CHARACTERIZATION OF SYNTHESIZED A-ZEOLITE
Simultaneous thermal analysis, X-ray diffraction, scanning electron microscopy and ICP-chemical analysis

M. M. Abdillahi, M. S. Gharami and M. A. B. Siddiqui

The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Abstract

Confirmations of the successful synthesis of a particular zeolite demand investigation of the crystals by XRD, SEM, MAS-NMR and chemical analysis. In this work, we have used the DTA exothermic lattice breakdown of the A-zeolite, which gives typical peaks at around 900–1200°C for characterization. The effects of *pH*, concentration, time of crystallization and temperature were studied and it was quickly and easily possible to distinguish A-zeolite formation from others originating from the synthesis matrix under different conditions by using DTA/TG analyses. The parameters were optimized for the synthesis of the zeolite and DTA measurements yielded enough information to identify the A-zeolite; this was confirmed by XRD and SEM.

Introduction

The zeolite frameworks are built up of regular or irregular sequences of AlO_4 and SiO_4 tetrahedral structures [1]. Secondary building units are truncated octahedra formed by connecting the tetrahedra about a number of oxygens to a plane network containing crystal water as well as various cations inside the pore of the zeolites. Type-A zeolite was first synthesized in the laboratory by Linde Air Products [2, 3] with a cubic structure, $a = 12.32$ Å, and a unit cell composition of $M_{12/n}[(AlO_2)_{12}(SiO_2)_{12}] \cdot NH_2O$ (n = cation charge, $N = 20$–30 and M = an exchangeable cation). The water molecules in the channels of the zeolites and those holding the crystals can be released by heating. The water in the pores can be removed without the structure undergoing decomposition. However, the bound water alters the structure when heating is applied at higher temperatures; others result in transformation [4]. Sticher [5] has shown the thermal effects of the synthetic zeolite K-G and demonstrated reversible dehy-

dration from ambient temperature up to 200°C, followed by irreversible dehydration at about 270°C, with characteristic DTA curves of transformations at higher temperatures.

Transformations of the A-zeolite are recognizable via two exothermic peaks, at around 900–1200°C. These transformations are caused by sintering and do not represent any phase changes from the mother crystal to daughter forms. This could be referred to as reconstruction of the A-zeolite crystal structure, after the original zeolite has been decomposed due to dehydroxylation. Dehydration of these zeolites at lower temperatures, signified by endothermic peaks coupled with the characteristic doublet exothermic peaks at higher temperatures, was the basis of our work, in order to identify the successful crystallization of the A-zeolite from the synthesis matrix of Na_2O-Al_2O_3-SiO_2-H_2O at various pH values, concentrations, times and temperatures.

This paper presents a simple, rapid simultaneous thermal analysis method for monitoring the successful synthesis of the A-zeolite and its subsequent characterization. Besides the thermal effects, XRD, SEM and chemical analysis were conducted for further confirmation.

Experimental

A-zeolite synthesis

The synthesis of NaA zeolite was carried out hydrothermally from a system containing Na_2O-Al_2O_3-SiO_2-H_2O. Sodium aluminate and sodium metasilicate (BDH) were used as the silicon and aluminum sources. Reactants per mole were 1 mole of SiO_2, 1 mole of Al_2O_3, 20 moles of NaOH and 550 moles of H_2O. Solutions of the aluminate, silicate and NaOH were stirred for 3.5 h at 368 K in a Parr autoclave. The effects of pH on the crystallization of the A-zeolite in the same synthesis matrix were investigated. In each case, the suspension was filtered off, washed repeatedly to neutral pH with doubly distilled water, and dried at about 110°C.

Characterizations

100 mg of the synthesized crystals and a similar amount of alpha-alumina were loaded on the sample/standard holders of simultaneous thermal analysis equipment (Netsch-STA-429). DTA and TG measurements were conducted at a heating rate of 10 deg·min^{-1} from ambient temperature up to 1200°C in an air atmosphere. A detailed experimental procedure was reported earlier [6]. The system was tested with different zeolite standards. Hence, the synthesized crys-

tals were subjected to thermogravimetry and differential thermal analyses simultaneously.

X-ray powder diffraction (XRD) analysis of the crystals obtained at various *pH* values was carried out by using a Philips PW/1730 diffractometer, with monochromatic CuK$_\alpha$ radiation, operating at 45 kV and 30 mA. The powder diffraction patterns were generated on a scanning vertical goniometer. The scanning speed and interval of data collection were 0.01 degree two theta/sec. The angles scanned were from 3 to 80 degrees theta, as shown in Figs 3 and 4.

The prepared crystals were mounted on aluminum holders and then coated with a layer of gold by a plasma spray technique to make the samples conducting. The scanning electron microscope (SEM) was operated at 20 kV and the probe current was varied from 1 to 6 amp. Several micrographs of each sample were recorded. Figures 5 and 6 illustrate the possible phase transformation of *A* to *P*-zeolite (Fig. 5) and the successful synthesis of the cubic crystals of the *A*-type under the right conditions (Fig. 6).

200 mg of synthesized samples was in turn weighed in platinum crucibles, with 800 mg of lithium metaborate, and fused in a muffle furnace at 900°C for about 15 minutes until a clear melt was obtained. The samples were cooled, dissolved and made up to 100 ml with deionized water in a volumetric flask. Inductively coupled plasma (ARL-3580) was employed for the chemical analysis of the gels and crystalline materials obtained at different *pH* values.

Results and discussion

The zeolite synthesis involves variations in composition in the solution, gel and crystallization stages. Therefore, there is no single unified route that explains the mechanism of formation of the *A*-zeolite. We carried out the synthesis with a matrix at various concentrations of OH$^-$ to adjust the *pH* from 10 to 14.

Effect of pH in the crystallization of A-zeolite

Zeolites can be crystallized in both alkaline and acidic media, but alkaline synthesis conditions have often been reported to favour the *A*-zeolite [7]. At very high levels of OH$^-$, the *A*-zeolite is rapidly formed, but it is equally converted to the *P*-zeolite [Fig. 5]. This can be suppressed by controlling the hydroxide content of the gel [7]. At high *pH*, the aluminate solution was found to contain only the tetrahedral [Al(OH)$_4$]$^-$, which is essential in the zeolite tetrahedral structural formation [8]. The silicate solutions contain a range of polymeric silicates, which depolymerize quickly in response to increased *pH*. In the most recent literature [9], it is possible to replace OH$^-$ by F$^-$ in the zeolite syn-

thesis. This has facilitated the formation of the soluble framework building species that has extended the usual alkaline *pH* synthesis to neutral or acidic level.

Thermal analysis

The TG and DTA curves of the products formed at different *pH* values are presented in Fig. 1. Figure 2 shows the TG and DTA curves of the synthesized *A*-zeolite. All crystals/amorphous samples formed from the same composition at various *pH* values underwent endothermic changes between 40 and 500°C, which is interpreted as the desorption of water. The endothermic peaks below 300°C with mass losses are due to the physisorbed water. The DTA endotherm shifted its peak temperature from 120 to 140 to 200°C, which could probably be taken as an indication of the relatively strong nature of the water bonding to the *A*-zeolite zeolite framework, and might indicate the formation of a proper *A*-zeolite. Some weak and broad endothermic peaks were observed between 300 and 500°C, which was related to the evolution of the water of crystallization. The endotherms evident at temperatures higher than 500°C are considered to relate to dehydroxylation of the aluminosilicate structures. Sticher [5] reported that zeolites heated above 500°C displayed small fissures in the contact zones between intergrown platelets. At around 1000°C, the *A*-zeolite recrystallizes, exhibiting the typical exotherms presented in Fig. 2. Table 1 summarizes the thermal analysis data on the products formed at different *pH* values.

Chemical analysis

The various samples obtained at the different *pH* values were mixed with borate in 1:4 ratio in platinum crucibles and were fused in a muffle furnace at 900°C. The solutions were analyzed by using an ARL-3580 inductively coupled plasma (ICP). After screening, the silica, aluminum and sodium contents of the crystals formed at *pH* $\geq$ 13 revealed Si/Al ratios approaching 1.0, typical of *A*-zeolite. The synthesized Na-A sample had the composition $SiO_2 = 32.2\%$, $Al_2O_3 = 28.3\%$, $Na_2O = 17.2\%$, $H_2O = 20.0\%$. This corresponds to the primary formula $Na_2AlSiO_4 \cdot 2H_2O$.

X-ray diffraction (XRD)

XRD is available for characterization of the crystalline and highly-ordered structures such as zeolites. The XRD patterns of the crystals obtained from the synthesis matrix at different *pH* values are reported in Figs 3 and 4. Below the optimum *pH* $\geq$ 13 for the synthesis of the *A*-zeolite, crystals of NaCl and
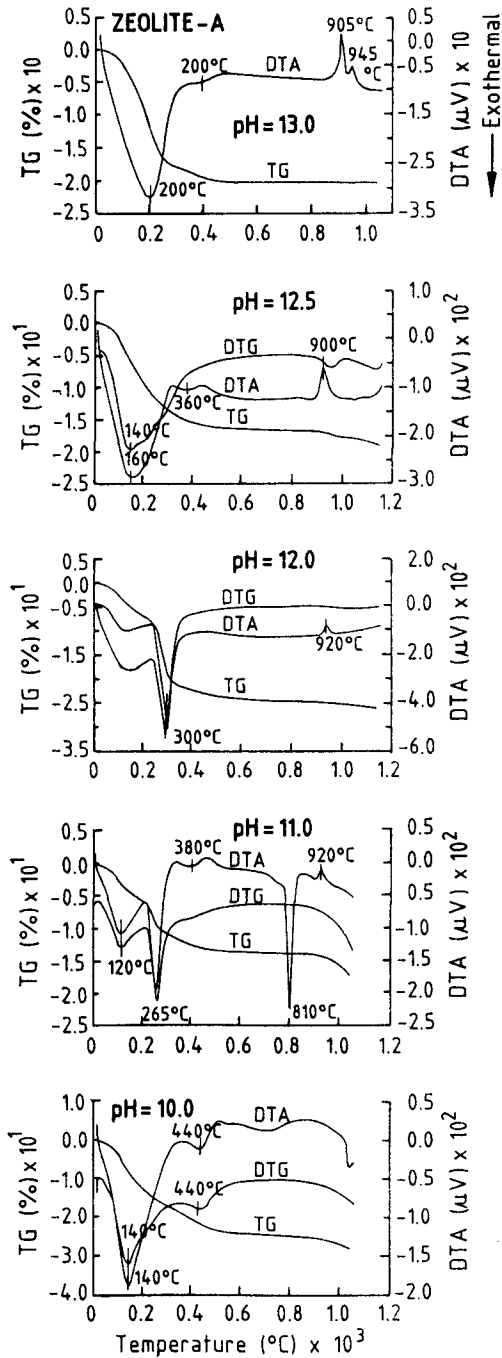
Fig. 1 TG and DTA curves for various crystallites at *pH* 10 to *pH* 13
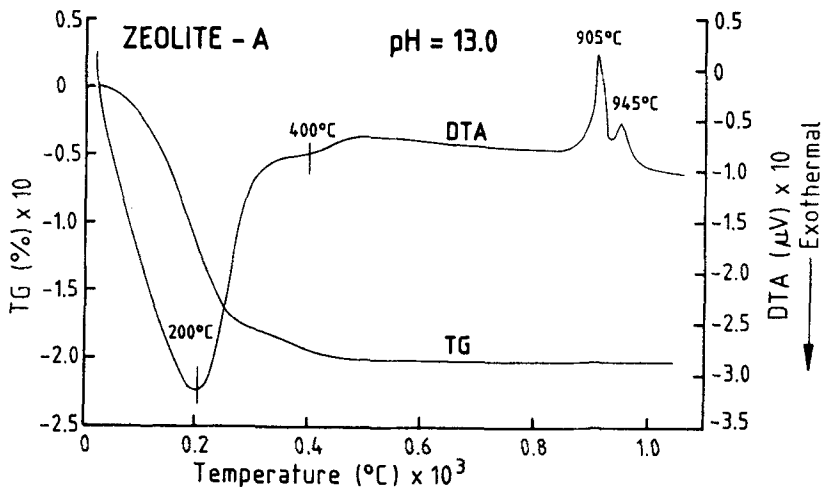
Fig. 2 TG and DTA curves of zeolite-A at $pH = 13.0$, showing the typical transformations

$Al(OH)_3$ were observed, as in Fig. 3a, b and c. Figure 3d shows that the sample is mainly amorphous aluminosilicate plus some NaCl crystals. The zeolite formed at $pH \geq 13$ was identified as of Na-A type and the powder pattern clearly revealed the differences between the crystals formed at $pH \geq 13$, identified as A-zeolite, and those formed from the same matrix at $pH < 13$. The diffraction patterns of the synthesized samples were matched with standards prepared by the Joint Committee of Powder Data Service (JCPDS), and are recorded under each XRD spectrum.

Table 1 Thermal analysis data on samples prepared at various pH values

Samples	TG	DTA		
$T=368$ K,	Mass loss / %	Removal of adsorbed H_2O	Loss of H_2O of crystallization	Maximum of exothermic peak /°C
		endotherm /°C		
1. pH 10	23.0	140	440	NA
2. pH 11	12.5	120,265	380	920
3. pH 12	23.0	140	300,420	920
4. pH 12.5	16.5	160	360	900
5. $pH \geq 13$	20.0	200	400	905,945

Scanning electron microscopy (SEM)

The size and morphology of the A-zeolite crystals were observed under the scanning electron microscope. The polycrystallites in Fig. 2 explain the recrystallization of the A-zeolite into the P-zeolite under the operating conditions. However, we found that this phase change is time-dependent: exactly 3.5 h of crystallization under the synthesis conditions yielded the A-zeolite, as illustrated in Fig. 6.
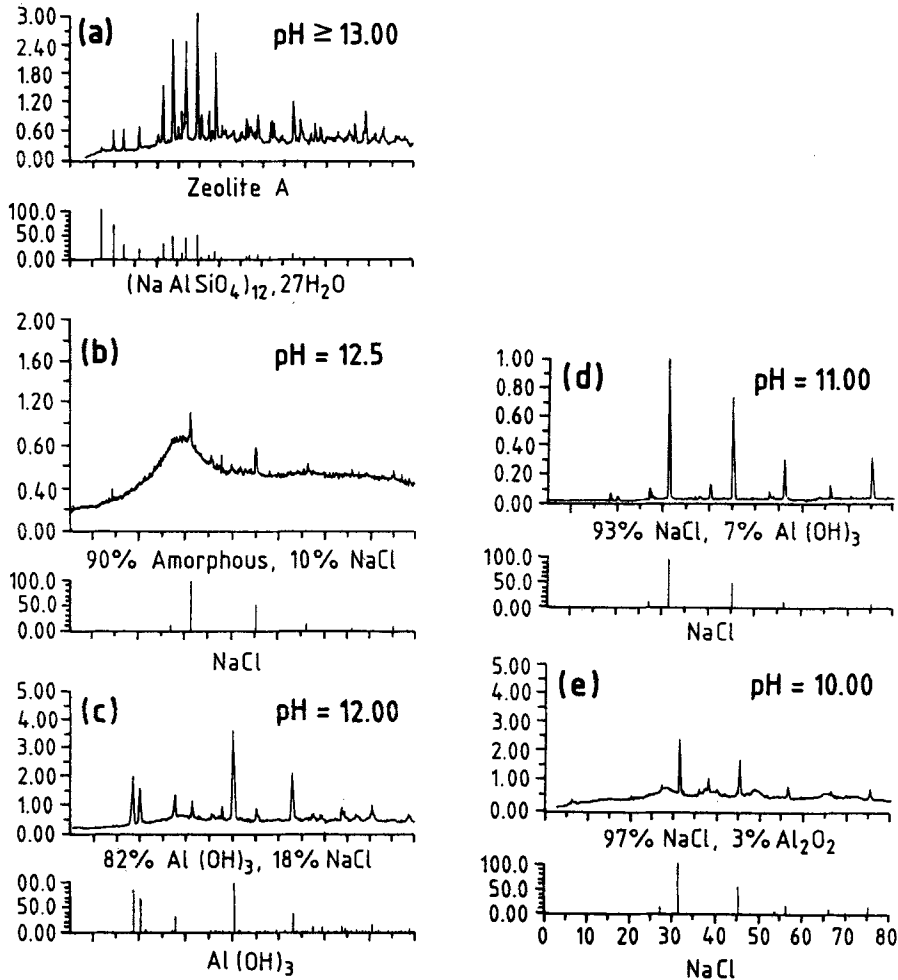

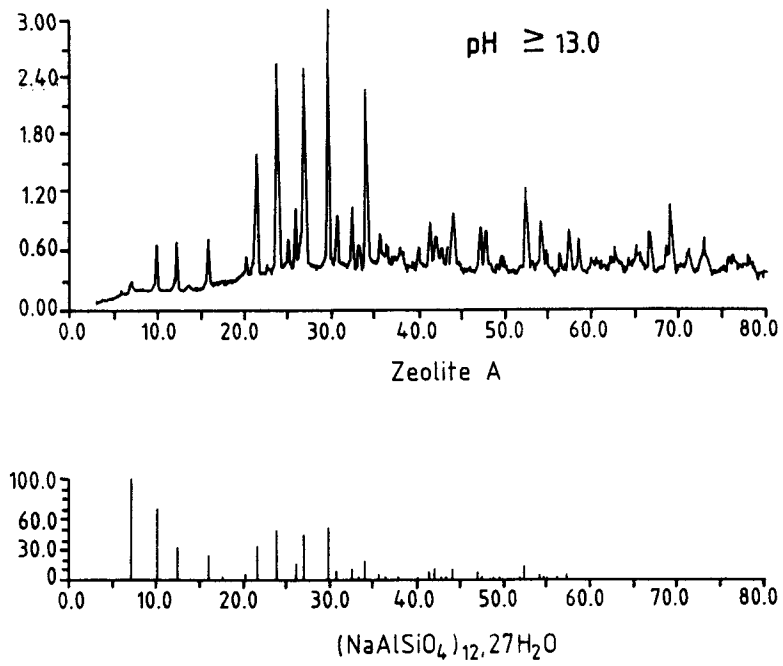Fig. 3 XRD patterns of the products obtained at pH 10.0 to pH 13

Zeolite A

$(NaAlSiO_4)_{12} \cdot 27H_2O$

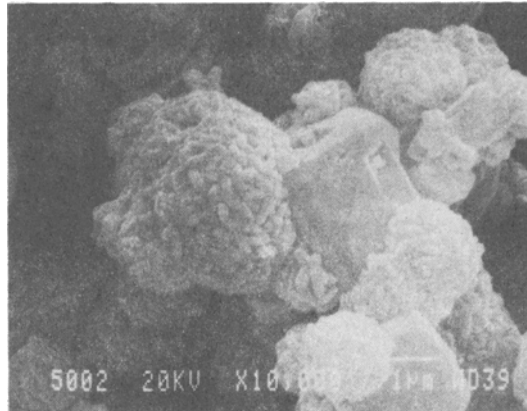**Fig. 4** XRD pattern of zeolite-A at $pH \geq 13.0$

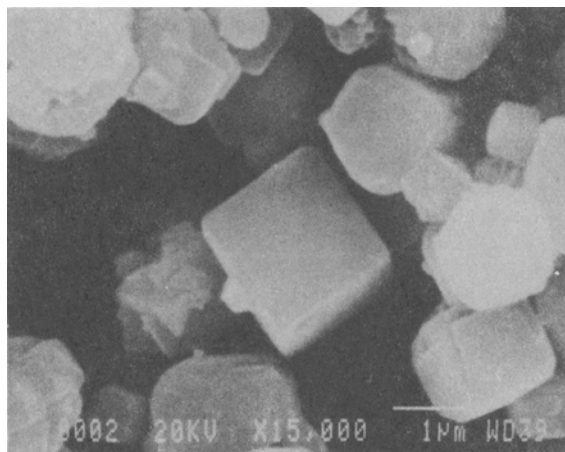**Fig. 5** SEM micrograph showing the crystallization of zeolite-A and the presence of P-zeolite

Fig. 6 SEM micrograph confirming the successful synthesis of zeolite-A at $pH = 13.0$ at 3.5 h

Conclusions

Simultaneous thermal analysis provides a useful means of monitoring the successful synthesis of the A-zeolite, and hence illustrates its thermal stability. The pH of the synthesis matrix was varied and optimized to be in the alkaline medium between 13 and 14. The characteristic transformation DTA peaks at around 900–1200°C were used to identify a preparation of the A-zeolite under the optimum pH conditions. The XRD powder diffraction patterns and the SEM micrographs provided evidence confirming the successful synthesis of the A-zeolite. Chemical analyses were used to obtain the zeolite primary formula composition.

* * *

References

1 R. M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, New York, London 1978, p. 31–44.
2 D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, J. Am. Chem. Soc., 78 (1956) 5963.
3 T. B. Reed and D. W. Breck, J. Am. Chem. Soc., 78 (1956) 5972.
4 W. Smykatz-Kloss, Differential Thermal Analysis-Application and Results in Mineralogy, Springer-Verlag, Berlin 1974 , p.88–91.
5 H. Sticher, Thermochim. Acta, 10 (1974) 305.

6 Y. D. Yeboah and A. M. Aitani, Thermochim. Acta, 149 (1989) 147.
7 D. W. Breck, Zeolite Molecular Sieves, John Wiley & Sons, New York 1974, p.277–279.
8 J. W. Akitt, N. W. Greenwood, B. L. Khandelwal and G. D. Lester, J. Chem. Soc. Dalton Trans 1972, 604–609.
9 J. L. Guth, H. Kessler, J. M. Higel, J. M. Lamblin, J. Patarin, A. Seive, J. M. Chezeau and R. Wey, Zeolite Synthesis, ACS Symposium series, 398 (1989) 176.

Zusammenfassung — Der Nachweis einer erfolgreichen Synthese spezieller Zeolithe erfordert die Untersuchung des Kristalles mittels XRD, SEM, MAS-NMR und mittels chemischer Analyse. Vorliegend wurde der im DTA exotherme Gitterzerfall von Zeolith-A verwendet, welcher zur Charakterisierung typische Peaks zwischen 900 und 1200°C liefert. Es wurde der Einfluß von pH-Konzentration, Kristallisationsdauer und Temperatur untersucht und eine Identifizierung der Zeolith-A Bildung war mittels DTA/TG-Analyse unter verschiedenen Bedingungen schnell und leicht möglich. Die Parameter wurden für die Zeolith-Synthese optimiert und DTA-Messungen boten genügend Informationen zur Identifizierung von Zeolith-A, was mittels XDR und SEM noch bestätigt wurde.