

Review

Zeolites as solid solvents¹

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Abstract

In addition to their natural appeal as crystalline solids possessing a void intracrystalline volume consisting of channels and cages, sometimes interconnected, zeolites also have remarkable features resulting from the surface curvature of their internal surface. These features involve non-covalent interactions between the framework of the zeolite and molecules adsorbed in their intracrystalline free space. These interactions extend beyond the molecular level and are thus of supramolecular nature. They are at the origin of confinement effects which govern their behaviour as sorbents and catalysts. By contrast to molecular shape selective effects which result from short range repulsions imposing restrictions on sorbates or reactants, reaction transition states, and/or products, the van der Waals interactions responsible for confinement effects are long ranged and attractive. They favour the adsorption of certain molecules vs. others, sometimes at specific locations in the intracrystalline volume, stabilise reaction transition states, and may eventually enhance the probability of bimolecular reactions. Because of such confinement effects, zeolites can be assimilated to solid solvents and several of their characteristics can be described using solvent effects as an analogy. This review analyses recent literature supporting this view with specific attention to the application of zeolites in selective adsorption and separation and their use as catalysts for fine chemicals synthesis. Some other consequences of confinement effects will also be discussed, in particular those relating to the measurement and optimal use of the acidic properties of zeolites. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Solvent; Intracrystalline free space; Sorbents; Catalyst

1. Introduction

The usefulness of many objects depends on the open space which they offer, just as the utility of a container is determined by its accessible empty volume...

Lao Che, Tao Te Ching, Chap. XI, in: A. Waley, *The Way and its Power*, Grove Press, New York, 1959.

Pleasantest of all ties is the tie of host and guest...

Aeschylus, 525 to 456 BC, *The Choëphoroe*.

Molecular sieves, zeolites in particular, are tridimensional crystalline solids which possess a large free intracrystalline volume consisting of channels and/or cages of atomic size, sometimes interconnected. Their ability to adsorb selectively and separate organic molecules [1,2] and their action as molecular shape selective

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catalysts [3,4] were first recognised in the 40s and 60s, mainly through the pioneering work of Barrer [1,2] and Weisz and Frilette [3] and Weisz [4], respectively.

The molecular shape selectivity (MSS) of zeolites results from short-range repulsions, i.e., constraints, arising from the interaction of sorbed molecules with their channels or cages of atomic size [4–9]. Reactant selectivity is observed when some reactants only can access their intracrystalline volume. Product selectivity occurs when reaction products have distinct diffusional behaviours in the zeolite pores. Restricted transition state selectivity prevents the formation of certain reaction transition states and inhibits the corresponding reaction steps.

The concept of confinement in zeolite channels and cages was introduced by us in the late 80s. By contrast to MSS, confinement effects stem from longer range and attractive interactions, e.g., van der Waals forces, which are of supramolecular nature. Confinement increases the physisorption energies of sorbates up to values which may become comparable to the activation energies for chemical reactions, enables the reactant(s) to recognise sites which are most favourable for their physisorption, and stabilises the reactant(s) and the reaction transition state(s) in an environment promoting the desired catalytic transformations, in a manner that may sometimes mimic the action of enzymes [10,11].

Consequently, two types of guest–host interactions and effects co-exist in zeolites, of which one will often predominate. This fact is unfortunately not always recognised today when discussing guest–host relationships and the selectivity of zeolite catalysts.

A specific consequence of confinement is that zeolites, e.g., molecular sieves in general, can be described as solid solvents when the sizes of the sorbate and of the channels or cages are comparable. Barthomeuf [12] was first to propose this idea in a paper introducing activity coefficients to rationalise the acidic properties of zeolites. However, no consideration was given at that time to the role played by intermolecular

forces between the sorbate(s) and the zeolite framework.

The present contribution addresses this problem by using as background the original confinement model [10,11]. In addition, some specific effects of confinement affecting the characterisation of acidity in molecular sieves and their observed acid activity, sometimes misquoted as acid strength, will also be discussed.

2. The confinement theory

The first qualitative proposal related to confinement effects is mentioned in a paper disclosing the ‘nest effect’ [13] based on results for the cracking of *n*-pentane on the protonated form of various zeolites [14]. It proposes that some of the remarkable properties of molecular sieves originate from their (somewhat flexible) open framework, possessing channels and/or cages acting as ‘pockets’, where the activation and conversion of substrates occurs. The ideas underpinning this proposal are the following,

- There will be situations where the selectivity of zeolites is dominated by positive (attractive) interactions, in contrast to the negative (repulsive) constraints which govern molecular shape selective catalysis.

- The substrate molecules and the zeolite framework may reciprocally optimise their respective structures to maximise their van der Waals interaction.

- Nesting may occur both in the intracrystalline volume of the zeolite and at the external surface which is made of ‘craters’ and ‘hills’ (the zeolite external surface cuts through cages and pore walls).

A model considering dispersion forces only was first elaborated to quantify the van der Waals interaction of a molecule with a surface whose curvature is at the atomic level [10,11,15]. This model explains in an unitary and quantitative manner several of the remarkable properties of zeolites as sorbents and catalysts. The key

variable is the dimensionless ratio of molecule size to cage/channel size, $s = d/a$ (d = distance of the molecule to the pore wall, a = pore radius), which is sufficient to quantify the magnification of dispersion forces relative to a flat surface of similar chemical nature ($W_r(s)$; $W(s)$ = energy for the system with curvature s , $W(0)$ = energy for the flat surface) when a molecule is adsorbed in a curved environment, as described in Eq. (1).

$$W_r(s) = W(s)/W(0) = (1 - s/2)^{-3} \quad (1)$$

When $s = 0$, corresponding to a flat surface ($a = \infty$), classical adsorption behaviour is expected and the physisorption energy is relatively small ($W_r(s) = 1$). However, when $s = 1$ corresponding to the situation for maximum confinement (tight fit) in this simple model, the physisorption energy is enhanced by a factor of 8, an effect already noted by de Boer and Custers [16]. For s -values larger than 0.5, physisorption energies are at least three times larger than those observed for the flat surface and may thus become comparable, in the $0.5 < s < 1.0$ range, to the activation energies measured for chemical reactions. Consequently, for microporous solids, their effect should not be overseen contrarily to the common perception that physisorption is

negligible relative to chemisorption. This model was used to quantify the behaviour of zeolites as molecular traps and to introduce new concepts such as ‘flotation’ and ‘reptation’ which are useful to describe the motion and the diffusional properties of sorbates in zeolite channels.

The confinement model was elaborated further to include different types of pore shape [17], as well as repulsion effects [18]. A rather complex relationship was derived in the latter case of which the main results are shown in Fig. 1. When repulsion effects are taken into account, the maximum magnification of the sorption energy, W , (relative to the flat surface case value, $W(F)$), is equal to 5.05 (rather than 8 for the simple model) in the optimal tight fit situation which is met for $s = d/a = 1.136$ (rather than 1.0 for the simple model). The variation of $W/W(F)$ vs. the curvature parameter s has the typical shape of a molecular energy curve (inverted). The magnification of the adsorption energy is still largely sufficient to explain the effects described hereabove, proposed on the basis of the simple van der Waals model.

It is enlightening to note that molecules can be strongly trapped in pores which are substantially narrower than their free (gas phase) sizes. The situation of lowest energy, $W/W(F)$ in

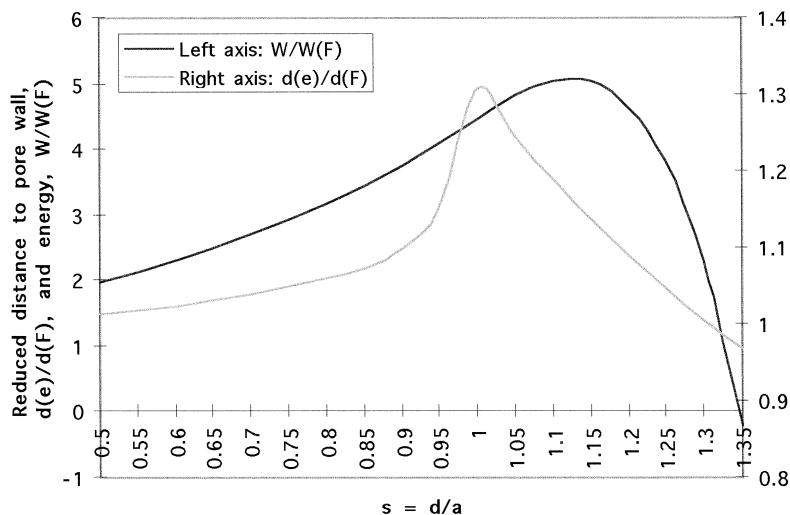


Fig. 1. Variation at equilibrium of the reduced adsorption energy, $W/W(F)$, and reduced adsorption distance, $d(e)/d(F)$, as a function of the curvature parameter, $s = d/a$.

Fig. 1, corresponds to a pore size equal to 88% of the free gaseous molecular size ($s = 1.136$) and the sorption energy remains favourable down to a pore size of only 75% of the free gaseous molecular size. This conclusion is sufficient to explain why molecules can be adsorbed in pores with size smaller than their cross-section in the gas phase. A typical case is that of benzene (van der Waals cross-section = 0.6 nm) which is easily adsorbed by MFI or MEL structure-type materials (ZSM-5, ZSM-11, silicalite; pore size = ca. 0.55 nm). In oversimplified terms, the reason for this is that the van der

Waals cross-section of an atom or a molecule is not a fixed ‘molecular’ property but a ‘collision’ parameter depending on the interaction of the atom or molecule with its neighbours or surroundings. The deeper the attraction potential well (i.e., the higher the confinement energy), the smaller will be the apparent van der Waals radius, within certain limits.

Looking at the equilibrium adsorption distance, $d(e)$, it is seen that the molecule remains in a tight fitting situation for $s \geq 1$, in which case $d(e)$ is determined by the pore radius, and after which for increasing pore radius (s de-

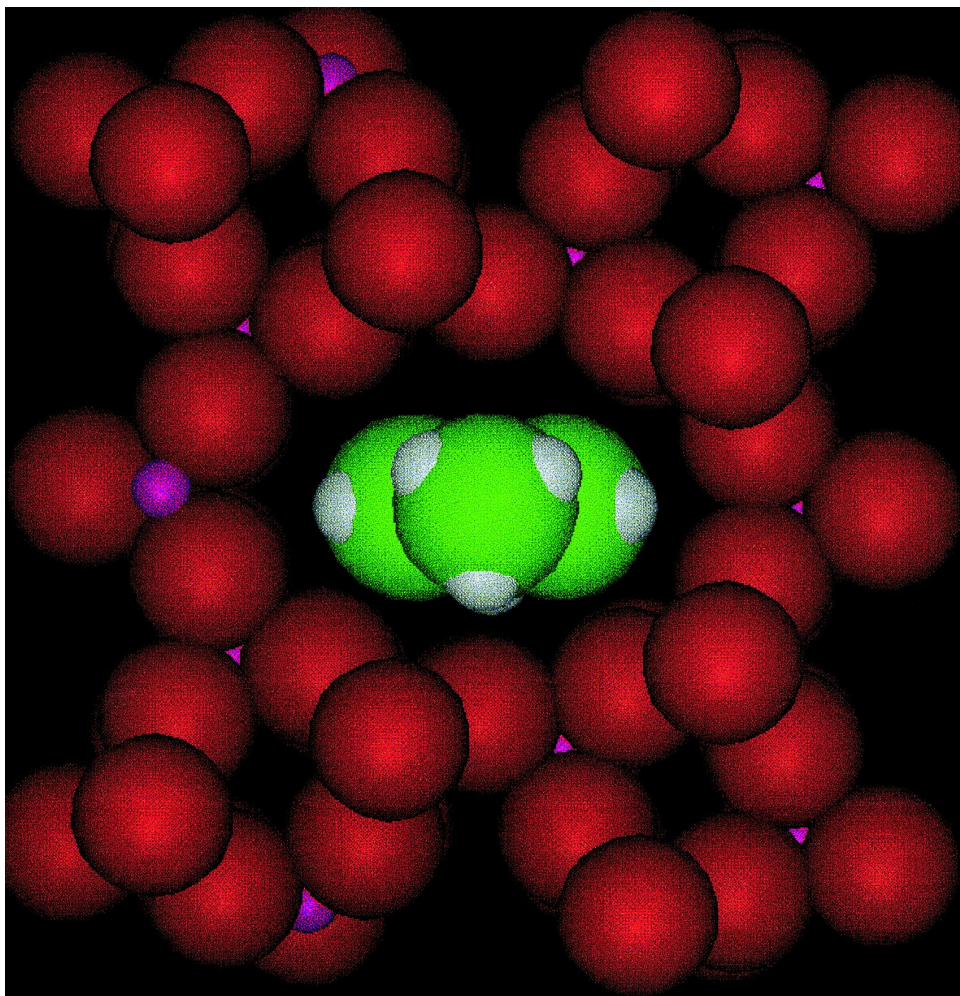


Fig. 2. *p*-Xylene ‘solvated’ by SAPO-11 (structure-type AEL with unidimensional highly elliptical channels (0.39*0.63 nm)).

creasing) the molecule sticks preferably to the pore wall and $d(e)$ decreases rapidly towards the value $d(F)$ observed for the flat surface situation (see $d(e)/d(F)$ vs. s in Fig. 1). It is concluded that molecules are preferentially adsorbed on the pore walls in large channels and may occupy more axial positions in smaller channels, and that the motion of molecules

across the channel (or cage) is an activated process whose activation energy becomes higher when channel (cage) dimension increases.

Both the simple and revised models were successfully used to correlate and predict the physisorption energies of non-polar molecules in various zeolites and other molecular sieves [18–20] on the basis of easily accessible molec-

A. Before

B. After

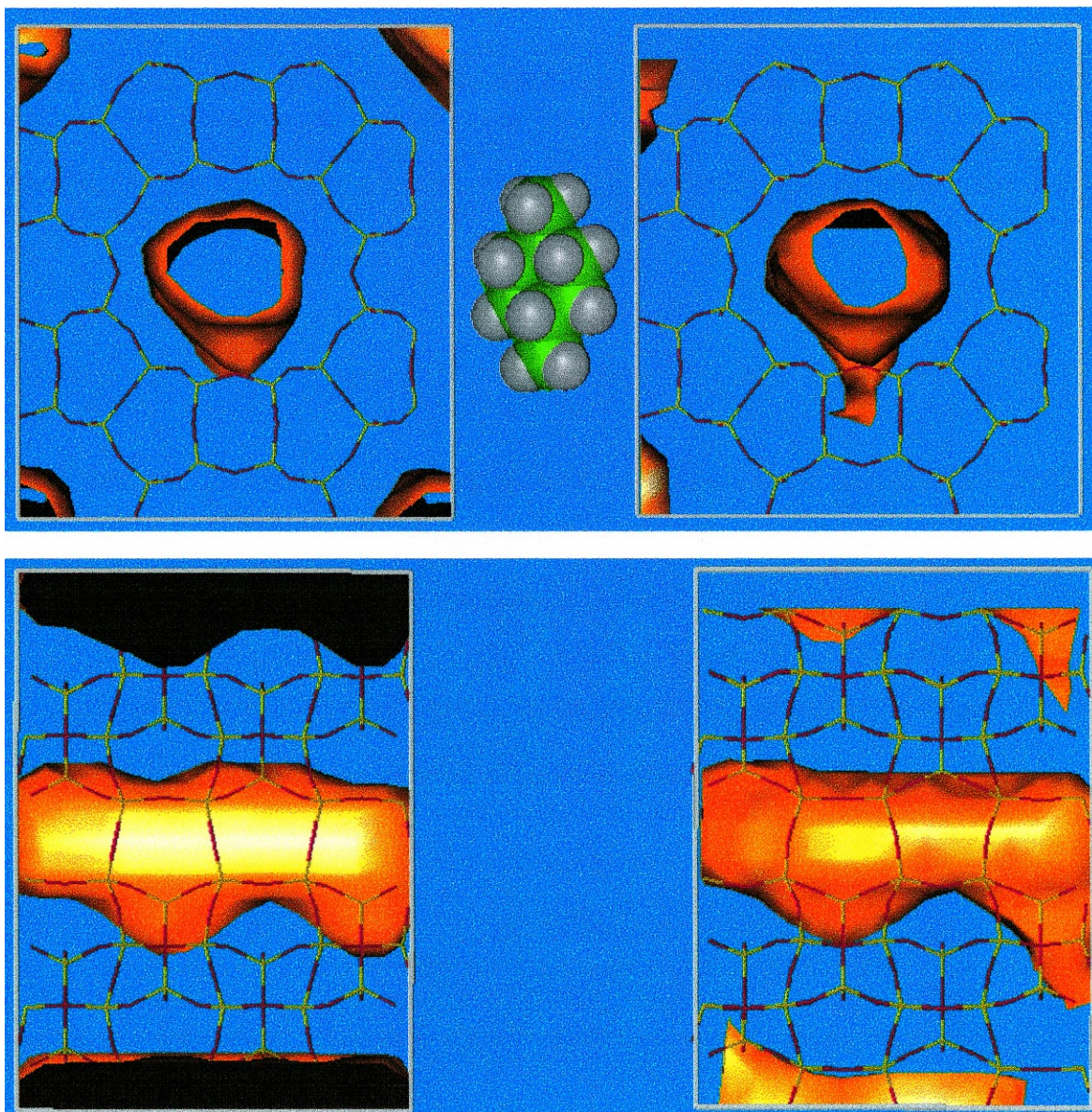


Fig. 3. Relaxation of the MOR framework upon adsorption of 1,4-dimethyl-cyclohexane. (A) Before adsorption. (B) After adsorption.

ular parameters (size and polarisability of the guest molecule) and a surface curvature variable ($s = d/a$) defined by the ‘guest molecule–zeolite host’ couple. Such a correlation shows that caution should be exerted when comparing calorimetric adsorption data for the same substrate in zeolites with highly different pore sizes or that of functionalised molecules with increasing chain length (or C number) in a specific zeolite [21]. It also suggests that even for a (small) molecule like NH_3 commonly used to count and measure the strength of acid sites in zeolites, the calorimetric heat of adsorption contains a non-negligible van der Waals contribution which increases for smaller pore sizes. Thus, the higher heat of adsorption of ammonia in ZSM-5 compared to mordenite and dealuminated zeolite Y does not entirely result from increased acid strength as commonly assumed but also from confinement effects as discussed later in this paper.

Several general conclusions can thus be drawn.

- Molecules adsorbed in the intracrystalline void space of a zeolite are in strong van der Waals interaction with their surroundings. They should not be considered or treated as being in the solid, liquid, or gas phase but rather as molecules solvated by the zeolite framework by analogy to solute–solvent interactions. Molecular modeling of *p*-xylene in SAPO-11 illustrates this point (Fig. 2). The fit between the *p*-xylene molecule and the zeolite channel shows that SAPO-11 is an excellent solid solvent for *p*-xylene. The physisorption energy of *p*-xylene in SAPO-11 is about 90 kJ mol^{-1} , thus comparable to the activation energy necessary to reach the transition state in several chemical reactions *p*-xylene may undergo. Zeolites and molecular sieves thus behave as solid solvents. In this respect, the adsorption of a gas by a zeolite can be described within certain limits by Henry’s law.

- Molecules can ‘contract’ to enter pores which have a size smaller (down to about 80%) than their free (gas phase) molecular size. This

is not unlike volume contraction effects which are observed upon mixing two liquids having a high affinity for each other. This observation may have paramount importance for the optimisation of selective sorption and separation processes, including the use of zeolite membranes for those.

- Similarly, it is expected that the zeolite framework will be distorted, at least locally, upon adsorption considering the magnitude of the physical interactions which are involved. Such distortions or lattice relaxations have indeed been reported experimentally upon adsorption of various molecules in zeolites such as ZSM-5 [22,23], RHO [24], and aluminophosphate sieves such as VPI-5 [25], and can now be predicted and illustrated by theoretical calculations and molecular modeling. Fig. 3 shows, for example, the channel of mordenite before (Fig. 3A, left) and after (Fig. 3B, right) adsorption of dimethylcyclohexane. It is seen that the zeolite lattice relaxes upon adsorption of dimethylcyclohexane which is tight-fitting, in order to reach an energy minimum by optimising van der Waals interactions and minimising repulsion [26].

3. Confinement effects in sorption and adsorption

3.1. Adsorption of simple molecules and hydrocarbons

Nitrogen and argon adsorptions are widely used to characterise solids in a high state of dispersion, among which zeolites. One routine method of analysis is the BET formalism which enables to calculate specific surface areas, assuming multilayer adsorption which is the statistical result of competitions between physisorption on the free surface of the solid and condensation on already existing adsorbate layers. Surface areas are derived by converting a calculated theoretical monolayer volume for the ad-

sorbate into an equivalent surface, knowing the area cross-section of the probe molecule. Although it was noted about 10 years ago that the BET formalism should be taken with a pinch of salt and preferably not used to characterise zeolites [10], the current literature still contains plenty of such examples.

Nitrogen adsorption at 77 K is certainly the most simple and quantitative method to evaluate the available intracrystalline volume of a zeolite sample. The amount of N₂ adsorbed at the plateau of the isotherm ($p/p_0 = \text{ca. } 0.2\text{--}0.35$) corresponds to the saturation of the channels and cages. Its comparison to the amount of N₂ adsorbed in the same conditions for an authentic and 100% crystalline sample enables the absolute and rapid determination of crystallinity. However, surface areas cannot be derived because of two reasons which contradict the hypotheses underpinning the BET model. The first one is that nitrogen, like all other molecules, is solvated by the zeolite framework and thus interacts strongly with its environment regardless of its exact position in the zeolite channel or cage. The second one is that multilayers as hypothesised in the BET formalism cannot be formed in channels or cages for geometrical reasons. For zeolites, it is thus recommended to use directly the plateau coverage (volumetric) value as described hereabove or possibly the theoretical monolayer volume which is part of the standard output of automated BET analysers. Both values generally agree within about 10% and can be used to characterise reliably the free intracrystalline volume and the absolute crystallinity of the zeolite.

The heat of dissolution of alkanes in an inert solvent increases proportionally to their chain length. Indeed, dispersion forces are responsible for mixing and solubility and the intermolecular forces and energetics which are involved are nearly proportional to the number of electrons of the solute. Similar observations have been made for the adsorption of alkanes in zeolites [27–29] and the following relationships were derived for the heat of adsorption, Q_s (kJ

mol⁻¹), of linear alkanes in zeolites MFI, LTL, and FAU [10]:

$$Q_s(\text{MFI}) = 15.0n(\text{CH}_3) + 9.7m(\text{CH}_2) \quad (2)$$

$$Q_s(\text{LTL}) = 13.6n(\text{CH}_3) + 8.4m(\text{CH}_2) \quad (3)$$

$$Q_s(\text{FAU}) = 11.0n(\text{CH}_3) + 7.0m(\text{CH}_2) \quad (4)$$

with $n(\text{CH}_3)$ and $m(\text{CH}_2)$ being the numbers of methyl and methylene groups, respectively. These equations show that the molecule–zeolite interaction is the sum of segmental contributions, an original proposal due to Barrer and Davies [29]. The values of the coefficients increase with confinement from FAU ($a = 0.37\text{--}0.59$ nm) to LTL ($a = 0.36\text{--}0.45$ nm) and MFI ($a = 0.27\text{--}0.38$ nm) ($a =$ pore radius; the first value corresponds to the channel size, the second to the cage or intersection diameter) and from CH₂ to the bulkier and more polarisable CH₃ group.

3.2. NMR evidence for the behaviour of zeolites as solid solvents

Raynes et al. [30] and Abraham and Holker [31] discussed the effect of van der Waals interactions to rationalise solvent effects on NMR chemical shifts in solution. Similar principles can be used to correlate and predict the ¹³C and ¹²⁹Xe NMR chemical shifts of organic species and xenon adsorbed in zeolites by considering confinement effects [32–34].

In molecular sieves, the pore wall consists exclusively of a dense arrangement of oxygen anions which polarise the electron density of the sorbed molecule. Thus, the screening by electrons of NMR sensitive nuclei will vary and the position of their NMR resonance will depend on pore size. Indeed, the fluctuation of the zeolite electric field whose square is not averaged out in time results in a paramagnetic contribution to the chemical shift. The latter depends on van der Waals interactions and is described by a relationship involving the reduced parameter $W_r(s)$ defined in Eq. (1).

Fig. 4 shows the variation of the paramagnetic contributions to the chemical shifts ($\Delta\delta$, ppm) of ^{129}Xe and ^{13}C in tetramethylammonium (TMA^+) [32,33] and tetrapropylammonium (TMP^+) [34] cations trapped in various zeolites. Zeolite structures are designated by their IZA code or conventional names. The following relationships were derived [11,35].

$$\delta_s(^{129}\text{Xe}, \text{ppm}) = -5.35 + 33.44 W_r(s) \quad (5)$$

$$\begin{aligned} \delta_s(^{13}\text{C} \text{ in } \text{TMA}^+, \text{ppm}) \\ = 55.63 + 0.375 W_r(s) \end{aligned} \quad (6)$$

$$\begin{aligned} \delta_s(^{13}\text{C} \text{ in } \text{TMP}^+, \text{ppm}) \\ = 8.03 + 0.30 W_r(s) \end{aligned} \quad (7)$$

with $d = 0.374$ nm for Xe, 0.483 nm for TMA^+ , and 0.508 nm for TMP^+ (d is the sum of the van der Waals radius of the sorbate and of the ionic radius of O^{2-} [18,19]).

This model provides a general and quantitative method for the characterisation of pore size and active site environment in zeolites and other microporous solids. Their channel or cage sizes, a , are readily evaluated using Eqs. (5)–(7) from the determination of the chemical shift, δ , and

the knowledge of the equilibrium adsorption distance, d (characteristic of the probe molecule).

3.3. Acid strength measurements by adsorption of NH_3 and amines

The determination of the heat of adsorption of NH_3 or simple amines by either calorimetry or quantitative analysis of temperature programmed desorption data are routinely used as a quantitative measure of the Brønsted acid strength of the protonated form of zeolites. It is generally assumed that the heat of protonation is measured by the heat of adsorption.

In view of the former discussion, it is obvious that the heat of adsorption of these probe molecules also includes a non-negligible contribution due to physisorption which will vary from one zeolite to another (depending on pore size) and with molecular size, as a function of the extent of confinement (Eq. (8)) [19].

$$Q_{\text{exp}} = Q_{\text{protonation}} + Q_{\text{confinement}} \quad (8)$$

Experimental values should thus be corrected for the contribution of physisorption before at-

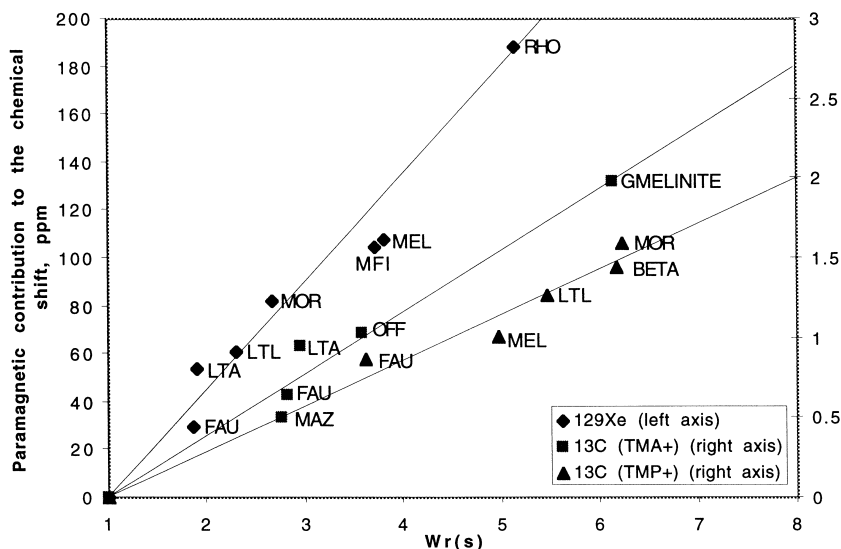


Fig. 4. Dependence of the chemical shifts of ^{129}Xe and ^{13}C in TMA^+ and TMP^+ cations adsorbed or ion-exchanged in a variety of zeolites on the reduced energy parameter $W_r(s)$.

tempting to correlate heat of adsorption and acid strength.

For ammonia, the approximate value of $Q_{\text{confinement}}$ is readily evaluated using Eq. (9), which is based on earlier proposals [19,35].

$$Q_{\text{confinement}}(\text{NH}_3) (\text{kJ mol}^{-1}) \\ = 1.44 + 5.41(1 - 1.88(r_p + 1.38))^{-3} \quad (9)$$

where r_p is the crystallographic pore (or cage) radius (in Å) of the zeolite. Typical values are listed in Table 1.

NH_3 physisorption energies span a range of about 30 kJ mol^{-1} from ferrierite to faujasite, the differences being 10.6 and 21.3 kJ mol^{-1} between ZSM-5 and mordenite or ZSM-5 and faujasite, respectively. The latter values are rather close to the differences in experimental calorimetric heats of adsorption observed when adsorbing NH_3 on ZSM-5, mordenite, and faujasite materials with low Al content. This observation indicates that the difference in acid strength of Brønsted sites in these zeolites is probably much less than was commonly accepted.

A similar effect should be observed for the heat of adsorption of alkylamines by the protonated form of zeolites. Heats of adsorption become larger as the chain length increases. This effect could be interpreted in terms of the higher proton affinity of the amine with increasing carbon number because of the inductive effect of the alkyl chain. However, this interpretation is questionable for two reasons. The first one is the rather rapid levelling of basicity with the

inductive effect (when the carbon number reaches about 3 to 4). The second one is related to confinement. As shown by Eqs. (2)–(4), the addition of $-\text{CH}_2-$ groups to an alkyl chain is indeed expected to progressively increase the physisorption energy by an amount (per C) which is larger for zeolites with smaller pore size, i.e., 7.0, 8.4 and 9.7 kJ mol^{-1} for FAU, LTL, and MFI, respectively. Thus, correction for confinement effects appears to be mandatory before drawing any valid conclusion from the use of such probes to characterise the acid strength of molecular sieves.

4. Zeolites as solid acidic solvents: acid strength and confinement effects

It is well established that the acid strength of zeolites depends on their Si/Al ratio and framework topology [36–39]. However, much less attention has been paid to quantify how confinement affects acid activity, considering that it is one of the factors determining the concentration of the reactants in the intracrystalline volume of the zeolite where catalysis occurs.

Rabo et al. [40] recognised in the early seventies that the concentration of molecules inside zeolite channels and cages was one of the major reasons for their remarkable performance as cracking catalysts, in particular, their higher selectivity to aromatics resulting from enhanced bimolecular hydrogen-transfer reactions. Fraissard [41] in his original ^{129}Xe NMR work in the early 80s mentioned that a high ‘virtual pressure’ exists in the zeolite intracrystalline volume, thereby increasing the collision probability of a reactant with the active sites and enhancing the reaction rate. Confinement rationalises these conclusions and throws additional light on the acid activity of zeolites as shown below.

As catalysis occurs in the zeolite pores, the correct expression for the reaction rate (assuming a simple first order reaction $\text{A} \rightarrow \text{B}$) is not:

$$r = k \cdot [\text{A}]. \quad (10)$$

Table 1
Contribution of physisorption to the heat of adsorption of NH_3 in various zeolites

Zeolite	$Q_{\text{confinement}}(\text{NH}_3)$ (kJ mol^{-1})
FER: Ferrierite	43.1
MEL: ZM-11	37.1
MFI: ZSM-5	36.0
MOR: Mordenite	25.4
OFF: Offretite	27.9
LTL: Zeolite L	18.6
FAU: Faujasite Y	14.7

It is better described by Langmuir–Hinshelwood kinetics:

$$r = k \cdot \theta_A \\ = k \cdot K_A [A] / (1 + K_A [A] + K_B [B]) \quad (11)$$

where k is the rate constant and K_A and K_B the adsorption equilibrium constants for the reactant and product, respectively. Eq. (11) shows that the reaction order becomes 0 when the zeolite intracrystalline volume is saturated by the reactant only ($K_B \ll K_A$ and $K_A [A] > 1$).

For gas phase reactions at rather high temperature, ($K_A [A] + K_B [B]$) is often much smaller than 1 and Eq. (11) becomes:

$$r = k \cdot K_A \cdot [A] \quad (12)$$

as described by us about 10 years ago [10]. By explicating the values of k and K_A , one obtains:

$$r = A \cdot \exp(\Delta S_A R) \\ \cdot \exp(-(E_A + \Delta H_A) RT) \cdot [A] \quad (13)$$

in which all parameters have their usual meaning.

Consequently, the reaction rate depends on confinement as $\Delta H_A = -Q_A$, where Q_A is the heat of adsorption of the reactant A which is a function of pore size and confinement according to Eq. (1). At constant acid strength, the reaction rate increases when confinement increases as the apparent activation energy, $E_{ap,A}$, is given by:

$$E_{ap,A} = E_A - Q_a \quad (14)$$

For linear alkanes, referring to Eqs. (2)–(4) and replacing Q_A by its value, one obtains:

$$E_{ap,A} = E_A - mQ_{CH_3} - nQ_{CH_2} \\ = E'_a - (n_C - 2)Q_{CH_2} \quad (15)$$

where $E'_a = E_a - 2Q_{CH_3}$ and $n = (n_C - 2)$. Eq. (15) predicts a linear dependence of the apparent activation energy on the number of the methylene groups in the alkane chain. It quantifies the experimental observations of Haag [42] and shows that the variation of the apparent activation energy with alkane chain length be-

comes more pronounced when the zeolite pore size decreases, i.e., it will be less important for FAU than for MFI. van Santen [43] has recently elaborated on these ideas by considering in addition the possible stabilisation of the transition state along the reaction pathway.

Eq. (13) also shows that the turnover frequencies, TOF, for the conversion of a given reactant by various zeolites assuming no change in the mechanism, will generally be affected by the zeolite pore size because of the dependence of ΔH_A on the curvature parameter s . It is unfortunate that such an effect is still not widely recognised today (most explanations still invoke only acid strength variation with framework topology and/or with Si/Al content) although published correlations support quantitatively the former view. One such correlation by us [10] is based on results of Kikuchi et al. [14] and holds for the cracking of n -pentane at 450°C by intermediate and large pore zeolites. A recent and impressive correlation including SAPO molecular sieves and MCM-41 mesoporous materials was also derived by Vogt [44] using original data.

These considerations point out again to the role of zeolites as solid solvents. Indeed, the situations we have described above are not unlike those encountered when conducting a biphasic acid-catalysed reaction in the presence of a liquid acid phase where the reactant is either gaseous or in a separate liquid phase. For those also, the reaction rate will depend on the solubility of the gas in the liquid phase (Henry's law) or on the partition of the reactant between both liquid phases.

5. Zeolite catalysis in liquid phase: application to organic synthesis

5.1. General principles

The principles of confinement and the consideration of zeolites as solid solvents sets a

new scene for the use of zeolites as heterogeneous catalysts in organic synthesis (fine/effect/specialty chemicals and pharmaceuticals). Because of practical considerations, such reactions are most often operated at rather low temperature and/or in the liquid phase.

Zeolite catalysis in liquid phase distinguishes itself from zeolite catalysis in vapour phase in several ways, as illustrated in Fig. 5 and listed below.

- The high concentration of reactants in the liquid phase leads to a high utilisation of the intracrystalline volume of the zeolite.

- The competition of the reactants for the zeolite intracrystalline volume is governed by MSS, confinement, and polarity effects.

- The possible adsorption of the solvent is a competitive and inhibiting process.

- The accumulation of product(s) in the solvent when operating in batch conditions will result in a progressively slower desorption of the products from the zeolite and a decrease in catalyst productivity as reaction proceeds. Indeed, the product is also partitioned between the external and the zeolitic solvents.

Maximum efficiency is achieved when the reactants are stoichiometrically adsorbed in the zeolite, when the products are easily desorbed, and when the solvent does not compete with the reactants. A solvent which has low affinity for the reactants and a high one for the product(s) will prevent accumulation of the product(s) inside the zeolite and promote the adsorption of the reactants by the zeolite. The distribution of reactants and products between the solvent and the zeolite, considered as a solid solvent, is determined by equilibrium constants which operate in a way similar to that of partition coefficients conventionally used to describe the distribution of a solute between two immiscible solvents. Thus, common approaches which could be used are: (a) phase-transfer catalysis when the zeolite has more affinity for the reactants than the solvent. Such an approach could be used to enhance the adsorption of the reactant(s) by the molecular sieve, (b) extractive catalysis when the (external) solvent facilitates the extraction of the products from the molecular sieve. Product inhibition will then be minimised.

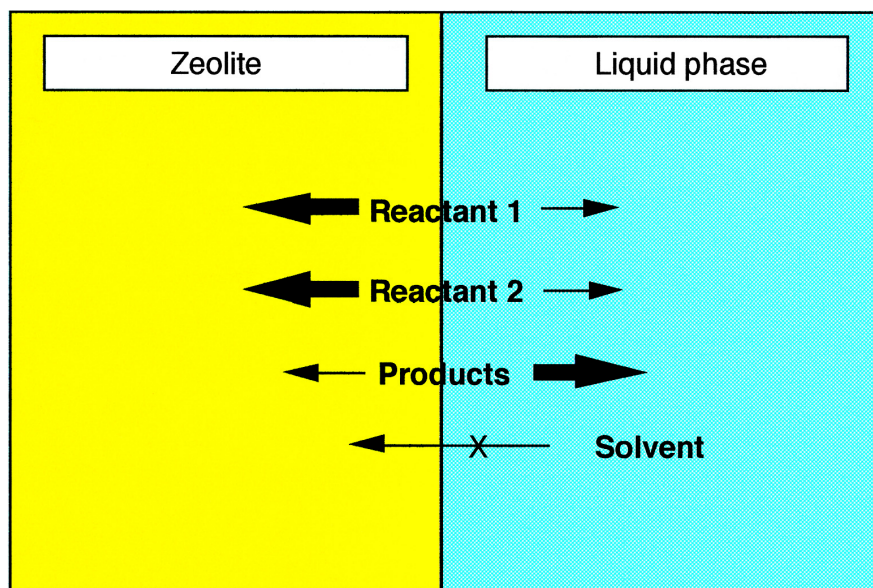


Fig. 5. Zeolite catalysis in the liquid phase: application to organic synthesis.

These principles can be illustrated by considering the simple reaction:



where R = reactant, P = product, with K_R and K_P being their respective adsorption equilibrium constants. The overall reaction rate, r , derived using Langmuir–Hinshelwood kinetics assuming competitive adsorption between R and P is given by:

$$r = k \cdot K_R [R] / (1 + K_R [R] + K_P [P]). \quad (17)$$

Fig. 6 shows the variation of the reaction rate as a function of conversion (conversion (%) = $100 \cdot (1 - [R])$) when $k = 1$, $K_R = 1$, and $[R] = 1$ at $t = 0$, the reaction being operated in batch conditions. K_P/K_R varies from 0 (no product inhibition) to 20 (high product inhibition).

Taking as baseline the situation where $K_P/K_R = 1$ (the reactant and product are equally adsorbed), the following conclusions emerge.

- Partition of the product between the external solvent and the zeolite affects dramatically the reaction rate. The effect is most apparent at low conversion when product inhibition immediately occurs.

- When the product is strongly adsorbed in the zeolite, e.g., $K_P/K_R = 20$, the reaction rate is already decreased by a factor of 5 at about 20% conversion. It means that the reaction should be conducted at low conversion and with high recycle of the unconverted reactant to maintain a reasonable rate. It points out to the need for continuous and/or otherwise modified batch processes.

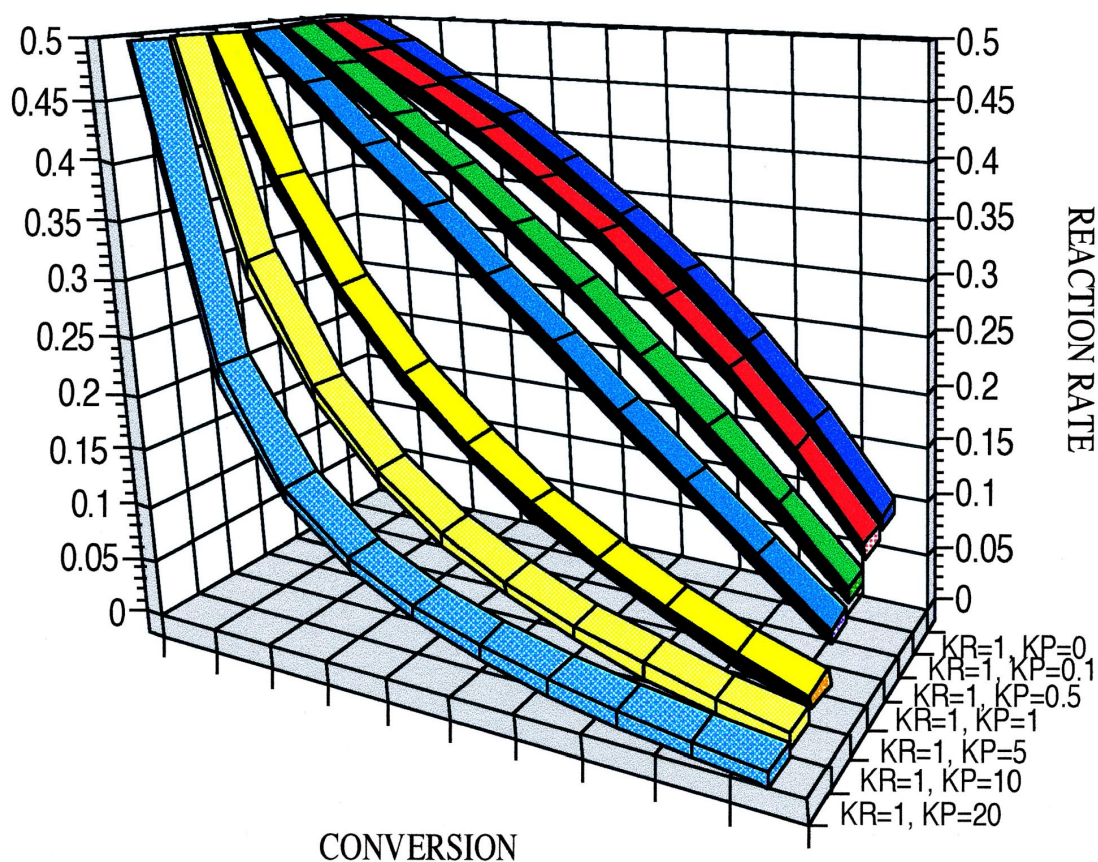


Fig. 6. Reaction rate vs. conversion as a function of increasing product inhibition ($0 \leq K_P \leq 20$) for a zeolite-catalysed model reaction operated in batch conditions.

• As the nature of the zeolite catalyst is determined by the reactants (MSS, confinement, or acidity/polarity requirements), the choice of the optimal external solvent becomes critical. An ideal solvent will not be adsorbed by the zeolite, will have a low affinity for the reactants and will solubilise extensively the products. Changing the nature of the solvent will enable to alter the K_P/K_R ratio. Mixed solvent could be used to vary continuously K_P/K_R .

These considerations hold also for bimolecular reactions and explain to a large extent why the application of zeolites as heterogeneous catalysts for organic reactions and fine chemicals synthesis has met severe limitations in the past. Such limitations include conversions smaller than those observed with non-microporous catalysts, the use of large amounts of zeolite (in some cases nearly equimolar to the amount of reactant(s)), and unsatisfactory mass balances (some of the products and reactants are trapped in the used catalyst when operating in batch conditions with large amounts of zeolite catalyst). Typical of such a situation is Friedel–

Crafts catalysis as practiced for aromatic acylation, benzoylation and alkylation.

5.2. Bimolecular reactions: Friedel–Crafts catalysis by zeolites

A general bimolecular reaction in which two reactants A and B, possibly differing by their size, yield a product P of higher molecular weight is:



Using Langmuir–Hinshelwood kinetics, and assuming competition between A, B, and P for the internal free volume of the zeolite, one derives the following rate equation:

$$r = \frac{k \cdot K_A \cdot K_B \cdot [A] \cdot [B]}{(1 + K_A[A] + K_B[B] + K_P[P])^2}. \quad (19)$$

In order to analyse the effects of product inhibition and of competition between the reac-

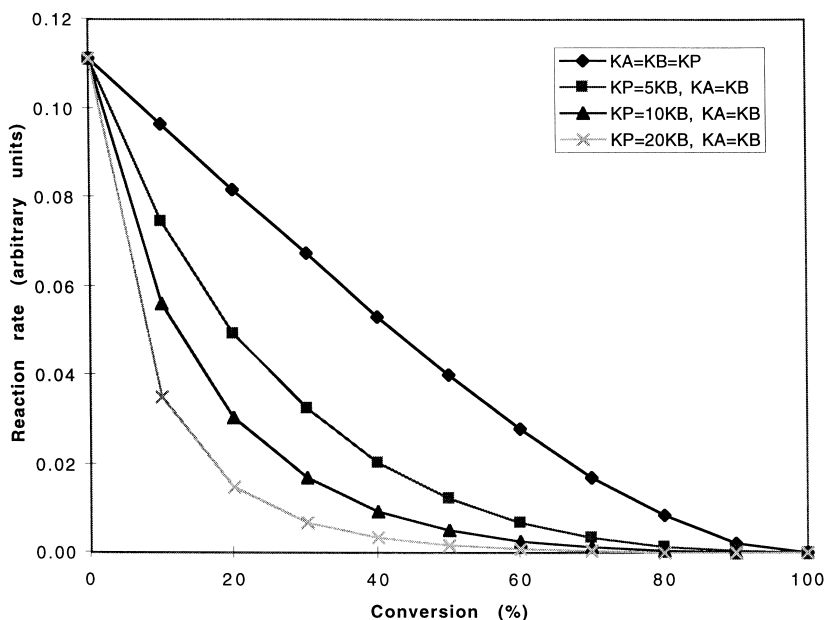


Fig. 7. Reaction rate vs. conversion for the bimolecular reaction $A + B \rightarrow P$ when $K_A = K_B < K_P$, for $[A] = [B]$ and $K_P/K_A = 1, 5, 10,$ and 20 .

tants, we assume in the following discussion that $k = 1$ and $K_B = 1$, and that $[B] = 1$ at $t = 0$. Thus, conversion at time t is:

$$\text{Conversion (\%)} = 100 * (1 - [B]). \quad (20)$$

The ratio $[A]/[B]$ at $t = 0$ can be varied to account for the presence of an excess of one reactant in the liquid phase and the values of K_A and K_P can be modified to simulate an enhancement in product inhibition (higher value of K_P) or the reduction in the adsorption of one reactant (lower value of K_A).

Two cases can be distinguished.

- Case 1: Inhibition by the product(s) only.

$$K_A \approx K_B < K_P \quad (21)$$

- Case 2: Inhibition by the product(s) and inhibition of the adsorption of A by B.

$$K_A < K_B < K_P \quad (22)$$

Fig. 7 shows the variation of the reaction rate as a function of conversion when $K_A = K_B = 1$ and $K_P/K_B = 1, 5, 10,$ or 20 . The dramatic effect of product inhibition is most obvious.

Compared to the situation where all entities are adsorbed with the same strength, the reaction rate is decreased by more than 50% at 20% conversion when K_P/K_B is equal to 5 or more, and the reaction rate becomes negligible above 50% conversion. As building up larger and more complex molecules inevitably leads to larger values of K_P/K_B , it is quite obvious that operation in batch conditions is not appropriate to perform such reactions with microporous or zeolite catalysts. Continuous or semi-continuous operation with recycle is preferable.

Fig. 8 shows the variation of the reaction rate as a function of conversion when $K_A = 0.2 K_B$ and $K_P = 5 K_B$, for two different reactant concentration ratios, i.e., $[A]/[B] = 1$ and 10 . The variation of the reaction rate when $K_A = K_B$ and $K_P = 5 K_B$ is plotted as reference. The initial reaction rate is reduced by more than 60% when $K_A = 0.2 K_B$ relative to $K_A = K_B$, illustrating the effect of non-stoichiometry inside the zeolite channels arising from differential adsorption. Increasing the concentration of A by a factor of 10, only enhances the initial reaction rate by a factor of 3 as a result of

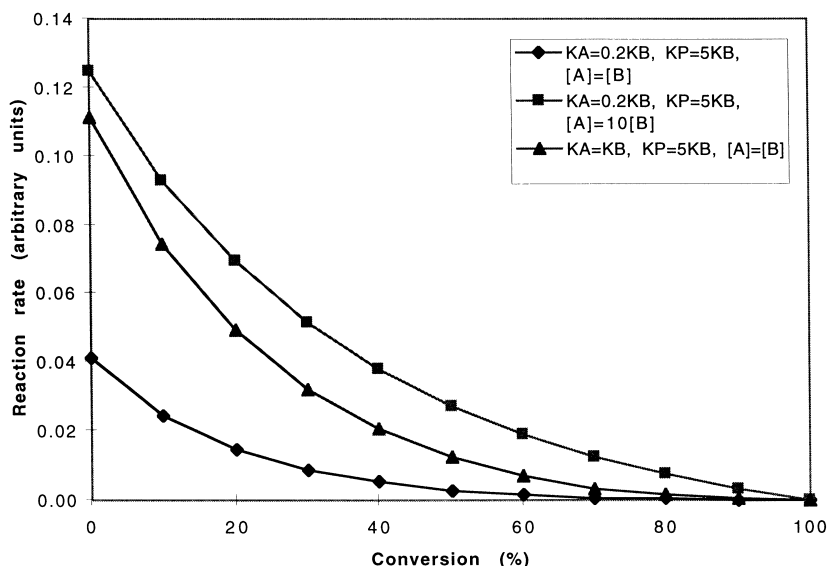


Fig. 8. Reaction rate vs. conversion for the bimolecular reaction $A + B \rightarrow P$ with $K_A = 0.2 K_B$ and $K_P = 5 K_B$ for $[A] = [B]$ and $[A] = 10 [B]$, and with $K_A = K_B$ and $K_P = 5 K_B$ for $[A] = [B]$.

competitive adsorption effects (A is less adsorbed than B), showing that this method is not suitable to determine reaction orders. However, the reaction rate decreases more slowly as a function of conversion because the adsorption of reactant A, in excess, is less inhibited by the reaction product(s).

Fig. 9 compares two situations with $[A] = [B]$ for which $K_A = 0.2K_B$ and $K_P = 5K_B$, or $K_A = K_B$ and $K_P = 20K_B$, respectively. The smaller initial reaction rate in the first case results from the smaller adsorption of reactant A. The faster decrease of the reaction rate in the second case is due to a stronger inhibition by the product(s).

Typical catalytic Friedel–Crafts additions correspond to these two cases. The first case would for example correspond to the reaction between acetyl chloride and toluene, in which case considering molecular sizes, the relative values of the equilibrium constants would indeed be in the order $K_A < K_B < K_P^{(A)}$ assuming that A is acetyl chloride, B toluene, and P the addition product A. The second case would then be representative of the alkylation of toluene by

benzoyl chloride for which $K_A \approx K_B < K_P^{(B)}$. $K_P^{(A)}$ should be smaller than $K_P^{(B)}$ as the addition product (A) in the first case has a lower molecular weight than the addition product (B) from benzoylation. Although the initial reaction rate is higher for benzoylation (benzoyl chloride is adsorbed more strongly than acetyl chloride), both reaction rates decrease rather rapidly and become nearly equal when conversion has reached about 20%.

This analysis suggests that acetic anhydride which has about twice the molecular weight of acetyl chloride should thus be adsorbed more strongly and behave as a better acylation agent. It also identifies some of the problems which may arise when performing Friedel–Crafts catalysis with zeolites or other microporous materials. Although quite a lot of attention was devoted to these and other related reactions, little real and commercial success has been met so far but for recent results on the acylation of anisole using acetic anhydride [45,46]. Possible reasons for reported failures or difficulties in this type of catalysis appear thus to be related to the behaviour of zeolites as solid solvents.

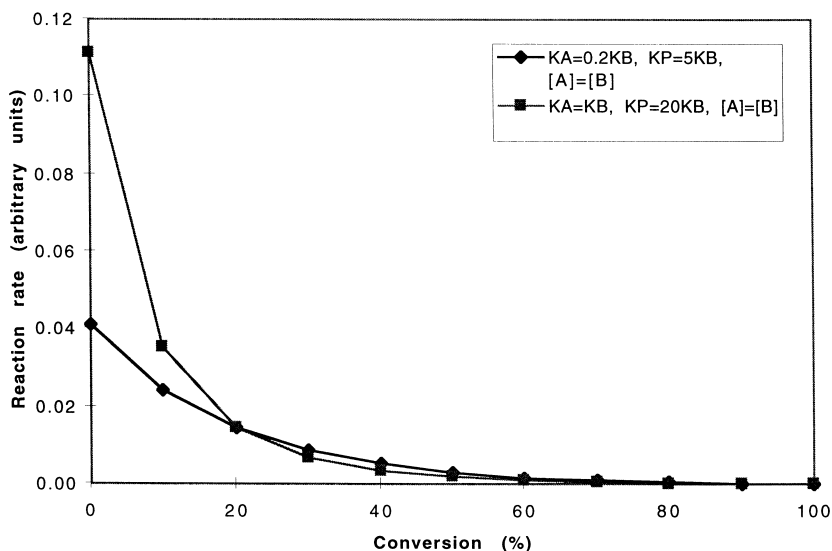


Fig. 9. Reaction rate vs. conversion for the bimolecular reaction $A + B \rightarrow P$ with $[A] = [B]$ and $K_A = 0.2K_B$ and $K_P = 5K_B$, or $K_A = K_B$ and $K_P = 20K_B$.

5.3. Zeolites as heterogeneous catalysts for organic synthesis: vistas

The aforementioned problems and pitfalls are expected to be rather common as synthetic organic chemistry generally consists of a sequence of reactions by which the size and the functionality of a molecule is increased stepwise, eventually leading to the desired product. Obviously, larger and more complex product(s) will always be more strongly adsorbed than the reactant(s), resulting in inhibition effects. Competition of the reactants for the intracrystalline volume of the zeolite will have to be mastered in order to achieve the correct reactant stoichiometry in the vicinity of the active sites.

To be circumvented, such problems need the combination of expertises provided by organic and zeolite chemists, and by creative chemical engineers. They require the understanding and the proposal of quantitative models for competitive adsorption, phase transfer, and extractive catalysis as described above, as well as the development of new semi-continuous and continuous (batch or other) reactor systems for liquid phase operation.

It must also be noted that these problems will be less apparent for mesoporous heterogeneous catalysts (e.g., MCM-41) as confinement effects become less important in larger pore size materials. However, the favourable concentration effect will also be reduced, possibly resulting in lower reaction rates if the intracrystalline volume of these materials is not optimally utilised.

6. Conclusions

Confinement effects play a major role in sorption and catalysis by zeolites. Because of their nature and magnitude, they have consequences in all fields where the behaviour and the reactivity of molecules are governed by non-covalent interactions extending beyond the molecular level, i.e., whenever supramolecular chemistry is involved.

Consequently, molecular sieves, e.g., zeolites, behave as solid solvents for molecules adsorbed in their intracrystalline volume as illustrated and demonstrated in this review by a number of observations: the variation of adsorption heats and NMR chemical shifts with zeolite pore diameter and molecular size, the adsorption of molecules in pores having a diameter smaller than their free gaseous phase size, and concentration effects affecting reaction rates of both liquid and gas phase reactions.

Further understanding and quantification of the behaviour of zeolites as solid solvents are likely to impact dramatically on their use as heterogeneous catalysts in organic and fine chemicals synthesis. The latter will require a transdisciplinary collaboration between organic and zeolite chemists as well as chemical engineers to tackle, quantify, and solve the various problems inherent to this field of heterogeneous catalysis.

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