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Thermal studies on MFI zeolites.
Part 1. Alkali metal and related exchanged forms of ZSM-5

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Abstract

Zeolite ZSM-5 has been converted into various ion-exchanged forms ($H_3O^+, NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+$). These were characterised by wet chemical analysis, X-ray fluorescence, scanning electron microscopy and surface area measurements.

Thermal analyses were performed (DTA, DSC and TG) and conclusions were drawn from the results at high temperature relating to their stability. Kinetic and equilibrium analyses of TG and DSC curves gave values for E_a and ΔH associated with water loss events. These were well correlated to cation size in most cases indicative of thermoanalytical data describing water–cation environments inside the zeolite framework.

INTRODUCTION

Synthetic zeolites used as cracking catalysts and molecular sieves need to have the appropriate thermal and hydrothermal stability to withstand the extreme conditions frequently involved in their use and regeneration.

Their properties can be modified by ion exchange and this has been common practice to achieve dual catalysts, to improve selectivity and to enable the cracking of crude oils containing impurities such as sulphur and nitrogen compounds as well as transition elements.

High-silica zeolites (i.e. those with high Si/Al ratios in their frameworks) are gaining in catalytic application, especially the zeolite ZSM-5. This MFI [†] zeolite can be used to catalyse cracking, hydrocracking, isomerisation, polymerisation reforming, alkylation and methanation reactions [1]. This paper describes part of a programme designed to investigate the thermal behaviour of ion-exchanged forms of ZSM-5 characterised by wet chemical and X-ray fluorescence analyses, as well as other techniques as appropriate.

[†] MFI is the code allocated to the ZSM-5 structure by the Structure Commission of the International Zeolite Association [2].

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EXPERIMENTAL

ZSM-5 was supplied by the Mobil Oil Corporation as washed cake. The cake was oven-dried at 118 ° C for 8 hours and then calcined in air for 16 hours at 540 ° C. Ion-exchanged forms were prepared by treating 2.5 g of zeolite with 25 ml of the appropriate salt solution (see Table 1) in a sealed ampoule for one week at 85 ° C. Stirring was maintained throughout the exchange period. All zeolite samples were stored in a desiccator over saturated NaCl solution for two weeks prior to analysis. This ensured that the equilibrium water content had been reached.

Thermal analyses were performed as follows: (i) DTA using a Du Pont 1090, sample size 10–20 mg, heating rate 20 K min^{-1} in nitrogen (flow 50 $\text{cm}^3\ \text{min}^{-1}$); (ii) TG using either a Du Pont 1090 or 950, sample size 10–20 mg, heating rate 10 K min^{-1} in nitrogen (flow 45 $\text{cm}^3\ \text{min}^{-1}$); (iii) DSC using a Du Pont 990 with a 910 DSC attachment, sample size 10–20 mg, heating rate 20 K min^{-1}, in nitrogen (flow 45 $\text{cm}^3\ \text{min}^{-1}$), using an aluminium pan as reference.

Characterisations were also carried out by XRD using a Guinier Camera, with Cu Kα radiation, XRF using a Phillips PW 1410 spectrometer and SEM using a Cambridge Stereoscam Microscope Mark 2A. Surface area measurements were carried out at Crosfield Chemicals, Warrington, Cheshire, UK. Wet chemical analyses confirmed Si/Al ratios and cation content.

RESULTS

Chemical analyses and characterisation of ion-exchanged samples

Table 2 shows idealised unit cell compositions of the ion-exchanged form of ZSM-5 calculated from XRF and wet chemical analyses.

SEM investigation showed no obvious change in morphology or surface detail; therefore, the results are not reproduced. Similarly XRD results are

TABLE 1

Ion exchange details

Cation form ZSM-5	Salt used and concn.
H^+	0.5 M HCl
Li^+	Saturated solution LiCl
Na^+	M NaOH solution
K^+	Saturated solution KCl
Rb^+	0.5 M RbCl
Cs^+	2 M CsCl
NH_4^+	Saturated solution NH_4Cl

TABLE 2

Chemical analyses and composition of ion-exchanged ZSM-5

Cation present	% Na_2O	% Al_2O_3	% SiO_2	% M_2O	Total	% H_2O	Si/Al	Unit cell composition
H^+	0.05	2.69	96.56		99.30	9.1	30.40	$H_{2.97}Na_{0.09}[Al_{3.06}Si_{92.94}O_{192}]\cdot 29.31H_2O$
Na^+	2.14	3.53	94.43		100.10	10.1	22.65	$Na_{4.06}[Al_{4.06}Si_{91.94}O_{192}]\cdot 32.92H_2O$
Li^+	0.16	3.88	94.79	1.06	99.89	11.0	20.69	$Li_{4.12}Na_{0.3}[Al_{4.42}Si_{91.58}O_{192}]\cdot 35.5H_2O$
K^+	0.02	3.62	91.26	3.30	98.20	8.3	21.35	$K_{4.25}Na_{0.04}[Al_{4.29}Si_{91.71}O_{192}]\cdot 27.9H_2O$
Rb^+	0.01	3.51	90.97	6.40	100.89	8.8	21.95	$Rb_{4.16}Na_{0.02}[Al_{4.18}Si_{91.82}O_{192}]\cdot 29.7H_2O$
Cs^+	0.01	3.40	88.29	9.34	101.04	7.0	21.99	$Cs_{4.15}Na_{0.02}[Al_{4.17}Si_{91.83}O_{192}]\cdot 24.35H_2O$
NH_4^+	0.04	3.80	90.03	3.05	96.93	10.8	22.6	$(NH_4)_{3.98}Na_{0.08}[Al_{4.06}Si_{91.94}O_{192}]\cdot 38.46H_2O$

TABLE 3

Thermoanalytical data for ion-exchanged ZSM-5

Cation	Weight loss (%)	DSC area under curve [a] ΔH (cm^2 mg^{-1})	E_a (kJ mol^{-1})	Surface area (m^2 g^{-1})
Na^+	10.1	2.66	14.66	424
H^+	9.1	3.14	12.39	406
NH_4^+	11.8	2.79	15.65	415
Li^+	11.0	2.10	13.75	405
K^+	8.3	2.39	15.41	400
Rb^+	8.8	2.22	12.66	404
Cs^+	7.0	2.41	12.38	393

[a] Temperature range from ambient to 250 ° C.

not included because they show only those minor changes in *d* spacing and intensity which could be expected from the introduction of different cations into the MFI framework. The surface area measurements (Table 3) also remained reasonably constant.

Thermal analyses

The TG results are included in Table 2. The profiles of all exchanged forms were similar, illustrating a smooth total water loss to about 200 ° C with small dehydroxylation peaks occurring in most cases in the region 400–500 ° C. The exception to this was, of course, the NH_4^+ form which lost NH_3 above 300 ° C.

The TG profiles were analysed by the rising temperature method to give a value for the energy of activation (E_a) corresponding to water losses (Table 3). The DTA curves are shown in Fig. 1. All show water loss features to about 450 ° C which all (except perhaps in the H_3O^+ form)

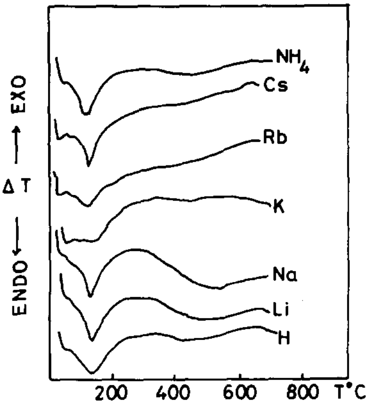

Fig. 1. DTA profiles of ion-exchanged forms of ZSM-5.

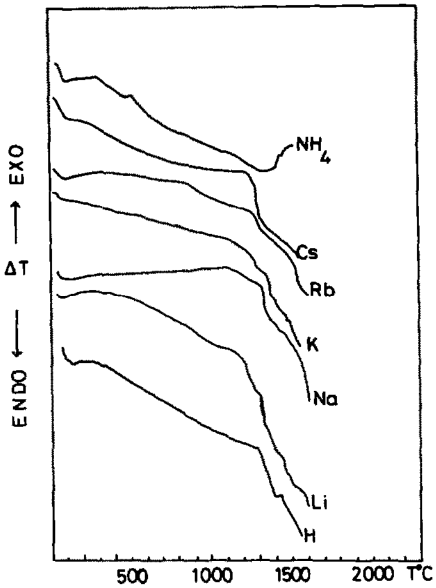

Fig. 2. DTA profiles at elevated temperatures for ion-exchanged forms of ZSM-5.

indicate more than one water site. Remaining features at higher temperatures correspond to dehydroxylation. The lower temperature feature was subjected to an area calculation from DSC results and expressed as the comparative ΔH values listed in Table 3. The DTA traces at higher temperatures showed endothermic events at above 1000 ° C (Fig. 2). These were shown by XRD to correspond to structural collapse. In some traces a small recrystallisation event subsequently occurred and lines appearing on the XRD could be taken as indicative of the presence of tridymite. This was true for all ion-exchanged forms.

Table 4 compares breakdown temperatures estimated by XRD to those from DTA from which it can be seen that DTA methods overestimate the thermal stability for the cations studied.

TABLE 4

Temperature of lattice collapse

Cation	XRD (° C)	DTA (° C)
H^+	1180	1240
NH_4^+	1180	1210
Li^+	1070	1100
Na^+	1030	1120
K^+	1130	1220
Rb^+	1150	1270
Cs^+	1170	1230

DISCUSSION

The chemical analyses show that ion exchange is very close to completion in all cases, in agreement with other workers. When H_3O^+ exchange is being carried out some loss of aluminium from the framework was observed, again as expected. The variations in Si/Al ratio, as seen in Table 2, are probably within the experimental error. The water contents are much higher than those observed by Gabelica et al. [3] when analysing different cationic forms of ZSM-5 prepared by direct synthesis. These workers measured water losses in the range 100–300 °C and their Si/Al ratio was between 32 and 48. They show that a reduction in hydrophobicity (i.e. Si/Al content) increases water content as expected, so the values quoted herein confirm this trend. That the water content noted is a function of the cation present is supported by the plot in Fig. 3 where a good correlation between ionic radius of the cation present in the MFI framework is observed.

Water loss events in zeolites which occur at lower temperatures are often not simple and can be symptomatic of complex cation and water sitings [4].

If the comparison between ΔH(comparative) and cation size made in Fig. 4 is considered, a monotonic relationship for the ions Na^+, K^+ and Rb^+ is noted. This is indicative of the major heat content change in these forms arising from one cation–water interaction. This is not so for the Li^+ form which displays an unusually low ΔH when it is considered that $Li\text{–}H_2O$ interactions are known to be very strong. That the H_3O^+ form has a high ΔH (not plotted) is in compliance with a contribution from dissociation of the type

$$H_3O^+ \rightarrow H^+ + H_2O$$

The situation for the loss of H_2O from the NH_4^+ form may be complicated by NH_3 loss.

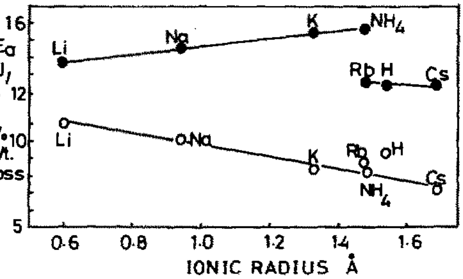

Fig. 3. Water loss (%) and energy barriers to water loss (E_a) as a function of cation size present in ZSM-5 (NH_4^+ value > 250 °C).

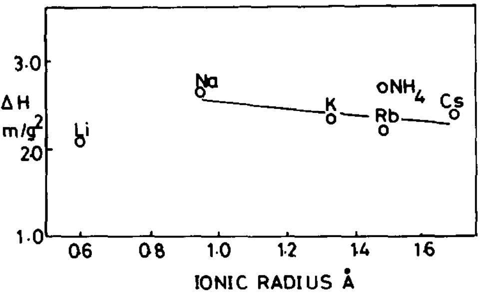

Fig. 4. Comparative enthalpy changes (ΔH) for water loss in ion-exchanged ZSM-5 as a function of cation size.

The kinetics of water loss is dependent on cation size for the ions Li^+, Na^+ and K^+ and on the loss of water up to 250 °C for the NH_4^+ form. These cases support the simple concept of water loss being impeded by the cation present. The values recorded for the Rb^+ and Cs^+ forms are lower than expected and are almost the same. An explanation for this might be that these larger ions completely fill the cation sites in the ZSM-5 structure and so water loss is from other unimpeded locations. The loss of water from the H_3O^+ form experiences a similar low energy barrier to migration, i.e. it could also be relatively unimpeded by the small H^+ cation created as suggested earlier.

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