reaction with benzyl alcohol is catalysed by Brønsted acid sites, and the $ZnCl_2$ effectively plays no role. Others have observed the very low activity of clayzic and similar catalysts towards aromatic alkylation with benzyl alcohol [8,10].

Since only Brønsted acid sites from the acid montmorillonite support are active in the benzyl alcohol reaction, the activity of clayzic relative to K10 should, in principle, reflect the extent to which the Brønsted acid sites on K10 are rendered inactive on clayzic by the deposition of $ZnCl_2$. The only data point for direct comparison shows 20% reactant conversion with clayzic and 100% with K10 catalysis. This means that, at most, 20% of the active Brønsted acid sites on K10 are still active on clayzic. Even though conclusions based on a single data point are necessarily tentative, the implication of this result is that, even at the relatively low $ZnCl_2$ loading of 1.0 mmol g^{-1} on clayzic used here, 80% or more of the Brønsted acid sites on the clay support are rendered inaccessible by coverage with $ZnCl_2$.

Table 1
Limiting reactant conversions for toluene alkylation with benzyl chloride and with benzyl alcohol, using silizic, clayzic and K10 catalysts

	Conversion of benzyl chloride after 15 min at 25°C (%)	Conversion of benzyl alcohol after 15 min at 110°C (%)
silizic	49	0
clayzic	38	20
K10	0	100

4. Conclusions

The results of this work provide partial quantification of the relative contributions of Lewis and Brønsted acid sites to the catalytic activity of clayzic under different reaction conditions. In alkylations with benzyl chloride, the $ZnCl_2$ Lewis acid centres are the most active sites, but polar reactants such as anisole can coordinate these sites leaving only a small proportion free to take part in reaction. Under these conditions the less active but accessible Brønsted sites can become significant contributors to the overall activity. Because reaction at these sites occurs with a higher activation energy than at $ZnCl_2$, their relative contribution to the activity increases with temperature. Aromatic alkylations with benzyl alcohol, in contrast, appear to be catalysed exclusively by surface Brønsted acid sites.

This work illustrates the need to optimise clayzic-type catalysts for particular reactions. The support used can vary from a mildly acid-treated clay (high Brønsted acidity but relatively little enhancement to supported $ZnCl_2$ activity) to a clay subject to more vigorous acid treatment or a mesoporous silica (low Brønsted acidity but highly active supported $ZnCl_2$). The choice of both optimum support and optimum loading of $ZnCl_2$ depend on the relative activities of the two types of acid site in the reaction in question and the temperature at which the reaction is to be carried out.

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