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Active Centres over HZSM5 Zeolites

I. Xylene Isomerization[1]

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The relationship between the concentration of surface hydroxyl groups, acidic sites, and the turnover number (TON) for the isomerization of *ortho*-xylene over HZSM5 zeolite has been investigated. Results from the temperature-programmed desorption of NH_3 from HZSM5 samples calcined at different temperatures reveal the existence of three types (weak, medium, and strong) of acid sites. A linear relationship (passing through the origin) was found between the TON and the concentration of the strong acid sites. Results from the adsorption of *ortho*-xylene on the same samples suggest that strong acid sites at channel intersections are the active sites for the isomerization reaction.

1. INTRODUCTION

The isomerization of xylenes is known to be catalysed by Brønsted rather than Lewis acid sites (*1*). It is an unimolecular process (*2*) and follows a single-site reaction model (*3*) involving the adsorption of xylene molecules on the protonic sites of the catalyst surface and subsequent intramolecular 1,2 shifts of the methyl groups (*2*) to form the isomeric xylenes. The reaction rate and selectivity for isomerization depends on the acid-strength distribution of the protonic sites (*4*). HZSM5 zeolite is active for the isomerization of xylenes (*5*). It contains two types of hydroxyl groups which absorb at 3600 and 3720 cm^{-1}, respectively, in the ir region (*6*) which can serve as potential Brønsted sites in acid-catalysed reactions. While zeolites, such as HZSM5, may contain different types of acid sites, all of them need not necessarily be equally active or selective in catalysing a particular reaction. For each reaction, the relationship between catalytic activity/selectivity and the type and concentration of acidic, active sites has to be established. Such a relationship has not been investigated for the isomerization of xylenes on HZSM5 zeolites, even though they are commercially being used in xylene isomerization processes.

The present study attempts at a semi-quantitative correlation between the concentration of the various acid sites measured by thermogravimetry and temperature-programmed desorption (TPD) of adsorbed NH_3 on the one hand, and the activity of HZSM5 zeolites for the isomerization of *o*-xylene, on the other hand. A linear relationship (passing through the origin) between the turnover number for the isomerization of *o*-xylene and the concentration of a particular, strong acid site is established. It is concluded that while HZSM5 zeolites prepared in the conventional way may contain many types of acidic sites only the strongest acid sites are selective for the isomerization of *o*-xylene.

2. EXPERIMENTAL PROCEDURES

A. Zeolite synthesis and characterization. The ZSM5 zeolite was prepared from solutions containing tetrapropyl ammonium ions according to the procedure described elsewhere (*7*). The composition of the unit cell of the zeolite in the sodium form was $Na_{2.12}[(SiO_2)_{93.82}(AlO_2)_{2.18}]18H_2O$. The NH_4

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form was obtained by ion exchange of the NaZSM5 using NH_4Cl solution. The zeolite was analysed by wet chemical analysis and flame photometry. The SiO_2/Al_2O_3 mole ratio of the NH_4ZSM5 was 86 and the sodium content 0.05 wt%. Samples 1–5 were prepared from the NH_4 form of the zeolite by calcination in static air for 8 h at 793, 933, 1123, 1323, and 1493 K, respectively. The temperature of the furnace was raised at a heating rate of 2 K/min. After the thermal treatment the samples were cooled to room temperature and kept over saturated NH_4Cl solution for 1 week.

The X-ray diffraction patterns of the calcined samples were recorded (Model Philips PW 1730) using nickel-filtered Cu$K\alpha$ radiation. The thermal analysis (DTA/TG) of water-saturated samples were carried out on an automatic derivatograph (MOM-102 Budapest). The sample weight was 200 mg and the heating rate was 10 K min^{-1}. The α-alumina was used as the reference standard. The BET surface areas of the HZSM5 samples were determined by the sorption of argon (77 K) using Accusorb unit (Micromeritics Model 2100 E). The void volume was calculated from the argon sorption data by the Dubinin method. The sorption of organic vapours was measured in a McBain quartz balance using about 250 mg of the sample. The acidity of the catalysts was measured by the TPD of NH_3. The catalyst (200 mg, 10–20 mesh particles) was loaded in a stainless-steel microreactor connected on-line to a gas chromatograph (AIMIL) and was activated in a flow of dry nitrogen at 823 K for 2 h and cooled to room temperature. NH_3 gas (RCF 99.5%) was purified by passing through KOH, activated CaO and finally through a column of molecular sieve 4A. The catalyst was completely saturated with purified NH_3 at ambient temperature and the physisorbed NH_3 was desorbed by flushing with nitrogen (100 ml min^{-1}). The catalyst was then heated at a linear rate of heating (10 K min^{-1}) in a stream of nitrogen and the amount of NH_3 desorbed was continuously monitored by a thermal conductivity detector to yield the TPD spectrum. Simultaneously the concentration of NH_3 in the exit gas was titrated using standard HCl (0.01 *N*). The total amount of NH_3 desorbed between 298 and 823 K was calculated from the titration data.

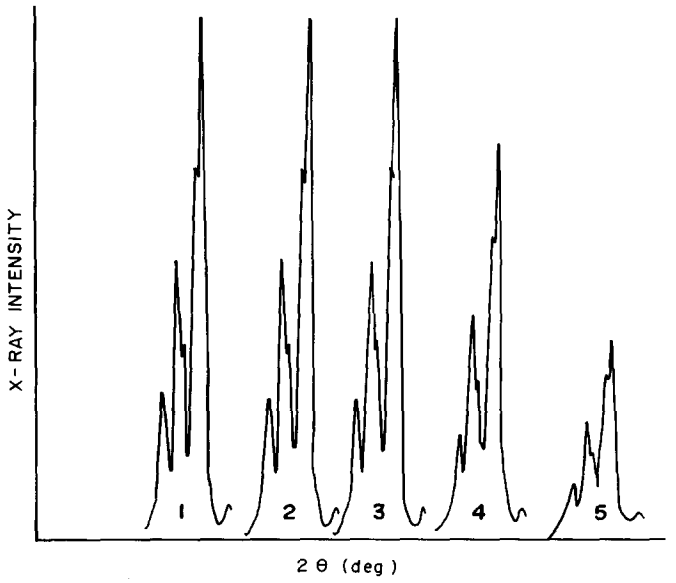

FIG. 1. X-Ray diffractograms of samples 1–5 in the region of 2θ = 21.5–25.5.

TABLE 1

Adsorption Data

Sample	Calcination temp. (K)	Adsorbate (mmol/g)		
		Argon	H_2O	*o*-Xylene
1	793	5.90	5.63	0.44
2	933	5.84	4.56	0.39
3	1123	5.75	4.05	0.22
4	1323	4.67	1.89	0.09
5	1493	0.91	0.35	0.02

Note. Adsorption was carried out at 77 K (for argon) and 298 K for H_2O and *o*-xylene, respectively. The adsorbate pressure: argon 188.7, H_2O 18.0, *o*-xylene 6.0 mm Hg, respectively.

B. Catalytic activity for o*-xylene isomerization.* The catalytic reactions were carried out in a fixed bed down flow, integral reactor. The zeolite (0.92 g, 10–20 mesh) was first activated in dry air at 723 K for 2 h and then cooled to reaction temperature (623 K) in a flow of dry nitrogen. Pure *o*-xylene (99.8%) and H_2 (IOL Bombay) were used. *o*-Xylene was fed (WHSV = 7.92, H_2/xylene = 2.3 mol) by a metering pump (Model 352, Sage Instruments) vapourized in a preheater assembly and then passed through the catalyst. The products were analysed by gas chromatography (Hewlett–Packard Model 5840 A) using 5% diisodecylphthalate and 5% Bentone-34 on chromosorb W column (2 m). The reproducibility of the data was about ±0.3%. Material balance checks indicated value better than about 99% wt.

RESULTS AND DISCUSSION

A. Structural Stability

The X-ray diffraction patterns of samples 1 to 5 (in the region of 2θ = 21.5 to 25.5°) are shown in Fig. 1. A partial structural collapse occurs beyond about 1200 K. The crystalline contents in samples 4 and 5 was only 77 and 53%, respectively. This fact could also be confirmed from surface area measurements. The surface areas were 445, 440, 450, 365, and 65 m^2/g for samples 1 to 5, respectively. The adsorption of argon, H_2O and *o*-xylene on these samples is shown in Table 1. Adsorption of argon is seen (column 2, Table 1) to be a more sensitive tool to discern the crystalline zeolite content than adsorption of either *o*-xylene or H_2O.

B. Catalyst Acidity

Figure 2 illustrates the TPD of NH_3 from all the samples. Three peaks at 373, 450–470, and 650–673 K are observed corresponding to adsorption on weak, medium, and strong acid sites, respectively. Topsøe *et al.* (*6*) have reported data on TPD of NH_3 from HZSM5. Three discrete peaks (333–373, 423–473, and 693–773 K) were observed of which the high-temperature one correlated with Na content. Acid sites, responsible for the 650–673 K peak in our TPD spectra (Fig. 2) are assigned to this

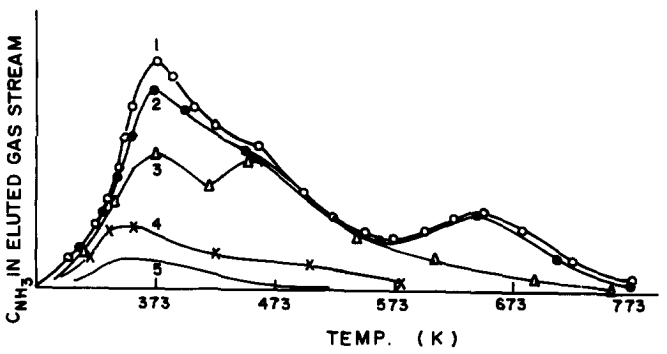

FIG. 2. Temperature-programmed desorption of NH_3 from samples 1–5.

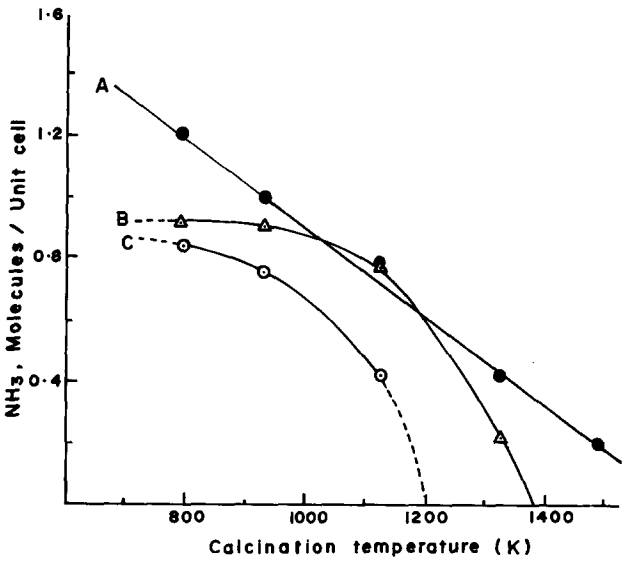

FIG. 3. The number of NH_3 molecules adsorbed on weak, medium, and strong acid sites (curves A–C, respectively) on samples 1–5 (calcined at 793, 933, 1123, 1323, and 1493 K, respectively).

species. The medium acidic sites (TPD peak at 450–470 K, Fig. 2) are similar to those characterised by others (*6, 8, 9*) as exhibiting a TPD peak around 450–500 K. The absolute concentration of these two acidic sites in samples calcined at various temperatures can be calculated from Fig. 2 as follows: The total amount of NH_3 desorbing from the sample in the TPD experiments was estimated by titration with a standard acid solution (see Experimental Procedures). Knowing the detector response (for NH_3) and the areas under the individual peaks, the number of NH_3 molecules corresponding to each TPD peak could be calculated. The data are shown in

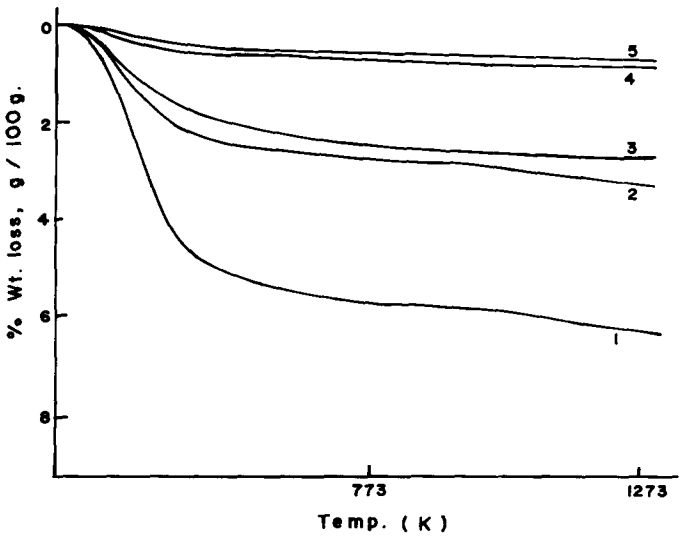

FIG. 4. The thermogravimetric weight loss from samples 1–5.

TABLE 2

Concentration of Surface Hydroxyl Groups and Acid Sites

Sample	Hydroxyl groups (No./unit cell)	Acid sites/unit cell		
		Total	Medium	Strong
1	4.8	3.0	1.0	0.84
2	4.5	3.0	1.0	0.76
3	2.4	2.0	0.8	0.4
4	1.2	0.6	0.2	0
5	1.0	0.2	0	0

Note. The concentration of the hydroxyl groups was estimated from thermogravimetry (see text). The concentration of the acid sites was obtained by TPD of NH_3 (see Fig. 3 and text).

Fig. 3. The concentration of NH_3 adsorbed on weak acid sites (curve A, TPD maximum at 373 K) decreases linearly with increasing temperature of calcination. On the other hand, the concentrations of the medium acid sites (curve B, Fig. 3) follow the zeolite content in the various samples and decreases sharply above a calcination temperature of 1200 K, when the zeolite structure begins to collapse.

An attempt was made to correlate the concentration of the various acidic sites (as estimated from the TPD of NH_3) with that of the surface hydroxyl groups (as estimated from the thermogravimetric weight loss of the sample between 773 and 1273 K (Fig. 4)). Column 2 of Table 2 gives the total number of surface hydroxyl groups per unit cell in samples 1 to 5. Assuming that all the NH_3 molecules are adsorbed as NH_4^+ ions (*10*), the number of surface OH groups that function as Brønsted acid sites and adsorb NH_3 (as NH_4^+) may be calculated (column 3, Table 2). Similarly, the concentration of OH groups that function as strong Brønsted acid sites (TPD peak maxima at 650–673 K, Fig. 2) may be estimated from the number of NH_3 molecules corresponding to the 650–673 K peak and the total number of surface OH groups. The values are given in column 5.

C. Catalytic Activity

Having characterised the surface acidic features of the samples in semi-quantitative detail, an attempt was next made to delineate the relationship, if any, between the activity of these samples in a typical proton-catalysed reaction such as the isomerization of *o*-xylene (*11*) and the concentration of the various acid sites. Towards this end, the turnover number (TON), de-

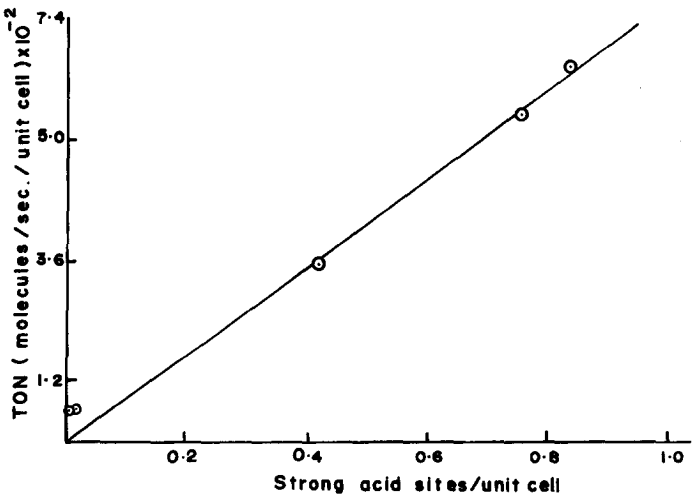

FIG. 5. The relationship between the turnover number of *o*-xylene isomerization (TON) and the concentration of strong acid sites.

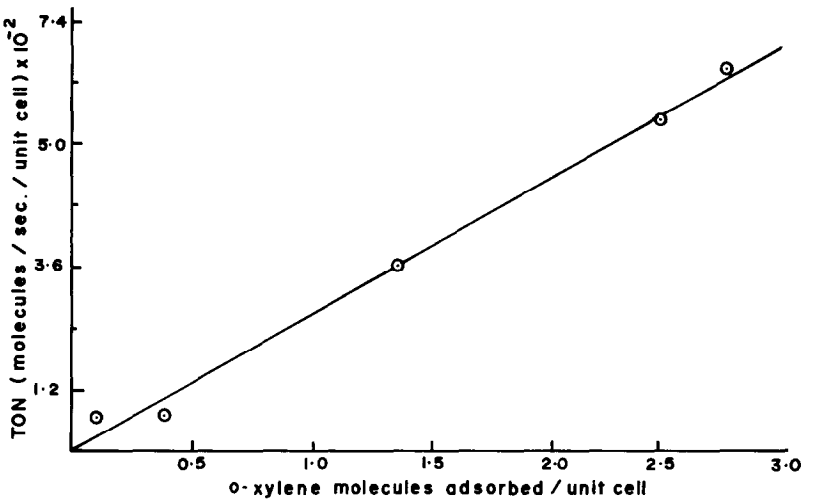

FIG. 6. The dependence of the turnover number (TON) for xylene isomerization on the amount of *o*-xylene adsorbed for samples 1–5.

fined as the number of molecules of *o*-xylene that undergo isomerization per second per unit cell of the zeolite was taken as the index of catalytic activity. It may be mentioned here, that at the low conversion and temperature levels of the present investigation, the dealkylation and disproportionation of *o*-xylene was not observed in any significant extent. A relationship was sought between TON and the concentration of the various acidic sites, i.e., strong acid sites (peak maximum at 650–673 K), medium acid sites (peak at 450–470 K) and weak acid sites (peak at 373 K). A satisfactory linear relationship was observed only in the case of the strong acid sites (Fig. 5). The fact that the straight line in Fig. 5 passes through the origin further supports our view that the acid sites responsible for the TPD peak maximum at 650–673 K are the main loci of catalytic activity in *o*-xylene isomerization.

What is the location of these sites? Further information on this point is available from Fig. 6 which illustrates the relationship between TON and the number of *o*-xylene molecules that are adsorbed per unit cell. The latter are calculated from the data of Table 1. Apparently, TON depends linearly on both the concentration of the strong acid sites as well as on the ability of the zeolite to adsorb *o*-xylene. Jacobs *et al.* (*12*) had earlier shown that sorption of xylenes, under conditions similar to those of the present study, correspond to one molecule per pore intersection in the zeolite channel system. The ZSM5 framework contains two types of intersecting channels, one sinusoidal channel system which has a near-circular pore opening of 0.54–0.56 nm, and the other straight channel system which has elliptical openings of 0.52–0.58 nm (*13*). The channel intersections have a critical dimension of nearly around 0.9 nm. The length of the xylene molecules is also around 0.9 nm. It is, hence, stereochemically feasible for an acid site, situated at the channel intersection to protonate the xylene molecule and initiate the intramolecular isomerization process. The latter process will be hindered in the channels which have much smaller critical dimensions (0.5–0.6 vs 0.9 nm). Hence, even though the xylene molecules can diffuse through the channel system, the isomerization reaction involving the migration of the methyl groups around the benzene ring is likely to occur mainly at the channel intersections.

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