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The thermal behaviour of sodium azide in zeolites

I. Hannus [a,*], Gy. Tasi [a], I. Kiricsi [a], J.B. Nagy [b], H. Förster [c], P. Fejes [a]

[a] *Applied Chemistry Department, József Attila University, H-6720 Szeged, Hungary*
[b] *Laboratoire de Catalyse, Facultes Universitaires N.D. de la Paix, B-5000 Namur, Belgium*
[c] *Institute of Physical Chemistry, University of Hamburg, D-20146 Hamburg, Germany*

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Abstract

Upon thermal treatment, NaN_3-doped zeolite transforms stepwise. After endothermic dehydration, the NaN_3 decomposes exothermically in air and under N_2 flow. The temperature of decomposition is higher than that of the pure azide. Part of the sodium azide remains intact up to 1000 K. The process was also monitored by IR spectroscopy. ^{23}Na NMR measurements revealed that metallic sodium clusters were formed.

Keywords: DTA; DTG; Sodium azide; TG; Zeolite

1. Introduction

In 1976, Barrer et al. [1] reported that the decomposition of sodium azide encapsulated in cancrinite is catalysed by the metallic sodium released previously. According to their DSC measurements, two endothermic peaks were observed at 393 and 523 K due to dehydration of zeolite. One exothermic peak was found at 693 K for a sample heated in air and was attributed to the oxidation of sodium metal and/or sodium azide as both processes are strongly exothermic. They assumed the decomposition temperature of bulk sodium azide to be near 558 K. From the two-stage nature of the process, an autocatalytic action of the sodium was assumed. As a result of sodium azide decomposition, coloured zeolites were obtained with a very broad line at $g \approx 2.0$ in the ESR spectrum due to the generation of charged sodium clusters inside the zeolite [1].

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* Corresponding author.

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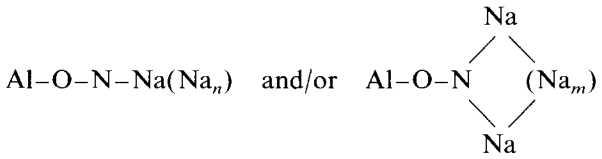
In the course of complex investigations of the NaN_3/NaY system, Fejes and co-workers [2,3] arrived at the following conclusions. Sodium vapour from the decomposition of NaN_3 eliminates the Broensted acidity of zeolites. For samples prepared by the impregnation technique, guest salt occlusion takes place, while for samples prepared by mechanical mixing this phenomenon could not be observed [4]. The occluded NaN_3 is not crystalline and amounts to nearly 2 azide ion per unit cell. The hosted azide decomposes above 1000 K, at a temperature much higher as compared to the decomposition of pure sodium azide, which is 653 K from our experiments.

In 1985, Martens et al. [5] used sodium vapour produced by in situ decomposition of sodium azide in zeolites for the preparation of catalysts of strong basic character. They changed the water solvent for methanol and applied higher sodium azide loadings than we did. Applying this procedure, excellent basic catalysts were prepared, the catalytic activity of which was demonstrated in several reactions [6]. From the investigation of azide decomposition, they concluded that instead of salt occlusion, as proposed by us, partial decomposition of sodium azide takes place resulting in nitrogen chemically bonded to the zeolite, consequently leading to an unusual thermal stability [7]. The envisaged "glued" complexes were represented as



$$\mathrm{Al{-}O{-}N{-}Na(Na_n)} \quad \text{and/or} \quad \mathrm{Al{-}O{-}N}\overset{\mathrm{Na}}{\underset{\mathrm{Na}}{\diamond}}\mathrm{(Na_m)}$$

Later, they revised this suggestion by partly accepting the salt inclusion phenomenon [8], which has been spectroscopically proven by us.

Concerning the conditions for the decomposition of azide, equivocal results have been obtained by different groups. We have reinvestigated the influence of experimental parameters on the decomposition of sodium azide in zeolites due to their importance in the preparation of basic catalysts. Results obtained by thermogravimetry, IR and ^{23}Na NMR spectroscopy are reported in the present paper.

2. Experimental

Sodium azide containing faujasite was prepared from NaY using NaN_3 in methanol following the recipe of Martens et al. [6]. The sample thus prepared contained 3.85 mmol NaN_3 per g NaY zeolite. In each experiment this sample was used.

For TG–DTA measurements, a Derivatograph Q (MOM Hungary) was used. The azide-loaded samples were placed on a plate series sample holder made from platinum and were tested in flowing air or nitrogen purified carefully to exclude traces of oxygen. The rate of the linear temperature program was varied between 1.25 and 10 K min^{-1}. TG, DTG, and DTA curves were recorded in the range of 298–1000 K. Samples for further analysis were taken after dehydration, before decomposition and after decomposition, the temperatures of which were initially determined.

Two methods of infrared spectroscopy were applied for analysing the process of decomposition and the products obtained after heat treatment of the sodium azide zeolite system. The KBr pellet technique was used for monitoring the changes which occurred upon baking the sample. For this, 100 mg of KBr and 2 mg of solid sample were carefully homogenized and pressed into discs of 1 cm diameter.

Self-supporting wafers were used for the in situ investigation of decomposition. For this purpose, a heatable stainless steel IR cell equipped with CaF_2 windows was applied. Spectra were recorded at preselected temperatures from the sample heated up linearly at a rate of 3 K min^{-1}. During recording of the spectra, the sample was held at a given constant temperature. In some cases the specimen was cooled down to room temperature.

The spectra were recorded on a Specord IR-75 spectrometer for the KBr matrix investigation and on a Digilab FTIR instrument for the in situ measurements.

MAS ^{23}Na NMR experiments were carried out on an MSL-400 Bruker spectrometer. The powdered samples were generally measured in a normal rotor. The decomposition was performed in situ in the NMR tube, according to the following procedure. The azide-loaded zeolite was filled into an NMR tube (5 mm o.d.) and dehydrated in vacuo at 473 K. Then the sample was heated at a rate of 3 K min^{-1} to 673 K under continuous evacuation and held at this temperature for one hour. The NMR tubes were carefully sealed to achieve proper balance and high spinning rate (3.8 kHz).

3. Results and discussion

3.1. Thermogravimetric measurements

According to the derivatographic pattern of pure sodium azide, there is only one decomposition step at 620 K (Fig. 1). However the DTG curve shows a broad peak which cannot be separated into several smaller components. Decomposition of sodium azide is exothermic. The broad DTA exotherm is in accordance with the DTG. From this it follows that the decomposition of pure sodium azide takes place in one step and not in two steps as proposed earlier in the paper [9] cited by Barrer et al. [1].

The thermal behaviour of the azide-loaded zeolite is different. Fig. 1 shows the derivatographic patterns at slow heating rate. Both the DTG and DTA curves contain two partially overlapping peaks for NaN_3/NaY. For comparison, the relevant curves of pure sodium azide are also shown in this figure. With increasing heating rate the resolution of these peaks becomes less complete. On the pattern registered at 5 K min^{-1} heating rate, no separation of peaks was observed at all (see Fig. 2).

An additional characteristic of the influence of heating rate was that the mass balance was found to be more complete for samples prepared by slow heating. This

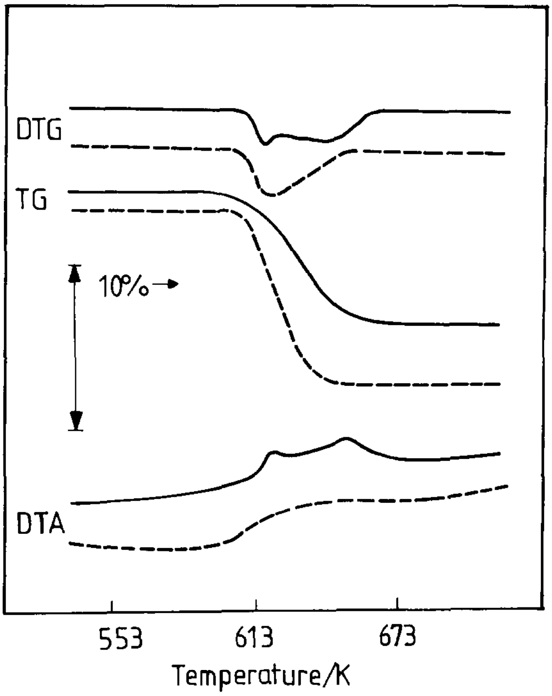


Fig. 1. Thermogravimetric patterns of NaN_3/NaY (——) and of pure NaN_3 (- - -) at 1.25 K min^{-1} heating rate.

result may be the consequence of a longer residence time of the released sodium in the cavities of the zeolite. This longer lifetime increases the possiblity for secondary reactions. Actually Martens et al. [6] showed that a fundamental difference exists between the state of sodium formed upon fast and slow decomposition of sodium azide. As the state of sodium determines the catalytic activity, they proved that neutral intracrystalline metal clusters are the active sites in several hydrocarbon transformations. These entities were formed when the decomposition was carried out slowly. Under these conditions the sodium atoms primarily formed may cluster rather than leave the pore system, generating catalytically inactive, neutral intercrystalline sodium agglomerates. The third type of entity which can be formed are charged Na_4^{3+} clusters, the characteristics of which are under study at present (see, for example, Ref. [10]). Investigations on the behaviour of these species are out of the scope of this work.

When the decomposition was carried out in air instead of nitrogen, a much more intense exothermic peak was observed which was due to the exothermic reaction between sodium and oxygen.

An additional small weight loss was found near 1020 K. As this peak is very small, the temperature of its occurrence cannot be determined accurately. The weight loss due to this step amounts to about 3%, in good conformity with a loading of nearly two azide ions per unit cell.

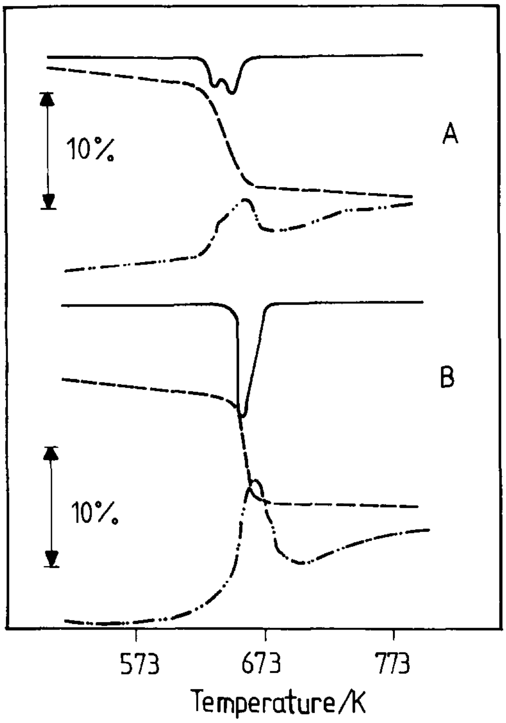


Fig. 2. TG (- - -), DTG (——) and DTA (- · · -) profiles of the NaN_3/NaY sample at 2.5 (A) and 5.0 (B) K min^{-1} heating rate.

3.2. IR spectroscopic investigations

Fig. 3 shows spectra obtained after treatment of an azide-loaded sample at different temperatures. The splitting of the band at 2115 cm^{-1}, present also in the spectrum of sodium azide, was already observed during azide loading as two bands were detected for NaN_3/NaY before heat treatment. After heating to 590 K, the splitting becomes more pronounced and in addition to the bands observed for the untreated material, here a new band is detected at 2090 cm^{-1}. After baking at 863 K only traces of azide remain in the zeolite, as shown by the very small bands in the spectrum taken from this sample. After thermal treatment at 1073 K no bands were found in the region of the azide vibrations. These results are in accordance with our former observations and prove that not only does decomposition of sodium azide take place, but also salt occlusion occurs, because azide bands of very low intensity are still present. It can be concluded that the distribution of sodium azide during preparation results in azide ions in different crystallographic surroundings.

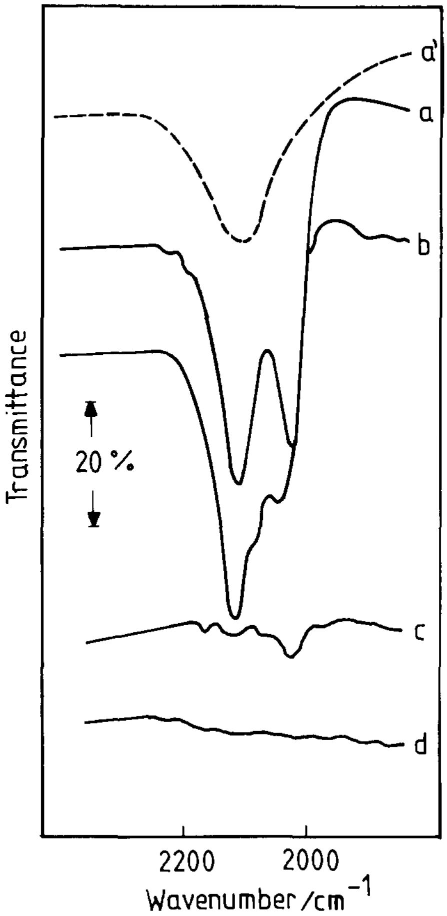


Fig. 3. IR spectra of NaN_3 (a') and of NaN_3/NaY treated at ambient temperature (a), 593 K (b), 853 K (c) and 1073 K (d). KBr matrix technique was used for preparation of these samples.

IR spectra depicted in Fig. 4 show that the band at 2080 cm^{-1} shifts to lower wavenumbers with increasing evacuation temperature, while a new absorption band appears at 2170 cm^{-1}. Below the decomposition temperature of sodium azide in zeolite two bands are present in the spectrum at 2060 and 2170 cm^{-1}. After heat treatment at 673 K, a strong decrease in their intensities was observed, as seen in Fig. 5. Comparison of the spectra taken at 673 K from the sample after treatment for 12 h at the same temperature with those recorded after cooling the sample down to room temperature shows that the bands are not separated at high temperature. This may be explained by the change in the rovibrational spectrum due to the dependence of the vibrational transition on temperature, the higher occupation of excited rotational levels and the enhanced mobility of the species leading to a

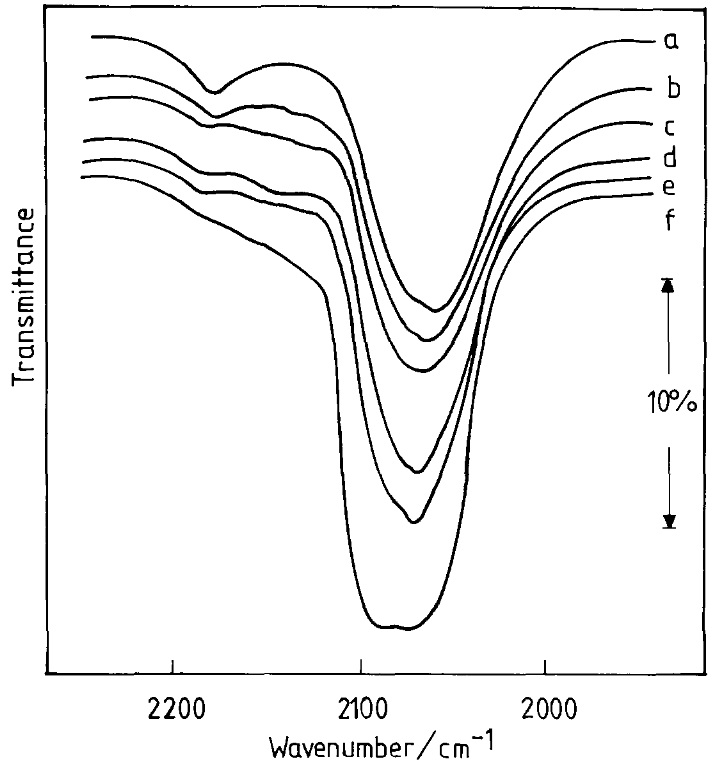


Fig. 4. IR spectra of NaN_3/NaY after treatment of the self-supporting wafer at 373 K (a), 473 K (b), 523 K (c), 573 K (d), 623 K (e) and 663 K (f) in vacuo. These spectra were recorded at the temperature of treatment.

different distribution in the zeolite pore system. As a consequence the spectrum becomes more complex at low temperature, in contrast to the more simple form at high temperature. As each spectrum in our former work was registered at beam temperature (approx. 330 K), this spectral change was not observed.

As the band at 2187 cm^{-1} develops slowly with increasing temperature, we assume that sodium azide moves from the supercages into the sodalite units with stabilization.

The mass deficit changes from 1% to 5%. The latter value is above the standard error of the measurement. Martens et al. have also found an incomplete mass balance on the basis of ^{15}N NMR measurements [8]. They proved that nitrogen is missing. To clarify this phenomenon further investigations are in progress.

3.3. *NMR spectroscopic investigations*

Fig. 6 shows the ^{23}Na MAS NMR spectra of NaN_3 (a), NaY-FAU (b), and NaN_3/NaY-FAU before (c) and after (d) decomposition of sodium azide. Aqueous

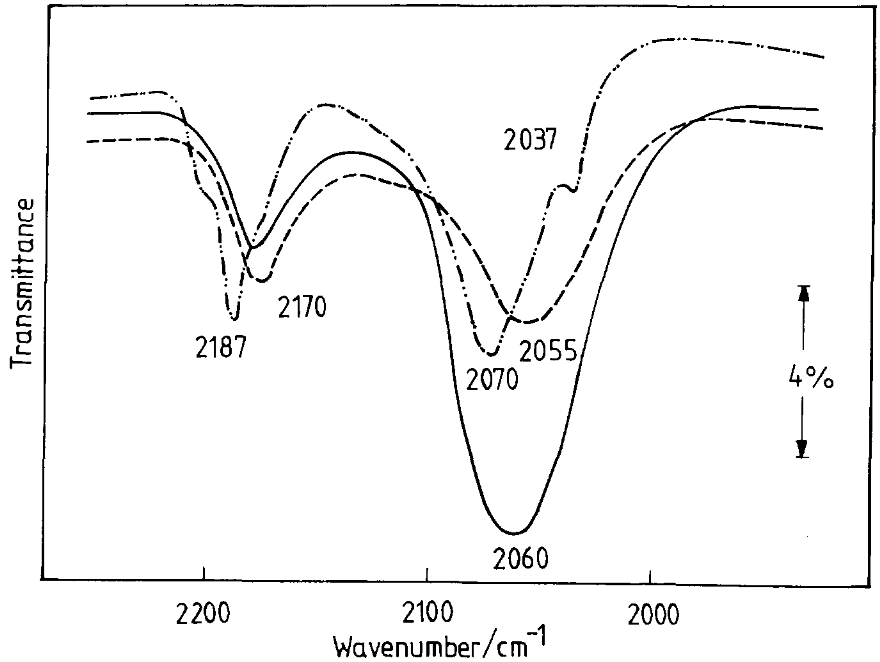


Fig. 5. IR spectra of a self-supported wafer pressed from NaN_3/NaY at 673 K after treatment at 673 K for 12 h in vacuum (——), the same sample measured at room temperature (– · · –), and at 673 K after repeated treatment at 673 K in vacuo (– – –).

NaCl solution was used as the reference (0 ppm). Spectrum b shows a sharp signal at −2.0 ppm due to the Na^+ ions in the supercages, the shoulder at −6.8 ppm characteristic for Na^+ ion in sodalite units, and an overlapping broad signal due to the presence of the Na^+ in hexagonal prisms [11]. Spectrum d contains a peak at −6 ppm which is composed of different signals including that of the Na^+ ions of the zeolite, undecomposed NaN_3 and the glass tube. The small peak at 640 ppm is attributed to a metallic sodium cluster, and is characteristic of a Knight shift. This signal has very rarely been observed before now [12].

4. Conclusions

From the results obtained in the course of the investigation of the decomposition of sodium azide in zeolite Y, the following conclusions can be drawn.

Decomposition of sodium azide in zeolites occurs at a higher temperature than in its pure form, independently of whether the sample preparation has taken place from an aqueous or methanolic solution of sodium azide.

The decomposition of sodium azide in zeolite is a stepwise process occurring at different temperatures.

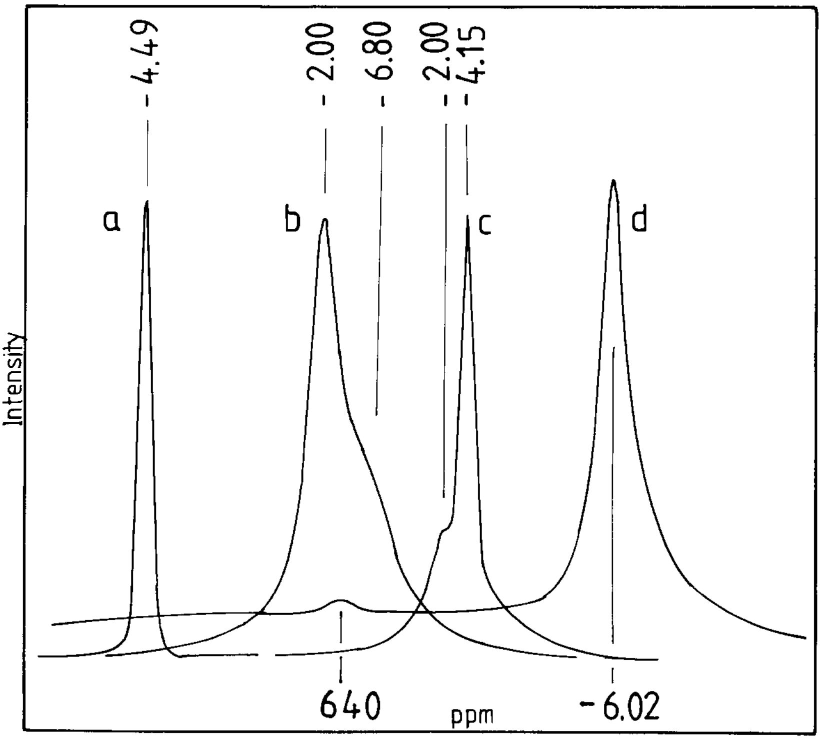


Fig. 6. ^{23}Na NMR spectra of NaN_3 (a), NaY-FAU (b), and NaN_3/NaY-FAU before (c) and after (d) decomposition of sodium azide.

A part of the sodium azide introduced into the zeolite does not decompose until above 1000 K, respresenting approximately 2 molecules azide per unit cell. This value is in agreement with our former results.

The stabilization procedure of sodium azide in zeolites can be monitored by IR spectroscopy. The number of bands attributed to azide in different surroundings in the zeolite pore system depends on the temperature. The spectra recorded at a high temperature showed less resolution than the low temperature data. This phenomenon can be explained by the increased mobility of guest molecules at high temperatures leading to broader absorption bands.

From the ^{23}Na NMR data, it follows that neutral sodium clusters are formed in samples prepared by in situ decomposition of sodium azide in zeolites.

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