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Mesoporous solid acid catalysts: relationship between amine TPD data and catalytic activities

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The concentrations of surface acid sites on Al^{3+}- and H^+-exchanged AlMCM-41 catalysts have been measured by temperature-programmed desorption (TPD) of a series of primary, secondary and tertiary amines, and by adsorption of ammonia. Surface acid site concentrations have been compared with cation exchange capacities (CEC's) and catalytic activities in the alkylation of toluene with benzyl alcohol. The results show that the catalytic activities of the two ion-exchanged forms of the AlMCM-41 are similar. This is reflected in the acid site concentrations measured with tri-n-butylamine, and to a lesser extent tri-i-butylamine, which are similar for both ion-exchanged forms of the catalyst, and close to the CEC. Acid site concentrations measured with smaller amines and ammonia are similar to those based on tributylamine TPD for H^+-exchanged AlMCM-41, but the Al^{3+} form of the catalyst appears to chemisorb significantly more of the smaller amines and ammonia, resulting in higher than expected acid site concentrations when these adsorbates are used. Larger amines than the tributylamines show very low chemisorption capacities on both forms of AlMCM-41, and appear to access only a small proportion of the surface acid sites. The primary amines tested show poor separation of chemisorbed and physisorbed amine in TPD experiments, making the determination of acid site concentration difficult. The results illustrate the importance of choosing an appropriate amine in using TPD to measure catalyst surface acidities.

Keywords: temperature-programmed desorption, TPD, ammonia, amine(s), mesoporous molecular sieve, MCM-41, AlMCM-41, exchangeable cation, surface acidity

1. Introduction

Temperature-programmed desorption (TPD) of ammonia or amine bases is often used to characterise surface acid sites on solid acid catalysts. The method assumes that the amines adsorb quantitatively on surface acid sites, and that desorption from acid sites can be distinguished from the desorption of physisorbed base on other sites [1,2]. The concentration of surface acid sites can be calculated from the amount of amine that desorbs from these sites, and some limited indication of the relative strengths of the acid sites can be obtained from the temperatures needed to bring about desorption.

The choice of base probe compound is important in obtaining TPD data which reflects catalytic behaviour. With zeolitic and similar microporous solid acid catalysts, small base compounds such as ammonia or pyridine are usually used, as these can generally access all the acid sites on these catalysts. Acidities measured with these bases can then be used for predicting catalytic activities in gas-phase processes involving similarly small reactant molecules.

For catalysts which are to be used for liquid-phase processes, or reactions involving larger reactant molecules, the choice of base probe molecule may be more critical, particularly in terms of the accessibilities of acid sites to probe molecules. This is examined in the current study, in which solid acid catalysts based on the aluminosilicate mesoporous molecular sieve AlMCM-41 are characterised with a range of basic probe compounds, and the resulting acidities compared with catalytic activities in a liquid-phase reaction.

The Brønsted acid form of AlMCM-41 is generally prepared either as the H^+-exchanged material (by ion exchange with NH_4^+ followed by calcination to decompose to NH_3), or through ion exchange with an acidic metal cation such as Al^{3+} which generates protons by polarisation of coordinated water molecules. Previous work has shown that these two forms of AlMCM-41 exhibit similar acid catalytic activities in a series of liquid-phase reactions [3]. An objective of this work is to examine the extent to which TPD experiments with alkyl amines reflect this similarity in catalytic activities, even though the nature of the Brønsted acid sites on the two forms of the catalyst are different.

The amines used include primary, secondary and tertiary alkyl amines. For comparison, surface acidities are also characterised by ammonia adsorption using a flow calorimetric method [4]. Catalytic activities are measured in the Brønsted-acid-catalysed alkylation of toluene with benzyl alcohol.

The amines are all of fairly similar base strengths (pK_b's and gas-phase proton affinities) and differ principally in terms of size and shape. It is the relationship between these properties of the probe amines and their usefulness in predicting catalytic activities in liquid-phase reactions that is the main focus of the work.

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An additional factor which can affect these TPD experiments is the possibility of the amine reacting on surface acid sites, yielding products that desorb at lower temperatures than would be expected for chemisorbed base. Primary amines generally react in this way on moderately strong surface acid sites, and the alkene products desorb as soon as they are formed [5]. If the alkene can be monitored separately from the desorbing amine this may aid the interpretation of TPD data but, if the sample weight alone is being monitored, TPD data can sometimes be difficult to interpret. Relatively little work has been reported using secondary and tertiary amines for TPD experiments [6] but, in principle, similar elimination reactions can occur with these probes. A further objective of the work is to establish the extent to which surface reactions affect the TPD of secondary and tertiary amines on solid acid catalysts.

2. Experimental

2.1. Catalyst preparation and characterisation

The synthetic procedure of Klinowski et al. [7], based on cetyltrimethylammonium ion template, was used for AlMCM-41 (formal Si/Al ratio of 15), and siliceous MCM-41 molecular sieves. Catalysts were characterised with powder X-ray diffraction, N_2 adsorption, ^{27}Al MAS NMR (University of Durham EPSRC facility) and elemental analysis for Al and Si (Butterworth Laboratories).

The Al^{3+} form of AlMCM-41 was prepared by treating calcined AlMCM-41 with 1 mol dm^{-3} aluminium nitrate solution in a molar ratio of 1 : 40 at 90 °C for 4 h. The catalyst was filtered and washed with hot water. The process was repeated and the catalyst air dried. The H^+ form of AlMCM-41 was prepared by ion-exchanging the calcined AlMCM-41 with NH_4^+ as above, followed by a second calcination in air at 540 °C for 20 h. The cation-exchange capacities of Al^{3+} and H^+ forms of AlMCM-41, and of siliceous MCM-41, were measured for samples dried at 100 °C for 1 h, by exchanging samples with Co^{2+} and measuring liberated Co^{2+} on back-exchange with hydrochloric acid [8].

2.2. Amine TPD and ammonia adsorption

Amines (AnalaR grade, listed in table 1) were dried over molecular sieve and used without further purification. Catalyst samples were dried at 100 °C for 24 h and then transferred to sealed vessels containing saturated amine vapour. Amine adsorption was carried out for 72 h at either room temperature or 100 °C (for the high boiling amines). Catalysts were transferred under nitrogen to a Stanton Redcroft STA 625 thermobalance and subjected to a temperature ramp of 10 °C min^{-1} under flowing nitrogen. The TPD data for the alkyl amines are compared with the adsorption capacities for ammonia measured at 180 °C, using a flow calorimetric technique on the same instrument described earlier [4].

Table 1
Adsorption capacities of AlMCM-41 catalysts for alkyl amines, and catalytic activities towards the alkylation of toluene with benzyl alcohol.

(i) *Amine TPD and ammonia adsorption – acid site concentrations*

Amine	Amine chemisorption capacities[a] (mmol g-cat.$^{-1}$) (measured by TPD: 275–500 °C)		
	H^+/AlMCM-41	Al^{3+}/AlMCM-41	MCM-41
Ammonia[b]	0.27	0.88	0.00
Diethylamine	0.33	0.54	0.06
Triethylamine	0.34	0.55	0.06
Tri-i-butylamine	0.32	0.41	0.05
Tri-n-butylamine	0.22	0.30	0.02
Tri-n-hexylamine	0.04	0.06	0.03
n-butylamine	0.52	0.66	0.15
i-butylamine	0.43	0.73	0.27

(ii) *Catalytic activities*

Thermal activation temperature (°C)	Pseudo-first-order rate constants[c] for the alkylation of toluene with benzyl alcohol ×10^{-5} (s^{-1})		
	H^+/AlMCM-41	Al^{3+}/AlMCM-41	MCM-41[d]
150	1.73	2.19	–
250	2.52	2.23	–
350	2.19	2.53	–

[a] ±0.04 mmol g^{-1}.
[b] Measured as adsorption at 180 °C (see text).
[c] $\pm 0.2 \times 10^{-5}$ s^{-1}.
[d] No detectable reaction within 1 h.

A limited number of base adsorption experiments were performed using a temperature-programmed solid insertion probe with a mass spectrometer, to make one-off measurements of the desorbing species. In each case, mass spectral peaks characteristic of the parent amine and of the alkene product of deamination were followed with temperature. There is some uncertainty over the exact sample temperatures in these experiments because the measuring thermocouple is necessarily slightly separated from the sample on the tip of the solid insertion probe. Reported temperatures are therefore termed "apparent" and must be treated as uncalibrated. Although this makes comparison with the weight-based TPD experiments slightly difficult, sample-to-sample comparisons are valid.

2.3. Catalytic measurements – alkylation of toluene with benzyl alcohol

All reagents were anhydrous and of AnalaR grade, and were stored over molecular sieve before use. Catalyst (100 mg) was activated at either 150, 250 or 350 °C under flowing dry air for 1 h. The catalyst was cooled to the reaction temperature of 90 °C and toluene/benzyl alcohol (10 g of mixture, 20 : 1 in mol), pre-heated to the reaction temperature, was added to the catalyst with stirring, maintaining the dry air flow. Samples were taken at 15 min intervals for 2 h, and analysed with GC using tetradecane as an internal standard.

3. Results and discussion

3.1. Catalyst characterisation

Elemental analysis for as-prepared AlMCM-41 (probably in the Na^+ form) gave a molar Si/Al ratio of 10. This is lower than the ratio in the synthesis mixture, suggesting that a proportion of the Si used was not incorporated in the lattice. The ^{27}Al MAS NMR spectrum (figure 1(a)) suggests that most of the Al is in tetrahedral lattice sites ($\delta = 50$–60 ppm), although a significant proportion is in octahedral sites (0 ppm). The pore size distribution and specific surface area (figure 1(b)) are typical of MCM-41 materials, showing a pore diameter maximum at about 3.2 nm.

The cation-exchange capacities (CEC's) of H^+-AlMCM-41 and Al^{3+}-AlMCM-41, measured by Co^{2+} uptake, were found to be 0.26 and 0.25 mequiv g^{-1}, respectively, based on the weight of hydrated catalyst, equilibrated under ambient condition. In principle, these values represent the maximum concentrations of surface Brønsted acid sites on the two catalysts. In comparison, the CEC of siliceous MCM-41 was found to be 0.13 mequiv g^{-1}. This material was used without ion exchange with acidic cations and is regarded as essentially non-acidic relative to the Al^{3+} and H^+ forms of AlMCM-41.

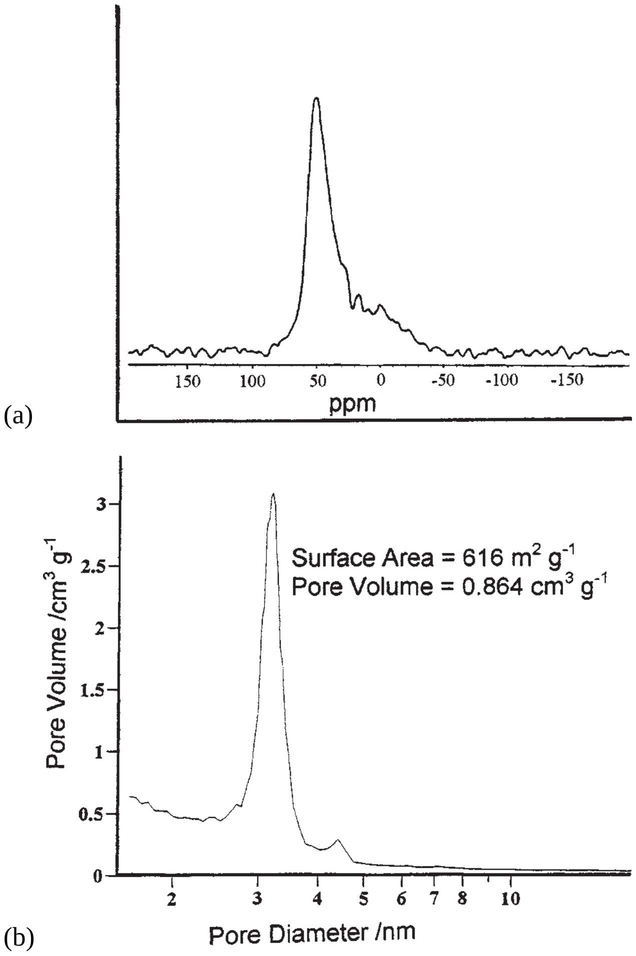

Figure 1. (a) ^{27}Al MAS NMR spectrum of as-prepared AlMCM-41 (probably in the Na^+ form). (b) Pore size distibution (BJH) and specific surface area (BET) taken from the N_2 adsorption/desorption isotherms at 77 K for as-prepared AlMCM-41.

3.2. Catalytic activities

Catalytic activities towards the alkylation of toluene with benzyl alcohol are shown in the table, for catalysts thermally activated at 150, 250 and 350 °C. Thermal activation was carried out at these temperatures mainly to demonstrate that the changes in catalytic activities over this range of activation temperatures are relatively minor. This is important because the amine TPD and adsorption measurements are made over a range of temperatures from 150 to 450 °C, on catalysts that have received no thermal pre-activation.

The most significant observation from the catalytic activity data is that the Al^{3+} and the H^+ forms of AlMCM-41 show broadly similar activities in the test reaction, and siliceous MCM-41 shows negligible activity.

3.3. TPD and amine adsorption capacities

3.3.1. Secondary and tertiary amines

Figure 2 shows the TPD weight curve for triethylamine on H^+/AlMCM-41. A change in slope can be seen between 200 and 300 °C. Similar breaks are seen for the

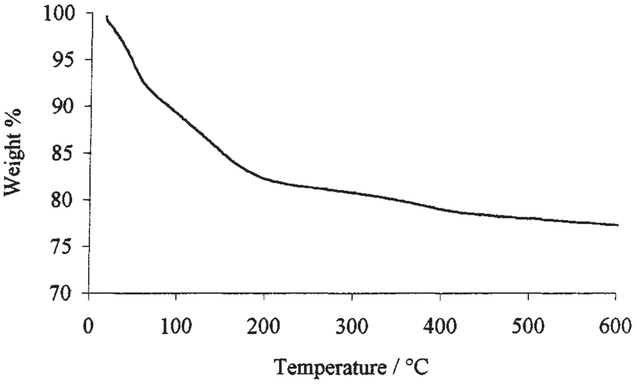

Figure 2. TPD curve for triethylamine adsorbed on H^+/AlMCM-41.

other secondary and tertiary amines over this temperature range on desorption from both Al^{3+}- and H^+-exchanged AlMCM-41.

The desorption profile for siliceous MCM-41 with these amines shows no desorption above 275 °C. As mentioned above, this material shows negligible catalytic activity, and is assumed to exhibit negligible acidity compared to the two ion-exchanged AlMCM-41 materials.

In equivalent TPD studies on acid clays [9] and zeolites [5,6] using a range of amines, other workers have found that the break between the desorption of physisorbed and chemisorbed amines generally occurs between 250 and 300 °C. In this work it has therefore been assumed that physisorbed amine is completely removed below 275 °C, and the desorption of chemisorbed amine occurs only above this temperature. The acid site concentrations are calculated from the amount of amine desorbed over the temperature range 275–500 °C. These are shown in the table.

3.3.2. Primary amines

The desorption characteristics of the primary amines n-butylamine and i-butylamine are different from those of the secondary and tertiary amines. No clear changes in the slope of the sample weight/temperature profiles are seen, and there is no clear difference between the desorption profiles for the AlMCM-41 materials and siliceous MCM-41, with both showing significant desorption above 275 °C. For this reason, data in the table for the two primary amines are considered unlikely to accurately represent surface acid site concentrations.

3.3.3. Ammonia

The flow calorimetric ammonia adsorption experiments were carried out at 180 °C. This temperature was also chosen to allow chemisorption but not physisorption [4].

3.4. Surface reactions followed by TPD-MS

Figure 3 shows the mass spectral TPD data for the desorption of a primary, secondary and tertiary amine together with the associated alkene products of deamination, from the H^+-AlMCM-41 catalyst.

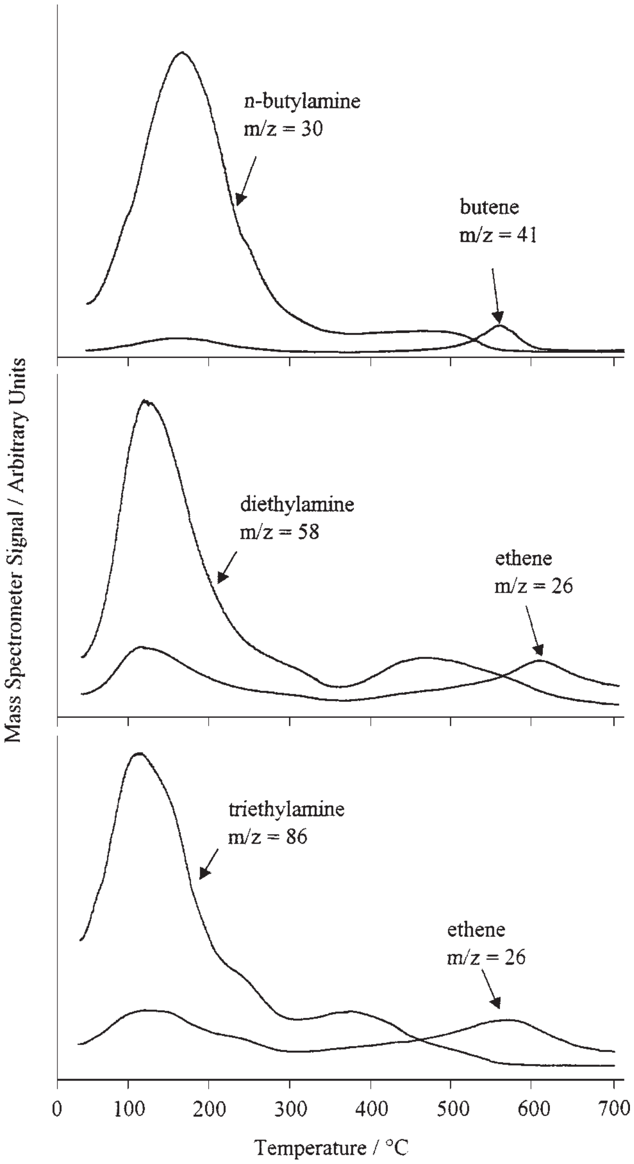

Figure 3. TPD-MS curves for n-butylamine, diethylamine and triethylamine on H^+/AlMCM-41. Note: the temperature scale is uncalibrated (see text).

In all cases, the desorption of physisorbed amine is seen at 100–200 °C (apparent temperature – see above). Amine desorption then continues to considerably higher temperatures (400–500 °C apparent), presumably as chemisorbed amine is lost.

For diethylamine and triethylamine, the desorption of chemisorbed amine is well resolved from physisorbed amine. The trace for the primary amine n-butylamine differs from the other two in showing poor separation between physisorbed and chemisorbed amine. This is consistent with the observation of poor separation between physisorbed and chemisorbed amine in the weight-based TPD experiments for primary amines, and supports the view that the determination of acid site concentrations using primary amine TPD is difficult with these catalysts.

For all three amines the formation and desorption of alkene appears to begin part way through the desorption of chemisorbed amine, and from then on alkene formation takes over from desorption of unreacted amine. Fortunately, because alkene formation only occurs at relatively high temperature, it does not affect the resolution between physisorbed and chemisorbed amine loss.

3.5. Amine TPD and surface acid site concentration

The TPD data for the primary amines studied here do not effectively differentiate between the acidic AlMCM-41 catalysts and the non-acidic, or very weakly acidic, siliceous MCM-41. Conclusions are therefore based on TPD data for secondary and tertiary amines, and ammonia adsorption.

It is reasonable to assume that the concentrations of acid sites on both H^+- and Al^{3+}-AlMCM-41 should be no greater than the cation-exchange capacities of the materials (0.26 and 0.25 $\mathrm{mequiv\,g^{-1}}$). The catalytic activities are consistent with this in that they are similar for the two forms of the catalyst.

The first catalyst, H^+-AlMCM-41 shows capacities for ammonia, and all the secondary and tertiary amines except for tri-n-hexylamine, which are similar and close to the cation-exchange capacity. There is a slight decrease in the adsorption capacities as the amines get larger up to tri-n-butylamine, and then an abrupt fall on going to the largest amine, tri-n-hexylamine. These results suggest that adsorption of amines on acid sites is essentially stoichiometric, but the accessibilities of acid sites are sensitive to the size of the probe base molecule.

In contrast, the capacity for chemisorbed amine or ammonia on Al^{3+}-AlMCM-41 is much more dependent on the nature of the base. The capacity for ammonia is over three times the cation-exchange capacity. Diethylamine and triethylamine also adsorb in excess of the exchange capacity, and it is only with tri-n-butylamine that adsorption is close to stoichiometric on acid sites. As with H^+-AlMCM-41, the largest base, tri-n-hexylamine, shows very low chemisorption.

4. Conclusion

Overall, for acid catalysts based on AlMCM-41, the primary amines n-butylamine and i-butylamine do not show sufficiently well resolved TPD profiles for the determination of surface acid site concentrations. Of the secondary and tertiary amines tested, tri-n-butylamine appears to reflect the surface acidities of the Al^{3+} and H^+ forms of AlMCM-41 better than any of the other amines studied.

The smaller amines and ammonia appear to be good probes for acid sites on H^+-AlMCM-41, but they adsorb in excess on Al^{3+}-AlMCM-41. A partial explanation may be that these small amines can coordinate exchangeable Al^{3+} ions in greater numbers than are required to simply neutralise the Brønsted acid sites, although this mechanism could not account for the apparent three-fold excess adsorption of ammonia. It seems that strong ammonia adsorption must additionally occur on sites other than those associated with the exchangeable cations in Al^{3+}-AlMCM-41.

The effect of using larger amines is difficult to judge since the only one used here (trihexylamine) is very much larger than the tributyl compounds. However, the trihexylamine appears to be too large to chemisorb to any significant extent in the mesoporous AlMCM-41 lattice (pore diameter 3.2 nm), clearly illustrating the sensitivity of measured acidity to probe molecule size.

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