Effects of Dry-air Calcination on the Physico-chemical and Catalytic Properties of HZSM-5 Zeolite

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A series of HZSM-5 zeolites has been prepared by dry-air calcination, in the range 833 to 1163 K, of samples from a single preparation of NH_4ZSM -5 containing 5.5 framework AI_T atoms per unit cell. A similar series of HZSM-5 zeolites has been prepared from NH_4ZSM -5 that had been bound with colloidal silica (Ludox) prior to dry-air calcination. The zeolites were characterised using mid-IR spectroscopy, ²⁷Al magic-angle-spinning nuclear magnetic resonance (²⁷Al MAS NMR) and temperature-programmed desorption (TPD) of NH_3 . It was shown that the zeolites are highly crystalline and that extensive structural dealumination does not occur at calcination temperatures below *ca*. 1000 K. Framework aluminium contents determined by ²⁷Al MAS NMR are considered to be a better measure of acid-site concentration that those given by TPD of NH_3 .

The activity of HZSM-5 zeolites as catalysts for ethylbenzene conversion at 573 K, to ethene, benzene and diethylbenzene, was only slightly suppressed by binding with silica. Reaction is believed to proceed by a dealkylation-alkylation mechanism; a maximum in activity for unbound HZSM-5 at $AI_T = 2.8$ suggests synergic interaction between framework and non-framework aluminium atoms. The conversion of propane at 808 K, to mainly methane, ethene and propene, showed an activity pattern closely similar to that of ethylbenzene.

HZSM-5 is a member of the pentasil group of zeolites, in which ten-membered rings form a medium-diameter pore system consisting of a three-dimensional array of intersecting channels. The high Si/Al ratio ensures that structural hydroxy groups located at channel intersections, or on the exterior surface of the crystallites, exhibit strong Brønsted acidity. It follows that HZSM-5 is an active catalyst for many reactions proceeding through cationic intermediates, where shape selectivity is frequently observed for reactions involving larger molecules such as dialkylbenzenes.

HZSM-5 can be prepared with a large range of Si/Al ratios and the activity for hexane cracking, hexene cracking, hexene double bond shift, toluene disproportionation and the conversion of methanol to hydrocarbons was found to be a linear function of total aluminium content when identical conditions were used for the activation of each catalyst.¹⁻³ The activity for hexane cracking on such catalysts was also found to be a linear function of the framework aluminium content, Al_T, determined by ²⁷Al MAS NMR.²⁻⁴ These linear relationships are lost following mild steaming, calcination or reactivation of the catalyst at high temperatures.⁵⁻¹² Activity for n-hexane cracking initially increased, passed through a maximum of considerably enhanced activity and finally fell with increasing severity of steaming. The effect has been investigated as a function of steaming pressure,^{5,6} temperature⁷ and time,^{8,9} whilst the framework aluminium content has been determined by ²⁷Al MAS NMR following systematic variation of all three parameters.¹⁰ Activity for propane conversion to aromatic hydrocarbons as a function of the temperature of dry-air calcination was at a maximum following pretreatment at 853 K.11 Similar effects following dry-air calcination were subsequently found for pentane, hexane and heptane cracking and o-xylene isomerisation.¹² However, evidence for two activity maxima, following pretreatment at 673 and 853 K,¹² suggested that dealumination generates two types of high-activity site. It is generally agreed 5-12 that the enhanced activity sites result from interaction between the bridged hydroxy groups, associated with normal Brønsted acidity, and non-framework aluminium species generated by mild structural dealumination.

The present paper reports on the characterisation and catalytic evaluation of a series of HZSM-5 zeolites prepared by dry-air calcination of samples from a single preparation of

 NH_4ZSM -5. Since commercial zeolite catalysts are normally bound with an oxide such as silica or alumina to improve their mechanical strength, HZSM-5 was studied both as a free powder and bound with colloidal silica. The catalytic test reactions were the conversion of ethylbenzene to benzene, diethylbenzene and ethene at 573 K and the conversion of propane to methane, ethene and propene at 808 K. These reactions were selected since the reactant molecules can be regarded as large and small, respectively, when compared with the dimensions of the zeolite pore system.

Experimental

Catalysts

The starting material for the generation of all catalysts was a single preparation of fully ammonium-ion-exchanged NH_4ZSM-5 zeolite, with a unit cell composition: $(NH_4)_{5.8}(AlO_2)_{5.8}(SiO_2)_{90.2} \cdot 18H_2O$. This material was prepared by subjecting 1 kg of NaZSM-5 with an Si/Al ratio of ca. 16 (synthesised by Laporte Chemicals using ammoniaethanol as the template) to acid washing with 1 mol dm⁻³ HNO₃ to remove soluble impurities, followed by three successive cation exchanges with 1 mol dm⁻³ NH₄NO₃ under reflux at pH 8. Between each exchange, the filtered solid was washed thoroughly with distilled water and oven-dried for 16 h at 393 K. No sodium could be detected in the final product by atomic spectroscopy, whilst plasma-source mass spectrometry showed sodium to be present only at concentrations below the ppm level. Comparison of the peak positions and relative heights of the powder X-ray diffraction pattern with published values,¹³ showed the product to possess the ZSM-5 crystal structure; there was no evidence of amorphicity or of other crystalline phases being present.

To assess the effects of a silica binder on catalytic properties and to provide granular catalysts with enhanced structural strength, four identical batches of silica-bound NH_4ZSM-5 were prepared. In each, 80 g of zeolite were combined with 80 g of 40 mass% ammonia-stabilized colloidal silica (Ludox); approximately 5 cm³ of distilled water were added to form a slurry which was thoroughly stirred for 0.5 h before oven-drying for 16 h at 393 K. The resultant cake, with a zeolite content of 70.3 mass% when fully dehydrated, was lightly broken and sieved to obtain granules of silica-bound catalyst with diameters in the range 0.5-2.0 mm. Such material is designated NH₄ZSM-5/B.

Both bound and unbound NH₄ZSM-5 zeolites were calcined within tubular silica vessels at selected temperatures in the range 833-1193 K using a flow of pure air that had previously been dried by passing through activated 4A molecular sieve. 3 g samples of unbound NH₄ZSM-5 were dehydrated in a 90 cm³ min⁻¹ flow of dry air for 1.5 h at 383 K before increasing the temperature at 8 K min⁻¹ to the final calcination temperature, which was maintained for 4 h before free cooling in the air flow to room temperature. Catalysts prepared in this way are designated HZSM-5/x, where x denotes the calcination temperature. Prior to measurements of catalytic activity in a flow system, accurately weighed 50 mg samples of NH₄ZSM-5 were calcined in situ in the reaction vessel. Initial dehydration for 12 h at 383 K in an 11 cm³ min⁻¹ flow of air preceded a 10 K min⁻¹ rise to the final calcination temperature. After 4 h at this temperature the catalyst was cooled to below 423 K before the gas flow was changed from air to helium. With the silica-bound zeolite, 6 g of NH₄ZSM-5/B was dehydrated for 16 h at 383 K in a 600 $\text{cm}^3 \text{min}^{-1}$ flow of air with a measured water content of 40 ppm; the temperature was then slowly raised to the calcination temperature which was maintained for 4 h before cooling to room temperature. Bound catalysts prepared in this way are designated HZSM-5/B/x.

Catalyst Characterisation

Mid-IR transmission/absorption spectra were obtained for all catalysts using a Perkin-Elmer 983G IR spectrometer, with attached data station, and KBr pressed discs containing 0.2 mass% zeolite.

A Jeol GX400 spectrometer operating at 104.05 MHz was used to determine ²⁷Al MAS NMR spectra of NH₄ZSM-5, NH₄ZSM-5/B and all calcined zeolite catalysts. The spectra were obtained by the Fourier-transform technique from 10000 scans, each possessing 4096 data points, with correction for baseline distortion. A computer program was used

to resolve peaks and integrate peak areas arising from aluminium atoms in environments of different symmetry. To obtain quantitative data for the aluminium content in these locations, the spectrometer was calibrated using a standard mordenite sample and care was taken to fill the sample spinner reproducibly.

TPD measurements were made in a continuously pumped vacuum system, where desorbed NH₃ was decomposed on an electrically heated tungsten wire before analysis as N₂ by an AEI MS10 mass spectrometer.¹⁴ Accurately weighed zeolite samples, 50–100 mg of particles from a broken disc pressed in an IR die, were vacuum-activated *in situ* for 1 h at 773 K. After cooling to 373 K the samples were exposed to 133 Pa of NH₃ for 0.5 h and subsequently evacuated at that temperature for 2 h to remove physically adsorbed NH₃. The samples was then heated at 8 K min⁻¹ to 873 K; mass spectrometer readings at m/e = 28 were computer-logged every 5 s and subsequently processed to give TPD spectra. The apparatus was calibrated by total desorption of NH₃ from different masses of an ammonium-exchanged Y zeolite of composition (NH₄)₃₈Na₁₇(AlO₂)₅₅(SiO₂)₁₃₇ · 204H₂O.

Catalysis of Ethylbenzene and Propane Conversion

All measurements of ethylbenzene conversion were made in a continuous-flow microreactor system operating at atmospheric pressure (10^5 Pa). For unbound catalysts, accurately

weighed 50 mg samples were first calcined in situ as described above and then further activated in a 30 cm³ min⁻¹ flow of helium for 16 h at 773 K before cooling to the reaction temperature of 573 K. Accurately weighed 50 mg samples of bound catalysts were activated at 773 K in a 30 cm³ min⁻¹ flow of helium for 16 h. After cooling to the reaction temperature of 573 K, a 30 cm³ min⁻¹ flow of ethylbenzene (279 Pa) in helium diluent, corresponding to an ethylbenzene feed rate of 3.26×10^{16} molecules s⁻¹, was passed through the catalyst bed. Samples of the product stream, taken at 15 min intervals over the first hour and then hourly, were automatically injected into an on-line Pye-Unicam GCD gas chromatograph coupled to a Pye-Unicam PU4811 computing integrator. The reactant-product mixture was separated on a 1.5 m column of 10% Apiezon L on diatomite C at 423 K. After activity measurements, the catalysts were purged of volatile material by flowing helium before cooling to room temperature in the same gas. The spent catalysts were subsequently analysed for carbon content using a Perkin-Elmer 240B elemental analyser.

For propane conversion, measurements were made in the same way as for ethylbenzene conversion, except that a catalyst mass corresponding to 100 mg of zeolite was used and that the reaction mixture was a 30 cm³ min⁻¹ flow of propane (36.5 Pa) in helium diluent, corresponding to a propane feed rate of 4.52×10^{15} molecules s⁻¹. The reactant-product mixture was separated on a 2.1 m column of Poropak Q at 313 K in the same chromatographic apparatus.

Results and Discussion

Mid-IR Spectroscopy

Unbound, calcined catalysts exhibited five absorption bands in the mid-IR region, centred at wavenumbers within the ranges given below. Following the published literature,^{15,16} these can be assigned to internal vibrations of the TO₄ tetrahedra at 1091-1101 cm⁻¹ (asymmetric stretch) and 450-453 cm^{-1} (T—O deformation), and to external, framework vibrations of the five-membered ring at 1221-1229 cm^{-1} (asymmetric stretch), 792-797 cm⁻¹ (symmetric stretch) and 544-548 cm⁻¹ (deformation). Closely similar spectra were observed for the bound, calcined catalysts, with bands at $1104-1108 \text{ cm}^{-1}$, $454-461 \text{ cm}^{-1}$, $1217-1223 \text{ cm}^{-1}$, 795-798 cm^{-1} and 545–548 cm^{-1} , although the band centred around 1220 cm⁻¹ was less well resolved. A further band at ca. 1410 cm^{-1} , assigned to NH_4^+ deformation, was present in the two uncalcined catalysts NH₄ZSM-5 and NH₄ZSM-5/B. The absence of this band with calcined catalysts confirms that complete deammoniation accompanies calcination.

The ratio of the absorbances of the bands centred about 550 and 450 cm⁻¹ (A_{550}/A_{450}) is a linear function of the extent of crystallinity of ZSM-5 zeolites, where a ratio of 0.75 corresponds to 100% crystallinity.^{16,17} Values of (A_{550}/A_{450}) and the percentage crystallinities they yield are given for the present catalysts in Table 1. For the unbound catalysts the overall level of crystallinity is ca. 100% for samples calcined at temperatures up to 1033 K, but drops following calcination at 1053 K or above. In the absence of information on the crystalline phase of the HZSM-5 zeolite, these results justify the choice of the limiting ratio of 0.75. Overall levels of crystallinity for the silica-bound catalysts consistently exceed the maximum value of 70% predicted by the zeolite-silica binder content and show little dependence on calcination temperature. These values show that the method is inapplicable when deliberate additions of foreign material are made to ZSM-5 zeolite. Fig. 1 presents plots of the peak wavenumber

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					²⁷ Al MA	S NMR			
mid-IR	spectroscopy	Al in different locations (mass%)		Al per	framework	NH ₃ desorbed in TPD			
catalyst	A_{550}/A_{450}	crystallinity (%)	Al _T	Al _{NFT}	Al _{NFO}	unit cell	Si/Al	/mmol g^{-1}	/molecules uc ⁻¹
NH₄ZSM-5	0.723	96	2.43	_		5.5	16	1.07	6.52
HZSM-5/833	0.725	97	2.02	0.36	0.11	4.6	20	0.902	5.50
HZSM-5/873	0.723	96	1.93	0.44	0.11	4.4	21	0.840	5.12
HZSM-5/913	0.753	100	1.88	0.59	0.11	4.3	21	0.810	4.94
HZSM-5/953	0.758	101	1.92	0.53	0.09	4.4	21	0.789	4.82
HZSM-5/993	0.752	100	1.77	0.67	0.10	4.0	23	0.785	4.79
HZSM-5/1013	0.735	98	1.37	1.08	0.08	3.1	29	0.666	4.06
HZSM-5/1033	0.743	99	1.24	1.05	0.11	2.8	32	0.611	3.73
HZSM-5/1053	0.692	92	0.93	1.35	0.11	2.1	43	0.451	2.75
HZSM-5/1073	0.693	92	0.94	1.19	0.13	2.1	43	0.436	2.66
HZSM-5/1093	0.703	94	0.74	1.31	0.13	1.7	54	0.550	3.36
HZSM-5/1113	0.651	87	0.56	1.57	0.12	1.3	70	0.322	1.96
HZSM-5/1163	0.650	87	0.45	1.78	0.12	1.0	91	0.260	1.59
NH ₄ ZSM-5/B	0.604	81	1.50	_	_	4.8	17	0.672	5.71
HZSM-5/B/833	0.593	79	1.62	0.19	0.09	5.2	17	0.660	5.61
HZSM-5/B/873	0.574	77	1.84	0.39	0.11	5.9	15	0.650	5.53
HZSM-5/B/913	0.597	80	1.79	0.23	0.08	5.7	16	0.672	5.71
HZSM-5/B/953	0.634	85	1.64	0.28	0.08	5.2	17	0.647	5.50
HZSM-5/B/993	0.598	80	1.25	0.19	0.06	4.0	23	0.624	5.30
HZSM-5/B/1033	0.625	83	1.26	0.24	0.10	4.0	23	0.577	4.90
HZSM-5/B/1073	0.582	78	0.81	0.63	0.06	2.6	37	0.436	3.71
HZSM-5/B/1113	0.581	77	0.46	0.74	0.10	1.5	62	0.303	2.58
HZSM-5/B/1153	0.615	83	0.44	0.96	0.10	1.4	65	0.230	1.96
HZSM-5/B/1193	0.583	78	0.23	0.60	0.07	0.7	133	0.218	1.85

Table 1 Catalyst characterisation

for the 1090 and 1220 cm⁻¹ bands for the unbound catalysts vs. calcination temperature. Notwithstanding a probable error of ± 1 cm⁻¹, both plots show a constant wavenumber up to ca. 1000 K followed by a linear increase with calcination temperature above this value. The peak wavenumber of the 1220 cm⁻¹ band is a linear function of the structural aluminium content,¹⁷ so that we take Fig. 1 as evidence for the onset of structural dealumination at ca. 1000 K, which is in accord with the crystallinity data for unbound zeolite.

Solid-state NMR Spectroscopy

The ²⁷Al MAS NMR spectra for NH_4ZSM -5 and NH_4ZSM -5/B consisted of a single signal with a chemical shift of 55 ppm from $[Al(H_2O)_6]^{3+}$, with spinning side bands at *ca.* 15 and *ca.* 95 ppm. The signal is assigned to tetrahedrally coordinated aluminium in the zeolite framework structure, Al_T . A series of spectra characteristic of dealuminated zeolites^{18,19} was obtained for the unbound, calcined catalysts; examples are shown in Fig. 2, where the signal maximum has been



Fig. 1 Peak wavenumber for the 1090 (\triangle) and 1220 cm⁻¹ (\bigcirc) IR bands of HZSM-5 catalysts vs. calcination temperature



Fig. 2 ²⁷Al MAS NMR spectra of HZSM-5 catalysts calcined at (*a*) 873, (*b*) 1013, (*c*) 1053, (*d*) 1113 and (*e*) 1163 K

expanded to an identical full-scale value for all spectra. The increase in noise with calcination temperature is an artefact arising from this expansion. The signal at *ca*. 0 ppm is assigned to non-framework, octahedrally coordinated aluminium, AI_{NFO} . The further, very broad signal, which underlies those at 0 and 55 ppm, is assigned to asymmetric, non-framework, tetrahedrally coordinated aluminium, AI_{NFT} .¹⁸ It is significant that this signal greatly increases with calcination temperature, whereas that for AI_{NFO} only shows a small increase. Fig. 3 presents a closely similar series of spectra from the bound catalysts, showing that the colloidal silica binder had little effect on the structural stability of the zeolite. It should be noted that the δ scale in Fig. 3 is only 70% as sensitive as that in Fig. 2.

The amount of aluminium in the three different environments was determined from the integrated areas of the resolved peaks and the sensitivity determined using mordenite as an external standard; values, expressed in terms of mass%, are given in Table 1. In principle, the sum of the aluminium content in these three locations equals the total aluminium content of the zeolite. X-Ray fluorescence (XRF) analysis gave an average total aluminium content of 2.68 mass% for the unbound catalysts, which reduces to 1.88 mass% for the bound catalysts after the silica binder is taken into account. For unbound catalysts the total aluminium content determined by MAS NMR is consistently lower than 2.68 mass%. However, for the bound catalysts there is reasonable agreement following low-temperature calcination, but the value from MAS NMR is lower following calcination at 993 K or above. This discrepancy between total aluminium content determined by XRF and MAS NMR, which increases with calcination temperature for both series of catalysts, is unlikely to be fully explained by errors in Al_{NFT}. It is more probable that some non-framework aluminium is in an asymmetric environment that renders it undetectable by MAS NMR. The low aluminium content of NH₄ZSM-5/B determined by MAS NMR, relative to that from XRF, probably arises from an error in the sample mass associated with incomplete dehydration; this material had not been heated above 393 K after the addition of colloidal silica. The band associated with Al_T



Fig. 3 27 Al MAS NMR spectra of silica-bound HZSM-5 catalysts calcined at (a) 833, (b) 913, (c) 1033, (d) 1113 and (e) 1193 K

allows us to calculate the number of structural aluminium atoms per unit cell and hence the Si/Al ratio of the framework; values for these are given in Table 1.

Fig. 4 and 5 present plots of the relative percentage concentrations of Al_T , Al_{NFT} and Al_{NFO} for both unbound and bound catalysts as a function of calcination temperature. Data for uncalcined NH_4ZSM -5 and NH_4ZSM -5/B, which only contain Al_T , are represented by filled points in Fig. 4 and 5. The plots emphasize the results obtained from IR spectroscopy, in that extensive structural dealumination does not occur unless catalysts are calcined at temperatures above 1000 K. Presumably, however, the initial fall in Al_T and the



Fig. 4 Relative percentage concentrations of Al_T , Al_{NFT} and Al_{NFO} in HZSM-5 catalysts *vs.* calcination temperature: \bigcirc , Al_T ; \triangle , Al_{NFT} ; \bigtriangledown , Al_{NFO} . The filled points are for uncalcined NH_4ZSM -5 which only contains Al_T .



Fig. 5 Relative percentage concentrations of Al_T , Al_{NFT} and Al_{NFO} in silica-bound HZSM-5 catalysts vs. calcination temperature: O, Al_T ; Δ , Al_{NFT} ; ∇ , Al_{NFO} . The filled points are for uncalcined NH₄ZSM-5/B, which only contains Al_T .

limited appearance of Al_{NFT} and Al_{NFO} following calcination at 833 K, accompanies deammoniation and dehydroxylation occurring at this and other temperatures below 1000 K.

TPD of Ammonia

TPD spectra for all the unbound catalysts were determined using accurately weighed samples of ca. 50 mg and a temperature-rise rate of 8 K min⁻¹; Fig. 6 presents examples for samples calcined at various temperatures. Following calcination at the lower temperatures, the spectra consist of a predominant peak centred around 580 K with evidence of a weak shoulder at ca. 420 K. As the calcination temperature is increased the peak at ca. 580 K diminishes, whilst the shoulder at ca. 420 K ultimately becomes a clear peak following calcination at the highest temperatures. From the variation in the temperature of the maximum of the ca. 580 K peak with rise rates between 3.1 and 34.0 K min⁻¹, an activation energy for NH₃ desorption from activated NH₄HZSM-5 of 162 ± 6 kJ mol⁻¹ was obtained. This is the same value as that obtained by Topsoe et al.20 and lies within the range of 137-169 kJ mol⁻¹ obtained by Post and van Hooff,²¹ in both cases this was for the highest-temperature desorption peak detected in a conventional flow system. The lowtemperature shoulder/peak at ca. 420 K was insufficiently resolved to obtain an activation energy for NH₃ desorption.

Similar TPD spectra to those shown in Fig. 6 were obtained for the silica-bound catalysts; the peak at *ca*. 580 K continued to predominate, whilst the low-temperature shoulder was more poorly defined. The activation energy for NH_3 desorption from HZSM-5/B/873 was determined to be 114 ± 5 kJ mol⁻¹. The considerable discrepancy between this value and that for the unbound catalyst may reflect NH_3 interacting with surface hydroxy groups on the silica binder during the desorption process.

Throughout the present work a single, broad desorption peak with a low-temperature shoulder is normally observed, whereas most published studies report three distinct desorption peaks.^{20,22,23} The low-temperature peak around 373 K is physisorbed NH_3 and thus no measure of catalytic sites. The next peak is considered to arise from NH_3 adsorbed on

Fig. 6 Ammonia TPD spectra of HZSM-5 catalysts calcined at (a) 833, (b) 993, (c) 1033, (d) 1073, (e) 1113 and (f) 1163 K

silanol groups on the exterior surface or at lattice defects, whilst the highest-temperature peak is associated with NH_3 adsorbed on the Brønsted and/or Lewis acid sites active in catalysis. The rigorous outgassing conditions presently used ensure that only this third peak is observed, so that the area under the peak is related to the number of catalytically relevant sites on the zeolite sample. Computer integration of the TPD plots, in association with calibration data, yields the values for the total NH_3 desorbed in mmol (g zeolite)⁻¹ and the corresponding number of NH_3 molecules per unit cell that are given in Table 1.

Fig. 7 presents a plot of the concentration of NH_3 molecules per unit cell from TPD vs. the concentration of framework tetrahedral aluminium AI_T determined by ²⁷Al MAS NMR. The difference between the experimental line (given by least-squares analysis to be y = 0.882x + 1.150 with a correlation coefficient of 0.95) and a theoretical 1:1 relationship is greatest for samples calcined at the highest temperatures. Since the low-temperature shoulder/peak was most prominent for these samples, we associate the difference with adsorption of NH_3 on extrastructural aluminium species. We conclude that ²⁷Al MAS NMR, rather than TPD of NH_3 , gives the best measure of the concentration of acid sites in calcined HZSM-5, whether it be unbound or bound with silica.

Ethylbenzene Conversion

In preliminary experiments at 493 K reaction was found to be exclusively disproportionation, the only detectable products were benzene and diethylbenzene. Isomers of diethylbenzene were not fully resolved under the experimental conditions, so that accurate rates for their formation could not be calculated. The ratios of the rates of benzene formation, $r_{\rm B}$, over those of diethylbenzene formation $r_{\rm DEB}$ ranged from 0.95 to 1.38 over 1 h on stream; values for the ratio exceeding unity indicate the preferential retention of diethylbenzene through either adsorption or reaction to involatile carbonaceous products. Unfortunately, the activity, which fell progressively with time on stream, became too low for accurate rate measurements, so that all further studies were made at 573 K. At this higher reaction temperature, dealkylation to ethene and benzene accompanied disproportionation; trace amounts of methylbenzene and dimethylbenzene were also detected.





Studies of alkylbenzene disproportionation on HZSM-5 catalysts,²⁴⁻²⁸ support high para-selectivity within the pore system, which increases with diffusion pathlength and hence crystal size. Subsequent isomerisation to the ortho- and metaisomers is associated with acidity on the exterior surface of the crystals, as evidenced by para-selectivity falling with the use of small crystals and increasing following the elimination of surface acidity. Similar considerations apply to the methylation of toluene and the isomerisation of xylene,²⁹⁻³¹ where para-xylene is formed preferentially in the pores, followed by isomerisation on the surface. Geometric constraints within the pores of HZSM-5 ensure that the disproportionation of ethylbenzene^{25,26} and *n*-propylbenzene²⁷ proceeds by the monomolecular, dealkylation-realkylation mechanism shown in Fig. 8. This mechanism also applies to the present results, where ethene formation at the reaction temperature of 573 K arises from the loss of a proton from the ethyl carbenium ion. The catalytic activities at 573 K, expressed as the rates of formation of benzene, diethylbenzene and ethene in molecules (g zeolite)⁻¹ s⁻¹, $r_{\rm B}$, $r_{\rm DEB}$ and $r_{\rm E}$, respectively, were determined for all catalysts as a function of time on stream. Throughout these measurements a standard ethylbenzene feed rate of 3.26×10^{16} molecules s⁻¹ was used. Consideration of the mechanism in Fig. 8 gives the relationship $r_{\rm EB} =$ $r_{\rm B} + r_{\rm DEB}$, where $r_{\rm EB}$ is the rate of conversion of ethylbenzene in molecules g^{-1} s⁻¹. With low fractional conversions of ethylbenzene, such calculated values of $r_{\rm EB}$ are more reliable than those determined from small differences in a large chromatographic peak.

Plots of r_{EB} vs. time on stream are given for four representative HZSM-5 and HZSM-5/B zeolites in Fig. 9. The activity falls relatively rapidly over the first 2 h, but then decreases almost linearly with time up to 24 h on stream. This is closely similar to the observation of Weitkamp *et al.*,²⁴ who also report on the shape selectivity of HZSM-5 in diethylbenzene



Fig. 8 Reaction mechanism for ethylbenzene conversion. Note that $r_{\text{EB}} = r_{\text{EB}(1)} + r_{\text{EB}(2)}$, shown in this figure.

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Fig. 9 Ethylbenzene conversion vs. time on stream. ○, HZSM-5/1028; ●, HZSM-5/B/1073; △, HZSM-5/1115; ▲, HZSM-5/B/1113.

isomer formation. Values for $r_{\rm EB}$ after 1, 5 and 20 h on stream are plotted as a function of calcination temperature in Fig. 10 and 11, whilst values of $r_{\rm B}$, $r_{\rm DEB}$, $r_{\rm E}$ and $r_{\rm EB}$ after 1 h on stream are given in Table 2. It would have been desirable to consider also the initial activities at zero time on stream in Fig. 10 and 11. However, initial activities calculated by computer-fitting a power series to plots of $r_{\rm EB}$ vs. time on stream were erratic and frequently gave values lower than those measured after 0.25 and 0.50 h on stream. For unbound HZSM-5 catalysts, Fig. 10, there is an activity maximum for material calcined at 1028 K and a peak/shoulder for material calcined at ca. 880 K. These are higher temperatures than the maxima observed by Sendoda and Ono,12 possibly reflecting differences in catalyst composition or humidity of the calcination gas. The latter is the more probable, since their starting material had a Si/Al ratio of 124, suggesting a higher thermal stability than the present catalysts with an initial Si/Al ratio of 16. Similar behaviour occurs with bound catalysts,

Table 2 Ethylbenzene conversion at 573 K after 1 h on stream

				_		
catalyst	r _B	r _{DEB}	r _E	r _{EB}	$r_{\rm E}$ (calc)	C (wt.%)
NH₄ZSM-5	2.90	1.04	1.48	3.94	1.86	1.86
HZSM-5/836	3.83	0.94	2.32	4.77	2.89	2.02
HZSM-5/877	4.03	1.03	2.44	5.06	3.00	1.84
HZSM-5/913	4.15	1.08	2.52	5.23	3.07	1.64
HZSM-5/957	4.78	1.28	2.93	6.06	3.50	1.76
HZSM-5/990	5.58	1.34	3.59	6.92	4.24	1.54
HZSM-5/1010	6.14	1.45	3.98	7.59	4.69	1.20
HZSM-5/1028	7.53	1.59	4.99	9.12	5.94	0.98
HZSM-5/1043	6.57	1.51	4.41	8.08	5.06	
HZSM-5/1053	6.24	1.25	4.24	7.47	4.99	_
HZSM-5/1093	4.35	0.94	2.97	5.29	3.41	1.08
HZSM-5/1115	3.35	0.74	2.17	4.09	2.61	1.03
HZSM-5/1161	1.56	0.47	0.89	2.03	1.09	0.86
NH ₄ ZSM-5/B	3.59	0.76	2.11	4.35	2.83	
HZSM-5/B/873	4.78	1.22	2.97	6.00	3.56	2.93
HZSM-5/B/913	5.53	1.14	3.47	6.67	4.39	2.43
HZSM-5/B/953	5.38	1.13	3.34	6.51	4.25	
HZSM-5/B/993	5.63	1.26	3.65	6.89	4.37	2.86
HZSM-5/B/1033	6.52	1.48	4.45	8.00	5.04	1.41
HZSM-5/B/1073	5.45	1.03	3.77	6.48	4.42	1.47
HZSM-5/B/1113	2.58	0.48	1.60	3.06	2.10	
HZSM-5/B/1153	1.36	0.33	0.71	1.69	1.03	1.34
HZSM-5/B/1193	0.87	0.23	0.37	1.09	0.64	1.56

 $r_{\rm B}$, $r_{\rm DEB}$, $r_{\rm EB}$ and $r_{\rm E}$ in units of 10¹⁶ molecules g⁻¹ s⁻¹.



Fig. 10 Activity of unbound HZSM-5 catalysts for ethylbenzene conversion vs. calcination temperature: \bigcirc , HZSM-5/x after 1 h on stream; \bigoplus , HZSM-5/x after 5 h on stream; \triangle , HZSM-5/x after 20 h on stream.

although the maxima in Fig. 11 are at slightly higher temperatures. Comparison of the activities shows the two series of catalysts to be similar, but with a 12% fall in the highest activity, so that binding with colloidal silica has little effect on ethylbenzene conversion.

Where ethene production occurs, the ratio $r_{\rm B}/r_{\rm DEB}$ will exceed unity, whilst the ratio $r_{\rm E}/r_{\rm DEB}$ is the rate of dealkylation relative to that of disproportionation. From the data in Table 2, average values of 4.05 ± 0.55 for $r_{\rm B}/r_{\rm DEB}$ and 2.59 ± 0.52 for $r_{\rm E}/r_{\rm DEB}$ with unbound zeolites are to be compared with the corresponding values of 4.57 ± 0.51 and 2.92 ± 0.40 for the bound zeolites, showing that the bound zeolites are slightly more specific for dealkylation. Further consideration of Fig. 8 gives the relationship $r_{\rm E} = r_{\rm B} - r_{\rm DEB}$; calculated values of $r_{\rm E}$ using this relationship are given in Table 2, where the calculated value for $r_{\rm E}$ is consistently greater than the measured value. This discrepancy is attributed to the further reaction of ethene to form trace volatiles and carbonaceous residues. Passage of pure ethene over



Fig. 11 Activity of bound HZSM-5 catalysts for ethylbenzene conversion *vs.* calcination temperature: \bigcirc , HZSM-5/B/x after 1 h on stream; \bigcirc , HZSM-5/B/x after 5 h on stream; \triangle , HZSM-5/B/x after 20 h on stream.



Fig. 12 Activity for ethylbenzene conversion $r_{\rm EB}$ after 1 h on stream, \bigcirc , and propane conversion $r_{\rm PA}$ after 20 min on stream, \bigcirc , vs. tetrahedral aluminium content in unbound HZSM-5 catalysts

freshly deammoniated NH₄ZSM-5 led to the formation of numerous products, principally in the C₈-C₁₂ range, but benzene was only a very minor product. Presumably the heavier products were formed on the exterior surface of the zeolite crystallites, since they are unlikely to diffuse from the pore system. The final column of Table 2 gives measured carbon contents, expressed as wt.% of zeolite present, after 24 h on stream and purging with helium at 573 K. Such carbonaceous material can be regarded as involatile and is probably located in the micropores or around their mouths.^{32,33} The carbon content decreases with calcination temperature for both bound and unbound catalysts, but is slightly higher in the bound material. Calculation suggests that the difference between the calculated and observed values of $r_{\rm E}$, integrated over a full run-time of 24 h, could supply sufficient carbon to account for the deposits. For example, the deposit on HZSM-5/1028 corresponds to 5.9×10^{20} (C atoms) g⁻¹, whilst the integrated discrepancy in $r_{\rm E}$ corresponds to 7.8×10^{20} (C atoms) g⁻¹.

Since the framework aluminium content, Al_T , is considered to be the best measure of the concentration of acid sites in calcined HZSM-5, r_{EB} for unbound catalysts after 1 h on stream is plotted vs. Al_T in Fig. 12. r_{EB} at 1 h on stream is selected since it represents an activity free from initial adsorption-desorption effects, but is also relatively free from the effects of poisoning by carbonaceous deposits. The plot is restricted to unbound catalysts since the possible generation of new acid sites from the interaction of dislodged aluminium with colloidal silica is obviated. There is a maximum in r_{EB} when Al_T is 2.8 per unit cell; this is close to half the Al_T content of 5.5 per unit cell prior to calcination.

Propane Conversion

The reaction was studied using a low propane pressure in the reactant stream (36.5 Pa) and a short residence time (0.33 s) in order to minimise interactions leading to oligomerisation, cyclisation and aromatisation. The results presented do not purport to be a full study of propane conversion, but they provide a comparison between large and small reactant molecules on the same series of HZSM-5 catalysts. At the chosen

Table 3 Propane conversion at 808 K after 20 min on stream

catalyst	r _M	r _E	r _{PE}	r _{PA} (calc)	C (wt.%)
NH ₄ ZSM-5	2.58	5.20	0.67	5.00	0.32
HZŜM-5/833	3.16	6.21	0.59	5.75	0.46
HZSM-5/873	3.26	6.61	0.63	6.12	0.42
HZSM-5/913	3.30	7.00	0.65	6.42	0.46
HZSM-5/953	3.67	6.66	0.48	6.14	0.40
HZSM-5/993	4.15	7.59	0.45	6.88	0.45
HZSM-5/1013	4.52	8.22	0.42	7.41	0.54
HZSM-5/1033	3.68	7.70	0.40	6.76	0.41
HZSM-5/1053	3.41	8.00	0.38	6.85	0.42
HZSM-5/1073	2.52	7.04	0.44	5.97	0.25
HZSM-5/1113	1.98	7.16	0.32	5.75	0.25
HZSM-5/1163	1.27	6.79	0.29	5.24	0.20
HH₄ZSM-5/B	1.69	3.61	0.69	3.66	0.27
HZSM-5/B/833	1.11	2.92	0.64	2.96	0.71
HZSM-5/B/873	1.42	4.84	0.65	4.35	0.46
HZSM-5/B/913	2.13	5.56	0.59	5.01	0.38
HZSM-5/B/953	2.26	5.91	0.66	5.35	0.44
HZSM-5/B/993	2.23	5.62	0.44	4.93	0.47
HZSM-5/B/1033	2.42	5.66	0.25	4.83	0.44
HZSM-5/B/1073	2.25	5.69	0.32	4.86	0.27
HZSM-5/B/1113	1.37	5.08	0.40	4.24	0.16
HZSM-5/B/1153	0.93	4.74	0.57	4.04	0.17
HZSM-5/B/1193	0.71	3.57	0.74	3.36	0.13

 $r_{\rm M}$, $r_{\rm E}$ and $r_{\rm PA}$ in units of 10¹⁵ molecules g⁻¹ s⁻¹.

reaction temperature of 808 K the major products were methane, ethene and propene, where $r_{\rm M}$, $r_{\rm E}$ and $r_{\rm PE}$ are their respective rates of formation in molecules $g^{-1} s^{-1}$. The only other detectable product was a trace of ethane. Rates of formation of the major products were determined for all HZSM-5 catalysts as a function of time on stream over 18 h. Product formation can be expressed in terms of the equivalent conversion of propane, r_{PA} , by the relationship $r_{PA} = (r_M)$ $+ 2r_{\rm E} + 3r_{\rm PE})/3$. However, this can only be an approximation since carbon loss through deposition was significant when considered in relation to reaction rates, which were an order of magnitude less than those observed for ethylbenzene conversion. Nevertheless, plots of r_{PA} vs. time on stream were almost linear and did not exhibit the rapid initial fall in activity observed for ethylbenzene. It follows that a representative activity can be selected at an earlier time in measurements of propane conversion; Table 3 presents values of $r_{\rm M}$, $r_{\rm E}$, $r_{\rm PE}$ and r_{PA} after 20 min on stream. The final column of Table 3 gives measured values of the carbon contents of the catalysts, expressed as wt.% of the zeolite present, after 18 h on stream and purging in helium. The value of r_{PA} for unbound catalysts is plotted against Al_{T} in Fig. 12; the curve is similar to that found for ethylbenzene, but the maximum is at the slightly higher value for Al_T is 3.1 per unit cell. We take this as evidence that similar high-activity acid sites participate in both ethylbenzene and propane conversion. The detailed reaction mechanism for propane conversion will be considered in a future publication, in conjunction with results obtained for aromatization on the same catalysts at high propane pressure. Few differences exist between bound and unbound catalysts, although the most active bound catalyst, HZSM-5/B/953, only exhibited 72% of the activity of the most active unbound catalyst, HZSM-5/1013.

Conclusions

Dry-air calcination of NH_4ZSM -5 at temperatures between 833 and 1163 K yields HZSM-5 catalysts of high crystallinity, where the framework aluminium content is more easily controlled than by conventional hydrothermal treatment. Binding the NH_4ZSM -5 with colloidal silica before calcina-

J. CHEM. SOC. FARADAY TRANS., 1994, VOL. 90

tion has little effect on the physical properties of the HZSM-5, but necessarily introduces amorphous material. Extensive dealumination of both bound and unbound HZSM-5 does not occur at temperatures below *ca.* 1000 K. ²⁷Al MAS NMR is taken to be the best technique to quantify the framework aluminium content and thence the potential acid-site concentration in the calcined zeolites.

The HZSM-5 zeolites are active catalysts for the conversion of ethylbenzene at 573 K and propane at 808 K, where reactant molecules can be regarded as large and small, respectively, in relation to the dimensions of the zeolite pore system. In all cases the activity of silica bound catalysts compares favourably with that of the corresponding catalyst in powder form. Maxima in the plot of activity of unbound catalysts *vs.* Al_T occurring at approximately the same value of Al_T, supports the thesis that both reactions proceed within the pore system on similar high-activity, acid sites. Almost equivalent concentrations of structural and extrastructural aluminium at the activity maxima supports the Brønsted acid–Lewis acid pair envisaged by Ashton *et al.*⁵ as the active centre.

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