Activation of Clayzic and its Effect on the Relative Rates of Benzylation of Aromatic Substrates

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The effects of the activation of K10 montmorillonite supported zinc chloride ('Clayzic') by different methods on the reactivity of the catalyst in the Friedel–Crafts benzylation of benzene and halobenzenes have been investigated. There is an optimum temperature for thermal activation in air at which point a rate enhancement, compared to unactivated Clayzic, in the benzylation of benzene of greater than 30 has been achieved. The rate limiting factor for these reactions is believed to be the ability of the aromatic substrate to enter the polar mesopores containing the active zinc ions in Clayzic, causing unexpected and activation-dependent rate trends to be observed. Activation of Clayzic is believed to reduce the polar nature of the pores, so aiding partitioning of the substrate into the catalyst.

Considerable academic and industrial interest has focused on the use of acid activated montmorillonite K10 supported zinc chloride (hereinafter referred to as 'Clayzic')[1–16] as a catalyst, since this remarkable material was first reported in 1989.[1] Most recently, interest has focused on cases where the activity of Clayzic can be suppressed by 'poisoning' due to complexation of the active zinc ion sites to oxygenated substrate or product molecules.[3,9,10,14] These studies have yielded some useful information about the nature of Clayzic, *e.g.* we have recently used a variable temperature study of the benzylation of anisole, to show that Clayzic has both Brönsted and Lewis acid sites.[3] The Brönsted acid sites were found to be due to the inherent acidity of the K10 support and the Lewis acid sites due to the supported zinc ions.[3] Of equal interest and of considerable importance is the question of how the activity of Clayzic can be enhanced *e.g.* by post-treatment.[15] In the case of solid acids post-treatment (or 'activation') methods are usually directed towards reducing the amount of solvating water in the catalyst and so enhancing the Lewis and Brönsted acidity of the material. To our knowledge no study of the activation of Clayzic has been reported. Considerable differences exist in the activation methods used to date. In this laboratory, thermal activation by calcination in air at 280 °C overnight has been used.[1,2] This was by analogy to the optimum calcination conditions determined for copper(II) chloride supported on K10 montmorillonite ('Claycuc').[1,16] Laszlo and co-workers have used calcination overnight in air at 120 °C.[7,12] Brown and Rhodes have used calcination under nitrogen at 150 °C for 1 h.[4–6]

Recent work has begun to explain the structural complexities of Clayzic. Brown and Rhodes have shown that mesoporosity in the support is necessary to the catalytic activity of Clayzic-type materials.[5,6] Pinnavaia[17] has reported that K10 is indeed mesoporous, having pore diameters in the range 60–100 Å. The size of these pores would suggest that no regioselectivity can be imparted to a reaction by structural constraints in the catalyst, as have been observed in zeolite catalysed processes. Laszlo's recent suggestion that the active sites are at the edges of the clay platelets[12] does not agree with the observations of Brown and Rhodes, who found no correlation between catalytic activity and surface area for Clayzic-type catalysts.[5] We have also recently shown the presence and explained the origin, of Brönsted and Lewis acid sites in Clayzic.[3] This study also showed that very useful information about the catalyst can be gleaned by varying the substrate in the Clayzic catalysed benzylation reaction.

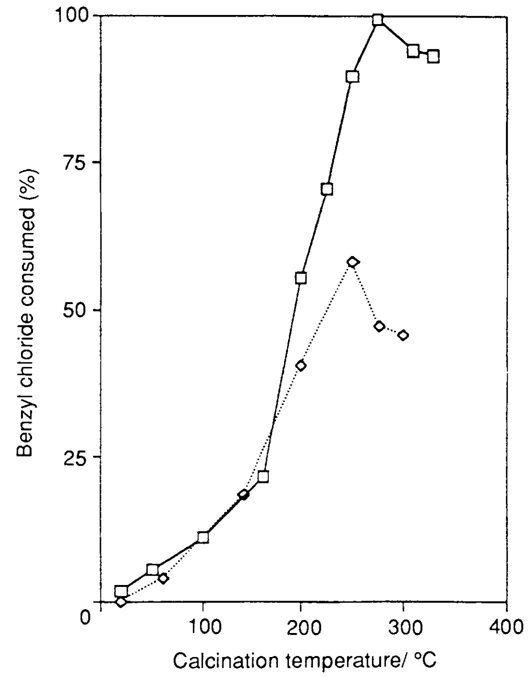

Fig. 1 Plot of benzyl chloride consumption in unit time (see text) *vs.* calcination temperature for clayzic and K10 clay, in the benzylation of cumene at 40 °C (four times as much K10 and two and a half times longer reaction time were used to obtain the plot for K10: see text); (□), clayzic; (◇), K10

We now report the results from our study on the activation of Clayzic and on the effects of different activation methods on the rates and selectivities of Clayzic catalysed Friedel–Crafts benzylation reactions of benzene and the halobenzenes.

Results and Discussion

The effect of different calcination temperatures on the activity of Clayzic was tested using the benzylation of cumene, a moderately activated substrate at 40 °C as a model reaction. The results of this study are shown graphically in Fig. 1.

Fig. 1 shows that there is an optimum calcination temperature for Clayzic. This appears at 275 °C and suggests that the effect of the calcination is more complex than simply dehydration of the catalyst to enhance the Lewis and Brönsted acidity. This optimum temperature is in good agreement with

Table 1 Effect of different activation methods on the catalytic activity of clayzic in the benzylation of benzene at 40 °C

Activation method	k ± sd/h^{-1}	$k_{\text{activated}}/k_{\text{unactivated}}$
Unactivated	0.064 ± 0.004	1.00
Azeotropic	0.158 ± 0.051	2.47
Thermal	2.01 ± 0.25	31.4

the optimum thermal activation temperature determined for Claycuc.[1,16] The effect of calcination on the catalytic activity of the K10 support is also shown in Fig. 1. It should be noted that four times as much K10 clay and a two and a half times longer reaction time were used to obtain the plots shown in Fig. 1. This observation demonstrates the much greater reactivity of Clayzic over the support, K10. The plot obtained for the K10 catalysed benzylation reaction shows that greatest catalytic activity is obtained at a calcination temperature of 250 °C. This also suggests that the effect of calcination is more complex than simple dehydration. It is possible that the calcination process causes structural changes to occur in the support, K10. The explanation for the observed differences in optimum calcination temperatures between K10 and Clayzic is not clear.

It was noticed that allowing thermally activated Clayzic to cool in air, rapidly reduced its activity. Cooling over phosphorous pentoxide in a desiccator preserved its activity and allowed reproducible results to be obtained. This suggests that thermally activated Clayzic is very hygroscopic.

The activities of untreated, thermally activated (by calcination in air at the optimum 275 °C overnight) and dehydrated (by azeotropic distillation to remove solvating water) Clayzic have been compared using the benzylation of benzene at 40 °C, as the test reaction. This reaction has been widely employed as a model reaction in studies of the activities of solid acid catalysts.[1–7,13] Pseudo first order rates of reaction were calculated to allow for differences in benzyl chloride concentration caused by the solvent remaining after azeotropic activation. These results are shown in Table 1.

The results in Table 1 show that both azeotropic distillation and thermal treatment of Clayzic do enhance the material's catalytic activity although the optimum conditions for the latter (by calcination in air at 275 °C overnight) are clearly a much more effective method. This is consistent with the suggestion that calcination in air at 275 °C does more than simply dehydrate the catalyst. The K10 support in Clayzic is known to be mesoporous[17] and the presence and dimensions of such mesopores have been shown to be important in the catalytic activity of Clayzic type materials.[5,6] It is possible that the calcination process alters the porous nature of the support in addition to removing solvating water. These effects are currently under investigation in this laboratory.

The halobenzenes are normally considered to be deactivated substrates in electrophilic aromatic substitution reactions (such as Friedel–Crafts benzylation), relative to benzene. The negative inductive (−I) effect of the halogen substituent destabilises the positively charged, σ-bonded, Wheland intermediate, formed in the rate determining step. These effects have been observed by Olah *et al.* in competitive aluminium trichloride–nitromethane catalysed benzylation reactions at 25 °C.[18] Olah has also shown that the observed *para-/ortho*-product isomer ratio in a Friedel–Crafts reaction can give information about the strength of the electrophile in a system.[19] The more reactive an electrophile, the lower the observed *para-/ortho*-ratio, as it will be less selective.

The calculated pseudo-first order rate constants,[3] mean *para/ortho*-ratios and calculated relative reaction rates (relative to benzene) for the unactivated Clayzic catalysed reactions, at 40 °C, are shown in Table 1. Non competitive reactions were used to prevent complicating co-reactant effects, such as those that have been observed by Laszlo *et al.*[7] Pseudo first order rate constants need to be calculated to allow for the differences in benzyl chloride concentration between reactions of different substrates.

The fact that rate differences between the substrates are observed is consistent with the rate determining step of the reaction being the attack of the aromatic substrate on the catalyst–benzyl chloride complex (the electrophile). The relative rates of Clayzic catalysed benzylations of the halobenzenes are surprisingly fast in relation to benzene and do not agree with Olah's observations under homogeneous catalysis.[18] We believe that the zinc ions in Clayzic reside in mesopores in the support structure which are likely to be hydrated and very polar in nature. The non-polar nature of the aromatic substrates will limit their ability to enter the mesoporous reaction space, *i.e.* the partitioning of the substrate between the polar, porous catalyst structure and the bulk reaction liquid strongly favours the latter. Thus the observed rate of reaction is limited by the ability of the substrate to enter the catalyst and so meet with the electrophile to effect reaction. The more polar halobenzenes might be expected to enter the polar mesopores more easily than benzene. Abraham's π^{H} values[20] (closely related to Taft's π^{*} and also a measure of a substrate's dipolarity/polarisability) could be expected to give an indication of the ability of a particular substrate to enter the catalyst structure. That the observed reaction rate of fluorobenzene is comparable to, and the reaction rates of the other halobenzenes are faster than, the reaction rate of benzene, can be explained by greater partitioning of the halobenzenes into the catalyst. The π^{H} value for benzyl chloride suggests that this reactant will experience relatively little difficulty in entering the catalyst structure. This is consistent with the formation of the electrophile not being rate limiting. This idea of reactant partitioning could help to explain the observations of Laszlo *et al.*, who found that in competitive reactions between benzyl chloride and benzyl alcohol, the alcohol can inhibit reaction completely or, surprisingly, react preferentially.[9] The greater dipolarity/polarisability of the alcohol over the chloride (as shown by their π^{H} values, Table 2) suggests that the alcohol will enter the mesopores containing the Lewis acidic zinc ions, preferentially (and once there, bind more strongly to the zinc ions, as the authors have suggested[9]).

The calculated pseudo first order rate constants,[3] mean *para/ortho* ratios and calculated relative reaction rates (relative to benzene) for the azeotropically activated[14] Clayzic catalysed benzylation reactions, at 40 °C, are shown in Table 3. After Clayzic has been activated by removing loosely bound water by azeotropic distillation with cyclohexane, the observed relative rates of benzylation are markedly different to those observed using unactivated Clayzic as the catalyst. In each case the observed reaction rate is higher than that seen for the unactivated Clayzic catalysed reactions. The reaction rate of benzene is found to have increased by the greatest amount. The rate enhancements for the halobenzenes are comparable. The reaction rate of benzene is now seen to be higher than those of fluoro- and chloro-benzene but lower than those of bromo- and iodo-benzene. The results suggest that the polar nature of the mesopores containing the active zinc ions, has been reduced and all the substrates find access to these pores less difficult. This suggestion is consistent with the reaction of benzene (the least polar substrate) showing the greatest rate enhancement after activation of the catalyst. The observed regioselectivities of the reactions are not informative of any change in the strength of the electrophile generated by the catalyst, as no consistent trend is apparent.

The calculated pseudo first order rate constants,[3] mean

Table 2 Calculated rate, selectivity and π^{H} data for the unactivated clayzic catalysed benzylations of benzene and the halobenzenes, at 40 °C

Substrate	$\pi^{H\,a}$	$k \pm \mathrm{sd}/\mathrm{h}^{-1}$	*para/ortho* ratio[b]	k_{ArX}/k_{ArH}
Benzene	0.52	0.065 ± 0.004	—	1.00
Fluorobenzene	0.57	0.064 ± 0.001	3.63	0.98
Chlorobenzene	0.65	0.081 ± 0.002	1.88	1.25
Bromobenzene	0.73	0.227 ± 0.018	1.87	3.49
Iodobenzene	0.82	0.154 ± 0.003	1.55	2.37
Benzyl Chloride	0.82	—	—	—
Benzyl Alcohol	0.87	—	—	—

[a] Ref. 12. [b] Ref. 10.

Table 3 Calculated rate and selectivity data for the azeotropically activated clayzic catalysed benzylations of benzene and the halobenzenes, at 40 °C

Substrate	$k \pm \mathrm{sd}/\mathrm{h}^{-1}$	*para/ortho* ratio[a]	k_{ArX}/k_{ArH}	$k_{azeotroped}/k_{unactivated}$
Benzene	0.158 ± 0.249	—	1.00	2.47
Fluorobenzene	0.084 ± 0.016	4.59	0.53	1.31
Chlorobenzene	0.094 ± 0.046	1.89	0.59	1.16
Bromobenzene	0.246 ± 0.018	1.78	1.56	1.08
Iodobenzene	0.190 ± 0.025	1.40	1.20	1.23

[a] Ref. 10.

Table 4 Calculated rate and selectivity data for the thermally activated clayzic catalysed benzylations of benzene and the halobenzenes, at 40 °C

Substrate	$k \pm \mathrm{sd}/\mathrm{h}^{-1}$	*para/ortho* ratio[a]	k_{ArX}/k_{ArH}	$k_{calcined}/k_{unactivated}$
Benzene	2.01 ± 0.25	—	1.00	31.4
Fluorobenzene	0.603 ± 0.085	5.52	0.30	9.42
Chlorobenzene	1.32 ± 0.20	2.04	0.66	16.3
Bromobenzene	1.73 ± 0.28	1.81	0.86	7.64
Iodobenzene	2.75 ± 0.24	1.77	1.37	17.9

[a] Ref. 10.

para/ortho ratios and calculated relative reaction rates for the thermally activated (by calcination in air at 275 °C overnight) Clayzic catalysed benzylation reactions, at 40 °C, are shown in Table 4. The observed relative rates of benzylation using thermally activated Clayzic are markedly different to the sets of data obtained using unactivated or azeotropically activated Clayzic. Again the reaction rate of benzene is seen to increase by the greatest amount, although the rates of all the benzylation reactions are seen to have increased significantly. Benzene is now observed to react more quickly than all of the halobenzenes except iodobenzene. The *para/ortho* ratios for these reactions are seen to be higher (with the exception of that of bromobenzene, which is comparable) than those observed with unactivated or azeotropically activated Clayzic (although only fluorobenzene shows a large change). This suggests that the reactivity of the system has been reduced by calcination, as a weaker electrophile appears to be generated. That a higher reaction rate is observed using a less 'active' catalyst, after thermal activation, is consistent with the turnover efficiency of the active sites having been improved by enhanced access of the substrates to the active sites. This suggests that the polar nature of the mesopores containing the active sites in Clayzic has been reduced further by calcination than by azeotropic activation. These suggestions are also consistent with our earlier suggestion that the calcination process causes structural changes to occur in the catalyst which aid reactivity.[1]

Experimental

Thermal Activation Studies.—Samples of 'Clayzic' (*ca.* 5 g, particle size 50–100 μm) were evenly spread in a glass container and heated in air overnight (16 h) at various temperatures. They were then cooled to ambient temperature in a desiccator over phosphorus pentoxide, weighed into the reaction flask and dried substrate added immediately. In this way, reproducible results from subsequent benzylations could be obtained.

Azeotropic Activation Studies.—'Clayzic' (2 g) was added to a pre-weighed flask and azeotropically distilled overnight (16 h) with 100 cm^3 of cyclohexane, using a Dean–Stark receiver. The flask and contents were then cooled to ambient temperature, re-weighed to determine the amount of cyclohexane remaining and dried substrate added.

Reactions.—The aromatic substrate [0.5 mol; dried (3 Å molecular sieves)] was added to the 'Clayzic' (2.00 g) and the mixture heated with vigorous stirring to 40 °C. Benzyl chloride (12.7 g; 0.1 mol) was then added in one aliquot. The reaction's progress was then monitored by GC (response factor corrected), and the products confirmed by GC–MS and by comparison to authentic samples. In the benzylation of the halobenzenes, small ($< 5\%$) amounts of the *meta* isomers were also detected.

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