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THERMOANALYTICAL STUDIES OF HIGH SILICA ZSM-5 ZEOLITES CONTAINING ORGANIC TEMPLATES *

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ABSTRACT

Novel shape-selective ZSM-5 zeolites acting as versatile catalysts for a variety of hydrocarbon conversion reactions are synthesised using quaternary ammonium compounds such as tetrapropylammonium bromide (TPA-Br), tetrapropylammonium hydroxide (TPA-OH), tetrabutylammonium hydroxide (TBA-OH), triethyl-*n*-propylammonium bromide (TEPA-Br) and triethyl-*n*-butylammonium bromide (TEBA-Br). These templating agents, occluded during synthesis, are found to play a structure-directing role and are found to influence structural, sorption and catalytic properties of these zeolite catalysts in their active form.

A course of the decomposition pattern of these quaternary ammonium compounds in order to achieve the zeolite in the active form is followed systematically by TG, DTA and DTG. TG and DTA curves indicate that pure quaternary ammonium compounds decompose in air around 180–200°C, while these, when occluded in the channels of the crystalline zeolites, decompose at much higher temperature around 400–500°C. This indicates that these templating organic species are localised and/or stabilised when occluded in zeolitic channels by some sort of physico-chemical binding forces. DTA curves further characterise the decomposition of these species by two pronounced, distinct exotherm maximas (at 410 and 470°C) due to their oxidative decomposition in air. This clearly indicates that occluded organic species possess two different environments. The weakly bound species indicated by exotherm maxima around 410°C, are probably situated near the channel intersections and not associated with acid sites. Comparatively more stabilised species decomposing by exotherm maxima at 470°C are believed to be associated with aluminium acid sites and acting as charge compensating cations. These observations are further supported by TG and DTG curves.

The nature of the decomposition products of these organic species are discussed with the help of IR spectra and sorption properties are found to complement these results.

INTRODUCTION

Increasing attention has been devoted over the last ten years to the synthesis and the properties of new zeolitic materials crystallised in the presence of organic cations [1,2]. Among such materials, zeolite ZSM-5 (Zeolite Socony Mobil) has received the greatest attention on account of its

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adsorption and catalytic properties for a variety of reactions such as methanol to gasoline, xylene isomerisation, toluene disproportionation, etc. [3,4]. A great variety of synthesis procedures has been disclosed in the patent literature [5].

The organic cations which act as templates [6] apparently play a prominent structure-directing role in ZSM-5 zeolite crystallisation. Thus, the study of their physico-chemical properties is important. Several adsorption, physico-chemical and catalytic properties have been described for ZSM-5 zeolite [7]. Present studies have been carried out to elucidate the behaviour of organic templates in the formation of high-silica ZSM-5 zeolite structure, influence on the sorption properties and the nature of the bond with zeolite framework.

In the present paper we report results obtained from TG/DTA/DTG, IR spectra and sorption studies of high-silica ZSM type zeolites.

MATERIALS AND METHODS

High-silica ZSM-5 zeolites were prepared under hydrothermal conditions according to the procedure described elsewhere [8]. The samples used in this work were synthesised at 180–200°C in a stainless steel autoclave (200 ml capacity) at autogenous pressure for 24 h–5 days having SiO_2/Al_2O_3 ratio 86. The reactant materials used were sodium silicate ($SiO_2 = 27.2\%$, $Na_2O = 8.4\%$, $H_2O = 64.4$ wt.%), aluminium sulphate (Merck), sulphuric acid (Analar grade, BDH), tetraalkylammonium compounds TPA-Br, TEPA-Br, TEBA-Br, and 40% aqueous solutions of TPA-OH, TBA-OH (Fluka AG). The samples were designated with 'Z' pre-fixed to the corresponding organic compound used. Part of the young gel-mix (Z/gel) was removed and dried at 100–110°C in an air oven.

The prepared zeolites were washed with distilled water to remove excess sodium, dried at 100–110°C, and kept over saturated ammonium chloride in the desiccator. The X-ray diffraction pattern of the initial (as-synthesised) form of the ZSM zeolite samples showed 100% crystallinity. The diffraction pattern was similar to that of ZSM-5 [8]. The sodium form of the zeolite (Na/ZSM-5) not containing an organic compound was obtained by heating the initial form of the zeolite in an air stream at 550°C in a muffle furnace for 4–5 h. The NH_4/ZSM form was obtained by treating Na/ZSM-5 with 5 N aqueous ammonium chloride (15 ml g^{-1} of zeolite) at 80–90°C for 12 h. The active protonic form (H/ZSM-5) was obtained by calcination of NH_4/ZSM-5 at 550°C in an air stream for 8–10 h. The derivatograms were recorded on a Paulik-Paulik-Erdey OD 102 type instrument in a dry air flow with 10 K min^{-1} heating rate. The sample mass was 100 mg. Sorption measurements were carried out on an all glass gravimetric unit using McBain type balance with silica spring (sensitivity 50 cm g^{-1}). The equilibrium sorption capacities were estimated at $P/P_0 = 0.5$, at 298 K for water and cyclohexane as sorbates. The IR spectra of the sample (Hexachlorobutadiene Mull technique) were recorded with an SP 300 Pye Unicam spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the DTA curves for various initial forms of high-silica ZSM zeolite samples along with the sample of dried young gel-mix (Z/gel). The figure reveals an endothermic effect with a minimum at 100–110°C (except in the case of Z/TPA-OH and Z/TBA-OH, which is at 50–70°C) and a very strong exothermic effect at 350–500°C with two pronounced maxima at 410 and 470°C.

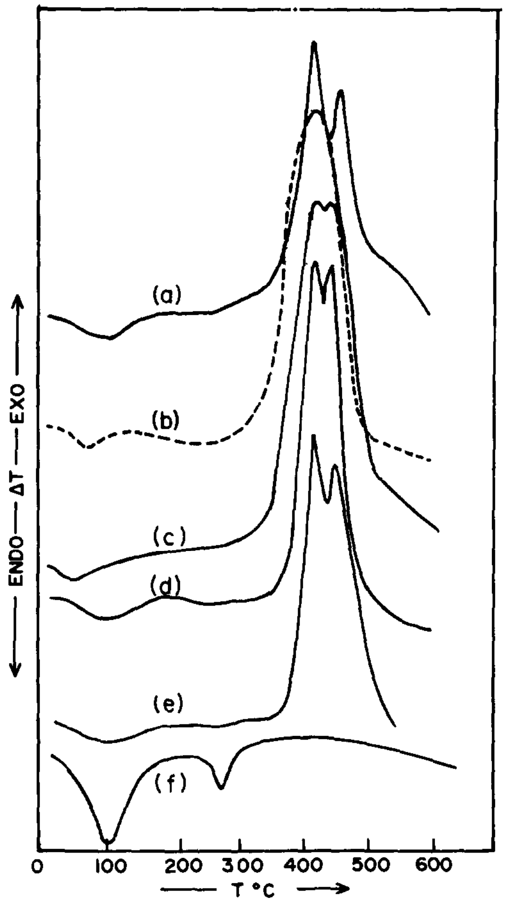

Fig. 1. DTA curves for as-synthesised forms of high-silica ZSM-5 zeolites (a) Z/TEPA-Br (b) Z/TBA-OH (c) Z/TPA-OH (d) Z/TEBA-Br (e) Z/TPA-Br and (f) Z/gel.

TABLE 1

Thermogravimetric data for high-silica ZSM-5 zeolites

Zeolite	Weight loss upon dehydration (%)	Weight loss upon organic cation decomposition (%)			Total % wt. loss up to 1000°C
		1st segment 350–420°C	2nd segment 420–500°C	Total	
Z/TPA-Br	2.5	6.0	4.0	10.0	13.0
Z/TEPA-Br	2.5	7.0	2.5	9.5	12.5
Z/TEBA-Br	5.0	5.0	3.5	8.5	14.0
Z/TPA-OH	5.5	5.0	5.0	10.0	16.0
Z/TBA-OH	7.0	7.0	3.0	10.0	17.0

The endothermic effect at low temperature is related to the removal of water which is physically adsorbed on the zeolite surface.

The inspection of exotherms on the DTA curves reveals major transformations at 350–500°C in the as-synthesised form of high-silica ZSM-5 zeolite samples which is accompanied by weight loss as summarised in Table 1. These transformations are irreversible and are not seen in a sodium form (Na/ZSM-5). This positive heat effect is related to the oxidative decomposition of organic compound stabilised in the zeolite framework. However, it is noted that pure organic compounds such as Pr_4NBr, Et_3PrNBr, Et_3BuNBr etc., melt and decompose in the temperature range 220–280°C (Fig. 2) with a sharp endothermic effect, which is in agreement with reported values [9]. Similarly, the DTA curve (Fig. 1) for Z/gel sample indicates that the endothermic decomposition of tetraalkylammonium compound contained in gel takes placed in the temperature range 250–270°C. However, tetraalkylammonium cations adsorbed or bound to the aluminosilicate framework are found to decompose in accordance with the literature [10,11] in the temperature range 350–500°C (Fig. 1). From this experimental evidence, it is concluded that these cations are probably ionically bonded to the aluminium anions (tetrahedra) in the zeolite framework during the hydrothermal crystallisation and get stabilised to the extent that they only decompose at the higher temperature range.

The exothermic peaks at 410 and 470°C on the DTA curve (Fig. 1) reflect the oxidative decomposition of the organic species stabilised in the zeolite framework in two steps. These exothermic transformations were also observed by Chao [12] and Bibby et al. [13]. However, the presence of two inflection points on the DTA curves indicates that this process is much more complex. This complexity is also revealed by the DTG (Fig. 3).

According to Flanigen [14] these organic cations are probably located at the intersection (3–4 TPA entities per unit cell) of the zeolite channels where they can also interact with framework negative charges. In support of this, we believe that the maxima and minima on the DTA and DTG curves,

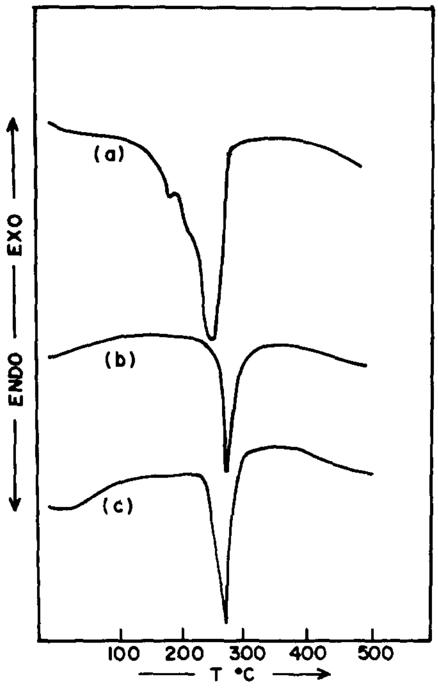

Fig. 2. DTA curves for pure organic compounds (a) TEBA-Br (b) TPA-Br and (c) TEPA-Br.

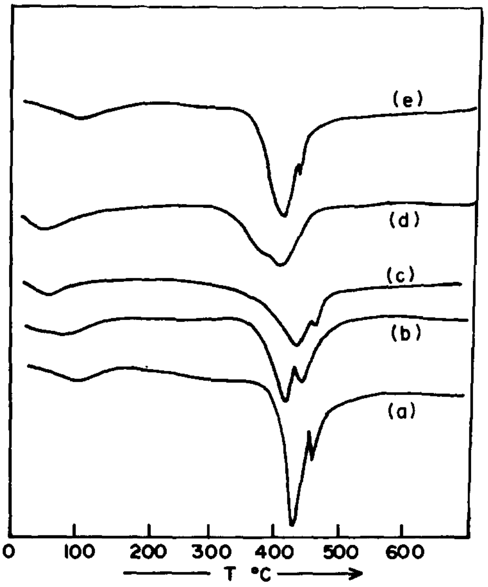

Fig. 3. DTG curves for as-synthesised forms of high-silica ZSM-5 zeolites (a) Z/TPA-Br (b) Z/TEBA-Br (c) Z/TPA-OH (d) Z-TBA-OH and (e) Z/TEPA-Br.

respectively, are related to the localisation of these organic cations at channel intersections. Apparently, the quaternary ammonium cations localised at channel intersection and not associated with acid sites and which are weakly bonded undergo oxidative decomposition (exotherm max. around 410°C, loss in weight 60 mg g^{-1} of zeolite) earlier than those which are strongly bonded with aluminium acid site (exotherm max. around 470°C, loss in weight 30 mg g^{-1} of zeolite). Similar observations have been reported by Parker et al. [15] while studing thermal decomposition of different silicalite and zeolite precursors using thermogravimetric techniques in conjunction with mass spectrometry.

Thus, we may assume that some of these cations are strongly bound to the high-silica zeolite framework during the synthesis process and, consequently, are not washed out by water and are not removed in subsequent drying at 100–110°C. This could explain the high stability of organic species in the nitrogenous high-silica ZSM-5 zeolite precursor. The tetraalkylammonium cations decompose releasing alkaline material, probably in a manner analogous to that for tetramethylammonium cations [10] according to the following scheme

$$[(CH_3)_4N^+O\text{-}Al\text{-}OSi] \xrightarrow{\Delta} [(CH_3)_3N + CH_2 + HO\text{-}Al\text{-}OSi]$$

It is interesting to note the pattern of the DTA curves marked (a) and (c) in Fig. 4. Curve (a) shows the usual oxidative decomposition pattern for organic material in the initial form of the high-silica ZSM-5 zeolite, while curve (c) is for the sample of Na/ZSM-5 which was placed in an aqueous

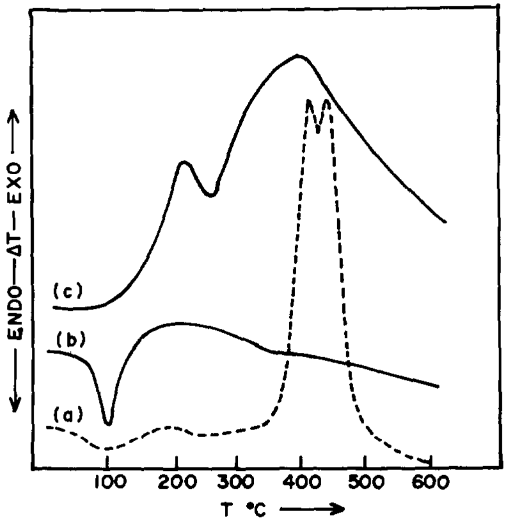

Fig. 4. DTA curves for (a) as-synthesised form of high-silica ZSM-5 (b) Na/ZSM-5 and (c) Na/ZSM-5 with adsorbed Et_3BuNBr.

solution of the respective tetraalkylammonium salt for 2 h, dried at 120°C and then admitted to record the derivatogram. Curve (c) indicates the exothermic effect in the temperature range 180–250°C and 300–600°C, which reveals that the physically adsorbed organic species on the surface of the high-silica zeolite decompose earlier (or at lower temperatures) and progressively keep on oxidising giving a broad shoulder in the range 300–600°C. Thus, the comparison of curve (a) and curve (c) reveals that the organic cations located at the intersection of the ZSM-5 zeolite channels during the synthesis process get stabilised to the extent that they decompose only at the higher temperature range with two characteristic segments on the DTA exotherm between 400 and 500°C. Curve (b) belongs to the Na/ZSM-5 (Fig. 3) sample which shows the increased endothermic effect in the low temperarure region 100–120°C as compared to that during calcination of (at 550°C, in an air stream) as-synthesised form of high-silica ZSM-5 zeolite. This is due to the additional amount of water adsorbed in the cavities and channels, which were occupied earlier by the respective organic cations.

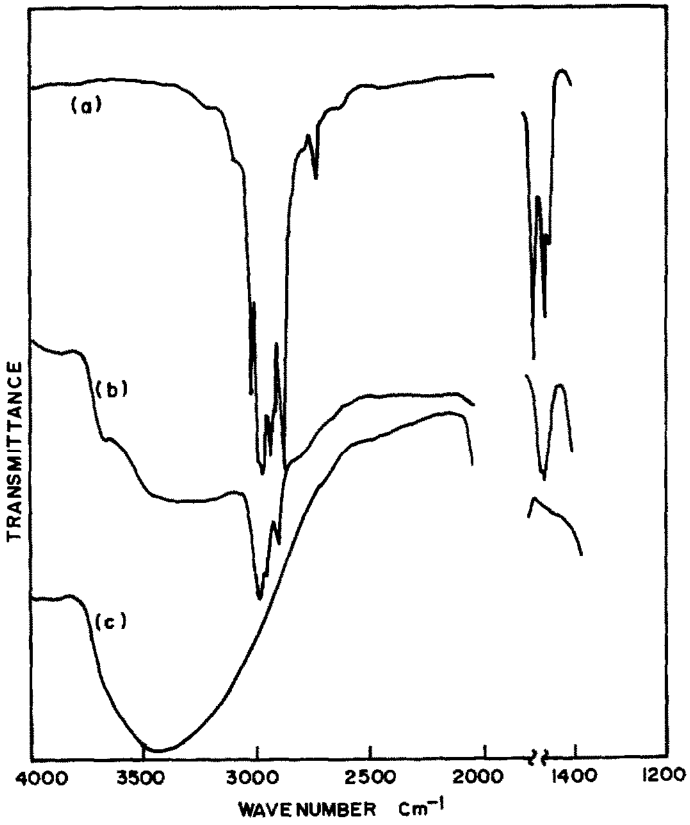

Fig. 5. IR spectra of (a) TPA-Br (b) Z/TPA-Br and (c) Na/ZSM-5 zeolite samples.

The infrared spectra of solid TPA-Br, Z/TPA-Br and Na/ZSM-5 in hexachlorobutadiene mulls are shown in Fig. 5. A medium strong band for pure $N^+(C_3H_7)_4Br^-$ at 3005 cm^{-1} is ascribable to CH_3 asymmetric stretching mode and additional weaker bands below 3005–2700 cm^{-1} have their origin in alkyl symmetric stretching modes [16]. Similarly, bands between 1400 and 1480 cm^{-1} are due to deformed (bending) CH_3, CH_2 asymmetric, symmetric modes, respectively. However, in the case of Z/TPA-Br sample the weak band at 2700 cm^{-1} due to alkyl symmetric stretching is absent. This may be due to some change taking place in the charge environment of $N^+(C_3H_7)_4Br^-$. This is likely since, during the synthesis process, the organic cation incorporated may undergo such change as to balance the electronegative part of the Al^{3+} in the tetrahedra. Thus, we may say that the electron donor sites of high-silica ZSM-5 zeolite may be the sites for both organic cation of the type $N^+(C_3H_7)_4$, $N^+(C_2H_5)_3C_3H_7$, $N^+(C_2H_5)_3C_4H_9$ and Na^+ cations. Finally, for the sample Na/ZSM-5 (obtained on calcination of as-synthesised form of Z/TPA-Br at 550°C) all the asymmetric and symmetric stretching modes below 3005–2500 cm^{-1} as well as CH_3, CH_2 asymmetric, symmetric modes at 1400–1480 cm^{-1} are absent. This also is obvious since the organic material is burnt off (decomposed) and removed from the high-silica ZSM zeolite framework.

The equilibrium sorption capacities of these high-silica ZSM zeolite samples in their protonic form (H-form) measured at 25°C and 0.5 relative pressure are summarised in Table 2.

In general, water adsorption values give the extent of hydrophobicity with varying SiO_2/Al_2O_3 ratio, however, no such correlation is found in the present study since all the samples have the same SiO_2/Al_2O_3 ratio. The probe molecule like cyclohexane in this context best acts as a pore-filling molecule. It appears from the data (Table 2) that pore volume (C_6H_{12} adsorption capacity) increases in order of size and molecular weight of templating cation.

TABLE 2

Equilibrium sorption capacity [a] for various high-silica H/ZSM-5 zeolites

Sample	Adsorption (g 100 g^{-1} zeolite)	
	H_2O	C_6H_{12}
Z/H/TEPA-Br	7.9	5.3
Z/H/TEBA-Br	6.8	6.7
Z/H/TPA-OH	5.6	7.0
Z/H/TPA-Br	7.0	7.15
Z/H/TBA-OH	7.4	8.13

[a] At 25°C, $P/P_0 = 0.5$.

CONCLUSIONS

The thermoanalytical data in this paper demonstrate the essential role played by various organic templates during the synthesis of high-silica ZSM zeolites. In particular, the DTA curves with two exothermic peaks between 400–500°C are characteristics of this type of zeolite. The two segments on the DTA curve are related to the localisation of organic cations at channel intersections. The decomposition of these organic cations occurs at higher temperature range, 350–500°C, than the pure parent organic species. This explains the increased stability of these templates in nitrogenous high-silica ZSM zeolite precursors. We believe that the electron donor sites of high-silica ZSM zeolite are the sites for both organic templates and sodium cations. This is well suported by the IR spectroscopy results.

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REFERENCES

1 E.M. Flanigen, Adv. Chem. Ser., 121 (1973) 119.
2 D.W. Breck, Adv. Chem. Ser., 101 (1971) 1.
3 C.D. Chang and A.J. Silvestri, J. Catal., 47 (1977) 249.
4 D.H. Olson and W.O. Hagg, U.S. Patent, 4 159 282 (1979).
5 M.P. Nicoletti and J.F. Van Krik, U.S. Patent, 4 159 283 (1979).
6 L.D. Rollmann, in R.B. King (Ed.), Inorganic Compounds with Unusual Properties, Vol. II, ACS, New York, 1979, p. 387.
7 J.R. Anderson, K. Foger, T. Mole, R.A. Rajadhyaksha and J.V. Senders, J. Catal., 58 (1979) 114.
8 S.B. Kulkarni, V.P. Shiralkar, A.N. Kotasthane, R.B. Borade and P. Ratnasamy, Zeolites, 2 (1982) 313.
9 W.K. Musker, J. Am. Chem. Soc., 86 (1964) 960.
10 T.E. Whyte, E.L. Wu, G.T. Kerr and P.B. Venuto, J. Catal., 20 (1971) 88.
11 A. Aiello and R.M. Barrer, J. Chem. Soc. A, (1970) 1470.
12 K.J. Chao, Proc. Natl. Sci. Counc., ROC, 3 (1979) 233.
13 D.M. Bibby, N.B. Milestone and L.P. Aldridge, Nature (London), 285 (1980) 30.
14 E.M. Flanigen, in L.V.C. Rees (Ed.), Proc. 5th Int. Conf. Zeolites, Naples, 1980, Heyden and Sons, London, 1980, p. 760.
15 L.M. Parker, D.M. Bibby and J.E. Patterson, Zeolites, 4 (1984) 168.
16 M.S. Agashe and C.I. Jose, J. Chem. Soc. Faraday Trans. 2, 75 (1979) 733.