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Acidity and Catalytic Selectivity in the Na–H–Mordenite System

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Changes in the acid-strength distribution of the sites generated at various levels of Na^+–H^+ exchange in synthetic, large-port sodium mordenite have been characterised by measuring the heat of adsorption of NH_3 on these sites. The activity and especially the selectivity behaviour of these sites in the isomerisation and disproportionation of *o*-xylene have also been studied. Acidic sites generated at higher degrees of Na^+ exchange have higher intrinsic heats of adsorption and also possess higher selectivity for disproportionation reactions at equal levels of conversion of *o*-xylene. By modulation of the Na^+–H^+ exchange level, it was hence possible to prepare catalysts with a high selectivity for the isomerisation reaction. It is postulated that a Brønsted acidic site associated with nonframework AlO^+ species formed during dehydroxylation of the zeolite is responsible for the enhanced activity observed at high levels of Na^+ replacement by NH_4^+.

INTRODUCTION

Acidic sites, which are capable of catalysing many hydrocarbon transformations such as isomerisation, alkylation, and cracking, are generated in mordenites when their nonframework cations, e.g., sodium, are progressively exchanged for protons. Changes in the acidic and catalytic properties of faujasites on replacing Na^+ by protons have been extensively studied (*1*). Even though the acid sites in mordenite bear many functional similarities to those in faujasites, steric effects on conversion and especially selectivity are more pronounced over mordenite with its smaller pore size. In the alkylation of benzene, for example, while the thermodynamically more favourable *meta*-diethylbenzene was found to predominate over the *para* isomer when ethylene was used as the alkylating agent, the *para* isomer with a smaller cross-sectional area was formed in much larger quantities when propylene was used as the alkylating olefin (*2*), revealing the overriding influence of the steric factor in determining the selectivity in product distribution. While the importance of steric factors in influencing the selectivity in reactions involving alkylaromatic hydrocarbons over mordenites is, by now, well recognised (*3*), it is quite possible that changes in the type and structure of the acid site may also affect the selectivity behaviour of mordenites. For example, are all the acidic sites, created at various stages of Na^+–H^+ exchange, structurally equivalent and do they possess similar, intrinsic, catalytic properties?

Minachev *et al.* (*4*) studied the dependence of the catalytic activity of mordenite on the degree of Na^+–H^+ exchange and found that the extent of isomerisation of cyclohexane into methylcyclopentane increases linearly as the exchange degree increases. They concluded that for the isomerisation reaction all the sites generated by the Na^+–H^+ exchange are uniformly active. In contrast to these results, Gray and Cobb (*5*) found that in the hydroisomerisation and hydrocracking of *n*-pentane, conversion increased slowly with increased degree of sodium replacement until about 80% exchange. Beyond 80% exchange, the conversion increased much more rapidly at a linear rate implying that the acid sites generated in the later stages of Na^+–H^+ exchange are different (at least as far as their catalytic properties are concerned)

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from those that are formed in the earlier stages of exchange. Similar low and high responses at low and high degrees of Na^+ replacement have been observed in the Na–H–Y zeolite system (*6, 7*). It is possible that the reaction by which activity is measured is important and can yield different responses to sodium replacement. However, it cannot be ruled out that the acidic sites generated by the removal of the last few sodium ions are structurally different from those that are formed in the early stages of replacement. The higher site density in samples wherein most of the Na^+ has been replaced by H^+ may also be an additional factor which modifies the intrinsic acidic and catalytic properties of the acidic sites.

In the present study, changes in the acid-strength distribution of the sites generated at various levels of Na^+–H^+ exchange in mordenite have been characterised by measuring the heat of adsorption of NH_3 on these sites. The activity and especially the selectivity behaviour of these sites in the isomerisation and disproportionation of *o*-xylene have also been studied. Our results indicate that the acidic sites generated at higher degrees of Na^+ exchange have higher intrinsic heats of adsorption and also possess higher selectivity for disporportionation reactions at equal conversion levels of *o*-xylene. By modulation of the Na^+–H^+ exchange level, it was thus possible to prepare catalysts having high and low selectivities for the isomerisation and disproportionation reactions, respectively.

EXPERIMENTAL

Materials

Sodium mordenite in the form of 1/16-in.-size extrudates (sample A) was obtained from Norton Company (Zeolon 100) and had the following composition (in wt%): SiO_2—76.1; Al_2O_3—11.2; Na_2O—6.56; Fe_2O_3—0.06; CaO—0.04, Balance—H_2O; SiO_2/Al_2O_3 (mole) = 11.5. Samples B, C, D, and E were prepared from sample A by successive ion exchange of sodium mordenite, A, with 2—MNH_4Cl solution at various temperatures until the desired replacement level of Na^+ was reached. The extent of ion exchange (of Na^+ by NH_4^+) in samples B–E was 36, 61, 71, and 100%, respectively. The NH_4^+-mordenites (5-g samples) were then dried in a "static air" oven at 110°C for 24 h and further calcined in the same oven at 550°C for 6 h. During drying and calcination, the samples were contained in porcelain dishes (5 cm × 3 cm × 1 cm). They were placed in the oven already preheated to 110 or 550°C for drying or calcination as the case may be. After the pretreatment, the samples were removed and cooled in a desiccator over saturated ammonium chloride solution. All the samples retained their crystallinity as could be verified from their X-ray diffraction patterns. The sum of the intensities of the peaks corresponding to *d* values of 9.01, 3.98, and 3.52 Å, respectively, was taken to be an index of the crystallinity of the sample.

Ammonia gas (>99.9%) was obtained from Air Products Ltd., USA.

Procedures

The adsorption isotherms of ammonia on samples A–E were measured volumetrically using a conventional high-vacuum adsorption system. Before the adsorption measurements, the samples (0.5 g) were degassed at 500°C for 6 h under a vacuum of 10^{-5} Torr. They were then cooled to the isotherm temperature and the adsorption isotherm was measured. A fresh batch of sample was used for each isotherm run. Duplicate runs were carried out in most cases to establish reproducibility of the results. The chemisorption of NH_3 in the temperature range 510–573 K on these samples was found to be reversible as most of the adsorbed NH_3 molecules could be desorbed on prolonged evacuation at slightly higher temperatures.

The reactions of *o*-xylene on these catalysts were studied at atmospheric pressure in a down-flow, fixed-bed reactor. About 1 g of catalyst particles (16–20 mesh) was diluted with quartz chips of the same size in the ratio 1 : 1. Experiments were carried out at various temperatures in the range 523–773 K and LHSV = 1–4. The products were analysed by a gas chromatograph (Toshniwal) using a flame ionisation detector and a (4-m × 3-mm-) column packed with 5% diisodecyl phthalate, 5% Bentone-34 on Chromosorb C. The column temperature was 363 K (isothermal). Hydrogen was used as the carrier gas (30 ml/min). Apart from unconverted *o*-xylene, the following compounds were also found in the effluent from the reactor: *m*- and *p*-xylenes, toluene, and 1, 2, 4-, and 1, 3, 5,-trimethylbenzenes. The 1, 2, 4-isomer was the predominant one in the trimethylbenzene fraction. Product samples were taken for analysis after 3 h of time on stream when the conversion level and product distribution had attained steady values for all the catalysts studied.

RESULTS AND DISCUSSION

Adsorption isotherms of ammonia on samples A–E at different temperatures in the range 510–573 K were measured. The isosteric heats of adsorption at various coverages were calculated using the Clausius–Clapeyron equation and are shown in Fig. 1. All the samples are observed to have a wide range of acid-site strengths. The change in ΔH_{iso}, the isosteric heat of adsorption, for sample E (H–mordenite) with coverage is quite similar to that reported by Kiovsky *et al.* (*8*) for a similar sample. The total theoretical acidity for mordenite (one molecule of NH_3 per Al ion) is about 58.5 ml (NTP) NH_3 per gram of zeolite. It is seen that, with the exception of sample E, the variation in the heat of adsorption is similar for all samples above about $\theta = 0.3$ (20 ml (NTP) of NH_3 per g). The influence of Na^+–H^+ exchange is seen mainly in the initial stages of adsorption ($\theta < 0.3$). Values of ΔH_{iso} and their variation with coverage for Na–H–mordenites containing varying amounts of Na^+ have not been reported in the literature so far. It is seen from Fig. 1 that even though acidic sites are formed even at low levels of Na^+–H^+ exchange, the increase in their strength and concentration with increasing degree of Na^+ replacement is neither uniform for all acid strengths nor

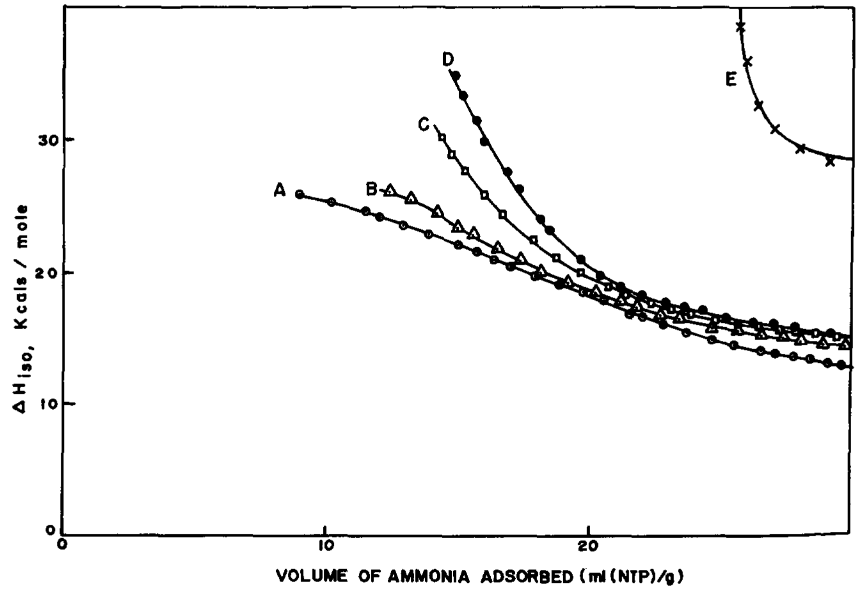

FIG. 1. Variation of the isosteric heat of adsorption, ΔH_{iso}, with coverage, for samples A–E.

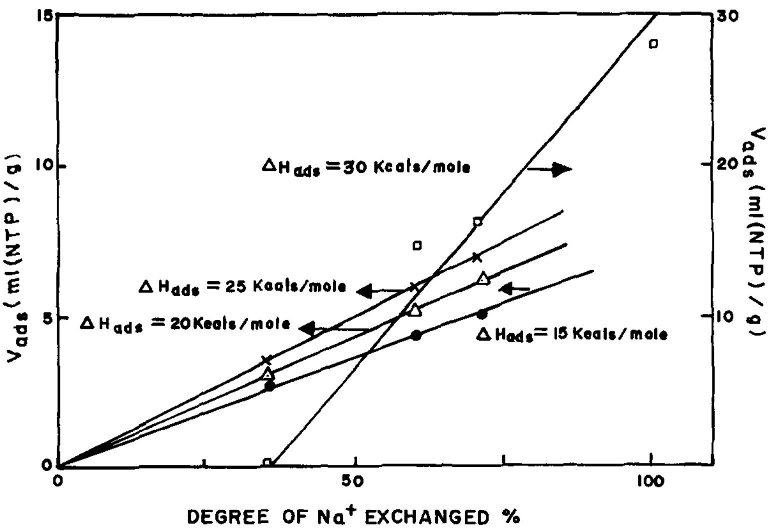

FIG. 2. Variation of the concentration of acid sites, expressed in terms of V_{ads} (ml(NTP)) of ammonia per g of catalyst, as a function of Na^+ exchange.

linear over the whole range. This is illustrated in more detail in Fig. 2. In this figure, the increase in the number of acid sites (of a given minimum strength) is plotted against the degree of Na^+ exchange. The data are taken from Fig. 1. It is seen that acid sites of different strength increase at different rates as more and more Na^+ ions are exchanged. The values of the slopes of the lines in Fig. 2, for example, are 0.155, 0.19, 0.22, and 1.0, respectively. Hence, the concentration of sites of higher acid strength increases at faster rates with the degree of Na^+–H^+ exchange. Another feature of Fig. 2 is that while sites with ΔH_{iso} less than 25 kcal/mole are formed even at low Na^+ replacement levels, stronger acid sites with ΔH_{iso} greater than 30 kcal/mole are formed only above about 50% Na^+–H^+ exchange. This is similar to observations on faujasites. In the case of Na–H–Y, while weak acid sites (3.10^{-4}% H_2SO_4) are formed even at low Na^+ replacement levels, strong acid sites (88% H_2sO_4) are formed only after 30% of the Na^+ are exchanged by H^+ (*9*).

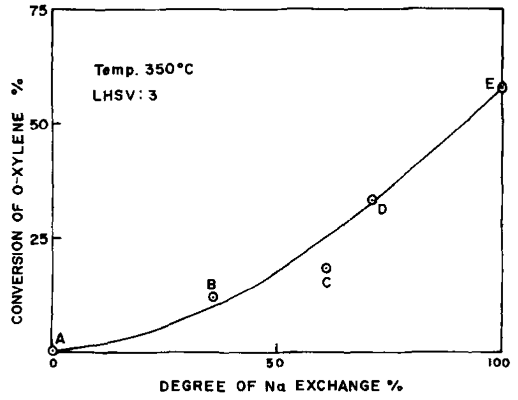

FIG. 3. The total conversion of *o*-xylene over catalysts A–E function of Na^+ exchange.

Catalytic Activity

In the presence of acidic catalysts, *o*-xylene undergoes intramolecular isomerisation to *m*- and *p*-xylenes. In addition, disproportionation of two xylene molecules to one of trimethylbenzene and one of toluene can also occur. One may ask whether the acidic sites that are active in intramolecular isomerisation are the same as those that catalyse the disproportionation reaction. Our results indicate that stronger acid sites are required for the disproportionation than for the isomerisation reaction.

The total conversion of *o*-xylene on mordenites containing varying amounts of Na^+ is shown in Fig. 3. The catalytic inactivity of Na–mordenite and the increase in *o*-xylene conversion right from the early levels of Na^+–H^+ exchange confirm the involvement of protonic sites in this reaction (*11–16*). Figure 4 illustrates the concentration of the products of the disproportionation reaction (toluene and trimethylbenzenes) as a function of the total conversion of *o*-xylene. In other words, Fig. 4 illustrates the selectivity of the catalyst for the disproportionation reaction. The most important feature of these results is that at any given degree of overall conversion of *o*-xylene, the selectivity towards disproportionation increases nonlinearly with the degree of Na^+ exchange. For example, even at a *o*-xylene conversion level of 40%, the disproportionation reaction does not occur over samples A–C. On the other hand, over catalyst E, the disproportionation assumes importance even at very low levels of conversion (Fig. 4). Hence, selectivity for the disproportionation reaction does not depend on the level of *o*-xylene conversion but rather on the type of acidic sites present on the catalyst surface. While the intramolecular isomerisation of *o*-xylene can occur on sites which are generated even at low levels of Na^+ replacement, only those acid sites which are generated above about 36% Na^+ exchange level are able to catalyse the disproportionation reaction. Now, it is already known (Figs. 1 and 2) that while acid sites with $\Delta H_{iso} < 25$ kcal/mole are generated at low levels of Na^+ exchange, stronger acid sites ($\Delta H_{iso} > 30$ kcal/mole) are formed only beyond about 50% Na^+ exchange (Fig. 2). It is therefore reasonable to conclude that acidic sites which adsorb NH_3 molecules with $\Delta H_{iso} > 30$ kcal/mole are active in the disproportionation reaction. Our finding that stronger acid sites are required for the disproportionation compared to the isomerisation reactions of alkylaromatic compounds over mordenites is similar to those observed in the case of faujasites by Hickson and Csicsery (*10*). These authors found that in the isomerisation and disproportionation of 2-ethyl toluene over deammoniated Y-type faujasites, the catalysts activated at 625°C possessed the maximum isomerisation activity. Maximum activity for the disproportionation, however, was possessed only by samples activated at 700°C and, hence, possessing sites of higher acidic strength (*10*).

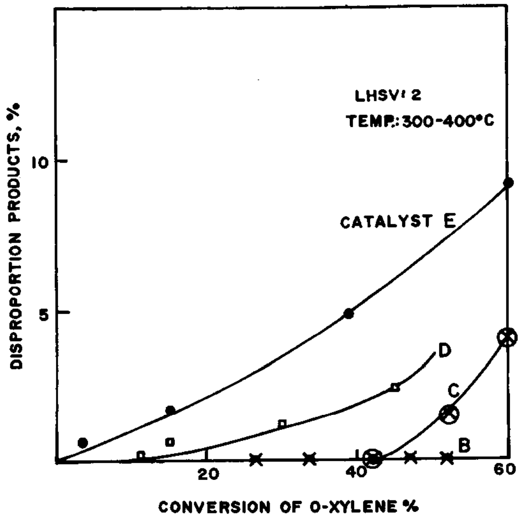

FIG. 4. Selectivity to disproportionation as a function of *o*-xylene conversion.

What is the structural nature of the strong acid sites that are generated at high degrees of Na^+ exchange? Investigating the relationship between the structural nature of acidic sites in zeolites and their catalytic activity in the isomerisation and disproportionation of *o*-xylene, Ward had shown (*11–16*) that all the active sites are Brønsted acids (proton). The heterogeneity in the acid-strength distribution (Figs. 1 and 2) indicates that these protons occur in different structural environments. When NH_4–mordenite is calcined, both ammonia and water are liberated. The deammoniation and dehydroxylation reactions overlap in the range of 525–620°C (*17*). Studies of the coordination of aluminium in dehydroxylated zeolites by X-ray spectrometry (*17*) suggest that only one-half of the aluminium is tetrahedrally coordinated (framework Al). Kühl had suggested (*17*) that the other half is probably present as AlO^+ cation to give the combination AlO^+ AlO_2^-.

The suggestion of Kühl (*17*) that the Lewis acid sites generated during the decomposition of highly ammonium exchanged zeolites do not consist of aluminium ions in trigonal coordination but nonframework oxoaluminium species has been confirmed for faujasites (*18*, *19*). Breck and Skeels (*19*) found that during the calcination of NH_4Y in dry air in a shallow-bed configuration at 200–700°C, spontaneous framework dealumination occurs. It was postulated that species like $AlOH^{2+}$, $Al(OH)_2^+$, and $[Al–O–Al]^{4+}$ are formed depending on the temperature of dehydroxylation and that these nonframework hydroxoaluminium cations are responsible for the acidity in deammoniated NH_4Y. It is likely that in the NH_4-mordenite system also, nonframework hydroxoaluminium species, formed by a mechanism similar to that postulated by Breck and Skeels for NH_4Y (*19*), are responsible for the strong acidity observed at high levels of Na^+–NH_4^+ exchange. Since the driving force for the removal of aluminum from tetrahedral sites in the lattice involves the reaction of the generated hydroxoaluminium species with the mobile protons (*19*), the phenomenon will be more significant at high levels of Na^+–NH_4^+ exchange as indeed was observed experimentally.

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