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INVESTIGATION OF ZEOLITE-Y FORMS USING DIFFERENTIAL SCANNING CALORIMETRY AND ELECTRICAL CONDUCTIVITY

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ABSTRACT

Differential scanning calorimetry (DSC) curves and electrical conductivity σ were measured for three forms of zeolite-Y, namely NaY, HY and dealuminated HY (DAY). The DSC curves gave dehydration endotherms for all the forms, whereas the σ values have a number of breaks indicating higher mobilities of the charge carriers. NaY exhibited by far the highest conductivity values, mainly resulting from a large number of Na^+ ions in the presence of freely diffusing water molecules. DSC indicated a lower free diffusion of water molecules in the HY form which, together with a relatively weaker acidity, contributes to its lower σ values despite its high water content. The production of a relatively large percentage of Al^{3+} ions in DAY by dealuminating the mother zeolite HY, together with the presence of freely diffusing water in the zeolitic channels (despite the low water content of DAY), results in its σ values being higher than those of HY.

INTRODUCTION

Zeolites contain mobile cations which are located in cavities in the channel walls and coordinated with water molecules within the channels [1]. The electrical conductivity exhibited by zeolites is ionic and arises from the migration of cations through the zeolite framework. Stamires [2] has found that the electrical conductivity of zeolite-A and zeolite-X increases with increasing water content. He also found that water molecules diffuse freely within the structures of the zeolites and that the self-diffusion constant of Na^+ ions increases regularly with increasing hydration of the zeolite. This indicates that hydrated zeolite crystals behave similarly to solid electrolyte solutions. The use of zeolites as ionic conductors in solid state batteries has been described and their high temperature performance at 500 °C has been reported [3].

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Differential scanning calorimetry (DSC) has recently been used in combination with thermogravimetry (TG) to determine the precise water content of zeolites [4] as well as the chemisorptive capacity of their acid sites [5–8].

In the present work, the electrical conductivity of three forms of zeolite Y, namely NaY, HY and dealuminated HY (DAY), has been determined from room temperature up to around 300 ° C, and correlated with their DSC–TG water contents. Their chemisorptive capacities of a base have also been determined using DSC.

EXPERIMENTAL

Treatment of zeolites

A 5 g sample of NaY zeolite was boiled in 50 ml of 1 M NH_4NO_3 solution under reflux for 18 h. The flask was cooled overnight, then washed with distilled water till free of NO_3^-, filtered and dried overnight at 110 ° C. This treatment exchanges all Na^+ ions with NH_4^+ ions. Decomposition of the NH_4–Y produced by heating at 530 ° C for 4 h gives the HY form [9]. Dealumination of the HY form using HCl-leaching [10,11] produces the DAY form.

Electrical conductivity measurements

The three zeolite-Y forms were pressed into pellets of 13 mm diameter and 2 mm thickness using a pressure of 1200 kg cm^{-2}. The pellets were then coated with silver paste and the resistance was measured using a two-electrode method under nitrogen atmosphere in a thermostat adjusted to within ± 1.0 ° C. A temperature gradient was established across the sample, using the axial heat-flow method to measure the sign of the carriers which contribute to the electrical conduction.

DSC measurements

A Mettler DSC-30 unit of the TA-3000 system was used with the following conditions: initial temperature, 50 ° C; heating rate, 20 K min^{-1}; final temperature, 600 ° C; full scale range, 25 mW; purge gas, nitrogen at 50 ml min^{-1}; and sample weight, 10.0 mg for dehydration and 2.5 mg for TEA chemisorption. A conventional technique with the reference cell being an empty aluminium pan, was used to obtain the DSC curves of the zeolite forms (Fig. 1), whereas the nullifying DSC technique was used for measuring the chemisorptive capacity for bases. A triethylamine-presorbing sample was placed in the sample cell crucible and a triethylamine (TEA)-free sample

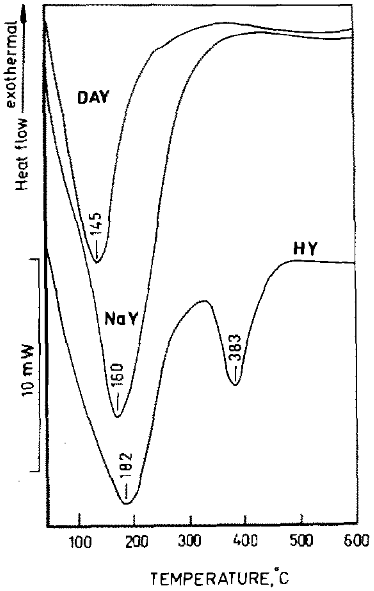

Fig. 1. DSC curves for NaY, HY and DAY using the conventional DSC procedure.

was placed in the reference cell. The enthalpy values obtained were taken to correspond to the chemisorptive capacity of the zeolite.

RESULTS AND DISCUSSION

The correlation of the electrical conductivities of zeolites with their DSC curves is not so direct as in the study of formulated compounds. Although the electrical conductivities in a given temperature range may show breaks and inflections due to phase transitions, the features appearing in DSC curves within the available DSC temperature range result from water desorption only, see Fig. 1. However, correlation of conductivity and DSC data gives useful information concerning the mobility of ions in zeolites.

Figure 1 shows the DSC curves of the three zeolite forms investigated using the conventional DSC measuring procedure. All features appearing in the 50–600 °C range available in the system employed are dehydration endotherms: peak temperatures (start, maximum and final) and dehydration enthalpies are listed in Table 1. Accordingly, the peak maximum temperatures are 160 °C for NaY, 182 °C and 383 °C for HY and 145 °C for DAY (the dehydration effect for HY is bimodal). The ΔH values obtained for these zeolite forms are 578 J g^{-1} (NaY), 322 J g^{-1} and 77 J g^{-1} (HY) and 215 J g^{-1} (DAY). Thermogravimetric evaluation of the DSC dehydration effects gives water contents of 36.5 wt.% (NaY), 20.9 wt.% and 5.1 wt.% (HY) and 14.0 wt.% (DAY). Thus, the water content of these zeolite forms is

TABLE 1

Enthalpy values for TEA-chemisorption [a] and DSC [b] and TG results for the three zeolite forms

Zeolite form	Chemisorption ΔH (J g^{-1})	First peak					Second peak				
		DSC results				TG water contents (wt.%)	DSC results				TG water content (wt.%)
		Temperature (° C)			ΔH (J g^{-1})		Temperature (° C)			ΔH (J g^{-1})	
		Start	Maximum	Final			Start	Maximum	Final		
NaY	965	50	160	340	578	36.5	–	–	–	–	–
HY	2009	50	182	300	322	20.9	300	383	450	77	5.1
DAY	145	50	145	220	215	14.0	–	–	–	–	–

[a] Using the nullifying DSC procedure for measurement.

[b] Using the conventional DSC procedure for measurements.

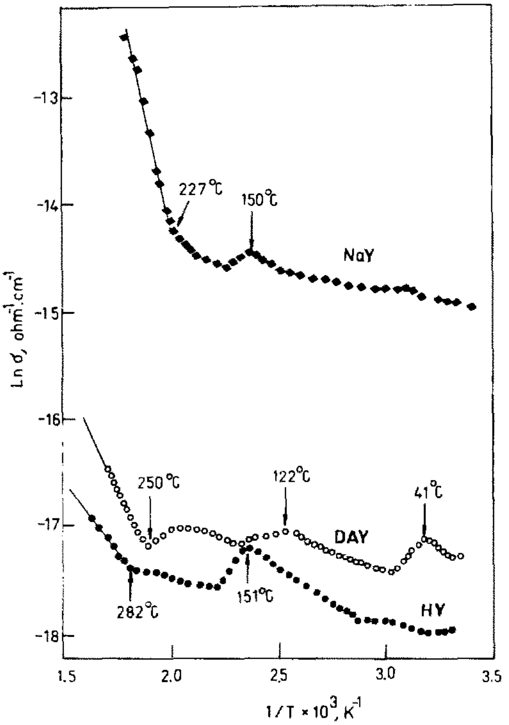

Fig. 2. Arrhenius plot of ln σ against $1/T$ for NaY, HY and DAY.

in the order NaY > HY > DAY. Removal of the Na^+ ions from the zeolite-Y structure produces a higher temperature dehydration peak indicating deeply situated, hindered water molecules and/or more strongly adsorbed water molecules. Removal of Al_2O_3 (to produce DAY) decreases the water content of the zeolite and considerably decreases its adsorption strength (Fig. 1 and Table 1), i.e. increases its free diffusion.

Table 1 also shows that the enthalpies obtained via TEA-desorption from NaY, HY and DAY are 965 J g^{-1}, 2009 J g^{-1} and 250 J g^{-1}, respectively. These enthalpies are proportional to the number of acid sites in the zeolites, which comprise both Brönsted (H^+ ions) and Lewis (Al^{3+} ions) types. Nevertheless, the chemisorptive capacities and, hence, acidities of the zeolites investigated are in the order HY > NaY > DAY.

Figure 2 shows the electrical conductivity, ln σ versus $1/T$ plots, where T is the absolute temperature, for the zeolite-Y forms studied. The conductivities decrease in the order NaY > DAY > HY; the conductivity of NaY is much larger by far than those of the two decationated forms, HY and DAY. The charge carriers in NaY are Na^+ ions together with H^+ and Al^{3+} ions, whereas in HY and DAY the charge carriers are H^+ and Al^{3+} ions only.

In the highest temperature region (Fig. 2), the ionic mobility in the zeolites is obtained by correlating the temperature at which the abrupt inflection of increasing conductivity appears, 227 ° C, 250 ° C and 280 ° C for NaY, DAY and HY, respectively, with the activation energies for this highest temperature region (beyond the conductivity inflections), 0.72 eV, 0.36 eV and 0.11 eV, respectively. Hence, the ionic mobility in this temperature region is in the order NaY > DAY > HY.

In the lower temperature range, several breaks appear in the conductivity values. These breaks are more pronounced for DAY than for NaY and HY, see Fig. 2. However, the common break at 150 ° C in the conductivities of NaY and HY implies similar thermal stabilities in their zeolitic structures. These two forms have the same $SiO_2 : Al_2O_3$ ratio (10 : 1) and so their ionic vicinities can be assumed to be structurally identical and different from that of DAY which has double this ratio (20 : 1). This above-mentioned break (at 150 ° C) appears to be shifted to the lower temperature of 122° C in the DAY conductivity curve. Moreover, a markedly lower temperature conductivity break appears as low as 41° C for DAY. This indicates the significantly larger mobility at lower temperatures of the charge carriers in DAY compared with those in NaY and HY. Hence an overall correlation of the conductivity curves in Fig. 2 may indicate that the highest temperature conductivity region is greatly influenced by the mobility of Na^+ ions, whereas the lower temperature conductivity is influenced by the acid-forming ions, particularly those produced by increasing the $SiO_2 : Al_2O_3$ ratio from 10 : 1 to 20 : 1. Kerr has found that 25% of the aluminium atoms in tetrahedral positions in the structure of zeolite-Y are converted to a cationic form after dealumination [12]. However, the mobility of oxygen ions in the framework structure of zeolite-Y can be excluded from this study as they were not measurable below 315 ° C [13].

Although DAY acquires the smallest number of water molecules compared with the other Y forms (see Fig. 1 and Table 1), its higher conductivity compared with HY (Fig. 2) can be attributed principally to its relatively higher Al^{3+} ion content, obtained during its dealumination; these ions are highly mobile in the presence of freely diffusing water molecules (the DSC peak maximum is 145 ° C, see Fig. 1). In contrast, the water molecules in HY are expected to be the least freely diffusing; this zeolite form has higher temperature dehydration peaks (with maxima of 182° C and 383° C).

The relatively higher ln σ values obtained for NaY, compared with HY and DAY (Fig. 2), can be principally attributed to the 56 Na^+ ions per unit cell freely diffusing with the largest number of water molecules (Table 1).

The increase in the strength of the zeolite acidity as a result of increasing the $SiO_2 : Al_2O_3$ ratio [14] may have a role in increasing the ln σ values of DAY relative to those of HY. Barthomeuf [14], Beaumont et al. [15] and Auroux et al. [16] have found that increasing the $SiO_2 : Al_2O_3$ ratio by removing part of the framework aluminium of zeolite-Y and ZSM-5 (dealumination) significantly increases their acid strength.

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