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STATE OF ALKALI AZIDES IN ZEOLITES STUDIED BY THERMAL ANALYSIS

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Abstract

Thermal behaviour of pure LiN_3, NaN_3, CsN_3 and their mixture with the respective LiY–FAU, NaY–FAU, CsY–FAU zeolite was investigated by means of thermogravimetry and IR spectroscopy. Thermodesorption of CO_2 was applied to compare the basicity of the alkali ion-exchanged Y zeolites. Two of the investigated systems, the NaN_3/NaY–FAU and the CsN_3/CsY–FAU gave single, well defined and reproducible azide decomposition features rendering these samples to apply as catalyst precursors for preparation of zeolite with basic character.

Keywords: azides in zeolites

Introduction

The thermal behaviour of sodium azide included in the interior of zeolite pore system and adsorbed on the outer surface of crystallites has been investigated by several research groups. The aims of their works were different.

Fejes and coworkers used the elementary sodium atoms generated by thermal decomposition of NaN_3 in the cavity of zeolites to eliminate the residual Brönsted acidity of the zeolite catalysts [1]. Martens *et al.* prepared zeolite with very strong basic sites and opened a new application of zeolites as catalysts since they were considered to have acidic character [2]. Förster and coworkers studied the decomposition of sodium azide in zeolites in order to shed some more light on the influence of zeolite structure on the decomposition temperature [3]. Kevan and coworkers evidenced and characterized the metal complexes generated upon decomposition of different azides in zeolites by ESR spectroscopy [4].

Recently, we reported the thermal behaviour of sodium azide in NaY–FAU zeolite [5] and the thermal characteristics of alkali metal azides in NaY–FAU zeolite [6].

In this communication we report on the thermal behaviour of alkali metal azides, particularly the LiN_3, NaN_3 and CsN_3 in the respective LiY, NaY and

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CsY zeolites. We intend to compare the results obtained for investigations of various azides in zeolites.

Experimental

From parent NaY zeolite LiY and CsY samples were prepared by ion-exchange. Ion-exchange degree was controlled by the uptake of the respective ions determined from the ion exchange solution by atomic absorption spectro- scopy and directly measuring the remaining sodium in the zeolite by ^{23}Na–NMR spectroscopy. Good correlation was found between the results determined by the two methods. NMR spectroscopy allowed us to identify those cation positions at which the Li^+ and Cs^+ ions are bonded. These are the ion positions situated in the supercages and the cubooctahedra.

LiN_3 and CsN_3 were prepared and described previously [6]. Before measurements azide salts were purified by recrystallization. The purity checked by atomic absorption and UV–VIS spectrophotometry was found to be over 90%.

LiN_3/LiY, NaN_3/NaY and CsN_3/CsY samples were prepared using wet preparation method. Zeolite powder was carefully mixed in concentrated solution of the respective azide in an appropriate ratio (3.84 mmol azide/1 g zeolite) followed by evaporation of water, under continuous stirring. The samples were kept at 388 K for five hours before thermogravimetric measurements.

X-ray diffraction analysis showed that there is no crystalline azide in the samples prepared by this method.

For TG measurements, Derivatograph-Q, Hungarian made equipment was used. Samples were placed on a plate-series holder in thin layer to avoid blowing due to azide decomposition. Measurements were performed generally between room temperature and 900 K using 5 K min^{-1} heating rate.

For temperature programmed CO_2 desorption measurements Chrom 4 gas chromatograph with TCD was used. The experiments were carried out in the 300–723 K range. In each case, the samples were pretreated in He flow at 723 K for 2 h. After cooling down, CO_2 (10 cm^3 min^{-1}) was adsorbed for 30 min. Then the CO_2 flow was shut off, the system was flushed with He until we got straight baseline for the gc. For desorption of CO_2 4.7 K min^{-1} heating rate was applied.

Results and discussion

Basicity test

Generally two distinct methods are described in the literature to prepare basic catalysts with microporosity. Both methods starts from zeolite rendering the pores of molecular dimensions. According to the procedure known for a long time alkali metal oxides are introduced in the alkali metal exchanged zeolites. The most frequently reported catalyst thus prepared is Cs_2O/CsY [7]. However, the internal volume of these materials is somewhat smaller than that of the parent zeolite.

By the second method alkali metal clusters are produced in the zeolite cavities [8]. The method of metal introduction used in the practice are as follows: treatment in alkali metal vapour generated by evaporation of the alkali metal or decomposition of alkali metal azide furthermore, deposition of alkali metal or its complex from solution of ammonia or naphtalene containing tetrahydrofurane. In our laboratory the application of the azide decomposition method became accepted.

CO_2 is regarded as acidic probe molecule used frequently for monitoring basic sites. To test the basicity of zeolite matrixes thermodesorption experiments were performed with CO_2 as probe.

As can be seen in Fig. 1 two desorption peaks were found for the ion-exchanged zeolites. The first peak is due to the physisorbed, weakly bonded CO_2 which desorbs at 335–340 K for each sample. The shape and maximum of the high temperature peaks are different although, the dominating amount of CO_2 desorbs at the same (440–673 K) temperature range. The determinated peak maxima for LiY, NaY and CsY are 571, 587 and 597 K, respectively. These values refer to the increasing strength of basicity of zeolite which is in the order: LiY, NaY, CsY. This trend is in agreement with the results of Barthomeuf, who measured the basicity with benzene adsorption [9].

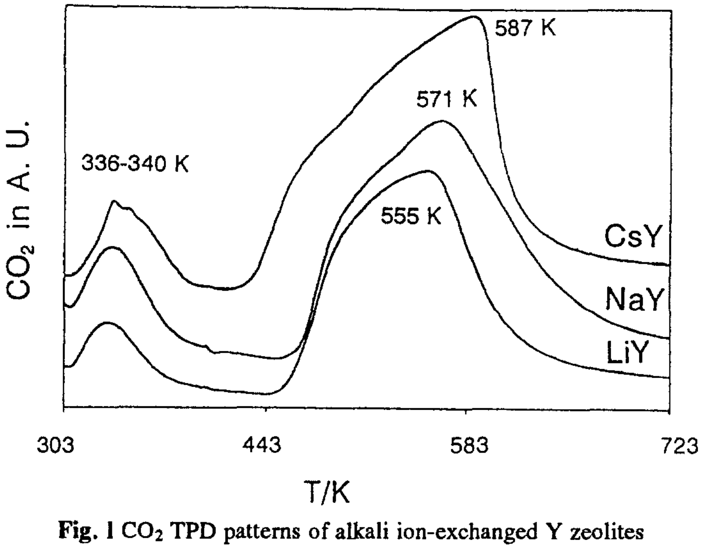

Fig. 1 CO_2 TPD patterns of alkali ion-exchanged Y zeolites

Thermoanalytical measurements

Thermal behaviour of alkali metal ion-exchanged zeolites

Derivatographic patterns of alkali metal exchanged faujasite zeolites show one weight loss step due to their dehydration. The temperature of these TG steps is practically the same, 400 K for each sample irrespective of the cations. The mass of water releases varies for the different samples. The results are summarized in the Table 1, where the compositions of the samples are also included. The data show that the water content of LiY–FAU is the highest, that of CsY–FAU is the lowest, while the water content of NaY–FAU lies in between. This order reveals the well known fact: the smaller is the ionic radius the higher the polarizing power of the ion.

Table 1 Composition and water loss of investigated zeolite samples

Sample	Unit cell composition	Water released *m*/%
LiY–FAU	$Li_{38}Na_{20}Al_{58}Si_{134}O_{384}$	31.4 (9.7)*
NaY–FAU	$Na_{58}Al_{58}Si_{134}O_{384}$	28.8 (9.0)*
CsY–FAU	$Cs_{50}Na_{8}Al_{58}Si_{134}O_{384}$	17.6 (7.3)*

*Samples dried at 388 K

Decomposition of alkali azides in their pure forms and in their mixture with zeolites

As the basic character of the alkali metal loaded catalyst varies with the nature of the alkali metals, the investigation of thermal stability of their precursors, the respective alkali azides is indispensable.

As can be seen in Fig. 2 the dominating amount of LiN_3 decomposes at 500 K. At lower temperature, at 350 K, the release of crystal water occurs. Note, LiN_3 is strongly hygroscopic material. At 530 K a third weight loss step is seen, attribution of which is uncertain yet.

The TG curve registered for the LiN_3/LiY system shows three distinct steps at around 450, 600 and 780 K. As these temperatures are far from those measured for the pure LiN_3, a complex decomposition feature is expected. Data obtained from the quantitative evaluation of TG curves are summarized in Table 2.

The nature of CsN_3/CsY system proved to be much simpler. The decomposition of pure CsN_3 occurs at 690 K as seen in Fig. 3. The CsN_3 decomposes at the same temperature in the CsN_3/CsY system. From this follows, that simple and reproducible decomposition behaviour is expected for this catalyst precursor system.

Similar behaviour was found for the NaN_3/NaY mixture, showing single well defined decomposition step at 630 K as TG curve in Fig. 4 shows.

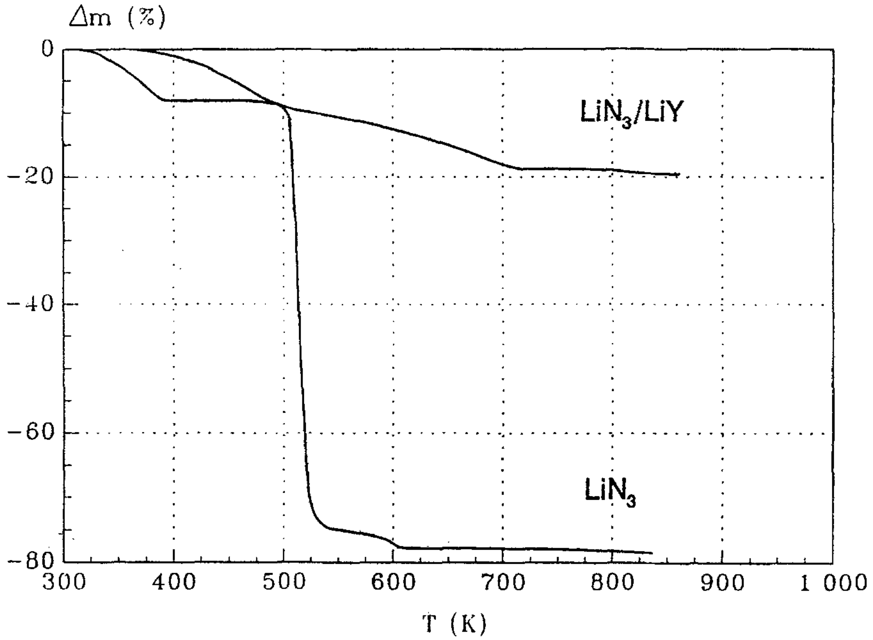

Fig. 2 TG profiles of LiN_3 and LiN_3/LiY

Table 2 Weight loss data of samples

Li system	*T*/K	*m*/%	*T*/K	*m*/%	*T*/K	*m*/%
LiN_3	298–423	8.0	423–530	61	530–900	8.5
LiN_3/LiY	298–513	8.8	513–728	9.2	728–900	0.8

Na system	*T*/K	*m*/%	*T*/K	*m*/%	*T*/K	*m*/%
NaN_3	298–1073	64				
NaN_3/NaY	298–623	7.6	623–900	13.4		

Cs system	*T*/K	*m*/%	*T*/K	*m*/%	*T*/K	*m*/%
CsN_3	298–680	0.5	713–900	22.5		
CsN_3/CsY	298–680	3.5	713–900	5.8		

In former papers we reported on the thermal behaviour of alkali azides introduced into NaY–FAU zeolite by wet method. In those cases we found that a small portion of azide did not decompose and remained in the cavities in the faujasite zeolite. The same feature was verified for either LiN_3/LiY or CsN_3/CsY system. After treatment of the LiN_3/LiY sample at some higher temperature than the decomposition temperature of LiN_3, a small amount of

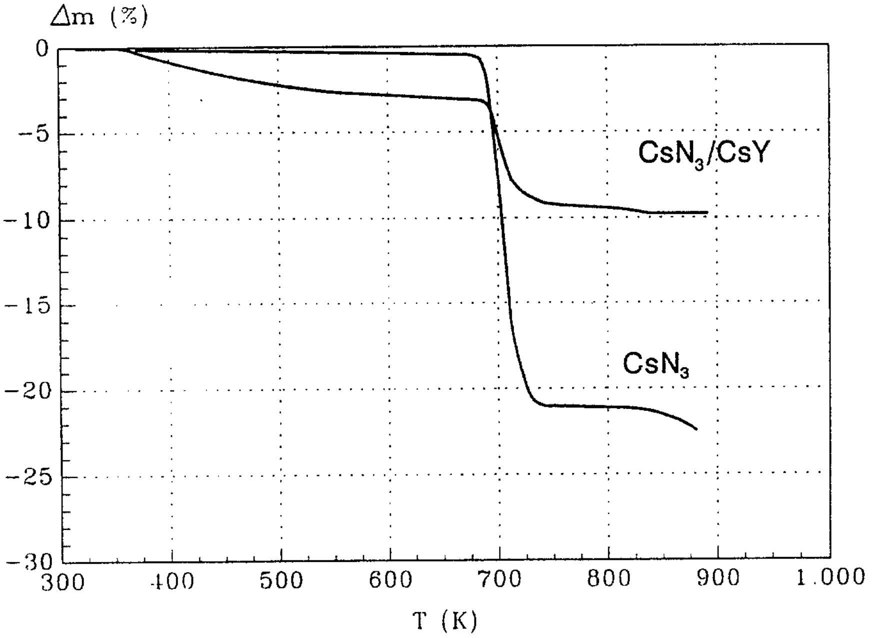

Fig. 3 TG profiles of CsN3 and CsN3/CsY

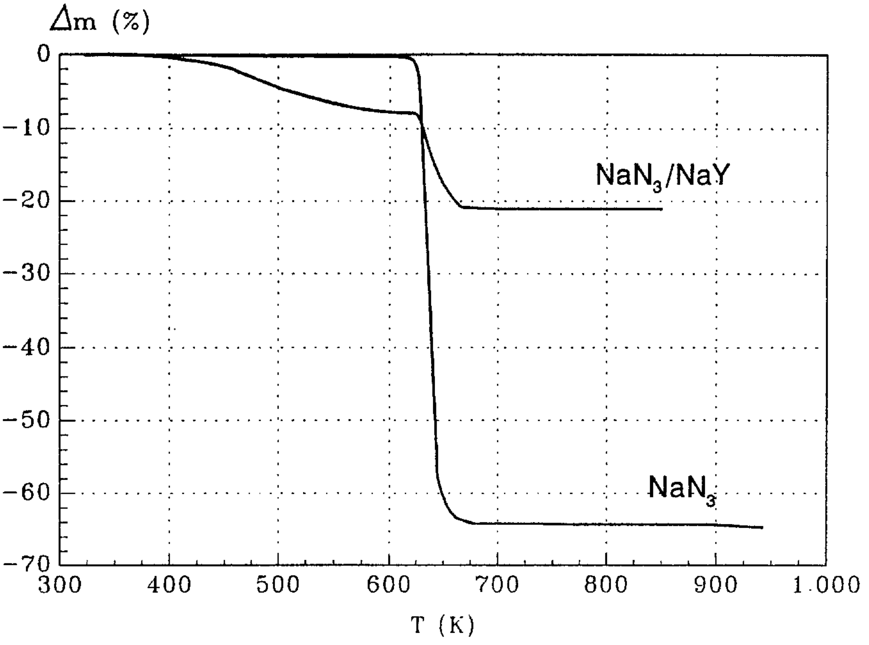

Fig. 4 TG profiles of NaN3 and NaN3/NaY

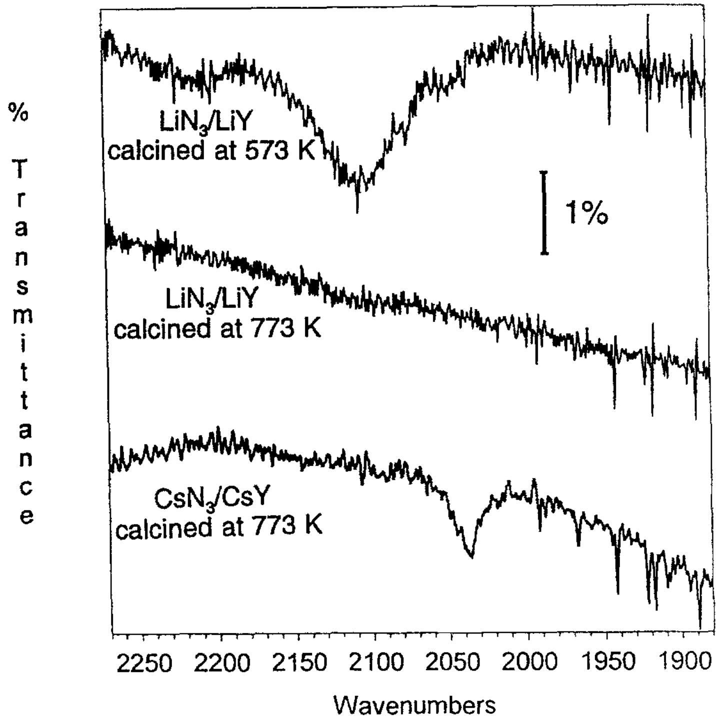

Fig. 5 IR spectra of calcined samples in KBr matrix

azide remained intact in the zeolite was detected by IR spectroscopy (Fig. 5). Heat treatment at 773 K resulted in the completion of the azid decomposition, azide band no longer was detected in the IR spectrum. The entire decomposition of CsN_3 in CsY–FAU zeolite was not achieved even after calcination of the sample at 773 K, almost 100 K higher than its decomposition temperature.

Conclusion

Thermal analytical measurements were performed in order to verify the optimal conditions of alkali azide decomposition used for preparation of zeolite based catalysts with basic character.

Two of the investigated systems, the NaN_3/NaY–FAU and the CsN_3/CsY–FAU gave reproducible azid decomposition features rendering these samples to apply as catalyst precursors for preparation of zeolite with basic character.

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