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Ignition of ammonia on various zeolitic substrates

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Abstract

The natural zeolites chabazite and clinoptilolite, and synthetic zeolites A and X in their ammonium forms were tested by thermodilatometry. Chabazite, A and X zeolites appeared to catalyze ammonia combustion, whereas clinoptilolite did not. The thermal effects relating to ammonia combustion were ascribed either to different heating rates or to different catalytic activity of the various zeolitic substrates. The different ignition temperatures of ammonia measured on different zeolitic substrates were taken to be a measure of the catalytic activity of the zeolitic substrate itself. © 1997 Elsevier Science B.V.

Keywords: Zeolites; Thermodilatometry; Ammonia combustion

1. Introduction

In previous papers [1,2], the thermodilatometry of various cation forms of a natural chabazite and synthetic zeolite A were investigated. These studies supplied useful indications in the characterization of the complex thermal behaviour of these two zeolites. Contrasting phenomena, often occurring simultaneously, such as thermal expansion, shrinkage arising from dehydration and thermal collapse of the less dense zeolitic structure and cation migrations from one site of the zeolitic structure to another were detected by this simple experimental technique. The same phenomena were not sufficient to interpret the thermodilatometric behaviour of the ammonium form of zeolite A [2]. The sudden increase in temperature occurring in the range 360–400°C was ascribed to the ignition of evolving ammonia upon heating. The usual ignition temperature of ammonia on steel (650°C) is higher than that recorded in thermodilatometric runs of the ammonium form of zeolite A. This lower ignition temperature was justified by the possible catalytic action of the acid sites formed in the microporous zeolite A structure after ammonia evolution [3].

The present investigation was undertaken aiming at a double goal. On the one hand, it further intends to confirm the supposition that acid sites, arising in zeolite structures from ammonia evolution, catalyze the ignition of ammonia itself. On the other, it intends to ascertain if thermodilatometry could be useful in the characterization of the catalytic activity of zeolitic materials. To fulfil these goals, ammonium forms of natural zeolites chabazite and clinoptilolite, and synthetic A and X zeolites were investigated by thermodilatometry.

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2. Experimental

The starting materials used in this investigation were the following: Carlo Erba reagent grade zeolites 4A and 13X, both in their sodium form, a natural chabazite from Mercogliano (Avellino, northeast of Naples) and a natural clinoptilolite from La Rioja (Argentina), both in their original composition. Chemical and mineralogical analyses of natural chabazite and clinoptilolite are reported in Refs. [4,5], respectively.

More or less homoionic ammonium forms of the reported zeolites were obtained by the following procedure: about 10 g of the various zeolites were suspended for 1 h, with continuous stirring, in 1 dm^3 of 1 M ammonium solution at 80°C. This solution was prepared starting from Carlo Erba reagent grade ammonium chloride. After the various zeolites were separated from the suspension by filtration, this same operation was repeated thrice. The resulting powder was washed with distilled water and dried overnight at 80°C. To allow water saturation of the zeolites, they were stored for at least seven days in an environment having more than 50% relative humidity.

By pressing such powders at 150 MPa, cylindrical pellets, having 10 mm height and diameter of 10 mm, were prepared. Such pellets, which are characterized by 35% average apparent porosity measured by the RILEM procedure [6], were tested by dilatometry either in an air or nitrogen atmosphere.

A mod. 402 E/7 Netzsch dilatometer was utilized adopting various heating rates: 3, 6.5, 10 and 30°C min^{-1}.

TG and DTA analyses were performed using a Netzsch STA 409 apparatus, adopting 100 mg sample, α-Al_2O_3 as reference and a 10°C min^{-1} heating rate.

X-ray diffractometric analyses were performed using a Philips PV 1730 diffractometer.

3. Results and discussion

The thermogravimetric curves of these zeolites, in their ammonium form, are depicted in Fig. 1. Their percent weight losses at 650°C, together with literature data concerning Si/Al ratios and framework density, are reported in Table 1.

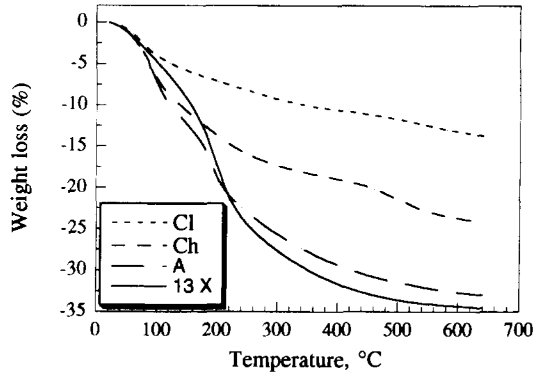

Fig. 1. Thermogravimetric curves of various zeolites in their ammonium forms.

Table 1
Percent weight losses at 650°C of the various zeolites in their ammonium form and literature data concerning Si/Al ratios and framework density

	Clinoptilolite	Chabazite	A	X
% Weight loss	13.8	23.8	32.6	34.4
Si/Al	3.01 [a]	2.26 [b]	1.00 [c]	1.25 [c]
Framework density, (g cm^{-3})	1.71 [d]	1.45 [d]	1.27 [d]	1.27 [d]

[a] Ref. [5]
[b] Ref. [4]
[c] Ref. [7]
[d] Ref. [3]

These weight losses can be mainly ascribed both to dehydration and ammonia evolution which occur simultaneously upon heating. It is well known that the water content of the zeolites increases with decreasing framework density, whereas the evolved ammonia, arising from the thermal treatment and turning the ammonium form of a zeolite into its hydrogen form, is related to the exchange capacity, i.e. to Si/Al ratio. As the exchange capacity increases with decreasing Si/Al ratio, the amount of evolved ammonia increases with decreasing Si/Al ratio. The weight losses of ammonium form of the zeolites seem to be more affected by their water content rather than the amount of evolved ammonia. Actually weight losses decrease according to the order: X $\cong$ A > chabazite > clinoptilolite, which is exactly the sequence in which the framework density increases.

In all the thermodilatometric curves, performed in air on chabazite, A and X zeolites in their ammonium

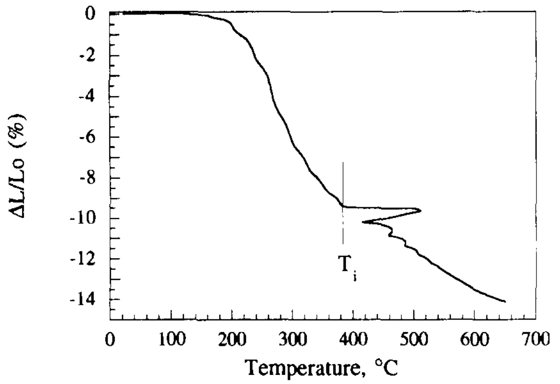

Fig. 2. Dilatometric curve in air of ammonium form of zeolite A at 10°C min^{-1} heating rate.

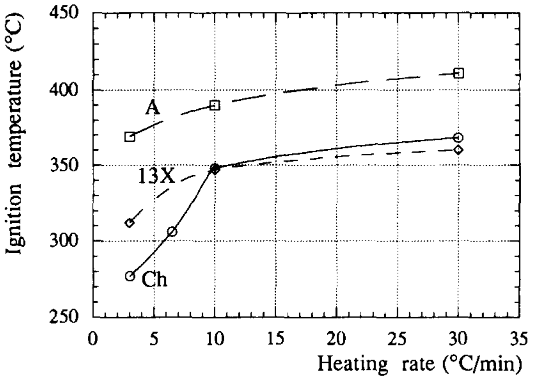

Fig. 3. Ignition temperature of ammonia as a function of heating rate for various zeolitic substrates.

form, sharp increases in temperature are recorded. An example of these curves is shown in Fig. 2 which depicts the thermodilatometric curve of zeolite A in its ammonium form at a 10°C min^{-1} heating rate. In this curve a sudden increase in temperature is evident starting at 390°C. All these thermodilatometric runs, when repeated in nitrogen atmosphere, did not exhibit any increase in temperature. The thermodilatometric behaviour of chabazite and zeolite X in their ammonium form appear very similar to that of ammonium zeolite A reported in Ref. [2]. Such behaviour appears to be amenable to the same interpretation and, thus, the suppositions developed for ammonium zeolite A in Ref. [2] seem to be valid even for ammonium chabazite and ammonium zeolite X. For these zeolites the acid sites, arising from ammonia evolution on heating [3,8], appear to catalyze the ignition of ammonia and its subsequent combustion giving rise to a sharp increase in temperature. This starts from different T_i values for each ammonium form. The DTA curves of ammonium chabazite and ammonium zeolite X do not exhibit, as ammonium zeolite A [2], any exothermic effect. Even in this case the same explanation appears valid for the three zeolites. The horizontal configuration of furnace chamber of dilatometer allows evolved ammonia to remain near the compact, whereas the vertical configuration of furnace chamber of DTA allows most of the evolved ammonia, which is lighter than air, to escape from the compact.

Other findings observed in Ref. [2] for ammonium zeolite A, are fully confirmed with ammonium chabazite and ammonium zeolite X. The thermal event related to the combustion of ammonia and the temperature at which the sudden increase starts, namely the ignition temperature of ammonia on the zeolitic substrate (T_i), steadily increases with increasing heating rate. The ignition temperature of ammonia on the zeolitic substrate is shown as a function of heating rate in Fig. 3. The fact that the thermal effect of ammonia combustion increases with increase in heating rate might be explained considering that even the process of deammoniation has its kinetics. At the lowest heating rate, a part of the evolved ammonia, at temperatures below ignition, has time to diffuse from the surface of the compact and, thus, does not burn. At the highest heating rate, ammonia have shorter times to diffuse giving rise to a more evident thermal effect due to the combustion. In this case, in fact, most of the ammonia present on the zeolite surface may burn at the same time.

A careful examination of the data reported in Fig. 3 may supply useful indication of the extent to which the zeolitic substrate catalyzes the combustion of ammonia. The presence of a zeolite in its hydrogen form dramatically lowers the usual ignition temperature of ammonia which is about 650°C on steel. The extent to which the ignition temperature of ammonia is lowered by a particular hydrogen zeolite could be taken as a measure of the catalytic activity of the zeolite itself, the lower the ignition temperature of ammonia the higher the catalytic activity. From this point of view, it appears that for heating rates lower than 10°C min^{-1} the catalytic activity decreases according to the order chabazite > X > A, whereas from 10°C min^{-1}

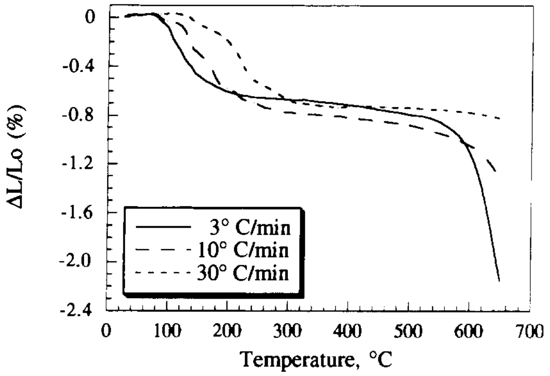

Fig. 4. Dilatometric curves in air of ammonium form of clinoptilolite at various heating rates.

onwards it decreases following the sequence chabazite ≅ X > A. This result appears to confirm the literature data. Actually the catalytic properties of zeolite Y, which is isostructural with zeolite X and differs from it only in the higher Si/Al ratio, are well known [3]. The high catalytic activity of chabazite should not be surprising. In fact, natural zeolites have not been considered of importance for catalytic uses mainly because they cannot offer the purity and homogeneity of synthetic zeolites. Nevertheless, the studies regarding the use of chabazite as a catalyst, reported in the literature [9–11], is evidence of its good catalytic activity towards various reactions such as the disproportionation of NO in N_2O and N_2O_3 or the oxidation of H_2S to S and H_2O.

Thermodilatometric curves of clinoptilolite in its ammonium form at 3, 10, 30°C min^{-1} heating rate are reported in Fig. 4. These curves do not display any sudden increase in temperature, which could be ascribed to ammonia combustion, at any heating rate. It looks as if the hydrogen clinoptilolite, arising from the thermal treatment of ammonium clinoptilolite, is not able to catalyze the combustion of the evolved ammonia unlike chabazite, A and X zeolites. However, the amount of ammonia evolved from ammonium clinoptilolite is lower than that evolved by chabazite, A and X zeolites owing to the lower exchange capacity. This lower amount of ammonia may not be sufficient to form a mixture with air whose composition falls within the flammability limits.

Another point that should be stressed is that the heating rate greatly affects the structural stability of clinoptilolite and, thus, its thermodilatometric behaviour. The three thermodilatometric curves display shrinkages of about 0.7% in the temperature range 20–300°C, whereas in the range 300–500°C there is a slightly decreasing trend. Above 500°C, the three heating rates give rise to markedly different behaviours. The curve performed at 3°C min^{-1} shows a very sharp shrinkage up to 2.2%, whereas the one performed at 30°C min^{-1} heating rate keeps its slightly decreasing trend with a final shrinkage of 0.8%. The curve performed at 10°C min^{-1} obviously exhibits a behaviour intermediate between the previous two. According to the findings of previous studies [1,2], the sharp shrinkage present in the final part of the thermodilatometric curve performed at 3°C min^{-1}, points out the thermal breakdown of the clinoptilolite with the subsequent formation of more compact phases. Such thermal breakdown only partially occurs at intermediate heating rate, as shown in Fig. 4. X-ray diffraction patterns of the samples subjected to thermodilatometric runs confirm these findings with increasing loss of crystallinity by decreasing the heating rate. The most likely explanation for this phenomenon is that a decrease in the heating rate keeps clinoptilolite for longer times at temperatures sufficiently high to undergo thermal breakdown, which does not occur at faster heating rates.

Fig. 5 reports the values of final shrinkage at 650°C for the zeolites in their ammonium form as a function of heating rate. Such shrinkages decrease in the order X > A > chabazite > clinoptilolite. This finding may be interpreted as follows: the lower the framework density the higher is the shrinkage. The framework density increases in the same order in which final

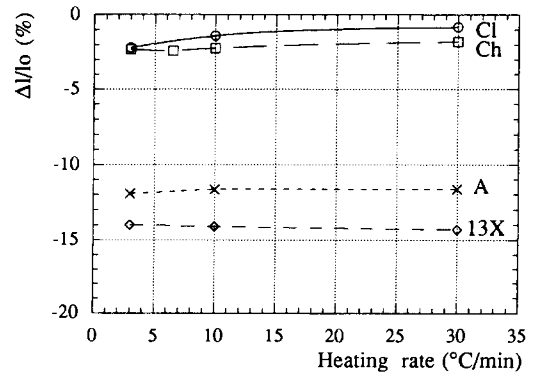

Fig. 5. Shrinkages at 650°C of various zeolites in their ammonium form as a function of heating rate.

shrinkage decreases. The heating rate does not sensibly affect the value of final shrinkage of zeolites A and X, unlike clinoptilolite for which the contrary holds. As far as chabazite is concerned, the increase in heating rate appears to slightly reduces the final shrinkage. These different behaviours may be explained considering that zeolites A and X do not undergo thermal collapse at any heating rates and that their low density structure allows fast dehydration and deammoniation kinetics. Chabazite do not undergo an evident thermal collapse but its slower dehydration and deammoniation kinetics gives rise to a slightly lower final shrinkage at the highest heating rate. The increasing final shrinkages of clinoptilolite with decreasing heating rate arise from the increasing extent to which thermal collapse occurs, as already pointed out.

4. Conclusions

This investigation was triggered off by the detection of an apparently anomalous thermodilatometric behaviour of ammonium zeolite A in a previous study [2]. This behaviour was ascribed to ammonia combustion catalyzed by the acid sites which arose in zeolite A microporous structure after thermal deammoniation. The results of this investigation appear to fully confirm this supposition inasmuch as ammonium chabazite and zeolite X display a thermodilatometric behaviour similar to ammonium zeolite A.

The difference in ignition temperature of ammonia on various zeolitic substrates, *ceteris paribus*, were ascribed to their different catalytic activity. Thus, the ignition temperature of ammonia might be interpreted as a measure of the catalytic activity of zeolite itself. Nevertheless, this supposition needs further confirmation, which appears to disclose a novel field of study: the use of thermodilatometry in the catalytic activity of zeolitic substrates.

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