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Activity–acidity relationship in zeolite Y
Part 3. Application of Brönsted type equations

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Abstract

The relation between activity and acidity in a variety of Y zeolite catalysts for the transformation of small olefins: ethene, propene, 1-butene and iso-butene, is presented. The acid site distribution of these samples was estimated by temperature-programmed desorption of ammonia, by using a numerical deconvolution technique. This information was then correlated with catalytic activity measurements using Brönsted type equations. Despite the complexity of calculations it is clear that this gas phase solid acid catalysed reactions follow simple rules, similar to the one observed in homogeneous processes. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many of the industrial catalytic applications of zeolites are examples of acid catalysed reactions on a solid surface. Thus, in the study of these catalysts a great effort has been made to characterise the acidity of the zeolites, and a great number of methods is currently used by researchers in this field [1–3]. Nevertheless, the wide range of acid strengths that can be found in the zeolites surface, depending on its structure and composition [4], makes the estimation of acid site strength distribution somewhat difficult.

The qualitative analysis of the influence of acidity in the transformation of light olefins has been done in part 1 [5] of this paper. In part 2 [6] we presented a digital decomposition method that allows the estimation of acid site strength distribution using a single temperature programmed desorption of ammonia experiment, and we will now combine this information to obtain a quantitative relation.

It is well known that the catalytic properties of zeolites, such as activity and selectivity, are extremely dependent on acidity. Qualitative relationships between activity and acidity are referred to in several works [7–16].

Acid catalysed reactions in homogeneous phase are known to abide certain rules that make the kinetic constant a function of the acid strength of the catalyst—the Brönsted equations [17]. Similar relations have been sought by those working in the field of heterogeneous catalysis

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[18]. The main problems that have hindered the solution of this problem are:

1. the characterisation and measurement of the acid strength distribution of solids;
2. the establishment of a unique scale of acidity strength similar for instance to the pK_A one in the solution;
3. the possible existence of different reactions mechanisms that operate simultaneously.

An additional problem is that even if the number of acid sites, and corresponding strength, are known, it may be difficult to know how many sites are accessible for a given reaction. Thus, it may be very difficult to quantify the effects of the number of acid sites and the strength of the acid sites in the catalytic activity for the reaction.

We have already presented a preliminary report [19] where we studied the acidity in a series of rare earth exchanged Y zeolite catalysts. This information was correlated with their catalytic activity towards the cracking of *n*-heptane. Brönsted-type equations were obtained in this case.

In this paper, we will start by presenting a description of the background that has to be considered in order to use Brönsted-type equations for heterogeneous catalysis. Then we will show how the acid site strength distribution results for two series of catalysts, HNaY and HNaUSY, can be correlated with the results of catalytic activity of the same zeolites for the transformation of ethene, propene, 1-butene and iso-butene.

2. Theory

In present work we intent to correlate the acid strength distribution data with the catalytic activity data. We will assume that the activation energy for ammonia desorption is a direct measurement of the strength of an acid site. By analogy with the Brönsted relations for homogeneous catalysis, the catalytic activity to an ensemble of sites with uniform energy, E^i, can be described by the following equation:

$$A_c^i = \alpha_c e^{\beta_c E^i} \tag{1}$$

where α_c is the constant which expresses the intrinsic activity of a chemical reaction, i.e., the activity when the catalyst acidity tends to zero and β_c the constant which expresses the chemical reaction sensitivity towards the acidity of the site. The parameters α_c and β_c should depend mostly on the reaction under study, in a way similar to the Brönsted relations for homogeneous catalysis but can also have some dependence on the catalyst structure itself.

The catalysts have sites with widely different acid strength and we will consider no significant interaction between sites with different energies. The acid side distribution on catalyst surface is characterised by the number of acid sites, q_{E0^i}, with activation energy for ammonia desorption, E^i. Thus, the global catalytic activity, A_c (mol/h g), will be the weighted summation of the contributions from all the possible energies, resulting in Eq. (2).

$$A_c = \sum_i q_{E0^i} \alpha_c e^{\beta_c E^i} \tag{2}$$

The E^i and q_{E0^i} values can be estimated applying the deconvolution method, described in part 2 [6] of this paper, on temperature-programmed desorption (TPD) of ammonia thermograms experimentally obtained.

The catalytic activity values computed by Eq. (2) can be compared with experimental values and the parameters α_c and β_c can be estimated by non-linear least square regression. The computations presented in this paper were performed in Excel 5 (© Microsoft) using the solver tool to minimise the sum of the square of the residuals.

3. Experimental

3.1. Catalysts

Two series of catalysts, based on two different forms of zeolite Y were used. The HNaY series of catalysts was obtained from the NaY zeolite (LZ-Y52—Union Carbide) by successive ion-exchange with NH_4NO_3 solutions and the HNaUSY series of catalysts was obtained from the NH_4USY zeolite (LZ-Y82—Union Carbide) by successive ion-exchange with $NaNO_3$ solutions.

Details of the preparation and composition of the catalysts have been given in parts 1 and 2 [5,6] of this paper.

3.2. TPD experiments

Adsorption of ammonia was carried out at 90°C, after which temperature increases with a linear heating rate of approximately 7.5°C/min from 90°C to 700°C.

Details about the TPD apparatus and the procedure used were described in part 2 [6] of this paper.

3.3. Catalytic experiments

The catalytic activity measurements for the transformation of ethene, propene, 1-butene and iso-butene were carried out in a fixed reactor at 350°C and atmospheric pressure.

Experimental details have been given in part 1 [5] of this paper.

4. Results

4.1. HNaY series of catalysts

The distribution of acid site strengths, in catalysts of HNaY series, as a function of activation energy for ammonia desorption (see part 2 [6] of this paper) were correlated with the results of catalytic activity of the same zeolites for the transformation of ethene, propene, 1-butene and iso-butene after 6 min of reaction (see part 1 [5] of this paper). Using the procedure described above the α_c and β_c parameters

Table 2
Calculated, A_c, and experimental, A_{exp}, catalytic activity values for the transformation of the olefins over HNaY series of catalysts

Reagent	Catalyst	$A_c \times 100$ (mol/h g)	$A_{exp} \times 100$ (mol/h g)
Ethene	NaY	0.03	0.10
	HNaY25	0.09	0.09
	HNaY40	0.09	0.08
	HNaY73	0.12	0.04
	HNaY80	0.06	0.05
	HNaY85.5	0.04	0.05
	HNaY91	0.12	0.12
Propene	NaY	0.74	0.13
	HNaY25	2.45	1.06
	HNaY40	2.70	2.10
	HNaY56	3.92	3.43
	HNaY73	3.90	4.23
	HNaY80	1.76	3.61
	HNaY85.5	1.38	3.79
	HNaY91	4.42	4.20
1-Butene	NaY	1.62	0.24
	HNaY25	5.08	3.59
	HNaY40	5.21	5.39
	HNaY56	6.53	6.28
	HNaY73	6.26	6.53
	HNaY80	3.38	5.81
	HNaY91	4.85	4.54
Iso-Butene	NaY	2.51	0.37
	HNaY25	7.85	7.88
	HNaY40	8.03	9.47
	HNaY56	10.03	8.90
	HNaY73	9.60	7.21
	HNaY80	5.21	7.30
	HNaY91	7.38	8.95

Table 1
α_c and β_c values of Brönsted equation estimated by fitting the catalytic activity calculated based on acid site distribution and the catalytic activity experimentally obtained to Eq. (2), for the transformation of small olefins on HNaY series of catalysts

	Ethene	Propene	1-Butene	Iso-Butene
α_c (mol/h g acid site)	1.1×10^{-11}	2.3×10^{-10}	1.1×10^{-9}	1.8×10^{-9}
β_c (mol/kJ)	5.0×10^{-2}	5.5×10^{-2}	4.2×10^{-2}	4.1×10^{-2}

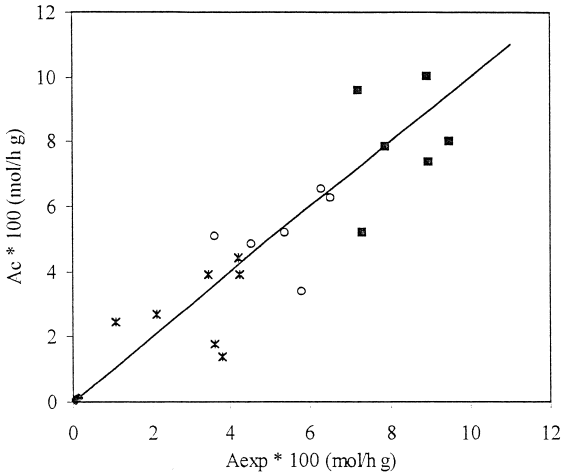

Fig. 1. Plot of the calculated, A_c, versus experimental, A_{exp}, activity values for the transformation of ♦—ethene, *—propene, ○—1-butene and ■—iso-butene over HNaY zeolites.

of Eq. (2) were estimated. The values obtained for the various olefins are collected in Table 1.

From the TPD results we can observe that NaY has a considerable amount of sites where ammonia is adsorbed although their activation energy for ammonia desorption is low [6]. This zeolite, however, has no significant catalytic activity in the transformation of the olefins under study [5]. Thus, it can be concluded that not all acid sites that adsorbed ammonia and are observed on TPD of ammonia are catalytically active. Thus, the fittings obtained were better when the sites with activation energy for ammonia desorption bellow 50 kJ/mol were not considered.

In Table 2 the catalytic activity values calculated using the Brönsted-type equation (Eq. (2)) and the experimental catalytic activity values for the transformation of the olefins under study after 6 min of reaction are presented. To present a graphical representation of the fitting, these values are plotted one against the other in Fig. 1.

Table 4
Calculated, A_c, and experimental, A_{exp}, catalytic activity values for the transformation of the olefins over HNaUSY series of catalysts

Reagent	Catalyst	$A_c \times 100$ (mol/h g)	$A_{exp} \times 100$ (mol/h g)
Ethene	HNaUSY3	0.25	0.06
	HNaUSY71	0.56	0.55
	HNaUSY83	0.59	0.88
	HNaUSY94	1.16	0.79
	USHY	1.35	1.55
Propene	HNaUSY3	1.20	0.19
	HNaUSY71	2.64	2.85
	HNaUSY83	3.08	4.20
	HNaUSY94	6.51	4.95
	USHY	8.07	8.83
1-Butene	HNaUSY3	2.46	0.28
	HNaUSY71	5.56	5.00
	HNaUSY83	5.16	6.22
	HNaUSY94	8.96	9.06
	USHY	9.81	9.74
Iso-Butene	HNaUSY3	2.53	1.72
	HNaUSY71	5.67	5.23
	HNaUSY83	5.54	6.74
	HNaUSY94	10.04	9.46
	USHY	11.25	11.41

4.2. HNaUSY series of catalysts

The distribution of acid site strengths, in catalysts of HNaUSY series, as a function of activation energy for ammonia desorption (obtained in Ref. [6]) were also correlated with the results of catalytic activity for the transforma-

Table 3
α_c and β_c values of Brönsted equation estimated by fitting the catalytic activity calculated based on acid site distribution and the catalytic activity experimentally obtained to Eq. (2), for the transformation of small olefins on HNaUSY series of catalysts

	Ethene	Propene	1-Butene	Iso-Butene
α_c (mol/h g acid site)	7.0×10^{-10}	2.6×10^{-9}	1.1×10^{-8}	9.1×10^{-9}
β_c (mol/kJ)	1.2×10^{-2}	1.6×10^{-2}	5.3×10^{-3}	8.0×10^{-3}

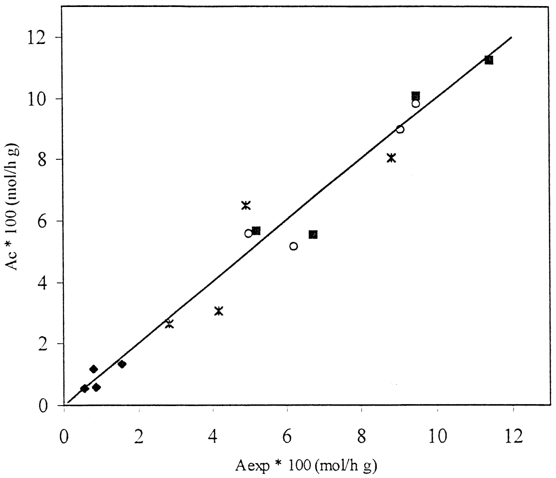

Fig. 2. Plot of the calculated, A_c, versus experimental, A_{exp}, activity values for the transformation of ♦—ethene, ∗—propene, ○—1-butene and ■—iso-butene over HNaUSY zeolites.

tion of the olefins after 6 min of reaction (presented in Ref. [5]).

Using the above described procedure the parameters for Eq. (2), α_c and β_c, were estimated and are collected in Table 3. As for the case of the HNaY series of catalysts, sites with activation energy for ammonia desorption bellow 50 kJ/mol are not considered in the computation of α_c and β_c.

In Table 4 the catalytic activity values calculated using Eq. (2) and the experimental catalytic activity values for the transformation of the olefins after 6 min of reaction are presented, while the quality of the fitting can be observed in Fig. 2.

5. Discussion

From the results obtained we can see that there is an excellent agreement between the activity values, computed using Eq. (2) and the fitted values of α_c and β_c, and the experimental values. This is indicative that acid catalysis rules that apply to homogeneous catalysis also hold for gas-phase acid-catalysed reaction in zeolites.

Some observations must be made in relation to the parameters α_c and β_c of Eq. (2), regarding their meaning and expected way of variation when the reactant is changed.

One would expect that, as the reagent transformation becomes easier, the α_c value increase for the catalysts belonging to the same series. In fact, for each series of catalysts we observed the following order for α_c values: ethene < propene < 1-butene ≈ iso-butene (see Tables 1 and 3). Nevertheless, there is no significant difference between the α_c values for the C_4 olefins, but it is also true that their reactivity, over these catalysts (mainly for HNaUSY zeolites), is very similar in magnitude although not in selectivity.

The β_c constant of Eq. (2) expresses the chemical reaction sensitivity towards the catalyst acidity. It would be expected that as the reactivity of the reagent molecules increases the β_c values decrease, i.e., the order for the β_c values should be: iso-butene < 1-butene < propene < ethene. This was, in fact, observed for each series of catalysts although, but as with the α_c values, the difference between the two C_4 olefins is small and also the values for C_2 and C_3 are very close.

A fact that is not clearly understandable is the difference between the parameters obtained in the two series of catalysts. In fact, we would expect that the α_c and β_c values depend mainly on the reaction and not on the catalyst, unless different sites were involved. The results clearly indicate that some difference does exist between the acid sites in the two series of catalysts, a fact which is probably related to the existence of extra-framework aluminiums and/or to the participation of basic Lewis sites (framework oxygens) in the reactional mechanism, specially in the less acidic series HNaY.

6. Conclusions

The most important conclusion is that Brönsted equations also hold for heterogeneous catalysis, and that its application is feasible in acid catalysed reactions over zeolites.

The parameters that are obtained by fitting Eq. (2) to experimental data can provide further information, at a basic level, on the reactions and the catalysts.

It can also be concluded that the activation energy for ammonia desorption is a good measure of the acid site strength, for the reactions under study, as well as for the transformation of *n*-heptane [19] and can be used in a fashion similar to how the pK_A is used in homogeneous acid catalysis.

The amount of computations that is needed to perform both the deconvolution of TPD thermograms and the correlation between activity and acidity is well within the power of modern desktop computers (details on the building of the worksheets are available upon request). Thus, this scheme which can easily be extended to other acid catalysts and other reactions would be extremely interesting to systematise a Brönsted-type approach to heterogeneous catalysis.

This can provide insight into the processes occurring at the catalysts and, of course, further work will be needed to understand why there are some differences between the parameters obtained with the two series of similar, although different, catalysts.

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