Activity–acidity relationship in zeolite ZSM-5. Application of Brönsted-type equations

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Abstract

In this paper the relation between activity and acidity in a variety of ZSM-5 zeolite catalysts, with different Si/Al ratios and different protonic content, is analysed and a quantitative correlation is obtained. The acid site strength distribution was estimated using temperature-programmed desorption (TPD) of ammonia by applying a digital deconvolution method to the curves. These data were then correlated with experimental catalytic activity data for the same catalysts towards n-heptane cracking reaction, by means of a Brönsted-type equation similar to the ones used for homogeneous acid catalysis and already used for other zeolites. It can be noticed that the same types of equation that are used for homogeneous acid catalysis also hold for heterogeneous acid catalysis and that the activation energy for ammonia desorption can be used as acid-strength scale for the purpose of correlation with catalytic activity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acidity is one of the most important characteristics of zeolites which make them very useful in acid catalysis. The catalytic properties, such as activity and selectivity, depend not only on the number of the acid sites but also on their specific activities. It is clear that this activity is related to the acid strength of the intervening sites.

The Brönsted equations have been used to describe the relation between the rate of homogeneously acid catalysed reactions and the acid strength of the catalysts [1]. A similar relation for heterogeneous acid catalysed reactions has been sought for a long time by researchers working in this field [2]. The major problem has been that, in any given catalyst, a wide range of acid strengths can be found on the surface, due to different structure, topology and chemical composition around each acid site [3,4]. This makes the estimation of acid site strength distribution somewhat difficult. Furthermore, it is not

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easy to establish a unique scale of acidity similar for instance to the pk_A for solutions.

A great effort has been made to characterise the acidity of the zeolites. Several experimental methods, like chemical titration, XPS, FTIR, NMR and thermal methods, are currently used by researchers in this field [5–7].

Temperature-programmed desorption (TPD) of ammonia is one of the major methods being used and some of the authors have proposed a numerical procedure to perform digital deconvolution of the curves obtained by single TPD experiments into the related mono-energetic component curves [8]. This method allows the estimation of acid site strength on a catalyst surface, using the activation energy for ammonia desorption as a measure of acidity of any given site. Some other authors [9–13] also proposed different calculation procedures to determine total acid strength, as well as acid strength distributions, at least at a comparative level.

The information about acid site strength distribution was quantitatively correlated with the catalytic activity for transformation of *n*-heptane and light olefins transformation in a variety of Y zeolites [14,15]. In these previous works it was verified that the acid catalysed reactions over Y zeolite could be described by the Brönsted-type relations.

Beyond the determinant factor of framework composition of the zeolites also the spatial distribution of acid sites across the framework is important, i.e., for a given composition, the structure type will modify the surface properties [4,16]. In order to systematise a Brönsted-type approach to heterogeneous catalysis, it is extremely interesting to know if the same kind of correlation between the activity and the acidity can be found for acid-catalysed reactions over acid catalysts with different structures, and to compare the corresponding parameters.

In this work, we characterised the acid site strength distribution of several ZSM-5 catalysts with different Si/Al ratio and different protonic content, applying the above mentioned deconvolution method on ammonia TPD curves. These

results were then correlated with the results for the catalytic activity for *n*-heptane transformation, using the same type of Brönsted equation.

2. Experimental

2.1. Catalysts

The ZSM-5 sample with Si/Al ratio 19 was supplied by UOP Molecular Sieves, the samples with Si/Al ratio 40 and 127 were supplied by PQ Zeolites and the zeolite with Si/Al ratio 29 was obtained from Leverhulme Centre for Innovative Catalysis. The acid forms of these zeolites were prepared by decomposing the template cations at 550°C under a flow of dry nitrogen during 3 h followed by calcination under a flow of dry air for 8 h.

The starting ammonium forms of non-templated and templated ZSM-5 zeolites whose Si/Al ratios are 26 and 42, respectively, were obtained from Angarsk Oil Chemical (Russia). Details of the preparation of NH_4-ZSM-5 zeolites have been previously described [17,18]. The acid form of the templated ZSM-5 was obtained as described above and the acid form of the non-templated sample was obtained by a simple calcination. Departing from the acid forms of ZSM-5 zeolites with Si/Al ratio 26 and 42, two samples and one sample, respectively, with different sodium content were prepared by successive ion-exchanges. The ion-exchanges were performed with 1 M sodium nitrate solutions using a solution volume (ml) to catalysts mass (g) ratio of 4 and mechanical agitation for 4 h at room temperature. The corresponding acid forms, HNa-ZSM-5, were obtained by calcination performed as described above.

All catalysts have been characterised by elemental chemical analysis. The characterisation of ZSM-5 zeolites which Si/Al ratio are 26 and 42 can be found elsewhere [19]. X-ray diffraction (XRD) in a Rigaku diffractometer with Cu

Table 1
Designation adopted for each ZSM-5 sample and chemical composition (Si/Al ratio and proton content)

Catalyst	Chemical composition	Si/Al	H^+ (% of total cationic positions)
ZSM5_19	$H_{4.8}[Al_{4.8}Si_{91.2}O_{192}]$	19	100
ZSM5_26	$H_{3.6}[Al_{3.6}Si_{92.4}O_{192}]$	26	100
ZSM5(38)_26	$H_{1.4}Na_{2.2}[Al_{3.6}Si_{92.4}O_{192}]$	26	38
ZSM5(11)_26	$H_{0.4}Na_{3.2}[Al_{3.6}Si_{92.4}O_{192}]$	26	11
ZSM5_29	$H_{3.2}[Al_{3.2}Si_{92.8}O_{192}]$	29	100
ZSM5_40	$H_{2.3}[Al_{2.3}Si_{93.7}O_{192}]$	40	100
ZSM5_42	$H_{2.2}[Al_{2.2}Si_{93.8}O_{192}]$	42	100
ZSM5(40)_42	$H_{0.9}Na_{1.3}[Al_{2.2}Si_{93.8}O_{192}]$	42	40
ZSM5_127	$H_{0.8}[Al_{0.8}Si_{95.2}O_{192}]$	127	100

$K\alpha$ radiation, scanning electron microscopy (SEM) with JEOL JMS-840 instrument and solid state MAS NMR measurements (for ^{29}Si and ^{27}Al) with a Bruker MSL 300 spectrometer were also performed.

In Table 1, we present the designation adopted for each ZSM-5 sample under study in the present paper as well as their chemical composition, Si/Al ratio and the proton content.

2.2. Temperature programmed desorption experiments

About 200 mg of sample were put in a Pyrex reactor and pre-treated, in situ, during 12 h at 450°C in a flow of nitrogen. After cooling to 90°C, ammonia adsorption was performed by feeding pulses of reactant grade ammonia(> 99.995%) to the reactor using a flow of dry helium (> 99%) of 60 ml/min. After the catalyst surface becomes saturated the sample was kept at 90°C for 2 h to remove the base excess. Ammonia was thermally desorbed by rising the temperature with a linear heating rate of approximately 7.5°C/min from 90°C to 700°C. The amount of NH_3 desorbed was measured by a TCD detector. The electrical signals from the detector and the thermocouple, which measures the temperature inside the cell containing the catalyst, were digitised by a CR3A chromatographic integrator and transmitted to a computer.

Details about the TPD apparatus used were described elsewhere [8].

2.3. Catalytic experiments

The catalytic activity measurements for the transformation of *n*-heptane were carried out in a continuous fixed-bed flow reactor, at 350°C, at total pressure of 1 bar, with nitrogen-to-hydrocarbon molar ratio of 9. A 60 ml/min flow of dry nitrogen was used and reagent fed at a rate of 3 ml/h. 200 mg of catalyst were used in the reactor. In all the cases the catalysts were pre-treated, in situ, at 450°C during 12 h under a flow of dry nitrogen (60 ml/min).

The reaction products were separated in an on-line gas chromatograph (Perkin Elmer 8420) equipped with a 50-m PLOT capillary column coated with alumina deactivated with potassium chloride and analysed by using a flame ionization detector.

Blank experiments showed that the thermal transformation of *n*-heptane under the operating conditions used is negligible.

3. Results and discussion

3.1. Determination of acid site strength distribution on the catalyst surface

In Fig. 1(I) and (II), the TPD of NH_3 thermograms obtained over all the catalysts under study are plotted. It can be noticed that for most of the catalysts two main bands can be observed which show a maximum in desorption rate around 450
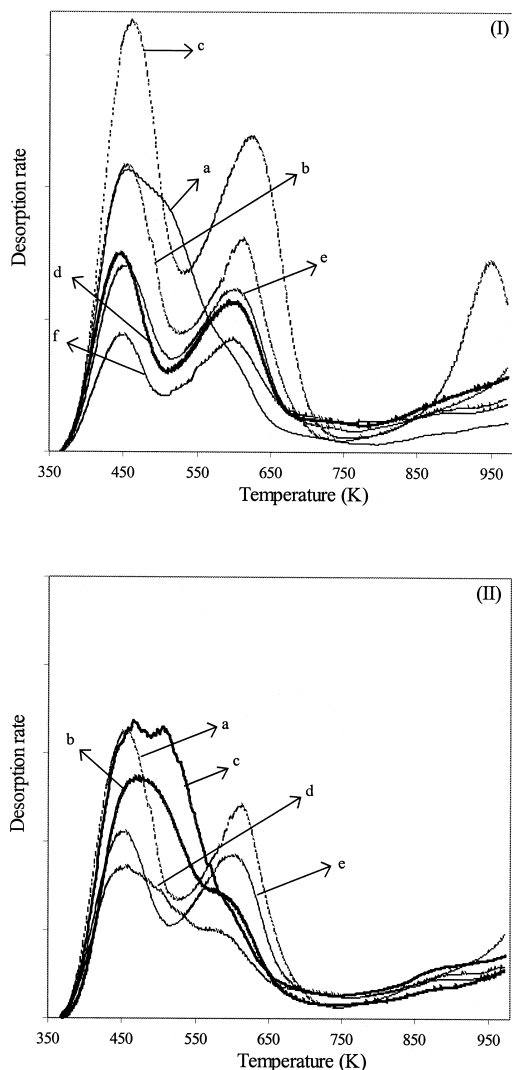
Fig. 1. TPD of NH_3 thermograms from the catalysts with (I) different Si/Al ratio: (a) ZSM5_19; (b) ZSM5_26; (c) ZSM5_29; (d) ZSM5_40; (e) ZSM5_42; (f) ZSM5_127, and (II) different protonic content: (a) ZSM5_26; (b) ZSM5(38)_26; (c) ZSM5(11)_26; (d) ZSM5_42; (e) ZSM5(40)_42.

the activity of this catalyst towards *n*-heptane transformation (Table 2) which means that there are factors other than the Si/Al ratio that lead to different acidity in ZSM-5 samples. A non-linear decrease in the number of acid sites when the Si/Al ratio value increases has been already reported by other authors for ZSM-5 [22].

Using the digital deconvolution method we have already proposed [8] we were able to determine the acid site strength distribution, for each catalyst, as a function of the activation energy for ammonia desorption from a single TPD experiment.

Experimental data were fitted to Eq. (1).

$$-\frac{\mathrm{d}q}{\mathrm{d}t} = \sum_i k_{E^i} \mathrm{e}^{-E^i/RT} q_{E^i} \tag{1}$$

where q_E^i is the amount of molecules adsorbed in acid sites presenting an activation energy for the desorption of ammonia of E^i and k_E^i is the corresponding pre-exponential factor.

k_E was considered a function of E, as proposed by Hashimoto et al. [23] using the following relation:

$$k_E = \alpha \mathrm{e}^{\beta E} \tag{2}$$

In order to determine the α and β parameters, a series of TPD of NH_3 experiments were carried out over ZSM5_26 zeolite by raising the ammonia adsorption temperature (T_0) by a small amount, ΔT [8]. Each pair of TPD thermograms

and 630 K, in good agreement with other previous reports [20,21].

As the Si/Al ratio increases the total number of acid sites decreases, so it would then be expected that the area below the TPD curve should also decrease. Nevertheless, this is not what can be observed in Fig. 1(I). For instance, the TPD curve for ZSM5_29 is the one with the higher area. This fact is in good agreement with

Table 2
Calculated, A_c, and experimental, A_{exp}, catalytic activity values for the transformation of *n*-heptane over the catalysts under study

Catalyst	$A_c \times 100$ (mol/h g)	$A_{exp} \times 100$ (mol/h0 g)
ZSM5_19	1.21	1.93
ZSM5_26	2.46	3.11
ZSM5(38)_26	1.03	1.61
ZSM5(11)_26	1.15	0.89
ZSM5_29	5.48	5.50
ZSM5_40	1.78	1.40
ZSM5_42	1.56	0.69
ZSM5(40)_42	0.94	0.17
ZSM5_127	1.08	1.00

with consecutive ammonia adsorption temperature was subtracted and curves for acid sites with approximately uniform strength were obtained. The TPD curves for acid sites with uniform strength and the corresponding fittings are plotted in Fig. 2. The estimated parameters, which lead to the relation (3), are collected in Table 3 .

$$k_E = 4.50e^{0.11E} \qquad (3)$$

Blank experiments have also been performed, without ammonia admission, using the same experimental conditions. A typical example of a TPD thermogram of NH_3 over ZSM5_29 and the corresponding blank experiment is shown in Fig. 3. As already mentioned elsewhere [8,21,24–26], the desorption peaks for temperatures above 750 K are associated with the dehydroxylation process since they are observed both in the TPD experiment and in the corresponding ''blank'' experiment. In the computations, before applying the deconvolution method on TPD curves these were base-line corrected using the corresponding ''blank'' experiment.

The discrete sets of energy values corresponding to the different types of acid site used

Table 3
E and k_E values estimated by fitting Eq. (1) to the TPD thermograms of NH_3 from acid sites having uniform acid strength carried out over ZSM5_26 catalyst

T_0 (K)	$T_0 + \Delta T$ (K)	E (kJ/mol)	k_E (s^{-1}) ($\times 10^{-2}$)
90	115	49.1	38.8
115	140	55.9	62.4
140	165	54.8	53.5
165	190	43.5	0.6
190	240	58.5	6.5
240	290	80.2	155.8

on the deconvolution method were optimised in order to obtain the best fittings of the experimental TPD thermograms and good precision in the final distribution.

All computations were performed in a commercial spreadsheet, Excel 5 (©Microsoft), using the solver tool to minimise the sum of the squares of the residuals by varying the values of q_{E0}^i.

In Fig. 4, a typical example of a thermogram, carried out over ZSM5_42 catalyst, with corresponding fitting and the component curves obtained by deconvolution method application, is shown. The relative numbers of acid sites as a function of the activation energy for ammonia
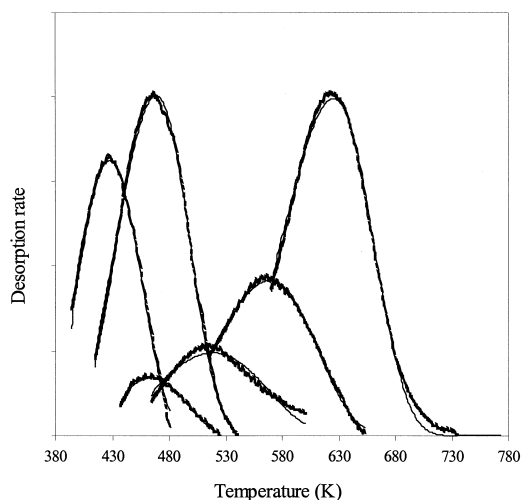

Fig. 2. TPD thermograms of NH_3 from acid sites having uniform acid strength (obtained subtracting thermograms performed with different ammonia adsorption temperature) carried out over ZSM5_26 zeolite. Lines are obtained by fitting Eq. (1) to the experimental data.
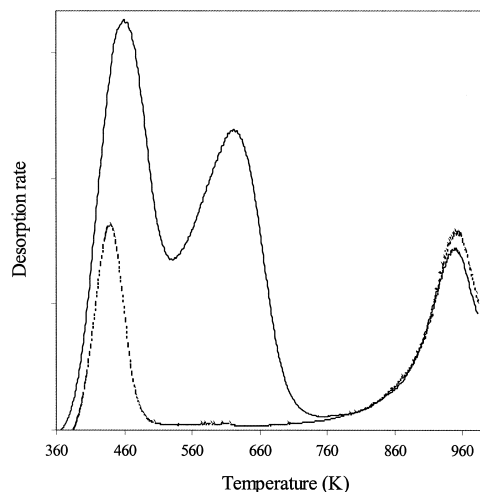

Fig. 3. TPD thermogram of NH_3 over ZSM5_29 catalyst (——) and the corresponding blank experiment, done over the same catalyst- and under the same experimental conditions but without NH_3 admission (– – – –).
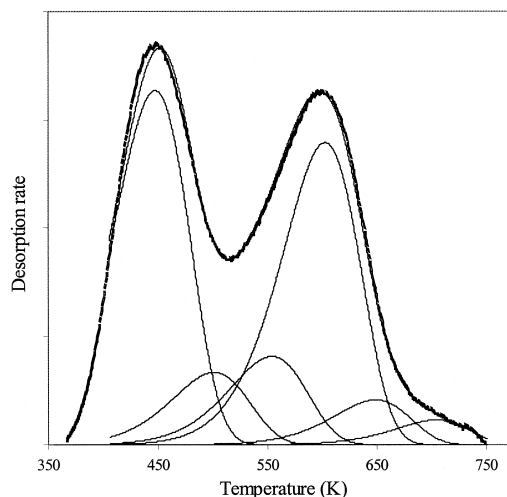
Fig. 4. TPD of NH_3 thermogram carried out over ZSM5_42 catalyst. Lines are the fitting and the component curves obtained by the deconvolution method application.

surement of the acid strength and, again, that there is no significant interaction between sites with different energy, Brönsted-type equations can be applied for the ensemble of acid sites with the same activation energy for ammonia desorption. Considering that the global initial catalytic activity of the zeolite is given by the summation for all the sites in the catalysts, it is described by Eq. (4).

$$A_c = \sum_i q_{E0}^i \alpha_c e^{\beta_c E^i} \tag{4}$$

where the q_{E0}^i are the number of acid sites with activation energy for ammonia desorption, E^i, α_c the constant which express the intrinsic activity of the chemical reaction and β_c the constant which express the chemical reaction sensitivity towards the acidity of the acid site.

desorption, for the catalysts under study, are collected in Table 4.

Activation energies for ammonia desorption values obtained are comprised within a range of values in accordance with other values already published [13,20].

It was observed that a smaller set of energies is required to describe NH_3 desorption from ZSM-5 than from Y zeolites (as found in Ref. [8]). The ZSM-5 samples under study have higher Si/Al ratio than Y zeolites previously studied so, the former present a lower cation concentration and consequently are expected to have a less heterogeneous surface.

3.2. Activity–acidity correlation

We have already demonstrated that it is possible to correlate the acid site strength distribution obtained as previously described with the catalytic activity data by means of Brönsted-type equations in a variety of Y zeolite for the transformation of several molecules [14,15].

Assuming that the activation energy for ammonia desorption can be used as a direct mea-

Table 4
Relative numbers of acid sites (%) as a function of the activation energy for ammonia desorption for all catalysts under study. Results obtained by decomposition method application on TPD thermograms

ZSM5_19						
Energy (kJ/mol)	41	63	78	103	–	–
% Acid sites	27	44	26	3	–	–
ZSM5_26						
Energy (kJ/mol)	48	61	80	97	120	–
% Acid sites	39	13	38	10	1	–
ZSM5(38)_26						
Energy (kJ/mol)	45	57	71	81	96	113
% Acid sites	37	28	13	18	3	1
ZSM5(11)_26						
Energy (kJ/mol)	39	65	80	102	–	–
% Acid sites	18	54	23	4	–	–
ZSM5_29						
Energy (kJ/mol)	49	66	80	88	98	–
% Acid sites	41	13	12	26	9	–
ZSM5_40						
Energy (kJ/mol)	46	64	79	93	120	–
% Acid sites	39	13	35	8	4	–
ZSM5_42						
Energy (kJ/mol)	45	55	67	80	96	116
% Acid sites	38	8	10	35	5	3
ZSM5(40)_42						
Energy (kJ/mol)	37	63	77	96	113	–
% Acid sites	16	36	36	7	5	–
ZSM5_127						
Energy (kJ/mol)	45	65	76	84	102	122
% Acid sites	31	9	36	15	7	3

Using the experimental catalytic activity data and the set of values (E^i, q_{E0}^i) previously obtained it is possible to estimate the values of α_c and β_c by non-linear least squares regression. It was already seen that not all the acid sites that adsorbed ammonia and are observed on TPD of ammonia are catalytically active [15]. This is verified for sites with low values of activation energy for ammonia desorption which correspond mainly to physical adsorption. Thus, the fitting obtained is better when the sites with activation energy for ammonia desorption below 60 kJ/mol are not considered.

The α_c and β_c estimated for the transformation of *n*-heptane on ZSM-5 catalysts under study are collected in Table 5. In Table 2 the catalytic activity values calculated using a Brönsted-type equation and the experimental catalytic activity values after 6 min of reaction transformation of *n*-heptane are presented. The quality of the fitting can be observed in Fig. 5.

The acid site strength distribution of several (RE)Y catalysts [14] has already been correlated with the experimental catalytic activity data towards *n*-heptane transformation by means of a Brönsted-type equation [14,27]. The α_c and β_c estimated are also collected in Table 5.

Some observations must be made in relation to the α_c and β_c parameters of Eq. (4) regarding their meaning. The α_c constant of Eq. (5) is proportional to the catalytic activity when the catalyst has no acidity. Thus, its value depends on the reactant and the mechanism of the reaction. As was expected, the α_c value is approximately the same over the ZSM-5 and Y zeolite catalysts.
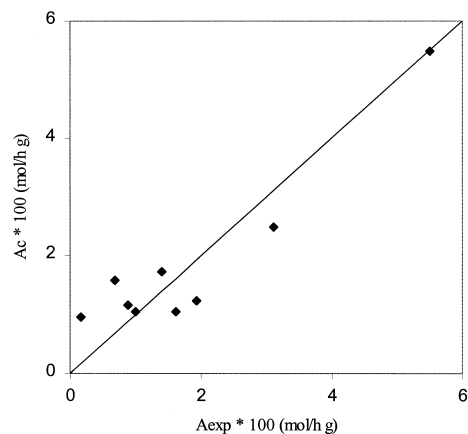

Fig. 5. Plot of the calculated, A_c, vs. experimental, A_{exp}, activity values for the transformation of *n*-heptane over all the ZSM-5 catalysts under study.

The β_c constant of Eq. (5) expresses the chemical reaction sensitivity towards the catalysts' acidity. From Table 5, it can be observed that the β_c value for the ZSM-5 set of catalysts is smaller than for the (RE)Y set of catalysts, meaning that the reaction of *n*-heptane is less sensitive to the acidity over ZSM-5 catalysts than over (RE)Y catalysts.

The product distributions obtained from the catalytic experiments performed over all the catalysts are always characteristic of a large preponderance of the β-scission mechanism, leading to a selectivity of $C_3 + C_4$ product formation around 75–80%. Nevertheless, there are significant differences in product distribution over the two structurally different sets of catalysts. In fact, whereas the *iso*-C_4/*n*-C_4 ratio in the cracking products over the ZSM-5 set of catalysts lies between 0 and 1, the same value (exception made for catalyst NaY) for the (RE)Y set of catalysts lies between 5 and 8. The fewer ramifications of the C_4 products observed on ZSM-5 catalysts compared with the Y catalysts is typical of smaller pore zeolites which limits the isomerisation step of the *n*-heptane prior to the scission step.

The shape selectivity effect over the ZSM-5 catalysts for the *n*-heptane transformation could be the explanation for the fewer sensitivity to

Table 5
The α_c and β_c values of the Brönsted equation estimated by fitting the catalytic activity calculated based on acid site distribution to the experimental catalytic activity, for the transformation of *n*-heptane on ZSM-5 catalysts under study in this work and on (Re)Y catalysts [14]

	α_c (mol/h g acid site)[a]	β_c (mol/kJ) ($\times 100$)
ZSM5	1.32×10^{-9}	1.69
REY	9.05×10^{-10}	3.44

[a]The number of acid sites is in arbitrary units.

the acidity over these catalysts compared with (RE)Y catalysts and leading to a smaller β_c value on the Brönsted-type equation found.

From these results it seems clear that the method we developed to obtain the acid site strength distribution has a definite catalytic meaning since the acid strength distribution data can be correlated in a quantitative way with catalytic activity of the catalyst. It is also clear that this correlation hold even for different zeolite structures. In this way it seems possible to accept activation energy for ammonia desorption as a practical scale of acidity for zeolites.

4. Conclusions

The most important conclusion of this work is that Brönsted relations hold for heterogeneous acid catalysis similarly as for homogeneous catalysis for different catalyst structures and reactions.

These relations were tested from the acid strength distribution obtained by applying a digital deconvolution method on TPD of ammonia curves. The activation energy for NH_3 desorption allows an adequate description of the acid site strength distribution that can be quantitatively correlated with the catalytic activity of different reactions under different zeolites. This means that, the activation energy for ammonia desorption can be used as a practical scale for zeolites samples with a catalytic meaning.

The computations involved in the establishment of these relations are complex; nevertheless, they are feasible within the power of modern desktop computers and in the reach of the experimental researcher.

The Brönsted equation parameters obtained teach us more, on a basic level, about the reaction under study.

A systematic approach to these Brönsted-type relationships for several acid catalysts and different reactions can be envisaged, so that a fast way to analyse and develop new catalysts could be used in acid catalysis by solids.

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