Evidence that Butane Disproportionation demands Adjacent Acid Sites

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In the disproportionation of butanes over protonic mordenites with a Si/Al ratio between 8 and 110, the activity of the acid sites increases with their density which shows that in this reaction at least two acid centres intervene.

In metallic catalysis it is clearly proven that many reactions require several sites for their catalysis (so called structure-sensitive reactions), whereas the same is not the case for acid catalysis. It has been suggested however, that adjacent acid sites are essential for the catalysis of various bimolecular reactions. Thus to account for the kinetics of disproportionation of alkylaromatic compounds, several authors[1—3] propose a mechanism involving as a kinetically limiting step a reaction between two aromatic molecules adsorbed over adjacent sites. Moreover on protonic mordenites the ratio between the disproportionation and the isomerization rates of xylenes decreases with the density of the acid sites; the only explanation for this decrease lies in the fact that if isomerization is an intramolecular reaction and requires one single acid centre for its catalysis, disproportionation, a bimolecular reaction, requires two.[4] We show in this paper that the density of the protonic mordenite acid centres is the parameter which determines their activity in butane disproportionation and that this reaction therefore requires adjacent acid sites.

The butane transformation rates were measured under the following conditions: recycling reactor, $\theta = 350$ °C, $p(H_2) = 0.9$ bar, $p(C_4) = 0.1$ bar, over a series of protonic mordenites prepared by dealumination. The Si/Al ratio of the samples varied from 7.5 to 110 and the total acid centre densities (n_t) from 1.8 to 0.14 mequiv. per gram (Table 1). The acidity of the mordenites was characterized by thermodesorption of NH_3. In agreement with the literature, the higher the Si/Al ratio, the stronger the acid centres. The difference in strength of the acid centres does not seem to be very significant, however; thus, whereas the ratio between the total number of sites of M and of MD_4 equals 13, the ratio between the number of sites of M and MD_4 capable of retaining NH_3 above 200 °C equals 7.5.

The butane transformation rates increase when the number of acid sites of the samples increases. However, the greater the value of the mordenite Si/Al ratio, the lower the density of the acid centres, and the lower the activity per acid centre. Figure 1 shows that this activity is roughly proportional to the square of the total number of the acid centres (n_t^2) and to the square of the number of the acid centres capable of retaining NH_3 adsorbed above 200 °C (n_{200}^2).

This decrease of the acid centre activity with density cannot be explained by the change in the strength of the acid centres since the lower the density the greater the strength. Neither can the different deactivation of mordenites explain this decrease since the stability of the samples increases with their Si/Al ratios. The most likely explanation is therefore that

Table 1. Characteristics of the mordenite samples.

Name	Unit cell	n_t mequiv. g^{-1}	n_{200},[a] mequiv. g^{-1}
M	$Na_{0.5}H_{5.2}Al_{5.7}Si_{42.3}O_{96}$	1.8	0.55
MD_1	$Na_{0.4}H_{5.2}Al_{5.6}Si_{42.4}O_{96}$	1.8	
MD_2	$Na_{0.4}H_{3.0}Al_{3.4}Si_{44.4}O_{96}$	1.05	
MD_3	$Na_{0.3}H_{2.4}Al_{2.7}Si_{45.3}O_{96}$	0.85	0.29
MD_4	$Na_{0.05}H_{0.4}Al_{0.45}Si_{47.55}O_{96}$	0.14	0.075

[a] n_{200} = density of sites capable of retaining NH_3 adsorbed above 200 °C.

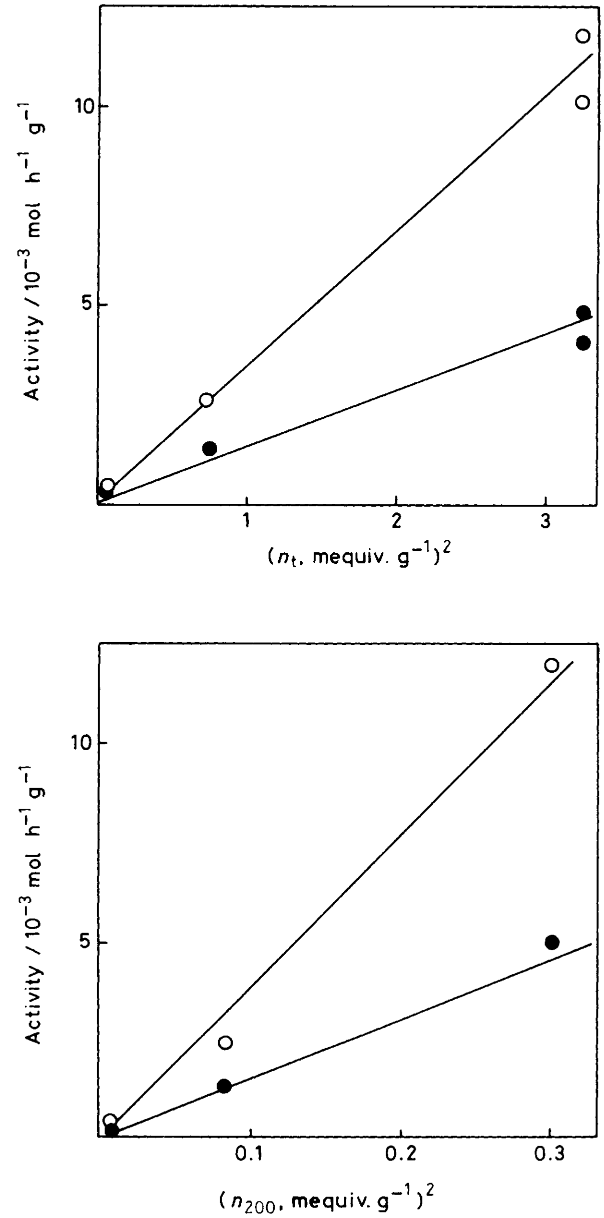

Figure 1. Iso- (○) and n-C_4 (●) disproportionation: change of the activity of the mordenites *vs.* square of the density of their acid sites: (a) n_t, total acid centre density; (b) n_{200}, density of acid sites capable of retaining NH_3 adsorbed above 200 °C.

butane disproportionation requires for its catalysis adjacent acid centres. This is in good agreement with the mechanism proposed for this bimolecular reaction[5] which implies as a first step the formation of two carbenium ions in C_4 and probably requires two adjacent Brønsted acid sites.

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