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# Activity–acidity relationship for alkane cracking over zeolites: *n*-hexane cracking over HZSM-5

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## Abstract

The acidity and the catalytic activity for *n*-hexane cracking of three related HZSM-5 catalysts have been determined. A method is described for obtaining the distribution of acid strength by deconvoluting ammonia TPD spectra and it is shown that a linear relationship exists between the enthalpy of the reaction and the activation energy for the desorption of ammonia. Both the Polanyi and the Marcus models were used to derive relationships between the reaction activation energy and the ammonia desorption activation energy. As expected, the former decreases when the latter increases; the reaction activation energy is lower on acidic sites of greater strength. Similarly, equations were derived relating the catalytic activity to the acid strength of the catalytic sites expressed by the activation energy for the desorption of ammonia. Observed activities for the cracking of *n*-hexane were correlated satisfactorily to theoretical ones evaluated using the Polanyi and the Marcus models, considering the distribution of acid site strength. For the cracking of *n*-hexane and the range of experimental conditions used, the Marcus model does not present a significant improvement relative to the Polanyi model. The strategy described in this work indicates that it is possible to predict the activity of a zeolite for a given reaction, provided the acid sites strength distribution is known; one simple method for obtaining the latter being ammonia TPD.

*Keywords:* Hexane cracking; ZSM-5; Acid catalysis; Acidity–activity relationship; Polanyi relationship

## 1. Introduction

The catalytic conversion of hydrocarbons over zeolites is applied in large petroleum-refining processes, among which catalytic cracking is the most important. It is generally recognised that the cracking performance of zeolites as catalysts, including activity and selectivity, depends on their acidity (number and strength of the acid sites) and their pore size (concentration and molecular shape selectivity effects) and ways to optimise such performance continue to be actively searched for.

The accelerated discovery, development, and optimization of catalysts that increase the efficiency and selectivity of chemical processes is a field that has witnessed increasing attention, both in industry and academia, over the last 10 years. High throughput experimentation (HTE) in catalysis is now recognised as a most valuable approach to speed up innovation in catalysis. HTE is mostly based on the development of highly automated techniques, underpinned in many ways by scientific computing in all of its aspects, from molecular modelling to data collection and mining.

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Another approach that can guide and accelerate discovery is to develop and establish structure–activity relationships that can guide the discovery process. Several pharmaceutical companies, searching for new drugs, have successfully implemented this strategy that, so far, has received much less attention in catalysis probably because of the problem complexity in the latter case. A catalytic system is resilient and many parameters are involved in its evaluation (from the catalyst preparation to its operation).

The classical manner to evaluate the behaviour of a potentially new catalyst for a specific chemical reaction is to perform a series of catalytic tests, where parameters such as temperature, pressure, amount and concentration of reactant(s), mass of catalyst, and contact time are varied. Although very reliable, this procedure is extremely time consuming, in particular, if the number of potential catalysts for the desired conversion is large. HTE is one approach that may help estimate the catalytic capabilities of new materials within a shorter time frame. Another one is the proposal of property/activity relationships (PAR) where the property can be quantitatively measured readily. Of course, it implies that all aspects of the catalyst(s) nature are well defined.

Among all solid catalytic materials, zeolites are unique as they have well-defined structures and compositions. Both are responsible for their Brønsted and Lewis acidic properties. The conversion of hydrocarbons over zeolites is catalyzed by their Brønsted acid sites whose acidity can be evaluated by various methods, temperature-programmed desorption (TPD) of ammonia being one of them. $NH_3$-TPD experiments can be performed, usually in a short time frame, readily and with a rather inexpensive equipment.

Linear free-energy relationships are used in physical organic chemistry to correlate kinetic and thermodynamic parameters for a family of reactions. One particular case is the Brønsted relationship that relates the rate constant of reactions catalyzed by acids or bases to the dissociation constant of the latter. It is thus conceivable that activity–acidity relationships could also be derived for reactions that are acid-catalyzed by solid acids, zeolites in particular. If so, characterizing the acidity of zeolites would provide an easy and fast way to estimate their catalytic activity for hydrocarbon transformations. In order to do so, two major issues have to be resolved: (1) a detailed description of the acidity spectrum (number versus strength) of the zeolite(s) must be acquired and (2) a practical way must be found to relate rate constant and acid strength, a measure of the latter being the activation energy for ammonia desorption as obtained from $NH_3$-TPD experiments.

Previous results have indicated that such relationships can indeed be derived from data obtained at a single temperature for a variety of hydrocarbons, both for Y zeolite [1–3] and for ZSM-5 [4], albeit only for isothermal conditions. The aim of this manuscript is to demonstrate that a general relationship between activity and acidity can indeed be derived for a given family of catalysts over a wide range of reaction temperatures and reactant concentrations, the cracking of *n*-hexane being used as a model reaction. Another important aspect of this contribution is that it deals with non-uniform kinetics resulting from the distribution of acid strength that is observed for solid acids, e.g., zeolites, that is, the understanding and modelling of the activity of multi-site catalysts [5].

## 2. Experimental

### 2.1. Catalysts

The parent HZSM-5 (MFI structure type, protonated form) zeolite was obtained from Zeolyst (CBV 3024G) and had a Si/Al molar ratio of 15. The original sample had virtually no sodium and it was partially Na-exchanged to modify its acidity. Two samples were prepared by ion exchange at room temperature with 0.5 and 1.0 M aqueous solutions of $NaNO_3$. These samples are referred to as HNaZSM-5(24) and HNaZSM-5(30), respectively, where the numbers in parentheses indicate the percentage of cationic sites that are occupied by sodium ions, as obtained by chemical analysis.

### 2.2. Catalyst pretreatments

All samples were dried at 120 °C for 12 h, calcined at 500 °C for 8 h under a flow of dry air of $0.5\,l\,h^{-1}\,g^{-1}$, and eventually equilibrated in a constant humidity container to prevent their contamination before use. Prior to the TPD measurements and catalytic tests, all samples were pretreated for 8 h at 450 °C under a flow of dry nitrogen.

### 2.3. Catalytic tests

The catalytic experiments with *n*-hexane were carried out in a tubular glass fixed-bed microreactor under plug flow conditions. Samples of about 75 mg of the zeolite catalyst were pretreated in situ as described above. Reactions were carried out at atmospheric pressure and at temperatures of 300, 350, 400 and 450 °C. The *n*-hexane feed was diluted with dry nitrogen to achieve *n*-hexane partial pressures of 0.19, 0.29 and 0.48 atm, the total gas flow rate being kept at 65 ml/min. The reaction effluent was analyzed using a Perkin-Elmer 8420 gas chromatograph equipped with a 50 m PLOT-type ($KCl/AlCl_3$) capillary column and a flame ionization detector.

### 2.4. Ammonia TPD

Temperature-programmed desorption (TPD) of ammonia was used to determine the acid strength distribution of the active sites. About 200 mg of zeolite were placed in a silica reactor and pretreated in situ as described above. The catalyst was then kept at 90 °C under a flow (60 ml/min) of dry helium. Pulses of ammonia were injected using a gas sampling valve, until no variation of the ammonia peak at the outlet was observed, meaning that the catalyst surface was saturated with ammonia. The sample was then purged for 30 min at 90 °C under a helium flow to remove any excess of ammonia not chemically absorbed. It was then heated up to 700 °C, at a rate of 10 °C/min, under a flow (60 ml/min) of dry helium. The effluent stream was monitored continuously with a thermal conductivity detector to determine the rate of ammonia desorption. Blank experiments, where no ammonia was adsorbed, were carried out to establish a base line for the regular experiments, in particular, to account for dehydroxylation which occurs at high temperature.

### *2.5. Molecular modelling – quantum calculations*

Computations were performed using Spartan'04 for Windows (©Wavefunction Inc.) using a hybrid HF/DFT B3LYP/6-31G$^{**}$ model. These computations aimed at establishing a relationship between the desorption enthalpy of ammonia estimated from the ammonia desorption energy profile (a measure of acid strength) and the activation energy for the a typical reaction over the zeolite sites. This reaction was only intended as illustrative of the relation that exists between the two parameters; the protolytic scission of *n*-hexane on the central C–C bond, as described by (Eq. (1)), was chosen as an example.

$$C_6H_{14} + HZ \leftrightarrows C_3H_8 + C_3H_7Z \tag{1}$$

To simulate modification of acid strength and its effect on the cracking of *n*-hexane, model sites of general formula $SiH_nCl_{3-n}OH$ ($n = 0$, 1 and 2) were used, the replacement of H by Cl resulting in an increasing acidity of the OH group. Model sites with higher acid strength were also obtained by shortening the Si–O bond length in $SiCl_3OH$. Such models are obviously very simple and do not account for long range, media or geometrical effects. They, however, provide information on how enthalpies for ammonia desorption and activation energies for *n*-hexane cracking can be correlated.

## 3. Theory

Deriving a relationship between the activity of a catalyst (in the present case, HZSM-5 for the cracking of *n*-hexane) and the distribution of its acid sites strength, in addition to the experimental determination of these parameters, involves two main steps: (i) the development of a method for characterizing the catalyst acid strength distribution and (ii) the proposal of a relationship relating acid strength to catalytic activity.

### *3.1. Determination of the acid strength distribution*

The objective is to correlate acidity (number and strength distribution of acid sites) with catalytic activity. The method selected in this work, among several others, for evaluating acid strength is $NH_3$-TPD which is well established. The strength of an acid site can be approximated by the activation energy for desorption of ammonia whose absolute value can be assumed to be equal to the ammonia adsorption enthalpy, as its adsorption has no or negligible adsorption activation energy.

Obtaining the distribution of acid strength from a $NH_3$-TPD profile requires its deconvolution into several components characterised by the number and strength of the acid sites. Several methods are available for this [6–14] and the method developed by some of the authors of this contribution was used [1,4,6]. It assumes that desorption from the acid sites is irreversible and kinetically first order, and that there is no interaction between two different acidic sites. The desorption rate from a set of sites with uniform adsorption energy is then given by an Arrhenius law (Eq. (2)):

$$\frac{dq_i}{dt} = -k_i\, e^{-E_{a(i)}^{NH_3}/RT}\, q_i \tag{2}$$

where $q_i$ is the amount of sites that are occupied by ammonia molecules at time $t$, $k_i$ a pre-exponential factor, $E_{a(i)}^{NH_3}$ the activation energy for the desorption of ammonia, and $R$ and $T$ are the ideal gas constant and the absolute temperature, respectively.

Acid sites in a zeolite have different acid strengths, depending on their position in the framework and their environment. Therefore, an experimental ammonia TPD spectrum (rate of desorption versus temperature) is the sum of several, more or less discrete, desorption curves corresponding to the different types of acid sites, as sites with different acid strengths will also have different activation energies for ammonia desorption. The deconvolution of the TPD spectrum into its components should thus, in principle, enable the determination of the sites acid strength distribution. For this purpose, a discrete energy grid may be used to represent, at least approximately, the range of desorption activation energy values which, in the limit, may be a continuum. Consequently, the overall TPD spectrum can be represented by Eq. (3):

$$\frac{dq}{dt} = -\sum_{i=1}^{n} k_i\, e^{-E_{a(i)}^{NH_3}/RT}\, q_i \tag{3}$$

where $dq/dt$ is the observed overall rate of desorption of ammonia at instant $t$ and temperature $T$. Fitting this equation to the experimentally observed desorption rate curve enables the determination of the amount of acid sites per unit mass of catalyst ($q_{0i}$ at $t = 0$) for each energy value ($E_{a(i)}^{NH_3}$) in the chosen energy grid that are present in the fresh catalyst.

In order to obtain through multi-linear least-square regression the values of $q_{0i}$, the pre-exponential factor must be known. To simplify the problem, it is assumed that $k_i$ and $E_{a(i)}^{NH_3}$ are related by Eq. (4), as proposed by Hashimoto et al. [9]:

$$k_i = \alpha\, e^{\beta E_{a(i)}^{NH_3}} \tag{4}$$

where $\alpha$ and $\beta$ are parameters that can be considered to be constant for a family of zeolites. For ZSM-5 type zeolites, these parameters have already been determined and are: $\alpha = 4.5\ s^{-1}$; $\beta = 0.11\ mol\ kJ^{-1}$ [4]).

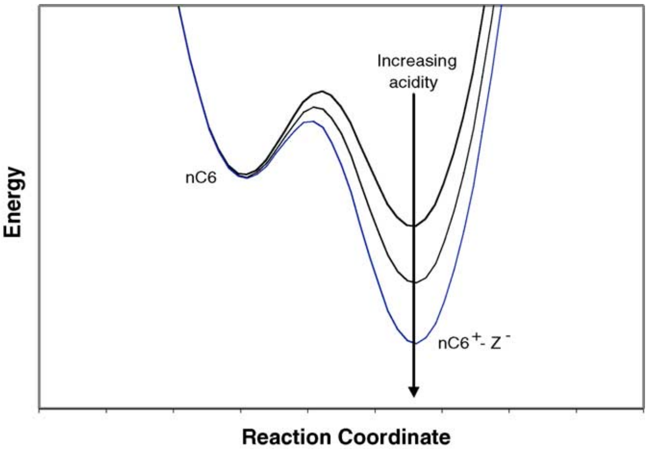

Fig. 1. Change in reaction energy profile for the protonation of *n*-hexane as a function of the acid strength of the site on which the reaction is carried.

### 3.2. Activity–acidity relationship

The test reaction used in the present work is the cracking of *n*-hexane. The latter can occur following direct protonation of *n*-hexane or by its reaction with a previously adsorbed carbocation. In either case, the reaction will have an exothermicity that will increase with the strength of the acid site as the chemisorbed carbocation will be more stabilized on acid sites of higher strength (see Fig. 1).

Several equations have been proposed to relate the rate of a reaction to its enthalpy when a family of reactions is considered [15]. For a family of reactions, the elementary steps are expected to be characterized by potential energy surfaces which exhibit roughly the same shape.

The simplest correlation has been proposed by Polanyi and states the following. If the enthalpy of reaction, $\Delta H_r$ (negative for an exothermic step), decreases by an amount $\Delta\Delta H_r$ from one member of the family to the next, then the activation energy barrier, $E_a$, will decrease by an amount $\Delta E$ equal to a fraction $\gamma_p$ of the change $\Delta\Delta H_r$, $\gamma_p$ being between zero and unity. This results in a linear relationship between the activation energy for a certain reaction and its enthalpy, according to Eq. (5):

$$E_a = E_a^0 + \gamma_p \Delta H_r \tag{5}$$

where $E_a^0$ is the activation energy for the athermic reaction and $\gamma_p$ is the sensitivity of the activation energy dependence on the enthalpy of reaction. In practice, both parameters can be adjusted for a given family of reactions. This approach has been used already by some authors to correlate reaction rate constants for a family of reactions [16] but it presents some drawbacks. In particular, it assumes that the reaction pathway is strictly the same for all the catalytic sites and it is seen from Eq. (5) that the activation energy may become negative for highly exothermic reactions.

Other equations have been proposed to solve these difficulties. One of them is the Marcus relationship that is an extension of Polanyi's proposal aiming at explaining some disparities observed for very endothermic or very exothermic reactions. Unlike the Polanyi relationship, this equation uses a second-order dependence of the activation energy on the reaction enthalpy (see Eq. (6)):

$$E_a = \left(1 + \frac{\Delta H_r}{4E_a^0}\right)^2 E_a^0 \tag{6}$$

The next step consists in relating the enthalpy of reaction, $\Delta H_r$, to the activation energy for the desorption of ammonia, $E_a^{NH_3}$, which as discussed above is equal but of opposite sign to the enthalpy of ammonia adsorption and is thus a measure of acid strength. Both the reaction and ammonia adsorption elementary steps involve the protonation of the substrate. We, therefore, propose and will assume hereafter that a linear relationship correlates the enthalpy of reaction, $\Delta H_r$, for the transformation under consideration and the activation energy for ammonia desorption, $E_a^{NH_3}$. The results of molecular modelling and quantum calculations described later in this paper support this assumption. Thus:

$$\Delta H_r = a + bE_a^{NH_3} \tag{7}$$

Using Eq. (7), the Polanyi (Eq. (5)) and Marcus (Eq. (6)) relationships, become Eqs. (8) and (9), respectively:

$$E_a = E_a^0 + \gamma_p a + \gamma_p b E_a^{NH_3} = E_a^{0N} + \delta E_a^{NH_3} \tag{8}$$

for the Polanyi approximation, where $E_a^{0N} = E_a^0 + \gamma_p a$ is the activation energy for the process carried out over a non-acidic site (zero activation energy for the desorption of ammonia), and $\delta = \gamma_p b$ the sensitivity of the reaction under consideration to the acid strength of the catalytic site, and

$$E_a = \left(1 + \frac{a + bE_a^{NH_3}}{4E_a^0}\right)^2 E_a^0 = \left(1 + \lambda \frac{E_a^{NH_3}}{E_a^{0N}}\right)^2 E_a^{0N} \tag{9}$$

for the Marcus approximation, where:

$$E_a^{0N} = \left(1 + \frac{a}{4E_a^0}\right)^2 E_a^0 \tag{10}$$

and

$$\lambda = \frac{b}{4}\left(1 + \frac{a}{4E_a^0}\right) \tag{11}$$

with $E_a^{0N}$ being the activation energy for the reaction carried out over a non-acidic site and $\lambda$ is the sensitivity of the reaction to the acid strength of the site.

Molecular modelling confirmed that Eq. (8) describes satisfactorily the relationship between the acidity of the site, as measured by the activation energy for the desorption of ammonia, and the activation energy for the transformation of propane [17]. Similar considerations for one of the possible pathways for the reaction being considered in this paper are dealt with below.

The last step consists in deriving a kinetic equation where the activation energy can be expressed using Eq. (8) or (9). In both cases, only two adjustable parameters will be used.

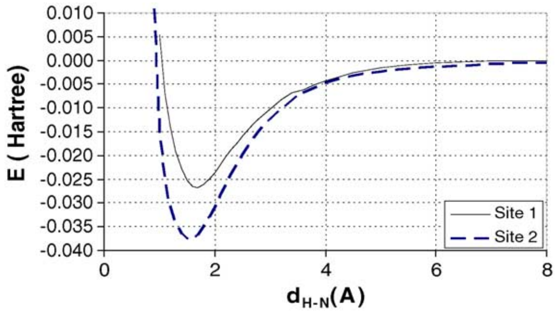

Fig. 2. Energy profile for the adsorption of $NH_3$ on acid sites of different strength. Site 1 is $SiCl_3OH$ with the computed equilibrium distance for the Si—O distance (0.1606 nm) and site 2 is the same cluster with the Si—O distance constrained to 0.13 nm. See text for calculation details.

Table 1
Energy values obtained by the HF/DFT B3LYP/6-31G** method for the activation energy for the protolytic scission of *n*-hexane and for the adsorption of ammonia over various acid site models

| | $\Delta H_{NH_3}$ (kJ mol$^{-1}$) | $E_a$ (kJ mol$^{-1}$) |
|---|---|---|
| $SiCl_3OH$ (0.13)[a] | −94.04 | 348.4 |
| $SiCl_3OH$ (0.14)[a] | −87.90 | 353.3 |
| $SiCl_3OH$ | −66.41 | 389.1 |
| $SiCl_2HOH$ | −62.70 | 401.1 |
| $SiClH_2OH$ | −56.10 | 400.2 |

[a] Numbers in brackets indicate constraints imposed on the Si—O distance (nm)—see text for details.

The kinetics for the transformation of *n*-hexane is usually observed to be of first order [18], and our results also indicate the same, and the general form of the kinetic equation is:

$$r = -kP_{\rm in}(1-x) = -k_0\,{\rm e}^{-E_a/RT}P_{\rm in}(1-x) \qquad (12)$$

where $k_0$ is a pre-exponential factor, $P_{\rm in}$ the partial pressure of *n*-hexane at the inlet of the reactor and *x* is the conversion of *n*-hexane.

The observable mean activity, $A_c$, for a plug flow reactor is given by:

$$A_c = \frac{F_{\rm in}x_{\rm out}}{W} \qquad (13)$$

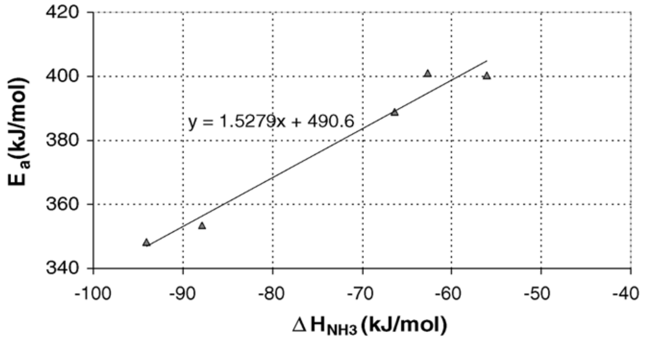

Fig. 3. Relation between the activation energy computed for the protolytic cracking of *n*-hexane and the adsorption enthalpy for ammonia as calculated by the HF/DFT B3LYP/6-31G** method.

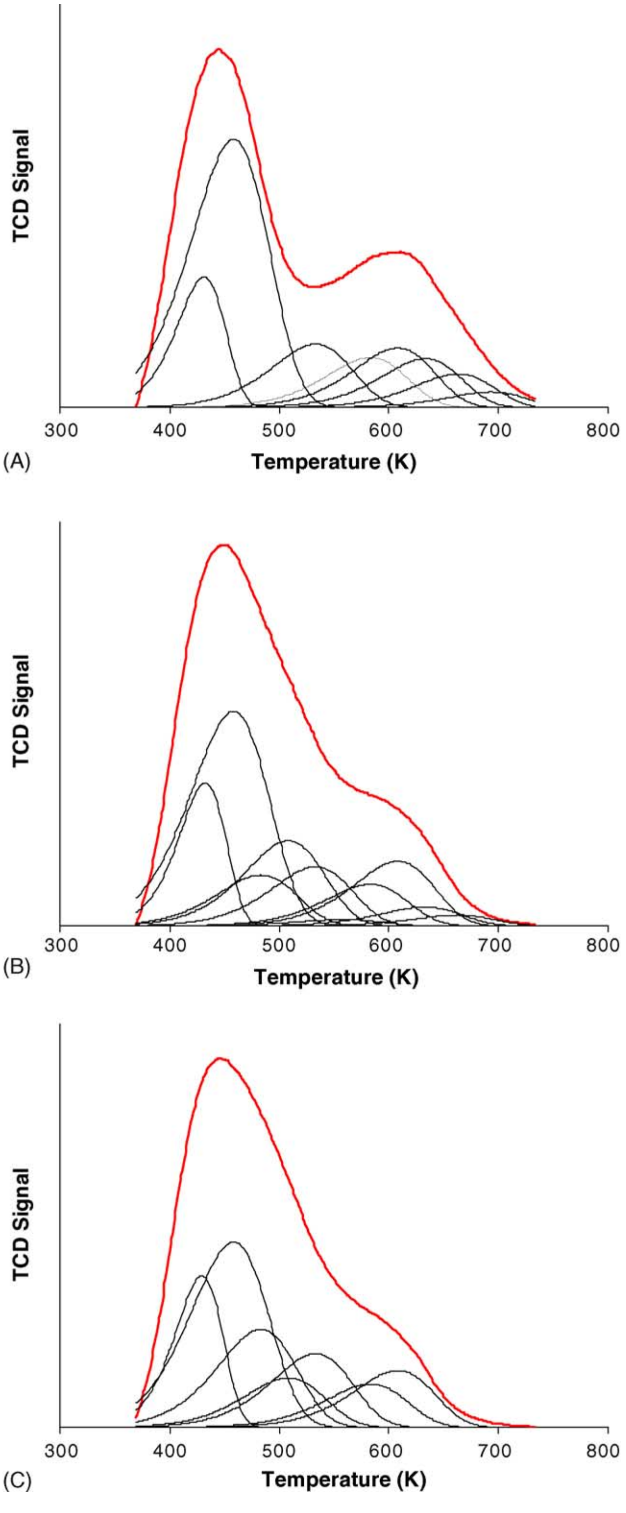

Fig. 4. Ammonia TPD spectra and discrete components obtained by deconvolution for the three different zeolites: (A) HZSM-5, (B) HNaZSM-5(24) and (C) HNaZSM-5(30). Thick line—experimental data; thin lines—individual components for desorption from uniform sites obtained by decomposition.

where $F_{\text{in}}$ is the molar flow of feed into the reactor, $x_{\text{out}}$ the conversion recorded at the reactor outlet, and $W$ is the mass of catalyst. Combining Eqs. (12) and (13), one obtains:

$$A_c = \frac{F_{\text{in}}(1 - e^{-kWP_{\text{in}}/F_{\text{in}}})}{W} \qquad (14)$$

where the parameter $k$ defined in Eq. (12) can be expressed as a function of the acidity of the active site (measured by the activation energy for the desorption of ammonia) by either the Polanyi (Eq. (8)) or the Marcus (Eq. (9)) approximation.

As there is a distribution of acid strengths, there will also be a distribution of rate constants and the observable kinetic rate constant will result from the activity of all the acid sites present at the surface of the catalyst. Accordingly, referring to Eqs. (8) and (9), the rate constants, $k$, to be used in Eq. (14) are:

for the Polanyi model :

$$k = k_0 \sum_{i=1}^{n} q_{0i}\, e^{-(E_a^{0N} + \delta E_{a(i)}^{NH_3})/RT} \qquad (15)$$

for the Marcus model :

$$k = k_0 \sum_{i=1}^{n} q_{0i}\, e^{-E_a^{0N}\left(1+\lambda \frac{E_{a(i)}^{NH_3}}{E_a^{0N}}\right)^2/RT} \qquad (16)$$

where the parameter $k_0$ is the pre-exponential factor for the reaction being considered and $q_{0i}$ are the amounts of acid sites, per gram of catalyst, that have been determined by the numerical decomposition of the TPD curves.

Both models are herein fitted to experimental data for the cracking of *n*-hexane on HNaZSM-5 zeolites with different distributions of acid strengths.

## 4. Results and discussion

### 4.1. Molecular modelling

Molecular modelling/quantum calculations were used to establish that the activation energy for the desorption of ammonia was a reasonable measure of acid strength and the validity of Eqs. (8) and (9) relating the activation energy for *n*-hexane cracking to the activation energy for ammonia desorption.

Model sites used in this work have the general formula $SiH_nCl_{3-n}OH$ ($n = 0, 1$ and $2$) where the electronegative chlorine atoms are used to increase the acid strength of the OH group. Other sites with stronger Brønsted acidity were also obtained by shortening and constraining the Si–O bond in $SiCl_3OH$ cluster.

Potential energy curves for the adsorption of ammonia were computed. The computations started with a full geometry optimization of the site with adsorbed ammonia to determine the minimum energy of the system and the equilibrium distance, $d_{\text{H–N}}$, between the nitrogen atom of ammonia and the hydrogen in the hydroxyl group. Subsequent minimizations were then carried out by systematically constraining the H–N distance to different values. All calculations were performed with the HF/DFT B3LYP/6-31G$^{**}$ model. This method was shown by other authors to supply satisfactorily results [19].

Fig. 2 shows typical potential energy curves for the adsorption of ammonia on Brønsted sites of different strengths. Site 1 is $SiCl_3OH$ with the computed equilibrium distance for Si–O (0.1606 nm). Site 2 is the same cluster where the Si–O bond has been constrained to 0.13 nm. As expected, the heat of adsorption of ammonia increases with increasing acid strength, accompanied by a decrease in the H–N bond length, $d_{\text{H–N}}$. In both cases, the adsorption of ammonia is not an activated process which is to be expected as no bond breaking occurs.

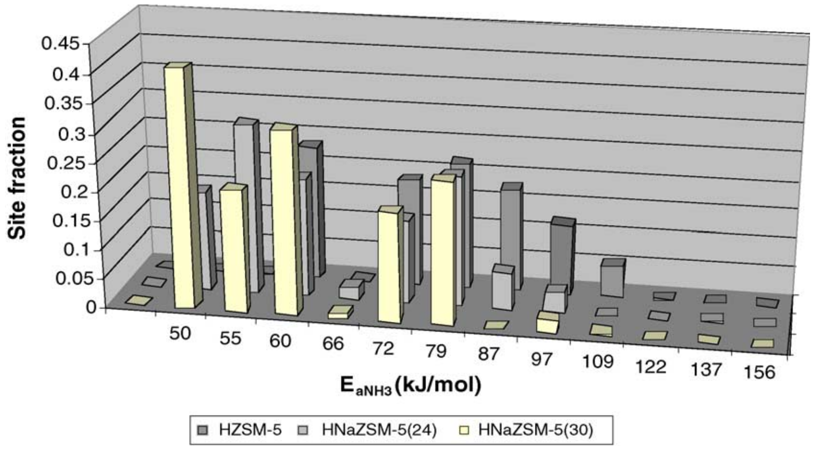

Fig. 5. Acid strength distributions for the three zeolites evaluated from the deconvoluted ammonia TPD spectra shown in Fig. 4.

To validate Eqs. (8) and (9), further computations were performed for a model reaction, which has been taken as an example. The reaction chosen for the example was the simple dissociative chemisorption of *n*-hexane (protolytic scission according to Eq. (1)) using the same model sites as for ammonia adsorption. Potential energies were computed for the whole system including the reactant, the model cluster, and the products. The results of the computations, i.e., the enthalpy for ammonia adsorption, $\Delta H_{\mathrm{NH_3}}$ (equal to $E_{\mathrm{a}}^{\mathrm{NH_3}}$) and the activation energy, $E_{\mathrm{a}}$, for the protolytic scission of *n*-hexane are presented in Table 1. The values obtained for the enthalpy of adsorption of ammonia are at the lower edge of experimental values and agree well with more elaborate computations using larger models [20,21]. It should be noted, however, that they do not include the contribution of confinement effects which was estimated to be about 20 kJ mol$^{-1}$, in the case of HZSM-5 [22]. Activation energies for the protolytic scission of *n*-hexane are on the high side compared to experimental values but here also it should be recognized that experimental values will be lower as a result of confinement effects [23].

Fig. 3 plots these results and shows that a linear relationship indeed exists between the activation energy for *n*-hexane cracking and the strength of the acidic Brønsted sites, evaluated by ammonia adsorption (see Eq. (17)):

$$E_{\mathrm{a}} = 491 - 1.53 E_{\mathrm{a}}^{\mathrm{NH_3}} \qquad (17)$$

This observation supports the assumptions made in the derivation of the activity–acidity relationships expressed by Eqs. (15) and (16).

### 4.2. Temperature-programmed desorption of ammonia

The $\mathrm{NH_3}$-TPD spectra for the three ZSM-5 samples under consideration and their deconvolutions into discrete components are shown in Fig. 4. Deconvolution of these TPD spectra using Eqs. (3) and (4), as described earlier, leads to the patterns shown in Fig. 4 from which the strength distribution of the acid sites can be derived.

Fig. 5 shows the acid strength distributions for all three catalysts. Although it might be expected that, for ZSM-5 the strength of the acid sites would be more uniform, the works such as the one by Olson et al. [24], indicate that for our catalysts, there is a significant heterogeneity of acid strengths; this is in accordance with our previous observations for other ZSM-5 catalysts [4], as well as those from other authors [25]. As expected, increasing $\mathrm{Na^+}$ ion exchange progressively reduces the number of strong acid sites, as shown by the intensity decreases of the high temperature desorption peak, the latter also confirming that exchange by sodium ions occurs preferably on the sites with greater acidity.

### 4.3. Catalytic activity for n-hexane cracking

Catalytic activity data expressed as the rate of *n*-hexane conversion (in mol/h/$\mathrm{g_{catalyst}}$) are shown in Fig. 6. Temper-

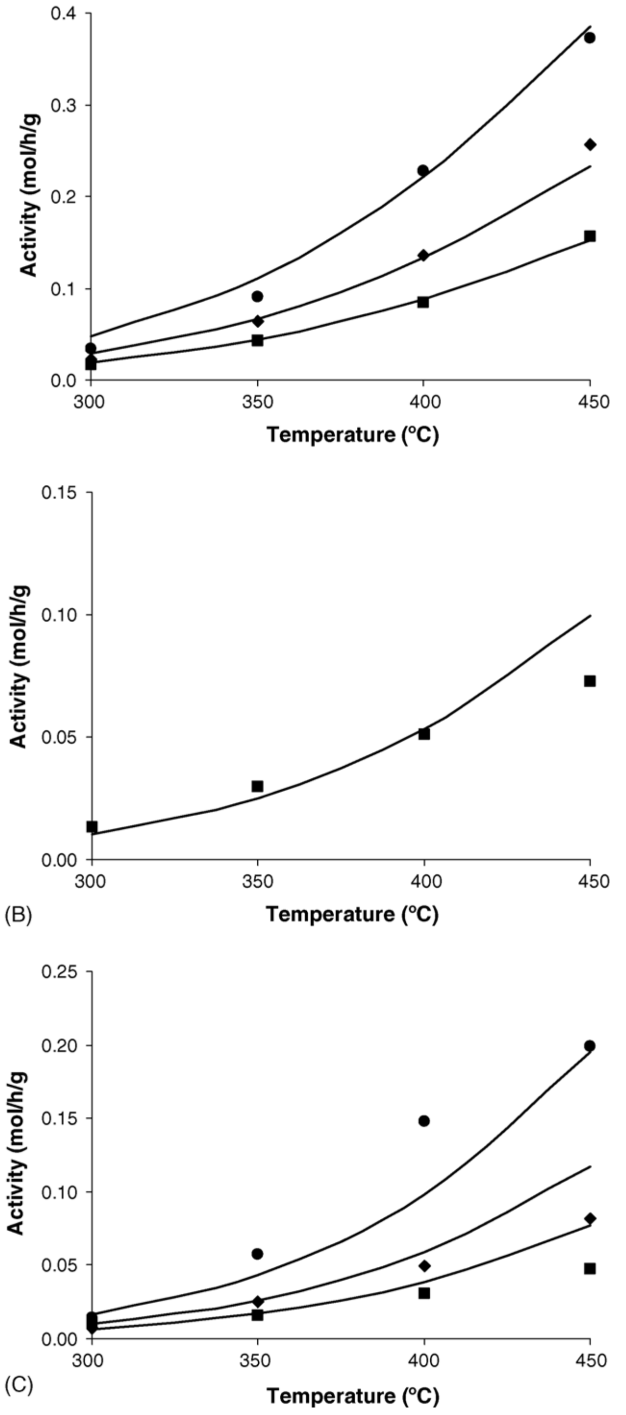

Fig. 6. Experimental catalytic activity for the cracking of *n*-hexane for different zeolites: (A) HZSM-5, (B) HNaZSM-5(24) and (C) HNaZSM-5(30). Symbols correspond to experimental data and lines to the model relating activity measurements to the acid strength distribution using the Marcus relationship. Partial pressures of *n*-hexane are: (■) −0.19 atm; (◆) −0.29 atm; (●) −0.48 atm.

Table 2
Fitted parameters

| Parameter | Polanyi model | Marcus model |
|---|---|---|
| $k_0$ (mol s$^{-1}$ g$^{-1}$ atm$^{-1}$ a.u.$^{-1}$)[a] | $1.19 \times 10^{-7}$ | $1.14 \times 10^{-7}$ |
| $E_a^{0N}$ (kJ mol$^{-1}$) | 82.5 | 85.5 |
| $\delta$ (Polanyi) or $\lambda$ (Marcus) | −0.332 | −0.209 |

[a] a.u. is an arbitrary unit that depends on the TPD equipment but that is proportional to the number of moles of active sites in the zeolite.

ature was varied from 300 to 450 °C as well as the partial pressure of *n*-hexane (from 0.19 to 0.48 atm). As expected, activity increases with temperature and partial pressure of *n*-hexane, and decreases with increasing sodium-ion exchange.

Symbols correspond to the experimental data points whereas the curves were obtained using Eqs. (14) and (16) fitting the experimental activity data assuming the Marcus relationship and the acid strength distributions determined by $NH_3$-TPD (Fig. 5). Good quality fits are observed.

### 4.4. Activity–acidity relationship

The catalytic activity results were correlated to the distribution of acid strength, measured by $NH_3$-TPD, using Eq. (14) and the expressions of the rate constants based on the Polanyi (Eq. (15)) and Marcus (Eq. (16)) models, respectively, using the least-square approximation. The values of $k_0$, $E_a^{0N}$, $\delta$ (Polanyi model), and $\lambda$ (Marcus model) are given in Table 2. Both models lead to nearly similar values for $k_0$, $E_a^{0N}$, $\delta$ and $\lambda$. The negative value for the latter two parameters confirms that the activation energy for the cracking of *n*-hexane decreases when the activation energy for ammonia desorption increases, i.e., when acid strength also increases. It should also be noted that the value of $E_a^{0N}$, ca. 85 kJ mol$^{-1}$, obtained from these fits for the symmetrical cracking of *n*-hexane is close to the experimental value, 97–109 kJ mol$^{-1}$, reported by Lukyanov et al. [26].

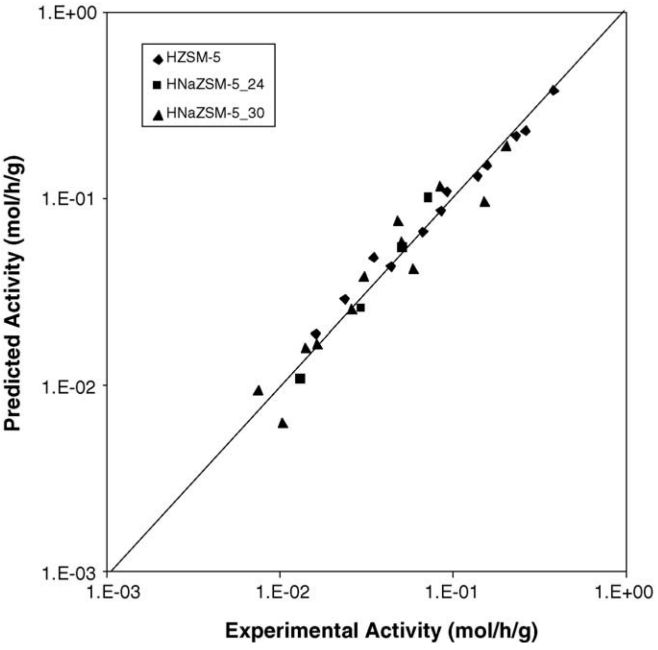

Fig. 7. Correlation between the experimental catalytic activity values and the theoretical values predicted by using the Polanyi model.

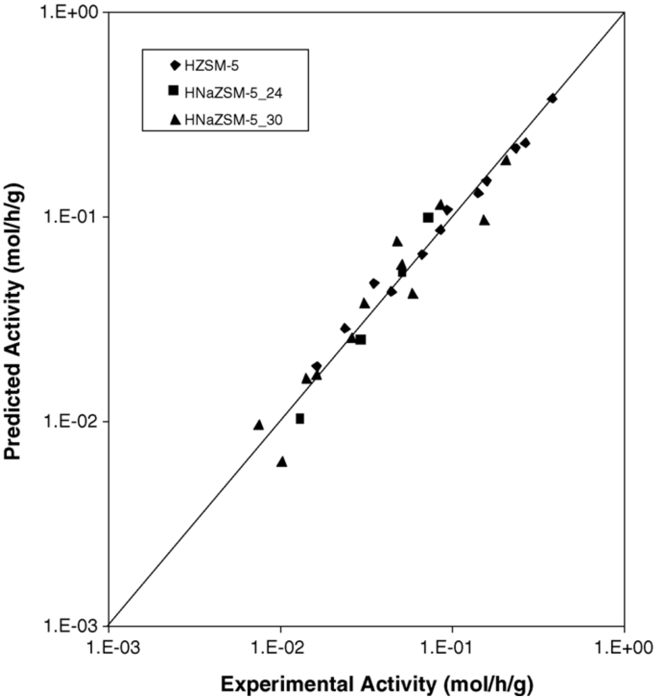

Fig. 8. Correlation between the experimental catalytic activity values and the theoretical values predicted by using the Marcus model.

The correlations according to the Polanyi's and Marcus's models between experimental and calculated (according to Eqs. (14), (15), and (16)) values between the catalytic activities obtained experimentally and the values calculated using the two proposed models are shown as parity plots in Figs. 7 and 8. In both cases, the agreement between experimental and theoretical data is most satisfactory. Both models describe well the behaviour of samples with different acid distributions in a broad range of temperatures and *n*-hexane partial pressures. This is to be expected as differences between the Polanyi's and Marcus's models are only expected when reactions are very highly endothermic or exothermic. However, the situation could be different for reactions that are very little or very highly demanding on the acid strength of the catalytic sites.

## 5. Conclusions

Experimental activities for the cracking of *n*-hexane can be correlated satisfactorily to theoretical ones evaluated using the Polanyi or the Marcus model, considering the distribution of acid site strength measured by ammonia TPD.

For the reaction considered in this study and the range of experimental conditions used, the Marcus model does not present a significant improvement relative to the Polanyi model, although this might be the case for reactions that are either much less or much more demanding on acid strength.

The strategy described in this work indicates that it is possible to predict the activity of a zeolite for a given reaction provided the acid sites strength distribution is known, one simple method for obtaining the latter being ammonia TPD. This approach appears most attractive, as it would considerably decrease the time necessary to evaluate their catalytic performance by reducing the number of catalytic tests to be performed.

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