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NOTES

Comparison Between Trapping of H Atoms Created by γ-Irradiation and Catalytic Activity of NaH-Y and Dealuminated Y Zeolites

Certain catalytic reactions proceeding by a carbonium ion mechanism such as isomerization or cracking reactions are generally associated with specific properties of the catalyst, e.g., nature of cation (*1*), acidic strength of Brønsted sites (*2*), etc. We have shown in a previous work (*3*), that for γ-irradiated zeolites, the formation and the trapping of H atoms should obey the following equilibrium:

According to this scheme it has been concluded (*3*) that the trapped H atom yield depends on three main factors: (i) the nature of the trapping site characterized by the EPR linewidth, ΔHpp, of the H atom doublet, (ii) the trapping strength of sites, characterized by the A_0–A shift between the hyperfine splitting constants of a trapped H atom, A, and a free H atom, A_0, (iii) the Brønsted acidity strength and number of structural hydroxyl groups, since for a given concentration of OH groups one would expect a correlation between the H atom yield and the Brønsted acid strength. Thus, if the two first factors are kept unchanged, the behavior of the H atom yield and of the Brønsted acidity are expected to be similar. In this respect, materials used for the present work have been chosen such that the values of A and ΔHpp stay constant in all experiments.

The starting material was NaY zeolite supplied by Linde Union Carbide Co. The Na^+ ions were conventionally exchanged by NH_4^+ ions from NH_4NO_3 solution until different levels were reached. The samples after deammoniation will be denoted Na H-Y. For some experiments, samples with 90% of Na^+ ions exchanged by NH_4^+ were more or less dealuminated by treatment in aqueous solution of EDTA (*4*). The samples will be denoted De H-Y after deammoniation. The crystal structures of these aluminum deficient samples as monitored by X-rays, are not disturbed until a critical level of dealumination is reached (25–30 extracted Al atoms per unit cell). However, a small shrinkage of the unit cell is observed with increasing degree of dealumination.

The samples were placed in EPR tubes, heated in 160 Torr of oxygen for 15 hr and then evacuated at 700°K and $10^{-5}/10^{-6}$ Torr to obtain the H form of the zeolites. Irradiation was performed at 77°K in a ^{60}Co cell and EPR spectra were recorded at 77°K.

For zeolites, each EPR line of the H atom doublet corresponds to the superposition of two underlying lines, B and N, due to H atoms trapped on two different sites. The peak to peak width values are, respectively, 3.6 (B) and 1.25 (N) Oe, and the A values are 499.8 and 501.8 Oe. For all samples the values of ΔHpp and A have remained constant for both lines indicating that trapping strengths and trapping sites have remained unchanged.

It was shown (*3*) that H atom yield depends on OH group content. According to

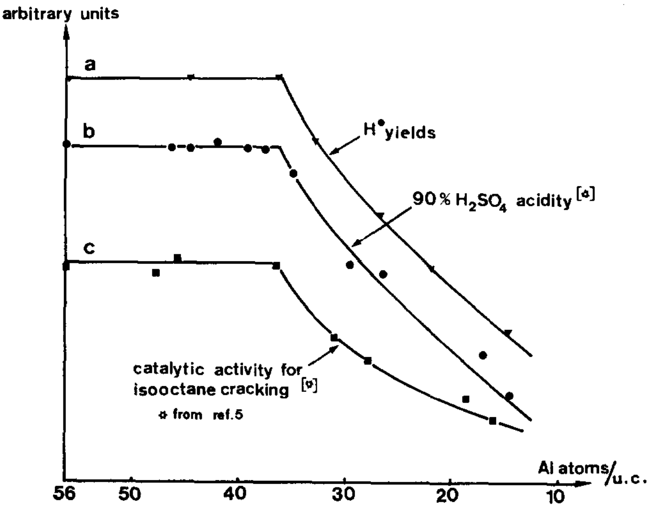

FIG. 1. H atom yields [lines N and B (a)], strong Brønsted acidity [$\geq 90\%$ H_2SO_4 (b)] from Ref. (*5*) and catalytic activity for isooctane cracking (c) from Ref. (*5*) as a function of dealumination of zeolite.

the above equilibrium it can be expected that the more acidic the OH groups, the more easily may the H atom be set free under irradiation. As a matter of fact for aluminum deficient zeolites De H-Y it can be observed that H atom yields (Fig. 1), strong acidity ($>90\%$ H_2SO_4) as determined using Hammett indicators (*5*) and catalytic activity for isooctane cracking (*5*) are closely correlated. These results agree with the conclusions of different authors (*6*) who have suggested that the active centers for cracking reactions on decationated and dealuminated zeolites are hydroxyl groups with mobile protons.

It has been observed that microwave saturation for line B is heterogeneous whereas it is mainly homogeneous for line N. Consequently, line B is due to an envelope of many individual lines of H atoms which may correspond to slightly different hyperfine constants, within a range of less than the linewidth, namely ±1.8 Oe with respect to the average value of $A = 499.8$

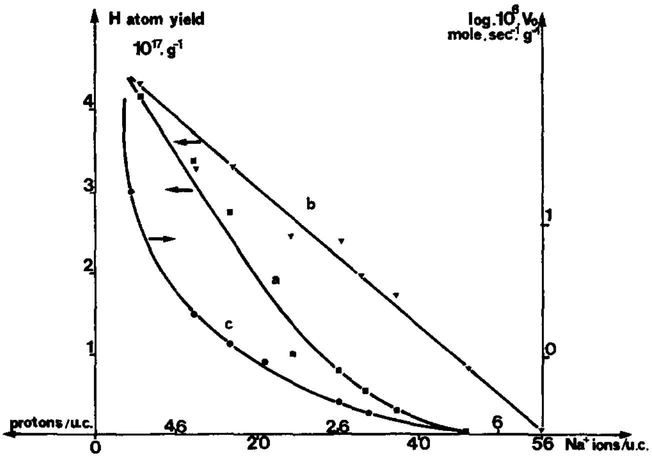

FIG. 2. H atom yields [lines N (a) and B (b)] and catalytic activity for isooctane cracking (c) from Ref. (*7*) as a function of Na^+ content.

Oe, i.e., to slightly different trapping strengths. Moreover, it is noteworthy that the average A_0–A shift for line *B* H atoms is larger than for line *N* H·, which may indicate that the line *B* H atoms are then more strongly trapped in their sites. Considering the above data, and the heterogeneity of the zeolite relative to the strengths of Brønsted acid sites (*5*), one may then suggest that the two lines, *B* and *N*, characterize the strong acid OH groups, but that the range of acidity measured via line *B* is spread towards weaker strengths of acidity than that of line *N*.

The curves in Fig. 2 represent the variations of the H atom yields corresponding to the two EPR lines compared to the catalytic activity for isooctane cracking (*7*) as a function of the exchange ratio of Na^+ by H^+ on Na H-Y samples. It can be observed that it is necessary to reach 30% of Na^+ ions exchanged by protons to obtain catalytic activity. This exchange level corresponds to the appearance of strong acid centers (*8*). This definite variation from linearity at low sodium contents was also observed for other reactions (*9–12*). Ward and Hansford (*9*) suggested that it corresponds to an increasing effectiveness per sites with increasing ion exchange.

Our results indicate that the strong acid OH groups giving rise to trapped H atoms, as evidenced by line *N*, markedly contribute to catalytic activity. According to the linear relationship between H atom yield for line *B* and the exchange level of Na H-Y samples, it may be concluded that not all the corresponding OH groups are active sites. However, as shown above, the latter groups correspond to a large range of acid strengths. Consequently it is possible that a part of them, namely the more strongly acidic ones, are also active sites.

The last 16 OH groups introduced into the zeolite lattice were shown by ir to be inaccessible to the reactant molecules. Moreover, it is interesting to note that the relationship between the H atom yield from line *N* and OH groups corresponding to the 3550 cm^{-1} ir band are similar as a function of exchange level (*13*). However, at variance with our findings, it is generally considered that 3550 cm^{-1} OH groups are not only inaccessible to reactant but also are nonacidic. In order to explain the catalytic activity described above, Ward and Hansford (*9*) suggested that a mutual enhancement of sites occurs as their separation decreases. Our results indicate that OH groups with protons of greater mobility are able to give rise to H atoms under γ-irradiation. We therefore suggest that the most mobile protons, which give rise to line *N* H atoms, and presumably also a part of the line *B* H atoms, are the active sites for catalytic reactions.

In conclusion, a correlation between H atom yields, strong Brønsted acidity and catalytic activity has been observed when trapping strengths and trapping sites of H atoms are kept unchanged. These results are in agreement with the conclusions of many authors who have suggested that only a fraction of the structural OH groups, namely the most acid ones, are active. In this respect the number of trapped H atoms ($\simeq 10^{16}$–10^{17}/g) is comparable with the number of active centers as generally postulated (*14*).

Although some parameters of trapping (strength and nature of trapping sites) are limiting, the method proposed allows one to distinguish Brønsted from Lewis acid sites and does not necessitate the use of any solvent, base or indicator. One may conclude that the active sites for reactions proceeding via a carbonium ion mechanism would be the most acidic structural OH groups, which under γ-irradiation yield H atoms which are trapped within the zeolite.

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