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THERMAL ANALYSIS OF ZEOLITES

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ABSTRACT

Thermal analysis has been used to characterize both natural and synthetic zeolites. Italian natural zeolites can be analysed for chabazite and phillipsite content by a simple thermoanalytical technique.

Various forms of the faujasitic zeolite Y can be characterized, especially dealuminated (ultrastable) forms and similar samples containing alumina. The high-silica zeolite ZSM-5 can be modified by boric acid treatment and its change in catalytic activity quantified by the microcalorimetric measurement of NH_3 uptake. Its crystallization from hydrogels, containing various ions with the tetrapropyl ammonium cation, can be monitored by TG/DTG and DTA to give information relating to the mechanism of synthesis.

Recrystallization of Na/NH_4 forms of zeolite A can be detected by DTA and confirmed by XRD and IR spectroscopy whilst the use of TMA to follow dimensional changes in Ca-substituted NaA zeolites is demonstrated using pressed discs and confirmed by Guinier–Lenne studies.

INTRODUCTION

The importance of synthetic zeolites as catalysts, drying agents and molecular sieves always has prompted a keen interest in their thermal behaviour [1]. Thermoanalytical techniques, by virtue of their speed of analysis, offer an attractive means to characterize zeolites. Similarly, natural zeolites have been growing in significance both in their geological importance as primary minerals [2] and in their potential applications in nuclear and waste water treatment, soil benefication and animal food supplementation [3].

PROGRESS REPORT

(a) Natural zeolites

Colella et al. [4] report a method for the evaluation of phillipsite and chabazite content in an Italian tuff for potential use as a thermal store in

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open systems. The method is based upon the relatively lower thermal stability of phillipsite whereby consecutive treatments at 240, 350 and 800 °C, interspersed with rehydration, quantify the amorphous, phillipsite and chabazite contents of the native rock.

(b) Synthetic zeolites

The faujasitic synthetic zeolites are the most commonly used cracking catalysts; especially as promoters in their stabilized forms. Alsdorf et al. [5] used DTA/DTG to characterize stabilized forms of zeolite Y dealuminated by two preparative methods. They show (Fig. 1) that no significant difference in thermal stability is noted when samples are prepared by thermochemical treatment (i.e. thermal decomposition of NH_4Y in the presence of water vapour) compared to those prepared using aqueous EDTA to leach Al from the NaY framework. Sorption capacities for both H_2O (from TG) and n-hexane (from adsorption isotherms) also were invariant with sample preparation (Table 1).

The high-silica zeolites (e.g. ZSM-5) are catalysts of high potential. Gabelica et al. [6] have used DTA to follow the course of a typical ZSM-5 synthesis based upon aluminosilicate hydrogels containing inorganic cations (Li, Na, K, Rb and Cs) with tetrapropylammonium ions as a specific structure-directing moiety. The reaction was interrupted at time intervals of up to 24 h and aliquots removed for XRD, TG/DTG and DTA analysis. The XRD results quantified the percentage crystallinity present whilst the thermal analytical data allowed the differentiation between TPA-OH species

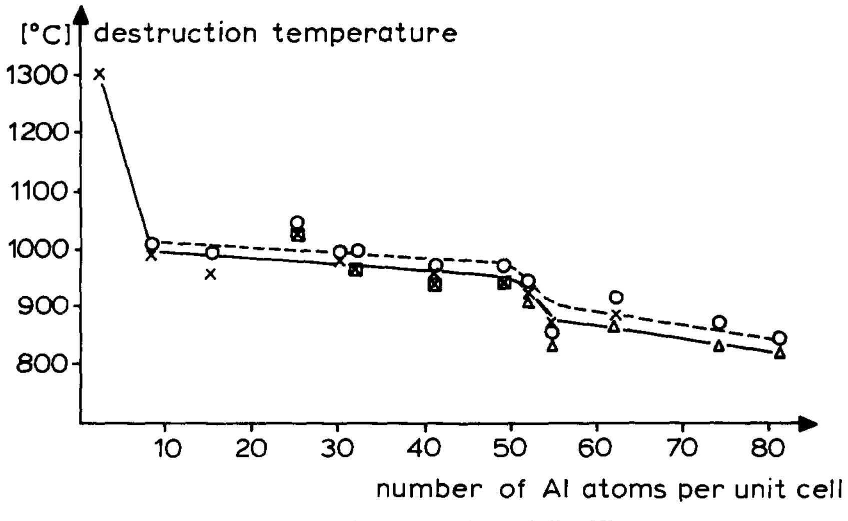

Fig. 1. Effect of sample preparation on zeolite stability [5].

TABLE 1

Effect of sample preparation on sorption capacity [5]

Sample	N_{Al} (number of Al atoms per unit cell)	Temperature of structure destruction (°C)		Adsorption capacity ($cm^3 g^{-1}$)	
		T_{on}(extr.)	T_p	H_2O (from the TG curve)	n-hexane (from adsorption isotherms)
NaX	81	830	855	0.28	–
NaX	74	840	880	0.26	–
NaY	62	875	895	0.26	–
NaY [a]	55	875 [b]	–	0.24	0.29
Series A					
1	52	933	946	0.25	0.27
2	41	959	972	0.24	0.27
3	30	980	992	0.21	0.24
4	15	~ 960	993	0.19	0.20
5	8	994	1003	0.10	0.18
6	2	> 1300 [b]	–	0.11	0.22
Series B					
1	49	944	972	0.25	0.29
2	41	945	972	0.24	0.27
3	32	965	995	0.23	0.26
4	26	1027	1044	0.23	0.24

[a] Parent zeolite for series A and B.

[b] Sintering.

trapped in Si-rich zeolite frameworks and TPA counterions in lattice "Al^-" centres. The results conformed to previous XPS and EDX investigations [7] demonstrating the presence of an Al gradient in the growing crystallites taken to show that the mechanism of ZSM-5 formation occurs via the formation of a silica-rich phase encapsulated by an Al-rich outer rim.

The zeolite ZSM-5 also is the subject of the work described by Auroux et al. [8]. Here the substrate is ZSM-5, impregnated with boric acid, examined by ammonia uptake. The uptake is monitored both microcalorimetrically and volumetrically using a microprocessor to automatically control the procedure. The strong surface acidity shown by NH_3 uptake is evaluated via a thermokinetic parameter previously used by Della Gatta et al. [9]. This parameter can be defined as $t_{1/2}$ being the time taken for one-half of the NH_3 to be desorbed at a given partial surface coverage. Use of this parameter more clearly defines the maximum interaction (see Fig. 2) and shows an acidity sequence correlating catalytic activity to weight of boron present in the ZSM-5. The increased activity with increased boron matches previous work [10] using boron-impregnated ZSM-5 as a catalyst for

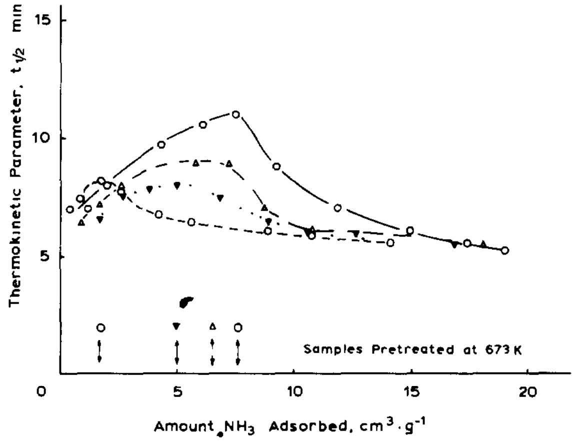

Fig. 2. Dependence of sorbate interaction strength ($t_{1/2}$) on NH_3 coverage [8].

methanol conversion, toluene disproportionation and toluene/methanol alkylation. Heat of adsorption data are also presented and the zeolite capacity for NH_3 is shown to decrease to some extent with increased impregnation.

Vendrine et al. [10] describe transformations in A zeolites heated to about 1100°C. The parent zeolite NaA was modified by varying degrees of ammonium exchange. Features occurring on DTA thermograms were checked using XRD and IR. The results demonstrated that, at high NH_4 content (more than $8NH_4^+$ per pseudo-unit cell), recrystallization of an amorphous phase to sillmanite occurs slowly from about 700°C and is complete at 890°C. When only one NH_4^+ ion was present in the pseudo-unit

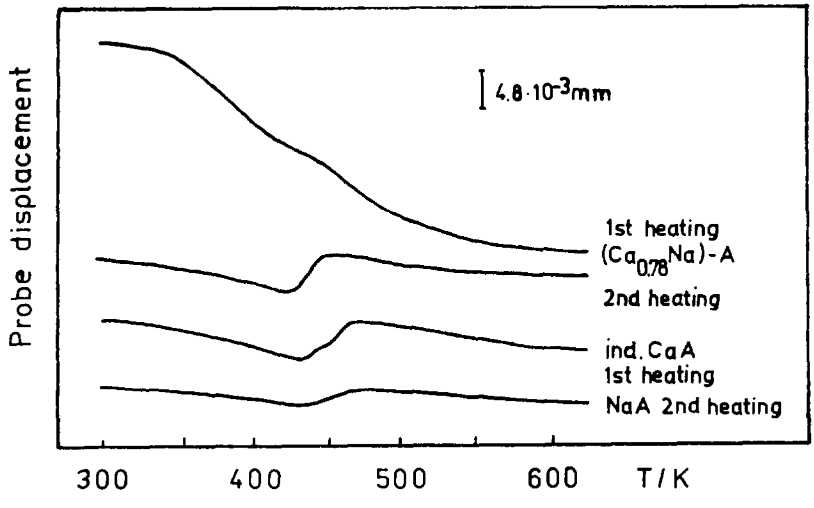

Fig. 3. TMA curves of discs of (Ca, Na)–A zeolites [12].

TABLE 2

Dimensional changes of (Ca, Na)–A zeolites [12]

Zeolite	TMA on discs $(\Delta l/l)\times 10^3$		Progr. heating X-ray $(\Delta d/d)\times 10^3$	
	300–670 K	420–470 K	300–670 K	420–470 K
$(Ca_{0.17}Na)$-A	3.3	2.9	3.1	2.6
$(Ca_{0.33}Na)$-A	3.1	2.6	3.0	2.5
$(Ca_{0.5}Na)$-A	2.9	2.5	2.9	2.5
$(Ca_{0.78}Na)$-A	2.3	4.7	0.1	4.5
$(Ca_{0.99}Na)$-A	1.9	8.1	0.1	9.5

cell, carnegeite forms from the amorphous phase at 790°C and subsequently recrystallizes to nepheline at higher temperatures—a behaviour like that of the parent zeolite—whereas the sillimanite framework collapses at 1100°C. The intermediate exchanges when Na is > 4 per pseudo-unit cell again form sillmanite.

The synthetic A zeolite is also the subject of work by Siegel et al. [11]. The systems studied are heteroionic (Ca, Na) forms of A of the type widely used as molecular sieves and drying agents. The method of analysis was that of thermomechanical measurements carried out both on pressed zeolite discs and packed powder beds. The pressed disc method of sample preparation was the more satisfactory despite an unusually high dimensional change introduced apparently by tensions created during the pressing. This feature reduced on subsequent reheating (see Fig. 3). Expansion and contraction features in the TMA curves were compared to dimensional changes occurring in the crystallographic unit cell observed by a Guinier–Lenne camera following a similar temperature programme to that of the thermal analysis (see Table 2). The features observed were interpreted in terms of cation and water movements within the unit cell operating both expansions and contractions.

CONCLUSIONS

The contributions clearly show the value of thermal analysis in interpreting data on zeolites. They show the whole range of applications from geophysical characterization through the measurement of surface acidity to synthetic studies, phase transformations, dimensional changes and modifications studies.

It is worth noting that only one paper uses an automatic and microprocessor driven approach. With the introduction of modern thermoanalytical equipment using microprocessor and minicomputer adjuncts, it can confidently be expected that thermal analysis will play an increasingly major role in the study of zeolites. Already very sophisticated software is being developed to interpret zeolite thermograms which is capable of giving a quick and detailed interpretation of sorption/desorption events on zeolites invaluable to their application [12].

One aspect of thermal analysis of zeolites not reflected in these proceedings is temperature-programmed desorption (TPD) which is increasingly finding very wide use in zeolite catalyst characterization [13].

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