

## Zeolites for Fine Chemical Production State of Art and Perspectives

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### Abstract

The paper analyses the role of catalysis and that of renewable resources in the frame of a sustainable development. The possible uses of natural feedstocks for chemical production and the application of catalytic methods to their transformations are reviewed, with emphasis on carbohydrates and vegetable oils and on zeolite catalysts, respectively. The problems arising from the embedment of active sites on the catalyst surface are discussed, with the aid of specific examples taken from oxidation and acid catalysed reactions.

### Introduction

An increasing part of chemical industry, pressed by environmental concerns on CO<sub>2</sub> emissions, recognises the potential benefits of using renewable raw materials. In the long term, crop-derived feedstocks are more sustainable than oil-based ones, while representing an opportunity of growth for agricultural economies. They are also generally non-toxic and can be biodegradable. They allow the natural recycle of CO<sub>2</sub>, reducing its growth in the atmosphere. For a major development in this direction, however, it is necessary that renewable raw materials are competitively priced and available in sufficient quantity to meet the needs of the market. It may be necessary, also, to reduce the transformation costs for they to become competitive with traditional routes. These aspects, *i.e.*, the valorisation of renewables and the means to achieve it, have been discussed in a recent Workshop [1].

Various authors envisaged a major role for catalysis (principally for heterogeneous catalysis) in the utilisation of renewable resources [2,3]. Actually, an intensive use of renewables for the production of chemicals and fuels will require a great effort in the development of new and effective catalytic technologies, in order that the transformations occur in a clean and efficient mode (*e.g.*, with low by-product formation and low energy consumption). A comprehensive discussion of the several studies, that are carried out with this clear objective, would be far beyond the scope of this paper. The focus will be on oxidation

and acid catalysed reactions, owing to the quantity and quality of wastes in the corresponding processes operated stoichiometrically and to the economic impact of these two classes of syntheses in chemical industry.

### Solid acid and redox catalysts for a sustainable chemistry

The use of solid catalysts, including zeolites, in acid catalysed and oxidation reactions allows major environmental benefits [4,5]. Solid acids are safe materials that can be recycled several times and finally disposed without the need of special procedures. Their advantages should be compared with the potential danger, for animal life and for environment, constituted by the use of soluble strong acids (risk of corrosive liquid and gaseous spills, stoichiometric production of liquid and solid wastes). Similarly, solid oxidation catalysts allow the use of relatively safe and inherently clean oxidants, *i.e.*, molecular oxygen and hydrogen peroxide. These avoid the production of wastes, sometimes of toxic nature, implied by the use of stoichiometric oxidants, such as heavy metal oxides, halogens, and organic peroxides [5].

Acid and transition metal substituted molecular sieves are among most studied solid catalysts. Besides sharing the typical advantages of heterogeneous catalysts, their attractiveness results also from the variety of structures and pore dimensions, from the tuneable acidity and redox properties and, in specific cases, from surface properties. The usefulness

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of acid zeolites has been hitherto proved by numerous applications in refining and petrochemical industries. Three commercial processes have been developed for redox zeolites. These are based on the use of hydrogen peroxide and titanium silicalite (TS-1), the most effective catalyst of this type [6-8]. Further applications are envisaged for both classes of catalysts in the transformation of relatively small sized intermediates, able to diffuse inside the micro and mesoporous volume of the solid, where active sites are located. Specific examples of ongoing research, related to the valorisation of natural resources, are listed below.

The viability of acid zeolites as catalysts, for the esterification and transesterification of carboxylic acids and their esters, has been studied by several groups since early 80s [4]. These are important reactions in the synthesis of biodiesel and oleochemicals. Other catalysts studied are sulfonic resins and hybrid organic/inorganic materials, prepared by grafting sulfonic and basic groups on mesoporous silica [9,10]. The correlation existing between adsorption phenomena, reactor engineering and catalytic performances was specifically addressed, with special emphasis on the esterification of fatty acids [11-13]. It was found that the increase of the hydrophobicity of mesoporous channels of MCM-41 significantly improved catalytic performances. This and other results are strong incentives for studies on the fine-tuning of surface properties, by either in-synthesis or post-synthesis chemical modifications.

Also related to the valorisation of oils and fats is the alkylation of benzene with long chain  $\alpha$ -olefins, to prepare alkylbenzene intermediates for the production of surfactants. In fact, terminal olefins can be derived from fatty acids, through the dehydration of corresponding fatty alcohol derivatives. These can be used, also, to carry out direct alkylation, eliminating the need for the preliminary dehydration to corresponding olefins [14,15]. Studies aimed at the valorisation of glycerol, co-produced in the transformation of fatty acids, are also increasing.

Several studies have been published on the synthesis of alkylglycosides, catalysed by acid zeolites and mesoporous silicas. The reaction is carried out similarly to the conventional Fischer route, obtaining the long chain alkylglycoside in a one- or a two-step method. The latter, based on the preliminary preparation of *n*-butylglycosides and then on transacetalation with the fatty alcohol, smoothes the differences in the solubility and in the adsorption of hy-

drophilic glucose and lipophilic fatty alcohol (*vide infra*) [16-18]. Of interest to the valorisation of natural products are also the hydroxyalkylation of furfural (obtainable from carbohydrates) and the rearrangement and hydration of terpenes. The first reaction has been carried out with aqueous formaldehyde on dealuminated mordenites, yielding 2,5-bis(hydroxymethyl)furan, a useful intermediate in the preparation of pharmaceuticals and, possibly, of polymers [19]. The conversion of terpenes, available as relatively inexpensive by-products in the citrus and pulp/paper industry, is of commercial interest. They have been isomerized, hydrated and esterified to various useful terpene derivatives, on different molecular sieves [20-22].

The clean oxidation of renewable materials, on redox molecular sieve catalysts, is the subject matter of a hitherto limited number of studies. Most of them concern the oxidation of olefin and alcohol compounds on Ti-containing molecular sieves.

The epoxidation of unsaturated fatty acid esters is a commercial route to the production of additives and polymer stabilisers. The usual oxidant is performic acid, a potentially unstable reagent, prepared for this reason *in situ* from hydrogen peroxide and formic acid. Recently, the oxidation with hydrogen peroxide, catalysed by Ti- $\beta$  and Ti-MCM-41 molecular sieves, has been studied as an alternative and safer route [23]. Similarly, the oxidation with hydrogen peroxide of various terpenes, to corresponding epoxides, is feasible on the same catalysts [24,25]. In the presence of bifunctional acid/redox molecular sieves, the rearrangement products can be obtained directly [26,27]. Accordingly, campholenic aldehyde, an intermediate used in the fragrance industry, could be prepared by the one-pot epoxidation/rearrangement of  $\alpha$ -pinene with hydrogen peroxide [26]. Similarly, furan and pyran derivatives, having rose scent, were obtained from linalool [27]. Large pore and mesoporous Ti-molecular sieves have been used as catalysts also for the oxidation of mono- and disaccharides with hydrogen peroxide [28,29]. Gluconic acid was mainly produced from *D*-glucose.

### Surface effects in zeolite catalysed reactions

As mentioned before, surface phenomena are determining factors, besides active sites, for the course of a reaction catalysed by a heterogeneous catalyst. They become even more relevant when the catalyst is a molecular sieve. It is opportune to stress here that

the pore diameter of zeolites is very close to the cross section of several organic reagents and products. As a consequence, adsorption energies are unusually high, often of a similar magnitude of activation energies of most reactions that the adsorbed compounds may undergo, justifying to some extent the definition of zeolites as inorganic solid solvents [30]. A second point to stress is the role of physical chemical properties of the surface relatively to those of the solvent, *e.g.*, the hydrophilic/hydrophobic nature and the size of the pores, in establishing selective adsorption phenomena.

The relation of adsorption energies and sieving effects with activity, selectivity and ageing of solid catalysts, particularly for liquid phase reactions, will be discussed with the help of suitable examples selected among reactions catalysed by acid and redox zeolites, regardless of whether they involve or not natural compounds. The conclusions will be of general value, holding for any reaction carried out on solid catalysts, including the transformation of natural compounds.

#### Adsorption and activity

Langhendries et al. studied the role of adsorption in the epoxidation of olefins with hydrogen peroxide, catalysed by Ti-molecular sieves [31]. They showed that the adsorption of the olefin increased with the increase of the polarity of the solvent (1-propanol < ethanol < methanol) and with the increase of the chain length of the olefin. It decreased with the decrease of the hydrophobicity of the pores (TS-1 > Ti, Al- $\beta$  > Ti-MCM-41). An analogous behaviour was reported for alkanes. The physical meaning of such results is that the combination hydrophilic/polar solvent (such as methanol) + hydrophobic pores (as in titanium silicalite) drives apolar molecules in the inner pore volume of the catalyst. Water and methanol are mostly repelled out. The desorption of the products is generally favoured (except for epoxides), since they are more polar than the substrate. As a result the content of the olefin is at maximum in the close proximity of the active sites, while water is at a minimum. The consequence for kinetics is a high rate of epoxidation.

The reverse phenomena occur when the pores are hydrophilic and the solvent is an apolar one. The layer of adsorbed water prevents the olefin from approaching the active site, retarding the rate of reaction. Actually, Ti-MCM-41 is a poor catalyst for the epoxidation

of olefins with hydrogen peroxide, similarly to soluble Ti-alkoxide catalysts. The reason is likely the same for both systems: the competition of water for active sites.

These arguments are confirmed by the epoxidation of olefins, catalysed by different Ti molecular sieves in various solvents. Table 1 shows the relationship between the epoxidation rates of 1-pentene on TS-1 and the corresponding partition coefficients, measured under comparable conditions to those of reaction. The decrease of the TOF closely parallels that of partition coefficients, in the order: methanol > ethanol > *t*-butanol [31,32]. Further support to the presence of a tight linkage between activity and adsorption is provided by the competitive epoxidation of 1-nonene and 1-hexene, carried out in methanol and on TS-1 (Table 2) [31]. Both the partition coefficient and the epoxidation rate of the longer chain olefin, 1-nonene, are approximately three times larger than those of 1-hexene.

**Table 1**

Epoxidation of 1-pentene on TS-1/H<sub>2</sub>O<sub>2</sub> and different alcohol solvents.

Solvent	K <sub>s</sub> <sup>a)</sup>	TOF (m/m <sub>Ti</sub> ×s) <sup>b)</sup>
Methanol	16.5	0.18
Ethanol	2.5	0.069
<i>t</i> -Butanol	≤0.8	0.041

a) Ref. 31.

b) Ref. 32.

**Table 2<sup>a)</sup>**

Competitive epoxidation of 1-nonene and 1-hexene on TS-1/H<sub>2</sub>O<sub>2</sub>.

Olefin	K <sub>s</sub>	r <sub>1</sub> /r <sub>2</sub>
1-Hexene	11	1
1-Nonene	>28	2.92

a) Ref. 31.

Finally, Table 3 shows that the TOF of the epoxidation of 1-octene decreases in the sequence TS-1 > Ti, Al- $\beta$  > Ti-MCM-41, paralleling the corresponding hydrophobicity order [33]. An analogous trend can be observed for the hydroxylation of aromatics on TS-1, Ti-MOR and Ti-MCM-41 [8].

Although a clear dependence of kinetics on adsorption is evident in the epoxidation of olefins, any undue generalisation might lead to arbitrary conclu-

**Table 3** <sup>a)</sup>

Epoxidation of 1-octene in methanol, catalysed by different Ti-molecular sieves.

	TOF (mol/mol <sub>Ti</sub> ·h)	H <sub>2</sub> O <sub>2</sub> Eff. (%)
TS-1	96.8	91
Ti-β	85.5	81
[Ti, Al]-β	41.8	65
Ti-MCM-41	7.2	54

a) Ref. 33.

sions. For instance, it is apparent from refs. [31] and [34,35] that the TOF follows, in the hydroxylation of *n*-hexane, a reverse trend with respect to that of partition coefficients. The result strongly suggests that the solvent can act by a multiplicity of ways on the reaction rate and that its effect on adsorption might not be the predominant one. For instance, the solvent can be directly involved in one or more steps of the reaction path [34]. The mechanism shown by Figure 1, *i.e.*, the intervention of the solvent in the oxygen transfer step, is such an example of the direct role of the solvent in the reaction [32,36]. The steric and electronic effects produced by the coordination on the active species sum up, in the epoxidation of the olefins, to the effects of adsorption. In the hydroxylation of paraffins, the various effects are most likely divergent, producing an inverse relation between partition coefficients and kinetics.

Analogous considerations hold for acid-catalysed reactions. This is nicely shown, for instance, by the acylation of alkylbenzenes on H-β (Fig. 2) [37]. In

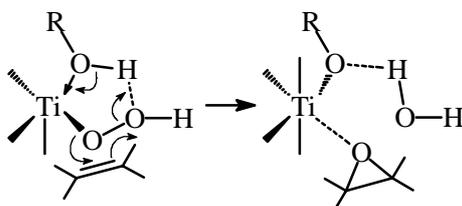


Fig. 1. Proposed mechanism for the epoxidation of olefins on TS-1.

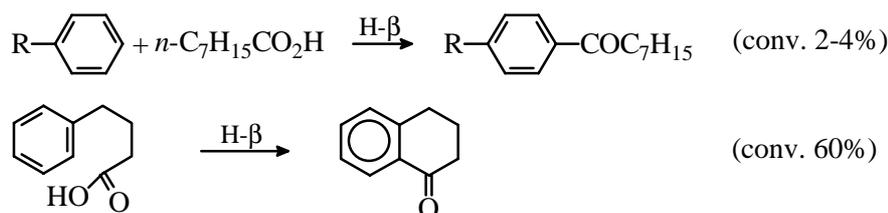


Fig. 2. Acylation of alkylbenzenes on H-β.

the reaction by the external attack of octanoic acid, the adsorption of apolar alkylbenzene is negligible in comparison to that of carboxylic acid. The latter is strongly favoured by the high affinity of the polar/hydrophilic head with the relatively numerous silanols on the catalyst surface. In fact, when the physical chemical properties of the reagents are very dissimilar, the population of one component, in the proximity of the active site, might predominate to such an extent that the reaction could not proceed significantly. Support to this interpretation is lent by the internal acylation of 4-phenylbutyric acid, for which the conversion is as high as 60%. Here, both reacting groups are on the same molecule, preventing any difference in the adsorption of the reactants.

The arguments above lead to a general conclusion of practical value. Acylation becomes a relatively easy reaction on aromatic compounds carrying donor polar groups, such as phenols, ethers and heterocycles. The presence of O-, S-, and N-functionalities improve the adsorption of the aromatic substrate, while increasing its nucleophilicity, owing to the higher affinity for the relatively polar surface of acidic zeolites and the electron donor properties, respectively [38,39].

#### *Modulation of adsorption via fine tuning of surface composition*

Since adsorption phenomena are a function of both the organic compound and the surface, it is possible to intervene in a given a reaction, by varying the physical-chemical properties of the surface. In acid zeolites, this is conveniently done through the fine-tuning of Si/Al ratio, either during synthesis or by post treatments. Decreasing the number of Al sites enhances the hydrophobicity of the surface and, therefore, the affinity of the catalysts for apolar compounds. On the same time, however, the density of active sites is decreased. Opposite conclusions can be drawn when decreasing the Si/Al ratio. In both cases, the final effect of varying the Si/Al ratio on catalysis cannot be predicted *a priori*, since the si-

multaneous variation of acidity and adsorption produce diverging effects. This is better illustrated by appropriate examples.

In the acylation of anisole with acetic anhydride on H- $\beta$ , the increase of Si/Al ratio had no effect on conversion (Fig. 3a, Table 4a) [40,41]. The diminution of the number of acid sites was likely compensated by a better-balanced adsorption of reagents, eventually leaving unchanged the rate of the reaction.

On the contrary, the acylation of anisole with acetyl chloride undergoes higher conversions on Y zeolite as the number of acid sites decrease, an apparently surprising result (Fig. 3b, Table 4b) [42]. However, this is a clear indication that the activity of the catalyst is essentially determined by sorption effects and less by the density of active sites. Other factors, such as the variation of mesoporosity in the catalysts, cannot be excluded.

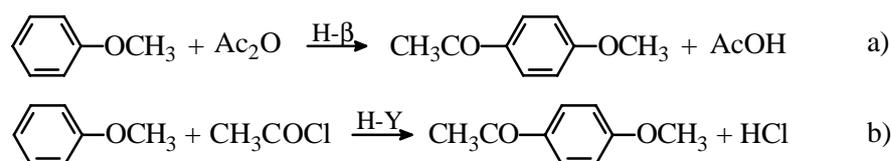


Fig. 3. Acylation of anisole on H- $\beta$  and H-Y zeolites.

**Table 4**

Acylation of anisole on H- $\beta$  (a) and H-Y (b) zeolites.

a		b		
Si/Al	Conv. (%)	N <sub>Al</sub> /u.c.	Yield (%)	TON (h <sup>-1</sup> )
11	66	53	4	3.6
25	65	30	15	38
		11	37	338
		7	46	739
		6	42	1043

### Adsorption and selectivity

Besides influencing activity, adsorption phenomena can have also an effect on selectivity. In the hydro-

xymethylation of furfural, the dealumination of mordenite catalyst, in addition to increasing conversion as in previous examples, improved selectivity up to 85% (Fig. 4 and Table 5) [43,44]. The mode of addition was also important. For high selectivities, formaldehyde had to be added as the first reagent and used in excess. The rationale proposed by the authors called upon adsorption phenomena. Furfural, generally adsorbed on less hydrophilic sites of mordenite, at relatively high concentration can also compete for acidic sites, inhibiting the adsorption and protonation of formaldehyde and, therefore, the formation of the nucleophile. Using excess formaldehyde reduces the competition of furfural for acidic sites, minimising both inhibition and side reactions.

Analogous results were obtained in the hydroxymethylation of guaiacol, carried out by a similar pro-



Fig. 4. Hydroxymethylation of furfural on H-mordenite

**Table 5**

Hydroxymethylation of furfural on H-mordenite.

a			b		
Si/Al	Conv. (%)	Sel. (%)	Mode of addition	Conv. (%)	Sel. (%)
11	4	40	Together	28	44
49	20	90	FA first	47	10
100	65	85	CH <sub>2</sub> O first	28	88

cedure on mordenite. Optimising the Si/Al ratio and the reaction parameters improved selectivity up to 80%, opening a new and cleaner route for the synthesis of vanillin, totally based on heterogeneous catalysis [45].

### Shape selectivity, advantages and drawbacks

Shape selectivity is probably the most popular property of zeolites. Organic synthesis can take advantage of it to prevent the formation of unwanted bulky products. One clear example is the high selec-

tivity in the synthesis of dihydroxybenzophenone (**I**), performed on microporous H- $\beta$  (Fig. 5) [38]. The channels of this catalyst are not large enough to allow the formation of sizeable dibenzoate ester (**III**) and xanthenone (**II**). The latter is a particularly undesirable compound, because it is deeply red coloured and difficult to separate from the main product, in the purification stage. Using macroporous acid catalysts, such as organic sulfonic resins, kinetics can be faster, but the formation of the side products is not prevented, as expected for a reaction occurring without steric restrictions.

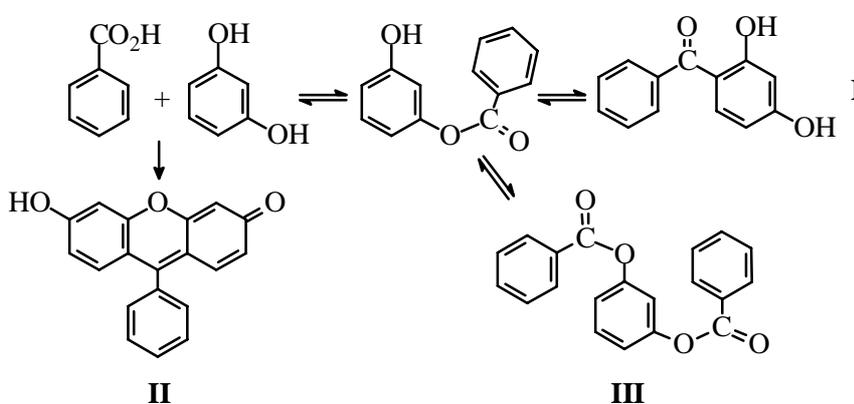


Fig. 5. Benzoylation of resorcinol.

Shape selectivity, however, is not the panacea able to solve any selectivity problem *via* size exclusion. In the acylation of 2-methoxynaphthalene (2-MN), the attack of acylium ion can occur at three different positions of the naphthalene ring (Fig. 6). At the 1-position, favoured by electronic factors and disfavoured by shape selectivity [46,47]. At the 6-position, favoured by thermodynamic and shape selectivity. At the 8-position, the least favoured one. The desired product is the 2,6-acyl methoxy naphthalene (2,6-AMN), a possible intermediate for the production of Naproxen. In this reaction, shape selectivity effects exercised by H- $\beta$  are not sufficient to override electronic factors driving the acylation at the 1-position.

The best reported isomer ratio is 9 [48].

It has been established by several studies that Ti-hydroperoxides are the active species or the precursors of active species in Ti-zeolites (Fig. 1). They show electrophilic behaviour in oxidation reactions, similarly to peracids and other peroxides [32]. Considering the epoxidation of olefins, the expected reactivity order, in the absence of steric restrictions, ought to be similar to that of peracids (Fig. 7). On the contrary, that shown by TS-1/H<sub>2</sub>O<sub>2</sub> is a completely different one. For instance, terminal olefins (*e.g.*, 1-pentene) react faster than internal ones (*e.g.*, *trans* 2-butene). Linear 1-pentene is epoxidized faster than branched pentenes. Most striking is the behaviour of 2-methyl-2-butene,

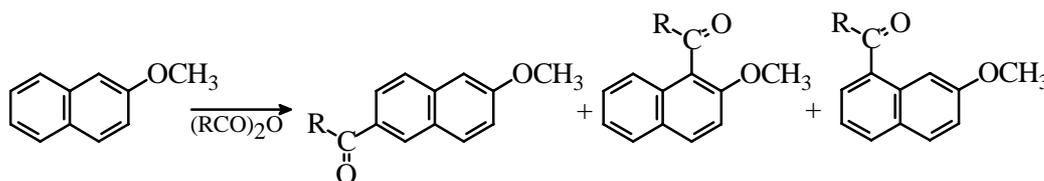


Fig. 6. Acylation of 2-methoxynaphthalene on H- $\beta$ .

reacting somewhat slower than 1-pentene, whereas its epoxidation with peracids is 240 times faster. Such striking discrepancies with peracids can only be ex-

plained by the predominance of steric restrictions, imposed by the micropores, over electron donation, as alkyl substitution increases on the double bond.

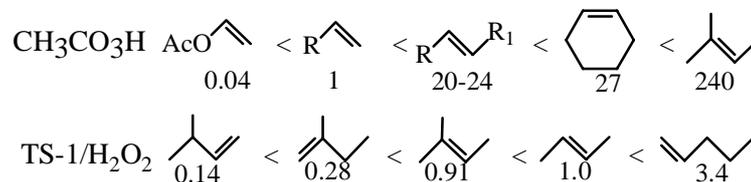


Fig. 7. Epoxidation of olefins. Relative rates.

Subtle differences in the molecular size can have major effects on reactivity, grace to shape selectivity [49]. For instance, *p*-xylene, freely diffusing in medium and large pore zeolites, was hydroxylated at the same rate on TS-1 and Ti-MOR. On the contrary, the reaction of the *o*-isomer, having a larger cross section, could be satisfactorily carried out only on large pore Ti-MOR.

## Conclusion

The number of studies aimed at the application of heterogeneous catalysts in the synthesis of fine chemicals, particularly in the areas of oxidation and acid catalysed reactions, denote the increasing perception of chemical industry for environmental issues. Actually, the introduction of catalysis in fine chemistry has to override a long established tradition, based on stoichiometric organic syntheses, and the intrinsic limitations arising from the typical organisation of production in this area of industry (batch reactors, multipurpose equipment, short development and commercialisation times). From a preparative point of view, these studies indicate that heterogeneous catalysis can be a promising tool for the clean production of fine chemicals. Hydrogenation has already been proved in many applications. Acid catalysed and oxidation reactions are two rapidly developing fields, with a few commercial processes already put into operation.

A second conclusion is that, for a larger diffusion of catalysis in fine chemistry, it is necessary to proceed further at least into two directions. The development of large pore and, more importantly, of mesoporous catalysts is mandatory. The effects of adsorption phenomena, on activity, selectivity and ageing, have to be studied in more details, taking into account the properties of both the solvent and the cata-

lyst. These considerations are particularly important for reactions occurring on zeolitic catalysts, owing to the comparable size of pores and reactants and the generally high adsorption energies. In fact, only reagents and products, freely diffusing in and out the micropores, can be concerned by zeolitic catalysis. Adsorption in a zeolitic pore can be compared, for importance, to solvation phenomena for reactions in liquid phase conditions.

Analogous considerations generally hold for the application of heterogeneous catalysts to the transformation of renewable feedstocks, with, in addition, some specific remarks. Actually, important renewable materials, like carbohydrates, possess very polar nature. Their reactions with apolar reagents can impose major difficulties in the design of appropriate catalysts, since any reactant has to adsorb in a well-balanced way with the others, for optimal catalytic activity. On the same time, the products should easily desorb to minimise both side reactions and ageing. These difficulties have already been highlighted in the studies on the synthesis of alkylglycosides and on the oxidation of glucose. More studies will be needed, particularly on the relation between adsorption/catalytic performances and the properties of surface/solvent. Cleanliness, mildness and selectivity of heterogeneous catalysts encourage further studies, both in academia and industrial laboratories.

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