Acidity–activity relationship in zeolite Y. A preliminary study for *n*-heptane transformation

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The transformation of *n*-heptane at 350°C has been studied on a variety of Y zeolite catalysts. The acidities of these samples were determined by temperature-programmed desorption of ammonia and, by using a numerical deconvolution technique, the acid strength distribution for the sites of each catalyst was obtained. Using these results we were able to correlate the catalytic activity with the acid strength distribution for all the catalysts using a Brønsted type equation, similar to the one that is used in homogeneous acid catalysis.

Keywords: acid catalysis, zeolites, catalytic cracking

1. Introduction

The Brønsted equation [1] describes the relation between the rate of an homogeneously acid-catalysed reaction and the acid strength of the catalyst, as measured by its dissociation constant. A similar relation for heterogeneous catalysis has been sought for a long time by researchers working in this field [2].

There are two main difficulties in obtaining this relation: one is the fact that the surface of the solids does not possess a unique acid strength, but rather a distribution of acid strengths, making it difficult to define a suitable *acid strength*, since the catalytic activity is the superposition of the catalytic activity of all the active sites with different acid strengths. The other difficulty lies with the measurement of acid strength distribution of the actual catalysts.

This last topic has been addressed by several authors [3–6] using temperature-programmed desorption of ammonia. The authors have also proposed a method for the numerical deconvolution of TPD data to obtain acid strength distributions.

In the present work we have characterised the acid strength distribution of a series of Y zeolite catalysts by means of the activation energy for the desorption of ammonia, obtained by temperature-programmed desorption (TPD), and measured their catalytic activity towards the cracking of *n*-heptane. A Brønsted type correlation between the activity and the acidity was obtained, of which we are presenting a preliminary report.

2. Experimental

The catalysts that were used have been obtained from the sodium form of Y zeolite (LZY52 – Union Carbide) by successive exchanges with ammonium nitrate and/or rare earth nitrate solutions. The final acid forms of the catalysts were obtained by calcination at 480°C for 8 h under a flow of dry air (0.5 ℓ/(h g)). The catalytic behaviour of some of these catalysts has been published previously [7–10]. The compositions of the catalysts that were used are presented in table 1.

Adsorption of ammonia was carried out at 90°C, after which the temperature was increased at a rate of approximately 10°C/min from 90 to 500°C. About 200 mg of catalyst was used with a flow of dry helium of 60 ml/min. The NH_3 that desorbed was measured by a thermal conductivity detector and the electrical signals from the detector and from the thermocouple (that measures the temperature inside the cell with the catalyst) were digitised by a CR3A chromatographic integrator and transmitted to a computer.

Table 1
Composition of the catalysts used in this work

RENaY series	NaY	$(Na)(AlO_2)(SiO_2)_{2.36}$
	LaNaY	$(La_{0.228}Na_{0.316})(AlO_2)(SiO_2)_{2.36}$
	CeNaY	$(Ce_{0.213}Na_{0.361})(AlO_2)(SiO_2)_{2.36}$
	PrNaY	$(Pr_{0.246}Na_{0.262}(AlO_2)(SiO_2)_{2.36}$
	NdNaY	$(Nd_{0.202}Na_{0.394})(AlO_2)(SiO_2)_{2.36}$
REHNaY series	HNaY	$(H_{0.703}Na_{0.297})(AlO_2)(SiO_2)_{2.36}$
	LaHNaY	$(La_{0.145}H_{0.307}Na_{0.258})(AlO_2)(SiO_2)_{2.36}$
	CeHNaY	$(Ce_{0.144}H_{0.309}Na_{0.259})(AlO_2)(SiO_2)_{2.36}$
	PrHNaY	$(Pr_{0.137}H_{0.346}Na_{0.243})(AlO_2)(SiO_2)_{2.36}$
	NdHNaY	$(Nd_{0.117}H_{0.389}Na_{0.260})(AlO_2)(SiO_2)_{2.36}$
REHY series	HY	$(H_{0.920}Na_{0.080})(AlO_2)(SiO_2)_{2.36}$
	LaHY	$(La_{0.191}H_{0.345}Na_{0.082})(AlO_2)(SiO_2)_{2.36}$
	CeHY	$(Ce_{0.155}H_{0.455}Na_{0.080})(AlO_2)(SiO_2)_{2.36}$
	PrHY	$(Pr_{0.147}H_{0.481}Na_{0.078})(AlO_2)(SiO_2)_{2.36}$

The catalytic activity measurement for the transformation of *n*-heptane was made in a fixed bed reactor at 350°C and atmospheric pressure. A 60 ml/min flow of dry nitrogen was used, and *n*-heptane was fed at a rate of 3 ml/h. 200 mg of catalyst were also used in the reactor. In all cases the catalyst was pre-treated in situ at 450°C for 12 h under a low flow of dry nitrogen.

3. Results and discussion

3.1. Temperature-programmed desorption data

Although the strength of adsorption of the sites in a particular catalyst is likely to follow a quasi-continuous distribution, we can consider that the acid strength distribution can be well approximated by a finite set of activation energies for the desorption of ammonia.

The rate of desorption $-\mathrm{d}q/\mathrm{d}t$ for a given temperature can then be computed as the summation of the contributions originating from the sites of each of the energies considered,

$$-\frac{\mathrm{d}q}{\mathrm{d}t} = \sum_i \frac{\mathrm{d}q_{E^i}}{\mathrm{d}t} . \qquad (1)$$

Assuming that desorption is irreversible, that there is no interaction between adsorbed species, and that the Arrhenius equation applies, each of the individual temperature-programmed desorption profiles, corresponding to sites with uniform energy, can be computed by integrating the equation

$$-\frac{\mathrm{d}q_{E^i}}{\mathrm{d}t} = k_{E^i} \mathrm{e}^{-E^i/RT} q_{E^i} , \qquad (2)$$

subject to the initial condition that, at $t = 0$, the total amount of sites is $q_{E^i 0}$. If one can compute the contributions from each of the energies in the set, it is possible to decompose an experimental thermogram by means of multi-linear regression to obtain the values of $q_{E^i 0}$, which corresponds effectively to the acid strength distribution, provided we consider that the activation energy for the desorption of ammonia is a good measure of the acidity of a site.

These contributions were computed using the expression proposed by Hashimoto to obtain the corresponding values of k_E as a function of E [3]. Using a least-squares regression technique in a commercial spreadsheet program, the values of $q_{E^i 0}$ were estimated. In figure 1 one of the fittings obtained is depicted, along with the acid strength distribution for some of the catalysts.

3.2. Acidity–activity correlation

We will next consider the possibility of correlating the acid strength distribution data with the catalytic activity data.

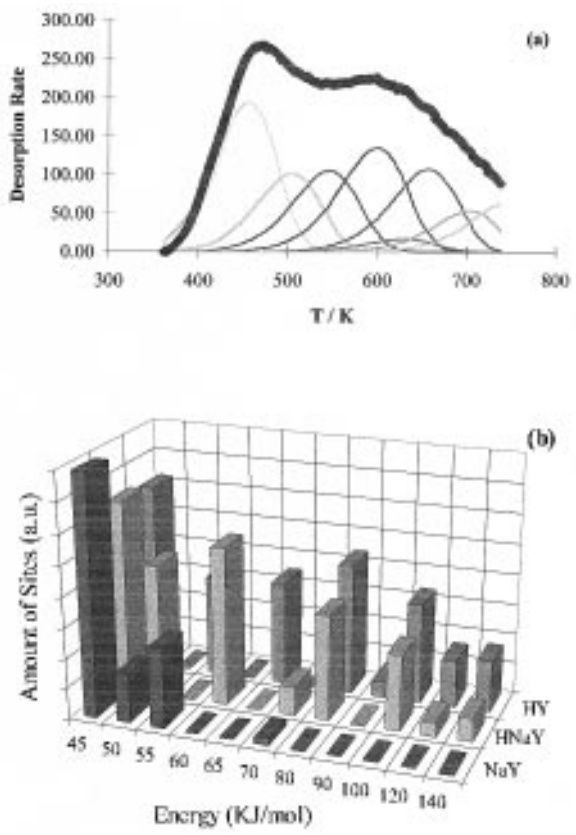

Figure 1. Fitting of the temperature-programmed desorption data for the HY catalyst and respective decomposition into mono-energetic desorption curves (a) and acid strength distribution for the NaY, HNaY and HY catalysts (b).

It is widely accepted that the model reaction used in this study of the cracking of *n*-heptane is mainly influenced by the acid strength of the sites in the catalyst. We consider, again, that there is no significant interaction between the sites with different energies and thus that we may apply a Brønsted type relation to the ensemble of sites having the same activation energy for the desorption of ammonia.

The global catalytic activity can then be computed as the summation for all the sites in the catalyst, as

$$A_{\mathrm{exp}} = \sum_i q^i_{E0} \alpha \mathrm{e}^{\beta E^i} , \qquad (3)$$

where α and β are parameters which should depend mostly on the reaction under study, in a way similar to the Brønsted relations for homogeneous catalysis. Using a least-squares technique, the activity data and the sets of (E^i, $q_{E^i 0}$) values obtained previously, the values of α and β were estimated. As seen in figure 2, a good correlation between experimental and calculated activity values is obtained.

4. Conclusions

Using NH_3 TPD it seems possible to characterise the

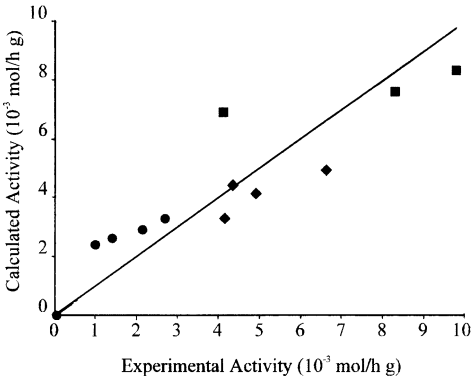

Figure 2. Correlation between experimental and calculated activity values for the transformation of *n*-heptane in the series of catalysts used in this work. (●) RENaY series; (◆) REHNaY series; (■) REHY series.

acid strength distribution of acidic zeolite catalysts and quantitatively to correlate this information to the catalytic behaviour of the catalysts using Brønsted type relations, like the ones used in homogeneous catalysis.

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References

[1] K. Laidler, *Chemical Kinetics*, 3rd Ed. (Harper and Row, New York, 1987).
[2] D. Barthomeuf, in: *Catalysis in Acids and Bases*, eds. B. Imelik et al. (Elsevier, Amsterdam, 1985) p. 75.
[3] K. Hashimoto, T. Masuda and T. Mori, in: *New Developments in Zeolite Science and Technology*, Studies in Surface Science and Catalysis, Vol. 28, eds. Y. Murakami, A. Iijima and J.W. Ward (Kodansha/Elsevier, Tokyo/Amsterdam, 1986).
[4] E. Dima and L.V.C. Rees, Zeolites 7 (1987) 219.
[5] H.G. Karge and V. Dondun, J. Phys. Chem. 94 (1990) 765.
[6] L. Forni and E. Magni, J. Catal. 112 (1988) 437.
[7] F. Lemos, F. Ramôa Ribeiro, M. Kern, G. Giannetto and M. Guisnet, Appl. Catal. 29 (1987) 43.
[8] F. Lemos, F. Ramôa Ribeiro, M. Kern, G. Giannetto and M. Guisnet, Appl. Catal. 39 (1988) 227.
[9] F. Lemos, J.M. Lopes and F. Ramôa Ribeiro, J. Mol. Catal. 53 (1989) 265.
[10] F. Lemos, J.M. Lopes, F. Ramôa Ribeiro and M. Guisnet, React. Kinet. Catal. Lett. 41 (1990) 390.