Superacid Sites in Zeolites

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Summary A scheme for solid superacids sites in zeolites is proposed which implies interactions between protonic sites and polymeric oxoaluminium deposits in the zeolite voids.

The high strength of protonic acidity in zeolites has long been thought to be related to an inductive influence of other species, such as cations[1,2] or, more generally, Lewis centres.[3,4] The subsequent increase in acid strength has been correlated with an improvement in the catalytic activity in carbonium ion reactions.[3,5,6] This suggested to Jacobs *et al.*[5,6] that the active sites are 'ultra-active' or 'superactive' hydroxyl groups. Very recently[7] it was suggested that in toluene disproportionation, some

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mordenite samples could activate hydrogen in the same way as a superacid medium does,[8] and this reduces coke formation. This very interesting suggestion led us to consider whether superacidity could originate in some zeolites from the combination of specific Brönsted and Lewis sites.

The mordenites studied[7] and described[9] previously show an acidity which depends on the pretreatment conditions. The programmed ammonia thermodesorption performed on dry-air pretreated and on steamed mordenites gives the curves depicted in the Figure. The broad 400 °C peak in the dry-air-pretreated mordenite [curve (a)] has been assigned to protonic acidity [ν(OH) 3610 cm^{-1}]. The steaming eliminates these sites [curve (b)] and at the same time a new peak of ammonia thermodesorption appears at 570 °C which may correspond to new and stronger sites. Simultaneously the catalytic activity in toluene disproportionation is improved from the original 2×10^{-4} mol g^{-1} h^{-1} of toluene converted at 500 °C for the dry-air-pretreated sample to 18×10^{-4} mol g^{-1} h^{-1} for the steamed catalyst.[9] We have previously shown that steaming removes some of the framework Al atoms,[10] in agreement with Kühl's statement,[11] to give polymeric oxoaluminium species, $(AlO)_p^+$, deposited in the channels. The high catalytic activity of the steamed mordenite may arise from two effects occurring upon steaming, the elimination of coking sites or the formation of active sites giving less coke. With regard to the latter hypothesis, we suggest that the new strong sites, indicated in thermodesorption by the 570 °C peak, may be superacids active in toluene disproportionation. The superacidity could arise from an interaction between protonic and Lewis sites such as occurs in, *e.g.*, the systems $AlCl_3$–HCl and SbF_5–HF, *etc.*[12] In this proposal the protonic sites are hydroxyl groups of the zeolitic aluminosilicic acid referred to as $(Si,Al)O_n(OH)_m$[13] and the Lewis sites are the $(AlO)_p^+$ species formed during steaming.[11,14] The latter are embedded in the zeolites as described in Y zeolites[15] or mordenites[11] and behave as if they were dissolved in the zeolite framework which itself acts as a crystalline acid liquid[13] and electrolytic medium.[16] Such a system, typical of zeolites, can be schematically represented as the couple:

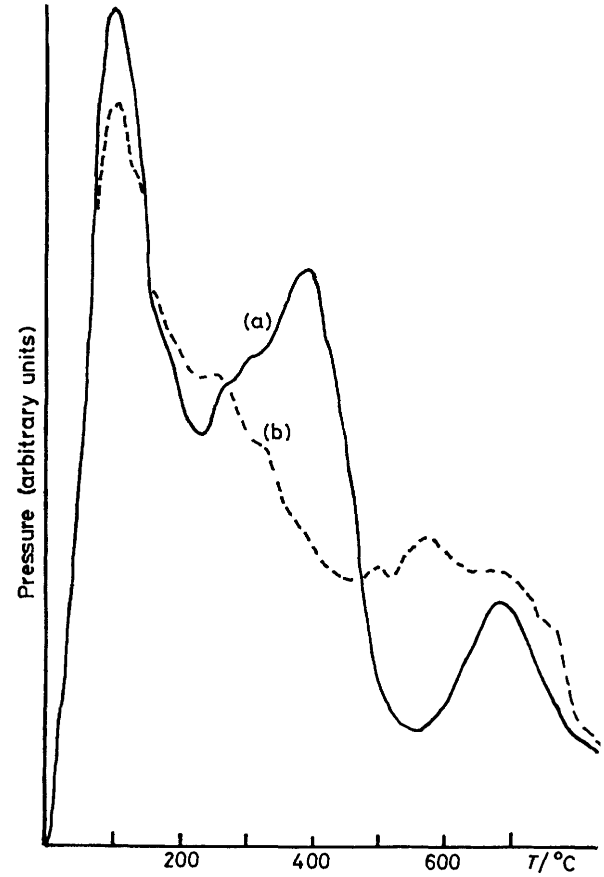
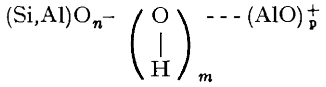


Figure. Changes in ammonia thermodesorption (heating rate 8 °C/min) as a function of temperature for dry-air-pretreated [curve (a)] or steamed [curve (b)] mordenite samples. (For experimental conditions see ref. 9).



$$(Si,Al)O_n\text{–}\left(\begin{array}{c}O\\ |\\ H\end{array}\right)_m \text{---}(AlO)_p^+$$

The interaction would consist of a partial electron transfer from the OH bond to the $(AlO)_p^+$ species which by decreasing the OH bond strength of the site would increase the proton lability and hence the acid strength of the site. The increase in protonic acid strength would be less than that observed in typical liquid fluorinated superacids but it is significant enough owing, presumably, to the high electronegativity of the oxygen atoms (intermediate between that of F and Cl atoms). Owing to the superacidity of these sites a small concentration would be enough to improve markedly the catalytic properties.

We thank Dr. Ch. Marcilly for the gift of the samples and Prof. M Guisnet for helpful discussions.

(*Received, 22nd September* 1980; *Com.* 1030.)

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