Microcalorimetric investigation of mordenite and Y zeolites for 1-methylnaphthalene isomerisation

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Adsorption microcalorimetry of pyridine has been used to determine the concentration and the distribution of strengths of the acid sites of Y zeolites and mordenite samples. 1-Methylnaphthalene was reacted over these samples at 623 K under atmospheric pressure in a continuous-flow fixed-bed reactor. For Y zeolites the relative extents of 1-methylnaphthalene isomerisation and disproportionation have been found to depend on the density of the acid sites. Coke growth favours isomerisation over disproportionation as time-on-stream increases. However, both disproportionation and coking are highly disfavoured in the channel system of mordenites, in spite of the relatively high density of the acid sites. The accumulation of strongly adsorbed feed and/or product molecules is responsible for the severe decay in activity of non-dealuminated mordenite.

Microcalorimetry has gained importance as one of the most reliable methods for the study of the surface acidity of solid catalysts. Ammonia, pyridine and other basic molecules can be conveniently used, according to specific needs, to assess the number and the strength of the acid sites. Surface acidity is a key parameter in the catalysis of a wide range of reactions of industrial interest. A potential route for upgrading low-cost, largely available polynuclear aromatic feedstocks is the conversion of 1-methylnaphthalene (1-MN) into 2methylnaphthalene (2-MN). The latter can be easily oxidised to 2-methyl-1,4-naphthoquinone, used therapeutically, under the name of Menadione, as a substitute for natural Vitamin K in the treatment of bleeding disorders. A further potential use of 2-MN is via its shape-selective methylation to 2,6-dimethylnaphthalene, used in the manufacture of films, fibres and engineering plastics. Zeolites are strong candidates as catalysts for the conversion of 1-MN to 2-MN: no pollution problems originate from these acid solids, whose pore structure is able to induce unique selectivity effects. 1-MN isomerisation to 2-MN was first reported to occur over magnesium-modified NaY zeolites.¹ The behaviour of Ω , X, Y and ZSM-5 was then investigated in our laboratory.^{2–5} All the zeolites were completely inactive in their fully Na-form; for H zeolites the sequence of the initial reactant conversion was $HY \approx H\Omega \gg$ HX \gg HZSM-5; selectivity to 2-MN ranged from *ca.* 70 to 100%; coking and activity decay were observed. Differences in the nature of the carbonaceous deposits formed during 1-MN conversion on zeolites of different structural types have been reported;6,7 besides coking, transalkylation was reported to be the main undesired reaction.

In the present work microcalorimetry was used to determine the acid properties of Y zeolites and mordenite, differing as to the extent of decationation and/or the Si/Al ratio; 1-MN was reacted over these samples in a fixed-bed flow reactor and their catalytic behaviour was interpreted by considering the combined influence of structure and acidity.

Experimental

NaY was a commercial sample from Union Carbide. The partially decationated NaHY sample was prepared from NaY by ion-exchange with NH_4Cl aqueous solution, 0.5 M, at room temperature, followed by overnight calcination in flowing air at 823 K (heating rate 3.5 K min⁻¹). To obtain the fully decationated HY sample ion-exchange was carried out under reflux at 368 K. HYd was prepared from HY by dealumination with SiCl₄ at 573 K, according to the procedure reported in ref. 8. Mordenite samples were commercial products from Norton and ZEOCAT. The chemical composition of the catalysts is reported in Table 1.

A Tian-Calvet heat flow equipment (Setaram) equipped with a volumetric vacuum line was used for microcalorimetric measurements. Each sample was pretreated overnight at 673 K under vacuum (10^{-3} Pa). Adsorption was carried out at 423 K, by admitting successive doses of pyridine and recording the thermal effect; the run was stopped at a final equilibrium pressure of 133.3 Pa. After overnight outgassing of the sample at 423 K, a second adsorption was carried out, giving an adsorption isotherm parallel to the first one. From the difference between the adsorption isotherms the amount of pyridine irreversibly adsorbed was evaluated.

The catalytic activity was tested in a fixed-bed flow microreactor. The zeolite samples were activated *in situ* by flushing with N₂ for 2 h at 773 K before reaction. Liquid 1-MN was fed by a syringe pump to the preheating section of the reactor, where it was vaporised and mixed with a H₂ stream (H₂/hydrocarbon = 30 mol/mol). The reaction was carried out at 623 K under atmospheric pressure; contact time, W/F, ranged between 0.23×10^2 and 3.28×10^2 g(cat) h [mol(1-MN)]⁻¹. The reactor effluent was collected in cold traps and analysed by capillary gas chromatography (GC) (carrier gas: H₂; column: 100 m Petrocol DH; oven programme: 1 min at 383 K, heating at 1 K min⁻¹ up to 493 K; detector: flame ionization).

The amount of coke was determined from the amount of CO_2 evolved when heating the catalyst at 773 K in an O_2 flow, after purging in N_2 to desorb reactant and/or products retained by the solid.

 Table 1
 Chemical composition of the zeolites

sample	unit cell formula
NaY NaHY HY HYd HMOR-5 HMOR-11	$\begin{array}{c} Na_{51}Al_{51}Si_{141}O_{384} \\ Na_{28}H_{23}Al_{51}Si_{141}O_{384} \\ H_{51}Al_{51}Si_{141}O_{384} \\ H_{30}Al_{30}Si_{162}O_{384} \\ H_{8}Al_8Si_{40}O_{96} \\ H_{4}Al_{4}Si_{44}O_{96} \end{array}$

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Results and Discussion

Microcalorimetric characterisation

Calorimetric results for the Y samples are reported in Fig. 1, where the differential heat of adsorption (Q_{diff}) is plotted vs. pyridine uptake (n). The initial values of Q_{diff} are in the range 240–195 kJ mol⁻¹. All the samples show a stepwise decrease in the differential heat with coverage. Non-specific adsorption could be responsible for the low differential heat observed at the higher coverages. Calorimetric runs carried out on silica samples (two commercial and one prepared by the sol-gel technique) actually showed that pyridine is adsorbed to some extent on pure silica, with differential heats not exceeding 60 kJ mol⁻¹. Accordingly, pyridine uptake originating differential heats $< 60 \text{ kJ mol}^{-1}$ were neglected. Some of the acid sites interact reversibly with pyridine. They have differential heats below 90–100 kJ mol⁻¹ (depending on the particular sample). The amount of the sites which adsorb pyridine irreversibly, n_i , is 88, 354, 746 and 566 μ mol g⁻¹ for NaY, NaHY, HY and HYd respectively. The number of sites with $Q_{\text{diff}} > 150 \text{ kJ mol}^{-1}$ is less than 50 μ mol g⁻¹ for any of the samples.

From the Q_{diff} vs. coverage curves of Fig. 1 the site energy distribution plots, $-dn/dQ_{diff}$ vs. Q_{diff} , were obtained. These are presented in Fig. 2 and can be regarded as the acidstrength spectra of the Y zeolites. The existence of different sets of sites, each set being homogeneous as to strength, is revealed for each sample by the presence of peaks in its spectrum. Most of the sites of the parent NaY are homogeneous, as indicated by the presence of a single, large peak around 84



Fig. 1 Differential heat of adsorption, Q_{diff} , vs. pyridine uptake for Y zeolites. Open symbols refer to readsorption after evacuation.



Fig. 2 Site energy distribution plots for Y zeolites

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kJ mol⁻¹; reasonably, these sites are the Na⁺ ions acting as Lewis centres. Accordingly, the large peak in NaHY can be associated with the reversible interaction of pyridine with the weakly acidic Na⁺ ions acting as Lewis centres. Accordingly, the large peak in NaHY can be associated with the reversible interaction of pyridine with the weakly acidic Na⁺ ions remaining after partial decationation, whereas the peak around 110 kJ mol⁻¹ indicates that a new set of sites of higher strength is formed. Complete decationation leads to HY; as expected, its spectrum no longer shows the low-energy peak, whereas the peak at 110 kJ mol⁻¹ appears markedly enhanced; another peak is also visible around 132 kJ mol⁻¹ The present results for HY are quite similar to those previously obtained for other commercial HY samples of similar Si/Al ratio9, whose acid-strength spectra for pyridine adsorption showed two sets of homogeneous sites with heats of adsorption between 145 and 115 kJ mol⁻¹; comparison of FTIR and calorimetric data allowed us to conclude that these sites were Brønsted in nature. The acid-strength distribution for HYd is similar to that of the parent HY, the effect of the mild dealumination being to decrease the number of acid sites.

Calorimetric results for mordenites are presented in Fig. 3. The initial differential heats of adsorption are between 250 and 220 kJ mol⁻¹ for HMOR-5 and HMOR-11, respectively. Increasing coverage causes a sudden drop in the differential heat to a plateau region, followed by a continuous decrease. The amount of irreversibly adsorbed pyridine is 788 and 625 μ mol g⁻¹ for HMOR-5 and HMOR-11, respectively. The sites with $Q_{diff} > 150$ kJ mol⁻¹ do not exceed 65 μ mol g⁻¹. The acid-strength spectra are shown in Fig. 4. HMOR-5 shows a large peak around 135 kJ mol⁻¹ (with a shoulder at 140 kJ mol⁻¹). The set of homogeneous sites observed on the mildly dealuminated HMOR-11 has a strength similar to that of HMOR-5.

Additional insight into the adsorption process can be obtained by considering the time over which the heat is evolved after each successive dose (thermokinetic parameter, t_0). This parameter is plotted vs. coverage in Fig. 5 for Y zeolites. For all the samples except NaY, t_0 first increases with pyridine coverage, passes through a pronounced maximum and then decreases. Comparison with Fig. 1 shows that the maxima correspond to the end of the stepped portion of the $Q_{\rm diff}$ vs. coverage plots, *i.e.* to the point beyond which reversible adsorption becomes established. The thermokinetic parameter for mordenites is shown in Fig. 6. Comparison with Fig. 3 shows that for these samples also the maxima occur at the coverages for which irreversible adsorption is complete. This indicates that surface diffusion is the mechanism by which the sites are selectively titrated during sequential exposure of the sample to pyridine.¹⁰ At low coverages, pyridine is adsorbed on the strong sites, where it remains irreversibly held, giving a low thermokinetic parameter. As coverage increases, the number of strong sites still available decreases and a competition between strong and weak sites takes place



Fig. 3 Differential heat of adsorption, Q_{diff} , vs. pyridine uptake for mordenites. Open symbols refer to readsorption after evacuation.



Fig. 4 Site energy distribution plots for mordenites



Fig. 5 Thermokinetic parameter, t_0 , vs. pyridine uptake for Y zeolites



Fig. 6 Thermokinetic parameter, t_0 , vs. pyridine uptake for mordenites

for the adsorption of pyridine molecules. Those eventually adsorbed on the weak sites are able to migrate to the stronger sites; the smaller the number of strong sites, the slower this surface equilibration process (as the molecules must diffuse over greater distances) and hence the thermokinetic parameter increases. After complete coverage of the stronger sites, only the exchange of pyridine among weaker sites occurs. This is a faster process resulting in a decrease in the thermokinetic parameter. The short time for the heat evolution observed for all the doses over NaY (Fig. 5) is in agreement with the weak (Lewis) acidity of this sample.

Catalytic behaviour

1-MN was reacted over the whole group of catalysts at 623 K. Fig. 7 shows the influence of the contact time, W/F, on the catalytic behaviour of HMOR-5, HMOR-11, NaHY and HYd after 30 min on-stream, *i.e.* the time needed for the establishing of stationary fluodynamic conditions. 1-MN undergoes selective conversion to 2-MN over both HMOR-5 (Fig. 7A) and HMOR-11 (Fig. 7B); on the latter, trace amounts of by-products (<1%) were revealed at $W/F = 1.36 \times 10^2$ g(cat) h [mol(1-MN)]⁻¹ and less than 3.5% of naphthalene (N) was formed at 3.28×10^2 g(cat) h [mol(1-MN)]⁻¹. Thermodynamic equilibrium (39% 1-MN and 61% 2-MN) is practically attained over both mordenites, but it requires working at the highest value of W/F in the case of HMOR-5, whereas this occurs even at $W/F = 0.82 \times 10^2$ g(cat) h [mol(1-MN)]⁻¹

The activity of HYd is remarkably high, as shown in Fig. 7C by the concentration of 1-MN in the effluent at the lower W/F value. Even under these relatively mild conditions, parasite reactions occur to some extent, as indicated by the moderate presence of naphthalene and dimethylnaphthalenes. As W/F is increased, a remarkable enhancement of N production is observed, while 2-MN decreases; also DMNs seem to decrease slightly. Over NaHY (Fig. 7D) DMNs are hardly formed (less than 2% at the highest W/F value). 2-MN increases up to a maximum and then smoothly decreases as W/F is raised. N is present only in very small amounts at $W/F = 0.82 \times 10^2$ g(cat) h [mol(1-MN)]⁻¹ beyond this point its concentration increases with W/F, with a trend similar to that for HYd.

NaY was found to be practically inactive at any W/F. The initial (30 min on-stream) results for HY at $W/F = 0.82 \times 10^2$



Fig. 7 Influence of the contact time, W/F, on the composition of the reactor effluent. (\bigcirc), 1-MN; (\square), 2-MN; (\diamondsuit), N; (\triangle), DMNs. Results refer to 30 min on stream.

g(cat) h $[mol(1-MN)]^{-1}$ were: 27.3% 1-MN, 52.8% 2-MN, 9.8% N and 10.1% DMNs. This catalyst was initially rather active, even at $W/F = 0.23 \times 10^2$ g(cat) h $[mol(1-MN)]^{-1}$: 45.8% 1-MN, 47.2% 2-MN, 3.5% N and 3.2% DMNs; however, it showed a dramatic activity decay, becoming practically inactive (naphthalene conversion *ca.* 2%) after 3 h onstream.

The influence of time-on-stream (TOS) on the catalytic behaviour of HMOR-5, HMOR-11, HYd and NaHY has been tested at $W/F = 3.28 \times 10^2$ g(cat) h [mol(1-MN)]⁻¹. Conversion and selectivity data are plotted vs. TOS in Fig. 8 and 9 respectively. HMOR-5 undergoes severe deactivation, whereas the other catalysts are still active after several hours on-stream (Fig. 8). In the case of HYd a variation in selectivity occurs along with conversion during deactivation (Fig. 9A). On the fresh catalyst, naphthalene production is strongly favoured, but it decreases dramatically with icreasing TOS, while 2-MN selectivity simultaneously increases. DMNs are also formed; after the early reaction period, their selectivity curve is practically superimposed on that for naphthalene. After several hours on-stream the amount of by-products is very low, 2-MN being produced with a selectivity higher than 90%. The selectivity of NaHY depends similarly on TOS (Fig. 9B) but in this case the formation of DMNs is always low (<8%). For both HMOR-5 and HMOR-11 the selectivity to the desired product was practically complete at any TOS. Coking occurs on the catalysts. The amount of coke deposited per g of cata-



Fig. 8 Influence of TOS on the conversion of 1-MN. (\bigcirc), HMOR-5; (\Box), HMOR-11; (\triangle), NaHY; (\diamond), HYd. Results refer to $W/F = 3.28 \times 10^2 \text{ g(cat) h } [\text{mol}(1-\text{MN})]^{-1}$.

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Fig. 9 Influence of TOS on selectivity for HYd (A) and NaHY (B). (\bigcirc) , 2-MN; (\square) , N; (\triangle) , DMNs. W/F as in Fig. 8.



Fig. 10 Influence of TOS on coke formation for HMOR-5 (\diamondsuit), HMOR-11 (\triangle), NaHY (\square) and HYd (\bigcirc). *W/F* as in Fig. 8.

lyst is shown as a function of TOS in Fig. 10. HMOR-5 appears to be 'saturated' by coke, after a few minutes of reaction, and a smooth coke increase seems to occur on HMOR-11. Catalyst 'saturation' by coke occurs also for the two faujasites, but it requires *ca*. 4 h on-stream for HYd and even a few more hours for NaHY.



Fig. 11 1-MN conversion as a function of the amount of pyridine irreversibly adsorbed, n_i , for Y zeolites

The acid properties of the samples are expected to determine their catalytic behaviour. The observed inactivity of NaY indicates that the weak sites, *i.e.* those adsorbing pyridine reversibly, are not able to catalyse the transformation of 1-MN. 1-MN conversion depends on the population of the acid sites strong enough to give irreversible interaction with pyridine (n_i) , as shown in Fig. 11 for Y zeolites. An interesting difference between NaHY and HYd is the occurrence of dealkylation practically without disproportionation over NaHY, whereas both reactions are present as well as isomerisation in the case of HYd (compare the composition of the reactor effluent in Fig. 7C and D). To correlate this difference with the acid properties the mechanism of the various reactions should be considered.

The isomerisation of mononuclear alkylaromatics occurs through intramolecular transfer of the alkyl group.¹¹ Reportedly, *m*-xylene isomerisation can also proceed *via* a bimolecular mechanism involving disproportionation products as intermediates,^{12,13} but this requires that the disproportionation reaction accompanies isomerisation to a relatively high extent. Accordingly, we can assume that 1-MN isomerisation is monomolecular over our catalysts, where isomerisation is, by far, the predominant reaction. A mechanism involving the formation of a diarylmethane intermediate is generally invoked for the disproportionation of monoalkylaromatics.¹⁴ While it is generally accepted that dealkylation requires stronger sites than isomerisation,14 the question whether the acid sites that catalyse intramolecular isomerisation are responsible also for disproportionation has been debated.¹⁴⁻¹⁸ It has been suggested that disproportionation requires stronger sites than isomerisation.^{15,17} Pyridine poisoning experiments¹⁸ support the view that both reactions demand acid sites of equivalent strength in the case of oxylene and 1,2,4-trimethylbenzene transformation over HY. Being a bimolecular reaction, disproportionation should be strongly dependent on the density of the acid sites; owing to the dimensions of the intermediate species, the structure of the zeolite should also play a fundamental role. Because of the several bimolecular reaction steps and the very bulky transition states involved, coking is very sensitive to both site density and zeolite structure.^{19,20}

The protonation of 1-MN should be the first step for both its isomerisation and dealkylation. Though the latter could occur before the protonated species has isomerised as well as after, the concentration profiles shown in Fig. 7D seem to suggest that, over NaHY, dealkylation follows isomerisation. The trend of naphthalene production for HYd (Fig. 7C) is similar to that for NaHY (Fig. 7D), being shifted upwards for the former because of the occurrence of disproportionation superimposed on dealkylation. The concentration profiles presented in Fig. 7C seem to suggest also that isomerisation and disproportionation occur through parallel pathways, which is consistent with different initial steps. The presence of a maximum in the 2-MN curve indicates the establishment of consecutive reactions, likely dealkylation and perhaps (at the intermediate W/F value) disproportionation. DMNs also seem to undergo further (very limited) transformation at the high W/F value.

The occurrence of disproportionation (besides dealkylation and isomerisation) over HYd and its absence over NaHY might stem from the presence on the former and the lack on the latter of some family of sites of particular strength. Calorimetric data allow us to rule out such a possibility. For HYd, 30% of the active sites have $Q_{\text{diff}} > 125 \text{ kJ mol}^{-1}$, 62% between 125 and 100 kJ mol⁻¹ and 8% <100 kJ mol⁻¹. For NaHY, 22, 50 and 28% of the active sites, respectively, are found in the same regions of strength. The two samples do not differ substantially as to their acid-strength distribution, in the sense that the fraction of the active sites populating each region is significant in both cases; furthermore, dealkylation (which is known to require stronger sites than disproportionation¹⁴) occurs over NaHY; this would enable disproportionation to occur if the strength was the relevant parameter.

Assuming competition between disproportionation and isomerisation on the sites with strength up to 125 kJ mol⁻¹,



and competition of both with dealkylation on the sites stronger than 125 kJ mol⁻¹, the concentrations of active sites able to catalyse both isomerisation and disproportionation are 566 and $354 \ \mu mol \ g^{-1}$ for HYd and NaHY, respectively. Accordingly, the occurrence of disproportionation over HYd is most likely related to its higher density of active sites in comparison with NaHY, where bimolecular disproportionation is disfavoured.

The route for coke formation is probably through the same intermediate involved in disproportionation, as shown in Scheme 1 (adapted from ref. 21 and 22). As expected, the higher disproportionation activity of HYd compared to NaHY is associated with a higher coking activity (Fig. 10). Dealkylation is suddenly suppressed as TOS increases (Fig. 9) because of poisoning of the stronger sites by coke; competition between disproportionation and isomerisation then occurs on the remaining sites. The size of the condensation products shown in Scheme 1 is such that they can only emerge with great difficulty from the supercages. Besides enhancing their tendency towards further condensation leading to polyaromatic coke, the location of these molecules in the supercages slows down the diffusion of reactants and products through the supercages. The formation of the cumbersome intermediate of disproportionation is thus hindered; furthermore, the diffusion of the cumbersome dialkylated naphthalenes would be slow compared to that of 2-MN. Thus, shape-selectivity effects induced by coke formation enhance isomerisation selectivity.

As expected, over HMOR-5 and HMOR-11, both disproportionation and coking are highly disfavoured (Fig. 7A and B and 10), as the channel system without large cavities in these zeolites is not spacious enough to allow the formation of the bulky reaction intermediates. The concentration of the acid sites able to catalyse 1-MN transformation is 788 μ mol g⁻¹ for HMOR-5 and 625 μ mol g⁻¹ for HMOR-11. In spite of this, HMOR-5 is less active than HMOR-11 (cf. Fig. 7A with 7B). This is due to the slow diffusion of the cumbersome reactant and products within the monodimensional channel system of HMOR-5, where hindering interaction with the active sites present at a high density is originated. The accumulation of strongly adsorbed feed and/or product molecules is responsible for the severe decay in activity of HMOR-5 (Fig. 8). This is supported by the finding that a deactivated HMOR-5 sample (4 h on-stream, conversion <10%) gave a renewal of activity (conversion >30%) after

simply raising the temperature at 773 K in N₂ flow until neither reactants nor products were revealed in the exit stream

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Paper 8/03931C; Received 26th May, 1998