Contributions for the study of the acid transformation of hydrocarbons over zeolites

P. Borges [a], R. Ramos Pinto [a,b], P. Oliveira [a], M.A.N.D.A. Lemos [a], F. Lemos [a,*], J.C. Védrine [c], E.G. Derouane [a,d], F. Ramôa Ribeiro [a]

[a] IBB – Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[b] ISCSP, Pólo Universitário do Alto da Ajuda, Rua Almerindo Lessa, 1349-055 Lisboa, Portugal
[c] Laboratoire de Réactivité de Surface, Université P. & M. Curie, 4 place Jussieu, F-75252 Paris, France
[d] Faculdade de Ciências e Tecnologia, Centro de Investigação em Química e Catálise, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

ABSTRACT

The acid-catalysed transformation of hydrocarbons constitutes a very important set of reactions for industrial applications of zeolites. These transformations have a high degree of complexity due both to the variability of the loads that are used, usually an intricate mixture of different hydrocarbons with various reactivities, and to the fact that zeolites possess acid sites with a wide range of acid strength distribution. In this paper we intend to give a contribution to the analysis of the transformation of hydrocarbons over zeolites taking into account this latter effect. An example on the conversion of propene over ZSM-5 catalysts, with Si/Al = 15 and 24, 30 and 32% H$^+$ exchanged by Na cations is described; in this example we show that it is possible to correlate the catalytic activity of a series of catalysts with their acid strength distribution, as measured using ammonia TPD, using Polanyi-type relationships. The use of these acidity–activity relationships allows the description of the behaviour of a set of catalysts using a single set of kinetic parameters that includes the sensitivity of the reaction to the acidity of the site and opens the way to the prediction of the activity of a catalyst based solely on the characterization of its acid site distribution.

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1. Introduction

Acid-catalysed transformations are very relevant reactions in many fields of the chemical industry and have been studied for a long time, both in homogeneous and heterogeneous phases.

Acid catalysis on homogeneous phases has been the subject of many studies to obtain quantitative correlations between the activity of a given catalyst and its acidity. The quest for these relationships has started in the beginning of the XXth century, with the pioneering works of Taylor [59] and Brønsted [60] and has been the basis for many other works, leading to the Seminov [1] and Polanyi [2][1] relationships and, in a more general form, to the development of linear free-energy relationships [3,4], which have found many uses in acid catalysis and organic chemistry [5].

In fact, correlating the rate of reactions with thermodynamic parameters has been a quest for chemists and chemical engineers for a long time. Hammond, started a paper published in 1955 [6] by

saying "Chemists have long been plagued by the lack of any general correlation between reaction rates and the positions of chemical equilibria". This quest has been the subject of many approximations that have been applied to the homogeneous catalysis. Since the original proposal by Polanyi which supports the previously presented Brønsted relationships for homogeneous acid catalysis, Marcus [7] and, more recently, Blowers and Masel [8] have proposed different schemes to relate the activation energy for a reaction with its thermicity.

Despite the fact that homogeneous acid catalysis has been successfully addressed by the approach of the linear free-energy relationships, the application of this concept to heterogeneous catalysis has been less pursued, although the gains that can be obtained from applying predictive techniques to heterogeneous acid catalysis can be very important for industrial and scientific applications. In the late 1960s and early 1970s Yoneda published a series of paper on the use of linear free-energy relationships for heterogeneous catalysis, including some on acid catalysis [9,10]

The reason for the slow application of this technique to heterogeneous catalysis is related to various issues.

The first issue is that there is no clear and universally accepted acidity scale for heterogeneous catalysts; whereas in aqueous medium pH is a simple enough scale to assess the acidity of a solution and the dissociation constant(s) of an acid species is a

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quantitative measure of the acidity of a molecular species. No such scales exist for heterogeneous acids, although attempts have been made to establish an indirect acid scale for zeolites based on model reactions [11–13].

The second issue is that homogeneous acids can be characterized by one, or, in the worst case, by a limited number of dissociation constants; on the contrary, a heterogeneous acid catalyst possess many different sites, a problem which is common to all comparisons between uniform or single-site catalysts, characteristic of homogeneous catalysts, and multi-site catalysts, typical of heterogeneous catalysts.

It is true that the characterization of the acidity of solid catalysts has been systematically carried out for various decades [14–16] by a variety of methods [17–19], and attempts have been made to correlate this acidity with activity [20,21], but, because no detailed description is used for the acidity of the solid catalysts, no direct correlation can be observed and the apparent kinetic rate constant per active site varies widely.

In this paper we will discuss the application of the concepts underlying the Brønsted relationships, as further developed by Polanyi, Marcus, Masel and other researchers to the acid transformation of hydrocarbons over zeolites and will apply them to the transformation of propene over acidic ZSM-5 catalysts showing that it is possible to quantitatively correlate, with a single set of kinetic parameters, the activity of a series of catalysts to the acid strength distribution.

2. Experimental

2.1. Catalysts

All catalysts were prepared from a parent HZSM-5 (MFI structure type, protonated form) zeolite, with a Si/Al molar ratio of 15, obtained from Zeolyst (CBV 3024G). The original sample had virtually no sodium and it was partially Na-exchanged to modify its acidity. Three additional catalysts were prepared from the same original zeolite by ion exchange with aqueous solutions of sodium nitrate with different concentrations. The catalysts prepared will be referenced as HZSM-5 (the unmodified catalyst) and HNaZSM-5_24, HNaZSM-5_30 and HNaZSM-5_32, where the last two figures correspond to the percentage of protons that was exchanged by sodium cations, as determined by elemental analysis.

2.2. Catalyst pre-treatments

All samples were calcined at 500 °C for 8 h under a flow of dry air of 0.5 l h^{-1} g^{-1}. After calcination, the zeolites were kept at room temperature in a constant and high humidity container. Prior to the ammonia TPD measurements and catalytic tests, all samples were pre-treated for 8 h at 450 °C under a flow of dry nitrogen.

2.3. Catalytic tests

The propene transformation was carried out in a fixed-bed continuous flow reactor with 75 mg of catalyst (wet basis). All reactions were carried out at atmospheric pressure and with a temperature range from 300 °C to 450 °C. The partial pressure of the reactant was varied from 5 to 30%, diluted with nitrogen. The total flow of reaction mixture was 120 ml min^{-1}. The reactant was fed for 3 min and then the effluent stream was sampled and analysed. After the first three analysis the time interval during which the reactant was fed was gradually increased so as to ascertain that no deactivation occurred during this period; the feeding interval was of 5 min, for the 4th–6th samples, 10 min, for the 7th and 8th, and 20 min for all the following ones. The catalyst was kept under a flow of pure nitrogen during the analysis. Fresh catalyst was used for each

run. No deactivation with time-on-stream was detected for up to 84 min of reaction. After the run the used catalyst was heated, under a nitrogen/air mixture, in a simultaneous TG/DSC apparatus, from ambient temperature up to 700 °C, to check for coke but none was detected.

External transport limitations were checked by varying the flow rate while keeping the same catalyst mass; no changes in reaction rate were observed. Internal limitations were checked using the Weisz–Prater criterion [22]. Using a diffusion coefficient of 9.7×10^{-9} m^2 s^{-1}, taken from [23], and assuming that the zeolite particles were always under 500 μm in size and total conversion (the worst case scenario) we obtained a value for the product of the effectiveness factor by the Thiele modulus, Φ, of 0.005, for 350 °C and for the lower gas phase concentration, which is significantly less than 1. Since the actual conversion is always less than 1, this criterion indicates that, within the range of experimental conditions used, there are no significant diffusion limitations.

The analysis of the effluent was carried out with a Shimadzu GC-9A gas chromatograph equipped with a Chrompack Plot CP7515 fused silica column and a flame ionization detector. The chromatogram was integrated with a Shimadzu C-R3A integrator.

2.4. Ammonia TPD

Temperature programmed desorption (TPD) of ammonia was used to determine the acid strength distribution of the active sites, as described in [24]. About 200 mg of zeolite were placed in a silica reactor and pre-treated *in situ* as described above. The catalyst was then kept at 90 °C under a flow (60 ml min^{-1}) 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 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^{-1}, under a flow (60 ml min^{-1}) 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 an *ab initio* Hartree Fock model with a 6-31G**basis set. These computations aimed at establishing a relationship between the desorption enthalpy of ammonia (a measure of acid strength) and the energy levels of the various steps involved in the reaction for the dimerization of propene.

To simulate modification of acid strength and its effect on the cracking of n-hexane, model sites of general formula SiH$_n$Cl$_{3-n}$OH (n = 0, 1 and 2) were used, the replacement of H by Cl resulting in an increasing acidity of the OH group. These models are obviously very simple and do not account for long range and media interactions, nor for geometrical effects. They, however, provide information on how enthalpies for ammonia desorption and the energy levels of the various steps involved can be correlated.

3. Theory

When we are interested in relating the acidity of a catalyst and its activity for a certain reaction, there are two levels of information that have to be constructed. The first one is to establish a suitable acid strength scale to characterize the acid catalysts and the second one is to obtain a quantitative correlation between the acidity

and the activation energy for the reaction that is being observed. We will start by looking at the main differences between homogeneous and heterogeneous acid catalysis and we will then discuss the establishment of a suitable acidity scale for the heterogeneous acid sites and its relation to the activation energy for the transformation of hydrocarbons over zeolites.

3.1. Differences between homogeneous and heterogeneous acid catalysis

The major difference between homogeneous and heterogeneous acid catalysis relates to the fact that homogeneous catalysts are essentially single-site catalysts, where it is relatively easy to characterize the active site by some properties, while heterogeneous catalysts usually possess a multitude of different sites, which not only have different quantitative interactions but also may exhibit different qualitative interactions with the molecules involved in the reaction scheme.

It is also important to note that, in many cases, the more relevant acid species present in an aqueous solution is the solvated proton, which can be represented by the H_3O^+ species and that the "acid strength" can be effectively measured just by the concentration of this species. In these cases the acidity of a solution can be measured by pH alone and, for this reason, the acidity and solvated proton concentration are often confused. In fact, when a stronger acid is used, since it presents a higher dissociation constant, this will also mean (for a given concentration of acid species) that a higher concentration of H_3O^+ will occur and, thus, pH is, in fact, a reasonable measurement of "acid strength", although it only measures the concentration of a specific acid species.

When moving to heterogeneous catalysis this is no longer true. The acid sites "work on their own" and an individual account of the number and strength of each one of them is required. Heterogeneous catalysts do not behave as single-site catalysts, i.e. a particular catalyst usually possesses acid sites of different strength and it is likely that they all contribute, with their own relative weight, to the activity of that catalyst. The usual approximation is to disregard the sites with lower acidity and consider only the stronger sites. However, most heterogeneous acid catalysts, for instance in the widely used zeolites, possess acid sites that are structurally different and have also different environments [25–27]. This produces a rather broad distribution of acid site strengths and, thus, in order to have a detailed view of the activity one should account for all, or at least, a large part, of the acid sites present in the catalyst. Attempts to relate the activity to the acidity usually results in non-existent or highly non-linear relationships [11–14,28,29], even if the correlation is made using only the number of stronger acid sites [30].

Acid strength distributions for solid catalysts can be obtained by various methods, most of which depend on the thermal desorption of bases from the acid sites to characterize and quantify the number and strength of the acid sites.

3.2. An acidity scale for heterogeneous catalysts

The establishment of an adequate acidity scale to measure the acid strength of sites in heterogeneous catalysts, and in particular in zeolites, is of paramount importance in the development of predictive quantitative relationships between acidity and activity.

For acids in aqueous solutions the acidity scale that is commonly used, the value for the dissociation constant of the acid, relies, in fact, on the measurement of the interaction of the acid with a "standard" base: water. The dissociation constant measures the ability of the acid to transfer a proton to a water molecule. It has also been proposed that, in a way similar to homogeneous catalysis, Hammet indicators could be used to establish a reasonable acid-

ity scale [31,32], and this scale has even been used to establish acidity–activity relationships [33].

It is reasonable to use a similar interaction between the acid site and a base molecule to establish a working acidity scale for heterogeneous acid sites and a lot of work has been done using the adsorption, and subsequent desorption, of bases as a way to measure the acid strength of catalysts (see, for instance [12]). Many studies have been done using ammonia as the base molecule. The use of ammonia has distinct advantages, since it is a strong base and a relatively small molecule, which is, thus, able to access most acid sites in a catalyst. These advantages are also linked to the disadvantages of using ammonia as a probe molecule, since ammonia can adsorb on many acid sites which are only accessible by small molecules or are too weak to be able to efficiently participate in catalysis. Note that accessibility can be probed by means of bases, usually amines, of different sizes [14] and an extension of the work described here for ammonia can be developed so that accessibility can also be taken into account.

However, ammonia adsorption and desorption has been used as a way to measure the acidity of zeolites and the adsorption energy of ammonia, as measured by NH_3-TPD, has been proposed as an acid scale for zeolites [24]. It has been also shown to be equivalent to acidity measured by ^{1}H NMR [34] and, very recently, to acidity measured by infrared spectroscopy [35]. It should be noted that the interaction of a NH_3 molecule with an acid site is likely not to involve an energy barrier for the adsorption step and, thus, the adsorption energy should be symmetrical of the activation energy for the desorption of the ammonia molecule from that site [24].

NH_3-TPD has been used for a long time to estimate the activation energy for the desorption of ammonia. This can be done by performing TPD experiments at various heating rates, and using the shift in desorption maximum to estimate the activation energy for the desorption (according to a method that can be found, for instance, in reference [36]). However, the dynamic experiment involved in NH_3-TPD can provide much more information and, for many years, various techniques have been developed to extract the full information regarding the acid strength distribution [37–47].

3.3. Determination of the acid strength distribution

To obtain the distribution of acid strength from a single NH_3-TPD profile we must perform a deconvolution of the thermogram into several components, corresponding to sites with uniform acidity and characterized by the number and strength of the acid sites [37]. 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. (1)):

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

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

The experimental ammonia TPD spectrum (rate of desorption vs. temperature) is the sum of the desorption curves corresponding to the different types of acid sites. A discrete energy grid was used to represent the different desorption activation energy values. As a consequence the overall TPD spectrum can be represented by:

$$\frac{dq}{dt} = -\sum_{i=1}^{n} k_i \, e^{-E_{a(i)}^{NH_3}/RT} q_i \tag{2}$$
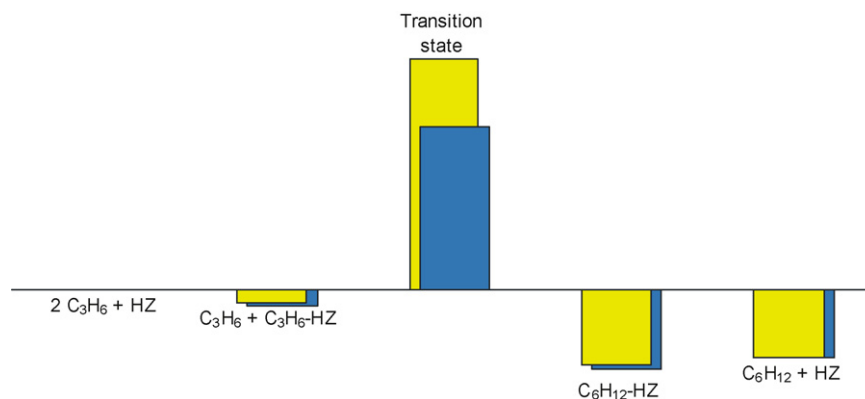
Fig. 1. Schematics for the first few steps in the transformation of propene over acidic sites, evidencing the influence of the acid strength of the site. (▢) weaker acid site, (■) stronger acid site. Relative energies computed using the *ab* initio HF/6-31G** quantum model described in the text.

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.

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. (3), as proposed by Hashimoto [40]:

$$k_i = \alpha e^{\beta E_{a(i)}^{NH_3}} \tag{3}$$

where α and β 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: $\alpha = 4.5\,s^{-1}$; $\beta = 0.11\,mol\,kJ^{-1}$ [48]).

3.4. Acidity–activity relationships

Having established a working acid scale for zeolite catalysts the next step is to relate the acidity of a site with the activity. For this purpose the easiest way is to transpose the old Brønsted relationships to heterogeneous catalysis in a way similar to the one proposed by Yoneda in the 1960s [9]. The easiest way to look at this rationale is to apply the Polanyi principle.

Let us consider what happens if we increase the acidity of a zeolite protonic site. An increase in acidity will lead to an increase in the interaction of that acid site with ammonia, but it will also imply an increase in the interaction with other base molecules, such as olefins, and also a stabilization of the carbocations or alkoxides that will be formed during the accept process for the transformation of hydrocarbons on acidic zeolite sites.

Let us consider the transformation of propene over acid sites. Fig. 1 depicts a schematic representation of the energy changes in the various steps in the initial stages of this transformation as computed using the quantum model described above for two acid sites of different acid strength. First a propene molecule is adsorbed onto an acid site, bonding to the acid site through the electrons in the double bond, and then this adsorbed olefin is converted into an alkoxide species, which is, in sequence, attacked by a second propene molecule to give a C6 alkoxide. The energy position of each of these stages, and in particular the activated step of the surface reaction, is correlated to the acid strength of the acid site where the transformation occurs. We will assume that the adsorption energy for the olefins (E_{ads}) is linearly correlated to the activation energy for the desorption of ammonia ($E_a^{NH_3}$), according to Eq. (4).

$$E_{ads} = b E_a^{NH_3} \tag{4}$$

where b represents the sensitivity of the adsorption enthalpy to the acidity of the site.

In relation to the activated step we will use the correlations mentioned above. The simplest correlation that can be used is the one based on the Polanyi principle. If the enthalpy of the surface reaction, ΔH_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 ΔE_a equal to a fraction γ_p of the change $\Delta\Delta H_r$. 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 γ_p the sensitivity of the activation energy dependence on enthalpy of reaction. This approach has been used already by some authors to correlate reaction rate constants for a family of reactions [49] but it has the drawback of assuming that the reaction pathway is strictly the same for all the catalytic sites and, as it can be seen from Eq. (5), the activation energy may become negative for highly exothermic reactions (very acidic sites).

As described above, other equations have been proposed to solve these difficulties. The Marcus relationship was proposed to explain some of the discrepancies observed for very endothermic or very exothermic reactions. While the Polanyi relationship can be obtained using linear approximations to the energy profile around the stable states, the Marcus relationship can be obtained if we consider that the energy profile around these stable states is described by a quadratic equation and leads also to a second order dependence of the activation energy on the reaction enthalpy (Eq. (6)):

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

Again we will consider that the enthalpy of reaction, ΔH_r, is linearly dependent on the desorption of ammonia, $E_a^{NH_3}$ according to

$$\Delta H_r = a + b' E_a^{NH_3}$$

where a is the non-catalysed reaction enthalpy and b' is the sensitivity of the reaction enthalpy to the acidity of the site. Substitution in Eq.(5) or (6), will give:

$$E_a = E_a^0 + \gamma_p a + \gamma_p b' E_a^{NH_3} = E_a^{0N} + \delta E_a^{NH_3} \tag{7}$$

and

$$E_a = \left(1 + \frac{a + b' E_a^{NH_3}}{4E_a^0}\right)^2 E_a^0 = \left(1 + \lambda \frac{E_a^{NH_3}}{E_a^{0N}}\right)^2 E_a^{0N} \tag{8}$$

for the Polanyi and the Marcus approaches, respectively. In both cases E_a^{0N} is the activation energy for the reaction carried out over a non-acidic site, given respectively by

$$E_a^{0N} = E_a^0 + \gamma_p a$$

and

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

δ and λ are the parameters that measure the sensitivity of the reaction to the acid strength of the site, respectively for the Polanyi and the Marcus approaches.

$$\delta = \gamma_p b'$$

and

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

Eq. (7) is, in fact, an extension of the well-known Brønsted relationships to heterogeneous acid catalysis and has already been applied successfully to the transformation of hydrocarbons over both Y [50] and ZSM-5 [48] zeolites. Eqs. (7) and (8) have already been compared for the transformation of n-hexane over H-ZSM-5 [24].

3.5. Molecular modelling as a tool to understand acidity–activity relationships

Polanyi, Marcus and Blowers-Masel relationships are based on approximations of the energy changes that take place along the reaction coordinate but nowadays, there are already a series of methods that can provide some insight into the pathway for the transformation of hydrocarbons over acidic sites.

Molecular modelling has been extensively used to understand the transformation of hydrocarbons but, although the influence of the hydrocarbon structure has been examined [51], the influence of acidity has only seldom be analysed [24,52,53].

From the studies that have been published it is clear that nearly linear relationships can be found between the acidity of a site and its catalytic abilities. In fact, using different molecular models, linear relationships have been found for the activation energy for the
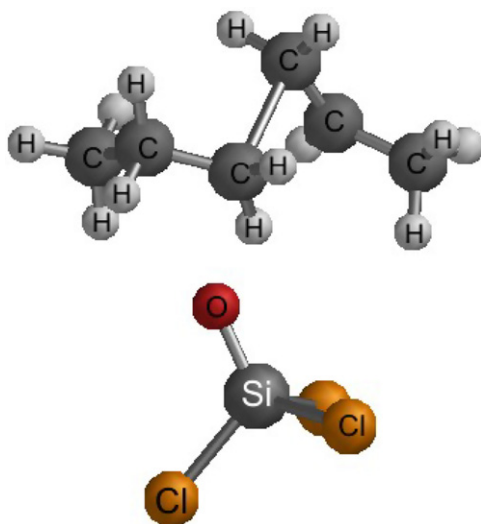
transformation of propane [53] and for the protolytic cracking of n-hexane [24]. Blowers has also found linear relationships between the activation energy for various reactions involved in the conversion of ethane with the deprotonation energy of the site [52].

These findings give full support for the use of a Brønsted type relationships to describe the influence of acidity on the catalytic performance of the acid sites in zeolites.

We have inspected the first step in the transformation of propene using an *ab initio* HF/6-31G** model. Full geometry optimizations were performed for the states corresponding to propene molecule
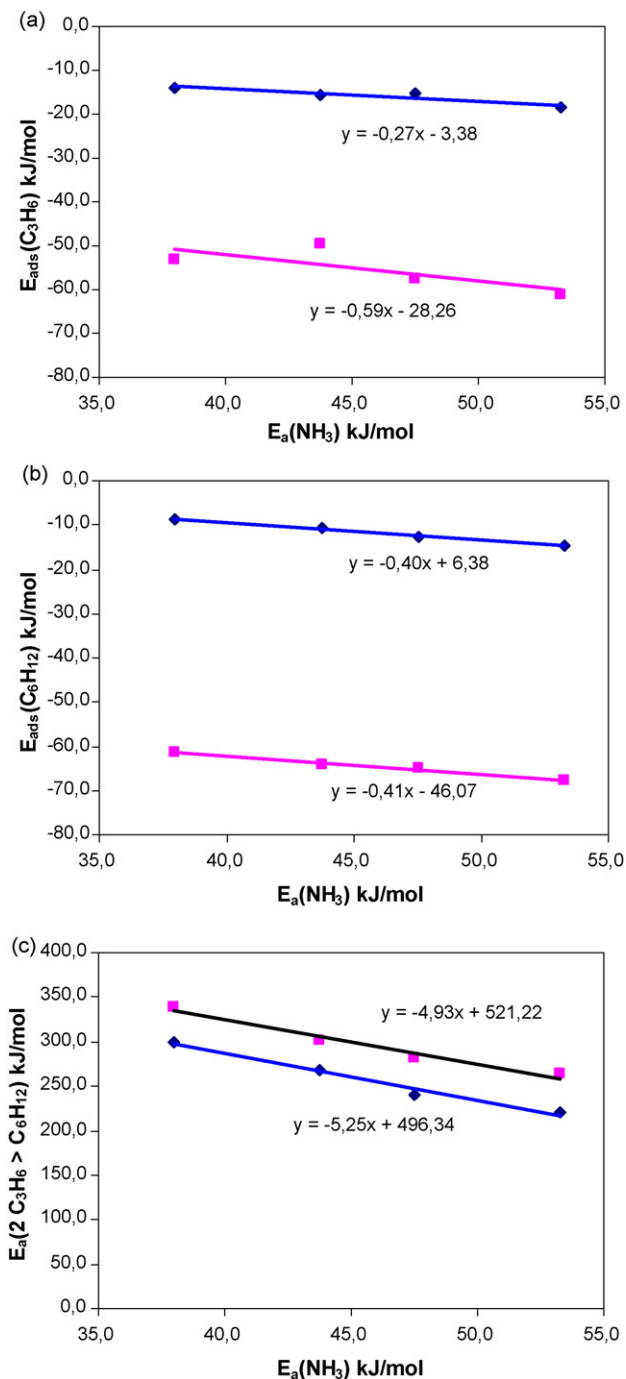
Fig. 3. Heat of adsorption of propene (a) or hexene (b) to the acid site by the double bond (◆) and by formation of the corresponding alkoxide (■) and activation energy for the surface reaction involved in the dimerization (c) as a function of the activation energy for the desorption of ammonia, as a measure of the acid strength, as computed by the HF/6-31G** molecular model (all values given in kJ mol^{-1}, see text for details).

Fig. 2. Transition-state for the dimerization of propene on a model acid site. The imaginary vibration frequency evidences the formation of the new C—C bond.

adsorbed by the double bond, the propyl alkoxide, the hexyl alkoxide and the hexane adsorbed by the double bond. A transition state search was performed to compute the energy of the transition state, for which the geometry is depicted in Fig. 2.

The results obtained also indicate that there is a linear relationship between the energy levels in all the steps in the transformation and the acidity of the site as measured by the activation energy for the desorption of ammonia (see Fig. 3).

Our main concern in analyzing these calculations is to verify that a linear relationship is expectable between the various energy differences in the steps involved in the mechanism for the dimerization of propene, which is true for all the possible steps, according to the quantum model that was used. As the acidity of the sites increase, corresponding to an increase in the activation energy for the desorption of ammonia, the adsorption energies become more negative (stronger adsorption) and the activation energy decreases (the reaction becomes easier), as expected. It can also be observed that there is some dependence of the adsorption energy on the size of the hydrocarbon, more pronounced for the alkoxide species.

It is also noteworthy that the activation energy for the surface reaction seems to be much more sensitive to the acidity of the site than the adsorption energy.

It is interesting to note that the results obtained from the quantum models indicate that the alkoxide forms are more stable than the forms corresponding to the olefins adsorbed by the double bonds; nevertheless the transition state that was obtained is closer, both in terms of energy and in terms of geometry, to the olefins
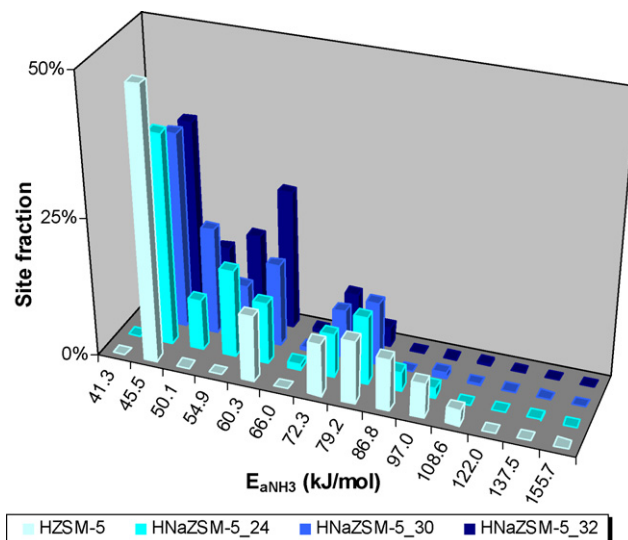

Fig. 4. Acid strength distributions of the HZSM-5, the HNaZSM-5_24, the HNaZSM-5_30 and the HNaZSM-5_32 catalysts, evaluated from the ammonia TPD experiments; see [24] for details.
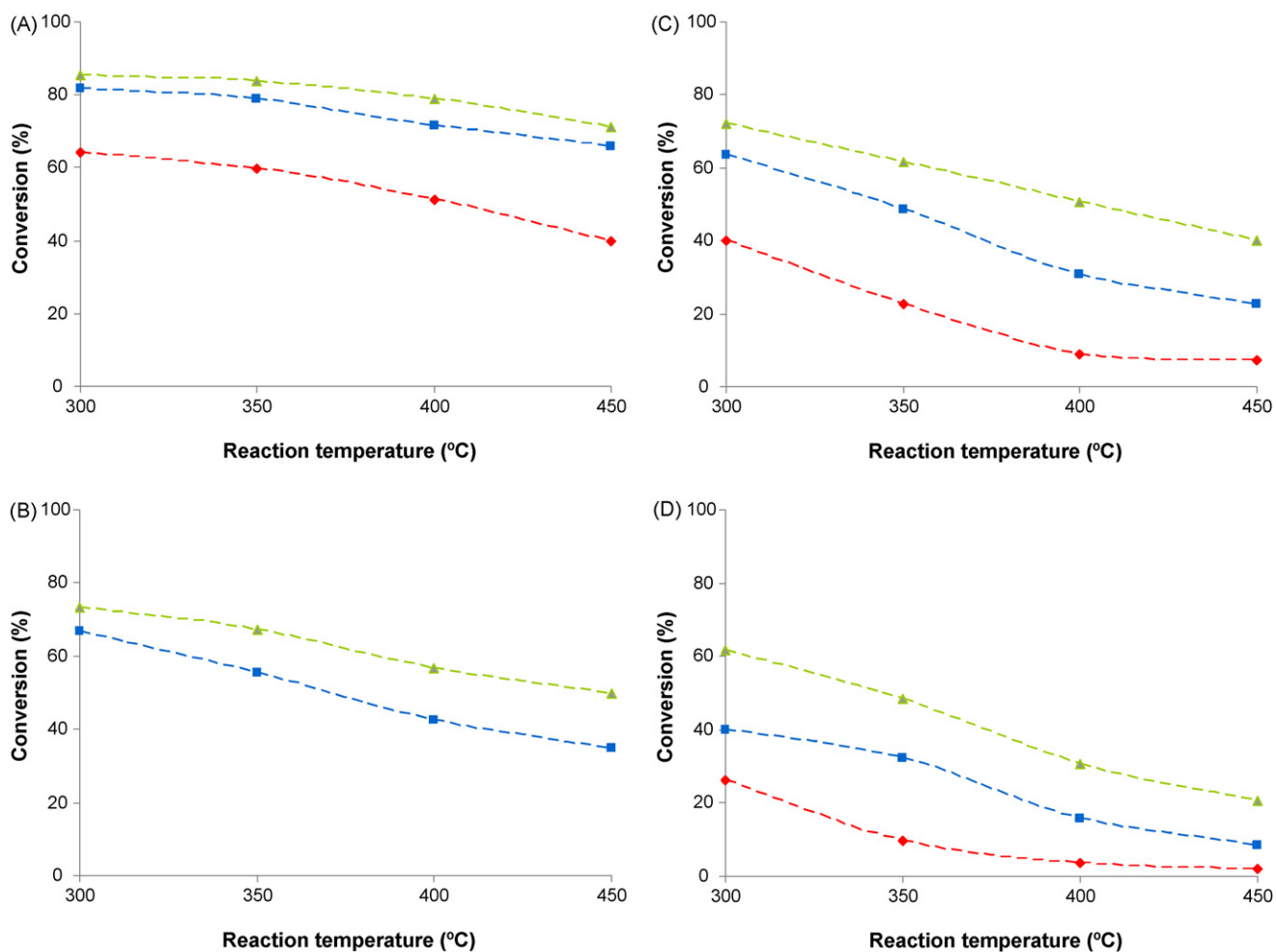

Fig. 5. Conversion of propene as a function of temperature, for various partial pressures of olefin in the feed (♦, 0.05 bar, ■, 0.15 bar, ▲, 0.30 bar). A–HZSM-5; B–HNaZSM-5_24; C–HNaZSM-5_30 and D–HNaZSM-5_32.

adsorbed by the double bonds than to the alkoxide species. This results in a higher activation energy for the surface reaction if we consider the reactant as being in the alkoxide configuration.

4. Results and discussion

The theory, outline above, will be used to correlate the activity towards the transformation of propene with the acidity, as measured by NH_3-TPD, in the series of catalysts that was prepared. We can expect that, besides the acidity, aspects related to the pore structure of the catalysts will influence their activity through confinement and pore structure effects [54,55]. However, since all catalysts were prepared from a single parent zeolite and the modifications, which were introduced by ion-exchange procedures to change the acidity, were not expected to change the pore structure of the catalyst, these effects should remain the same for the whole series of catalysts. Thus, only the acidity will have a bearing on the differences observed among the various catalysts.

Fig. 4 depicts the acid strength distributions that were obtained from ammonia TPD, by the procedure described above, for the four catalysts studied during this work. Since we expect the acid strength distribution in the zeolite to be continuous, each peak in the figure corresponds to the number of acid sites that have an activation energy for the desorption of ammonia around the value that is quoted; the peaks for activation energies of 41.3 and 45.5 kJ mol^{-1}, however, correspond to ammonia that is still physically adsorbed on the zeolite at the beginning of the desorption process and, thus, is not related to actual acid sites. These peaks have not been included in the correlation with catalytic activity.

As to the transformation of propene, for the experimental conditions that were used, no significant deactivation was observed in any of the experiments that were carried out. Part of the data on the transformation of propene over HZSM-5 has already been reported in a previous paper [56].

Fig. 5 depicts the propene conversion, as a function of temperature, for various partial pressures of reactant, for the all catalysts that were used, while Fig. 6 shows an example of the product distribution that was obtained for catalyst HNaZSM-5_24.

As it can be seen, as the temperature increases the conversion lowers; it was also observed that the product distribution is shifted towards lighter products with increasing temperature. On the other hand, as the partial pressure increases the conversion increases and heavier products are obtained.

The main products that are observed can be rationalised as resulting from a reaction scheme where the oligomerisation of the reactant is eventually followed by cracking, as suggested, for instance by Derouane in the case of ethene [57]. As a result, the main products are olefins, although significant amounts of aromatic and paraffinic products are also observed, resulting from other secondary transformations, such as aromatization and hydrogen transfer reactions. Since the catalysts used are fairly acidic we did not observe any of the heavier olefins which are readily cracked into lighter products under the operating conditions that were used.

It has been shown [56] that this behaviour could be interpreted assuming an oligomerization mechanism involving the adsorption of the propene molecule followed by cracking of the larger molecules. This has led to the following reaction rate law:

$$(-r_0) = \frac{kKC_L p_0 p_{O\,inlet}}{1 + Kp_{O\,inlet}} = \frac{kKC_L p_{O\,inlet}^2 (1 - x)}{1 + Kp_{O\,inlet}} \tag{9}$$

where k is the kinetic rate constant for the surface reaction by which a propene molecule is added to the adsorbed chain and K is the equilibrium constant for the adsorption of an olefin to the acid site, C_L is the surface concentration of acid sites and $P_{O\,inlet}$ is the olefin concentration at the reactor inlet. These are expressed as a function
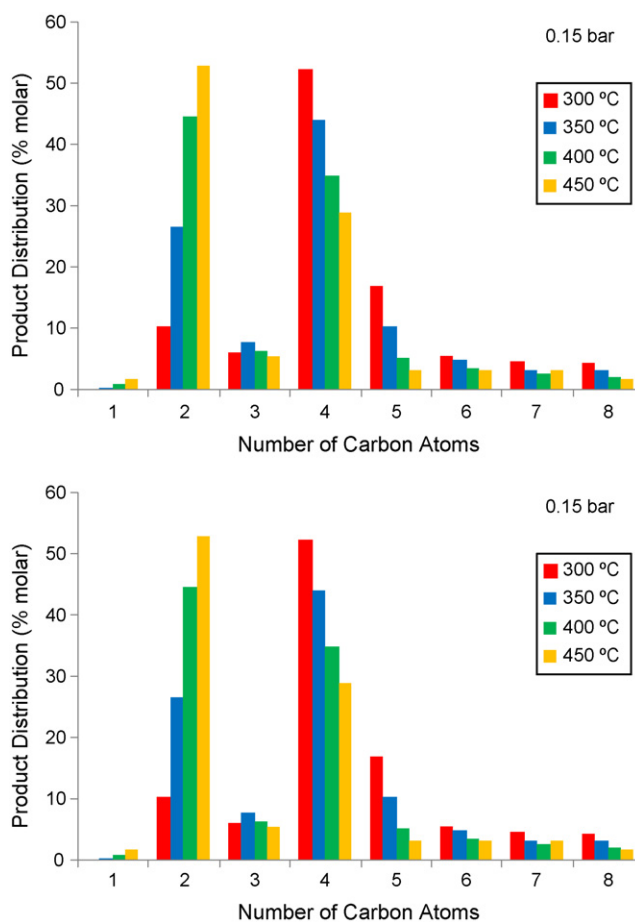

Fig. 6. Product distribution in the transformation of propene with the HNaZSM-5_24 catalyst.

of temperature, by the Arrhenius

$$k = k_0\, e^{-E_a/RT} \tag{10}$$

and Van't Hoff equations,

$$K = K_0\, e^{-\Delta H_{ads}/RT} \tag{11}$$

respectively.

Notice that Eq. (9) is equivalent to a simple first order kinetics but with the kinetic rate constant given by

$$k_{eff} = \frac{kKC_L p_{O\,inlet}}{1 + Kp_{O\,inlet}} \tag{12}$$

We will now consider that both the rate constant and the equilibrium constant depend on the acidity of the site over which the reaction is being carried out. The activation energy will depend on the acidity according to Eq. (7) (Polanyi approach) or to Eq. (8) (Marcus approach) and the adsorption energy will depend on acidity according to Eq. (4). Then, the effective rate constant for a catalyst with multiple sites will be given by

$$k_{eff} = k_0 K_0 C_L p_{O\,inlet} \sum_{i=1}^{n} q_i^0 \frac{e^{-(E_a^{0N} + \delta E_i^{NH_3})/RT}\, e^{bE_i^{NH_3}/RT}}{1 + K_0\, e^{bE_i^{NH_3}/RT} p_{O\,inlet}}$$

$$= k_0' \sum_{i=1}^{n} q_i^0 \frac{e^{-(E_a^{0N} + \delta E_i^{NH_3})/RT}\, e^{bE_i^{NH_3}/RT}}{1 + K_0\, e^{bE_i^{NH_3}/RT} p_{O\,inlet}} \tag{13}$$

Table 1
Fitted parameters for the complete model with propene. Confidence intervals were estimated using a bootstrap methodology [52] and are given to a 95% confidence level.

Parameter	Polanyi	Marcus
k_0 (mol s^{-1} g^{-1} a.u.$^{-1}$ *)	$3.2 \times 10^{-14} \pm 0.7 \times 10^{-14}$	$2.49 \times 10^{-14} \pm 0.8 \times 10^{-14}$
δ	$-2.65 \times 10^{-9} \pm 1 \times 10^{-15}$	–
λ	–	$-2.59 \times 10^{-9} \pm 1 \times 10^{-15}$
E_a^{0N} (kJ mol^{-1})	6.9 ± 0.4	7.2 ± 0.6
K_0	$3.6 \times 10^{-5} \pm 0.8 \times 10^{-5}$	$2.5 \times 10^{-5} \pm 0.6 \times 10^{-5}$
b	-0.80 ± 0.02	-0.83 ± 0.02
Least Squares Sum (mol^2 s^{-2} g^{-2} a.u.$^{-2}$)	2.37×10^{-9}	2.37×10^{-9}

* a.u. is generic unit that depends of the TPD equipment but that is proportional to the number of moles of active sites on the zeolite.

for the Polanyi approach and by

$$k_{\text{eff}} = k_0 K_0 C_L p_{\text{O inlet}} \sum_{i=1}^{n} q_i^0 \frac{e^{-(1+\lambda(E_a^{NH_3}/E_a^{0N})^2 E_a^{0N}/RT)} e^{bE_i^{NH_3}/RT}}{1 + K_0\, e^{bE_i^{NH_3}/RT} p_{\text{O inlet}}}$$

$$= k_0' \sum_{i=1}^{n} q_i^0 \frac{e^{-(1+\lambda(E_a^{NH_3}/E_a^{0N})^2 E_a^{0N}/RT)} e^{bE_i^{NH_3}/RT}}{1 + K_0\, e^{bE_i^{NH_3}/RT} p_{\text{O inlet}}} \quad (14)$$

for the Marcus approach.

From Eqs. (9) and (13) or (14), according to the approach considered, the conversion was computed at the outlet using a plug flow model for the reactor. Using the values obtained from the ammonia TPD for the amounts of sites (excluding the peaks corresponding to activation energies of 41.3 and 45.5 kJ mol^{-1}, as explained above), the models were fitted to the experimental data using k_0, K_0, E_a^{0N}, b and δ or λ as fitting parameters. Confidence intervals for the various parameters were estimated using a bootstrap methodology [58]. The estimated parameters are given in Table 1 along with the corresponding confidence intervals. Parity plots for the fittings are shown in Fig. 7.

As it can be seen from the parity plots, although the confidence intervals for some of the parameters are relatively large, this model describes with reasonable accuracy the experimental results that were obtained, notably in the cases where higher activity is observed, that is, for the more acidic catalysts. It is worthy to note that the model was applied with a single set of kinetic parameters, which include only five parameters for each model, the ones presented in Table 1, to all experiments, covering not only all partial pressure and temperature variations but also the use of different catalysts.

As a conclusion from our results, one can say that this model is quite useful as practical computational model for the reaction at hand, although some care should be taken in analysing the kinetic and thermodynamic parameters that were estimated, since some of them have relatively large confidence intervals. Looking at the parameters that were estimated, one can see that, contrary to what could be expected from the sensitivity computed using the molecular modelling results (see Fig. 3), the activation energy for the surface reactions seems to be much less sensitive to the acidity of the site, as it can be seen by the δ or λ values, than the adsorption of the olefins (see the value of b); however if we look at the sensitivity computed using the molecular modelling results, and if we take into account that the activation energy for the desorption of ammonia from these model sites is very low, indicating that they are very weakly acidic, we may find an explanation for this discrepancy. In fact, using the equation shown in Fig. 3(c), it is possible to compute the strength of the acid site that would result in zero activation energy for the surface reaction step. This would occur for a site with an activation energy for the desorption of ammonia of only 94.6 kJ mol^{-1} (for the reaction starting with the olefin coordinated by the double bond) or 105.8 kJ mol^{-1} (for the reaction starting from the alkoxide species), which are in fact very close to the actual activation energies for the sites in the catalysts, as mea-

sured by the TPD experiments. Above these values the activation energy computed by the linear approximation would be negative and, thus, not physically viable. According to the modifications on the Polanyi equation, both introduced by Marcus and by Blowers and Masel, in this case the sensitivity of the reaction towards the acidity should become very low for high acidity values, as it is in fact observed by the values of either δ or λ.

On the other hand, the estimated value for the sensitivity of the adsorption energy on the acidity is -0.80 or -0.83 (respectively for the Polanyi and Marcus approximations), which compares very well with the values given in Figs. 3(a) and (b).
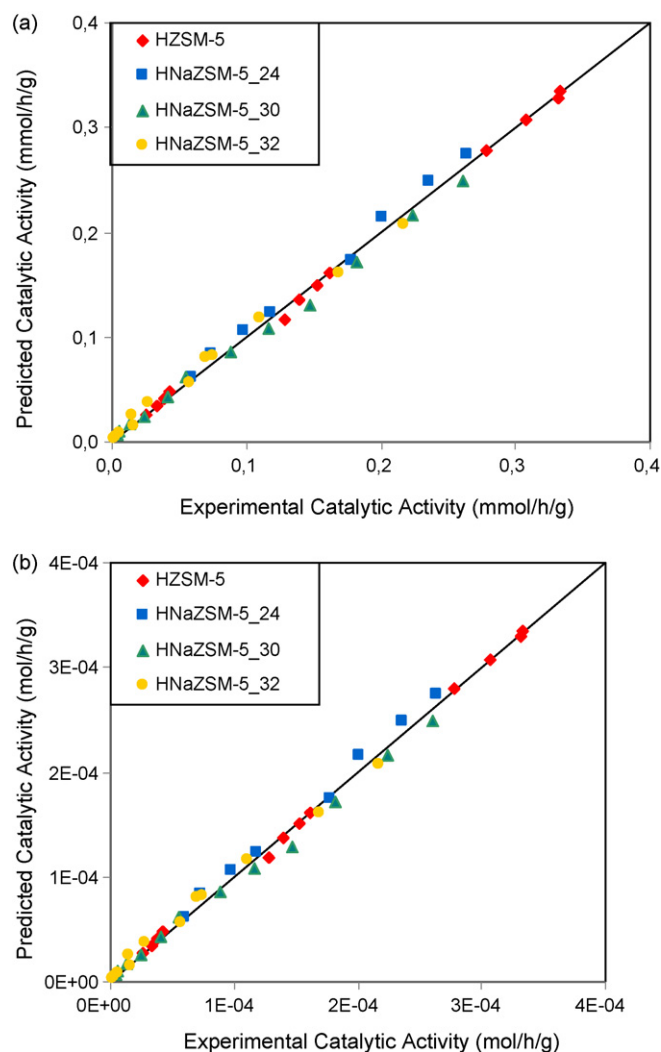

Fig. 7. Parity plots for the fittings of the kinetic models accounting for acid strength distribution using a Polanyi (A) and a Marcus (B) approach. All temperatures, partial pressures and catalysts tested are depicted.

5. Conclusions

The results that have been obtained so far clearly indicate that it is possible to establish acidity–activity relationships for heterogeneous catalysts in a manner which is similar to the ones that have been used for homogeneous catalysis for decades. These relationships account for the heterogeneity of the strengths of the acid sites present in solid acid catalysts and require the use of suitable acid scale. Similarly to the acidity scale that is accepted for homogeneous acids, the interaction of the acid site with a standard base is adequate and ammonia is a suitable choice since it has been used for quite a long time.

The use of these acidity–activity relationships allows the description of the behaviour of a set of catalysts using a single set of kinetic parameters that includes the sensitivity of the reaction to the acidity of the site and opens the way to the prediction of the activity of a catalyst based solely on the characterization of its acid site distribution.

Although molecular modelling indicates that all steps in the reaction network may be influenced by acidity, the fittings, obtained for the series of HNaZSM-5 catalysts on the transformation of propene, indicate that the largest influence is on the adsorption step, generating the adsorbed active species (which is likely to be an alkoxide species). This apparent discrepancy may be due to the fact that the model sites that were used are only very weakly acidic. The search for more suitable acid site models to be used in molecular modelling calculations, as well as the use of different quantum models, may provide answers to this issue.

Although the work done so far indicates that it is possible to obtain a single set of parameters for a certain reaction and a given family of catalysts, it is certain that further work is needed to compare different catalysts and obtain a universal description for heterogeneous catalysts.

Acknowledgments

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