

# Role of hydrophobic effects in organic reactions catalysed by zeolites

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## Abstract

The role of hydrophobic effects of dealuminated mordenites (Si/Al ratios varying from 7 to 100) has been investigated in two reactions carried out in aqueous/alcoholic media: hydroxymethylation of furfuryl alcohol with aqueous formaldehyde and hydration of phenyl-acetylene in alcohol medium. For both reactions, initial rates and turn over frequencies (TOF) increase in a significant extent with increasing Si/Al ratios. It is shown that the differences thus observed in the TOF values are characteristic of variations in the hydrophobicity of the various dealuminated mordenites, which is confirmed by the corresponding increase of the hydrophobicity parameter  $h$ , determined by thermogravimetric analysis of such samples. The hydrophobic character of the zeolites is also discussed in terms of the softness and activity of the corresponding Brønsted acid sites. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrophobic effect; Dealuminated mordenites; Hydration; Hydroxymethylation; Aqueous media

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## 1. Introduction

Hydrophobic effects play a key role in many chemical phenomena in aqueous solution [1,2].

A hydrocarbon-like molecule dissolved in water is surrounded by water assemblies along its exposed surface. This process is entropically very unfavorable, as typically shown for transfer of methane from the gaseous to the aqueous phase. The hydrophobic interaction, most simply expressed,

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is the tendency of a hydrocarbon-like molecule to reduce these water assemblies by making contact at its surface with the surface of another hydrocarbon-like molecule.

The hydrophobic interactions that refer to the attractive forces between two or more apolar solutes in water play an essential role in molecular self-assembly such as the formation of biological membrane structures, micelle formation of amphiphiles and micellar catalysis [3].

Hydrophobic interactions are also invoked to explain solvent effects in highly aqueous media. A typical example is the Diels–Alder reaction which is dramatically accelerated in water. According to Breslow [4], the hydrophobic packing of diene and dienophile is the most likely explanation for the observed rate effects.

This hydrophobic interaction contributes in a significant way to the hydrophobic recognition by cyclodextrins [5]. In fact, cyclodextrins have a hydrophobic cavity of appropriate size occupied by water molecules in the absence of a guest molecule. However, when a specific ‘guest’ molecule is added into the cyclodextrin solution, it drives water out of the cavity by occupying it by itself. A variety of factors such as Van der Waals and London dispersion forces are proposed to interpret the binding of cyclodextrins with substrates.

All these results, obtained mainly in solution, have led to the determination of hydrophobicity scales, for example the Hansch hydrophobicity parameter  $p_x$  which relies on partitioning phenomena [6].

However, in heterogeneous catalysis, such a parameter is not clearly defined. In the case of crystalline aluminosilicate zeolites, the silica and alumina tetrahedra are arranged in a rigid three-dimensional framework which, in effect, is porous. The adsorption of water molecules in zeolites involves the specific interaction between the water molecules and the hydrophilic centers, which are silanol groups or cations associated with the framework aluminum atoms. As a matter of fact, it was found that the amount of water adsorbed is strongly dependent upon the Si/Al ratio [7]. Upon dealumination, the net electrostatic charge due to the presence of tetrahedral aluminum atoms decreases and so does the ability of the zeolite to adsorb strongly polar molecules. Consequently, dealuminated zeolites are hydrophobic. It is well established that highly siliceous materials show a marked hydrophobicity on their surfaces [7,8]. Therefore, high-silica zeolites are expected to have a high activity as solid acid catalysts in aqueous solution [9] due to the preferential adsorption of organic materials, based on London-type interactions.

Recently, the hydrophobicity index (HI) was introduced as a quantitative measure for the hydrophobic properties of molecular sieve adsorbents or catalysts [10,11]. It was determined via competitive gas phase adsorption of toluene and water. Zeolites with different structures but similar Si/Al ratios possess different hydrophobicities. For example, zeolites Y (Si/Al = 35) and ZSM-5 (Si/Al = 30) give HI values of 15 and 0.5, respectively. Another experimental method proposed in the literature for characterizing the hydrophobic surface properties of zeolites is the hydrophobicity parameter  $h$  [12] determined by desorption of water in a thermogravimetric analysis experiment.

As part of our programme on transfer of concepts from homogeneous to heterogeneous catalysis [13], the present paper deals with the evidence of hydrophobicity in heterogeneous catalysis. Two reactions, carried out in aqueous/alcoholic medium have been chosen as examples to illustrate this approach in the presence of hydrophobic zeolites to prevent a total deactivation by water. Thus, hydroxymethylation of furfuryl alcohol with aqueous formaldehyde [14,15], and hydration of phenylacetylene [16,17] have been studied in the presence of various mordenites in a protonic form and with increasing Si/Al ratios (from 7 to 100). The aim of this paper is to depict more particularly the relationship between the hydrophobic character of zeolites of same structure and activity of such catalysts in aqueous media.

## 2. Experimental

### 2.1. Catalysts

H-Mordenite (Zeolon 100-H, Si/Al = 6.9 from Norton, H-M 1) and three dealuminated mordenites identified respectively as H-M 2, H-M 3, H-M 4 (Si/Al = 11, 49, 100), from Zeocat, were used. Typical properties of these catalysts are shown in Table 1.

### 2.2. Hydroxymethylation of furfuryl alcohol

The reactions were carried out in a glass reactor working in the batch mode. The general procedure was as follows: 6 ml of formalin were added to the zeolite (250 mg). The resulting suspension was magnetically stirred at 338 K for 0.5 h before adding furfuryl alcohol. Samples were withdrawn periodically and analyzed by high performance liquid chromatography (HPLC), using a Shimadzu pump LC-6A with a  $0.5 \text{ ml min}^{-1}$  constant flow, a Shimadzu UV spectrophotometer SPD-6A detector at 230 nm and controlled by a PC with a software package (ICS). A Kromasil C18 column (15 cm, 5 mm) was used and the mobile phase was acetonitrile/water (30/70 by volume).

### 2.3. Hydration of phenylacetylene

The reactions were carried out in a 0.1 l stirred autoclave operating in a batch mode and equipped with a system for sampling of liquid during the reaction. The autoclave was charged with the freshly calcined zeolite (calcination overnight at 773 K in air, prior to use) (500 mg) and phenylacetylene (1 g) together with 50 ml ethanol and 1 ml distilled water, and then heated to 433 K. As soon as the temperature of 433 K is reached, a first sample is withdrawn, which is considered sample  $t = 0$ . Samples were analyzed by gas–liquid chromatography (Alltech OV1-capillary column 10 m), 323 to 373 K,  $5 \text{ K min}^{-1}$ .

### 2.4. Thermogravimetric analysis

Thermal analysis was performed on a Setaram TGC 85 differential thermal analyzer in a steam of air ( $100 \text{ ml min}^{-1}$ ). Hydrophobicity  $h$  is calculated as the ratio of the weight losses measured by thermogravimetric analysis at 423 K and 673 K. In fact interstitial zeolitic water is of two kinds: the highly mobile water which is lost at relatively low temperatures (ca. 423 K) and the more strongly bound water which is not removed until temperatures close to 673 K are reached. If the sample is extremely hydrophilic  $h = 0$ ; for very hydrophobic samples  $h = 1$ .

Table 1  
Catalysts properties

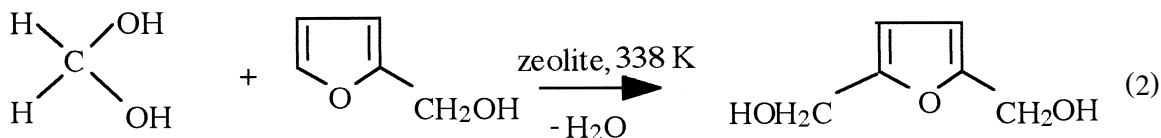
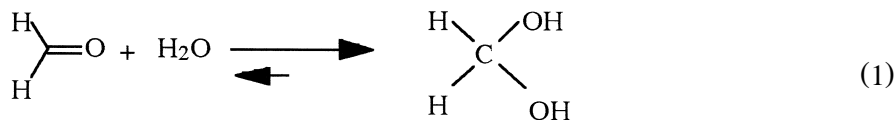
Catalyst	Composition			Si/Al atomic ratio	Number of sites $\text{g}^{-1} (\times 10^{-20})$	Porosity		Specific surface area $(\text{m}^2 \text{g}^{-1})$
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> (wt.%)	Na <sub>2</sub> O			micro $(\text{cm}^3 \text{g}^{-1})$	meso $(\text{cm}^3 \text{g}^{-1})$	
H-M 1	73.10	18.10	0.05	6.9	12.5	0.204	0.040	497
H-M 2	92.79	7.17	0.01	11 <sup>a</sup>	8.45	0.192	0.056	486
H-M 3	98.29	1.70	0.01	49 <sup>a</sup>	1.99	0.178	0.132	485
H-M 4	99.15	0.84	0.005	100 <sup>a</sup>	0.98	0.183	0.144	522

<sup>a</sup>Total and framework Si/Al ratios are identical.

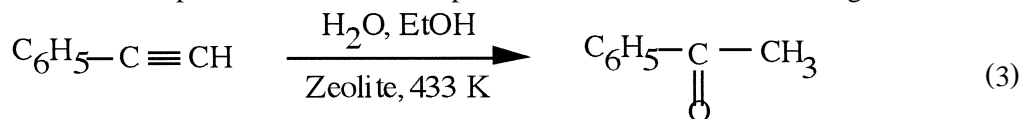
### 3. Results and discussion

The two model reactions have been carried out in the presence of mordenite zeolites chosen as reference catalysts due to their expected high activity in aqueous solution.

The hydroxymethylation of furfuryl alcohol with formalin (37 wt.% aqueous formaldehyde with 10–15% methyl alcohol) leads, under the conditions described above, to 2,5-bis(hydroxymethyl)furan (BHMF), according to reactions (1) and (2):



The hydroxymethylation reaction takes place at low temperature (338 K); under such conditions, the hydration reaction does not occur. Consequently, the latter has been studied at higher temperature (433 K), temperature for which acetophenone is easily and quantitatively produced from the hydration of phenylacetylene over short periods of time in the presence of mordenites, following reaction (3):



As an example, Fig. 1 shows the results obtained in the two reactions by using H-M 4. In 10 min, the conversion of substrate in both cases is near 75%.

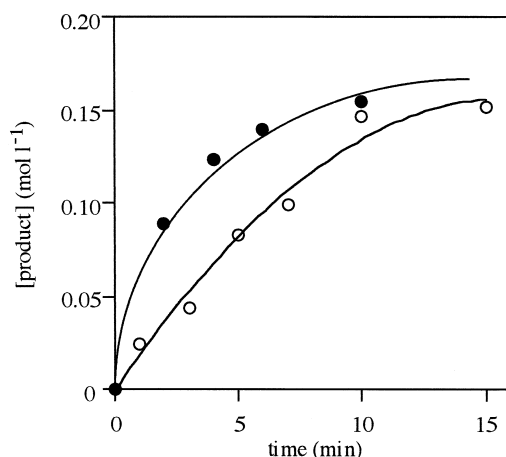


Fig. 1. Formation of acetophenone (○) and BHMF (●) vs. time in the presence of H-M 4. Hydration: phenylacetylene 0.2 mol l<sup>-1</sup>, water 1 ml, ethanol 49 ml, catalyst 0.25 g,  $T = 433$  K. Hydroxymethylation: furfuryl alcohol 0.23 mol l<sup>-1</sup>, formalin 6 ml, catalyst 0.25 g,  $T = 338$  K.

Table 2

Initial rates for hydration of phenylacetylene and hydroxymethylation of furfuryl alcohol as a function of Si/Al ratio of mordenites

Catalyst	Si/Al	$r_0$ hydration (mol s <sup>-1</sup> g <sup>-1</sup> ) × 10 <sup>6</sup>	$r_0$ hydroxymethylation (mol s <sup>-1</sup> g <sup>-1</sup> ) × 10 <sup>6</sup>
H-M 1	6.9	2.1	<sup>a</sup>
H-M 2	11	27	1.3
H-M 3	49	65	10
H-M 4	100	43	36

<sup>a</sup>Over the sample Si/Al = 7 the hydroxymethylation reaction is too slow to determine initial rate.

Such experimental curves of product concentration vs. time allow to determine the initial rates of the reactions. Table 2 shows the values of initial rates for both reactions using mordenites with different Si/Al ratios.

For both reactions, initial rates increase in a significant extent with increasing Si/Al ratios, except for hydration reaction where a decrease is observed from Si/Al 49 to 100. Such a result can be attributed, in a first assumption, to the low number of active sites present in that catalyst ( $0.98 \times 10^{20}$  sites g<sup>-1</sup>, Table 1). This result is in agreement with the work of Cambor et al. [18] about the preparation of alkyl glucosides over zeolites with different hydrophobic–hydrophilic properties.

In order to establish a valid comparison between the different mordenites, and as the total number of acidic sites per gram of solid changes with the Si/Al ratio (Table 1), the results must be better expressed in terms of turn over frequencies (TOF) which are obtained by dividing the initial rates by the number of acid sites (or aluminum atoms) per gram.

Table 3 reports the TOF for the hydration of phenylacetylene and for the hydroxymethylation of furfuryl alcohol for various mordenites together with the corresponding values of  $h$  measured according to Klinowski's method [12].

It is clear that the TOF increases with the Si/Al ratio of the zeolite whatever the reaction considered. As, by definition, the TOF is independent of the total number of active sites, its value reflects both the acidic and hydrophobic character of one site. According to Barthomeuf [19], every acid site of the three dealuminated mordenites (H-M 2, H-M 3, H-M 4) presents the same strong acidity; in the case of mordenites, it can be considered that the maximum acid strength is obtained for samples with framework Si/Al > 9.4. Consequently, it can be assumed that the differences observed in the TOF values are characteristic of variations in hydrophobicity. Such an assumption is confirmed by the measured values of  $h$  (Table 3), which increase with an increasing of the Si/Al ratio. As it can be seen in Fig. 2, the evolution of TOF for both reactions against the hydrophobicity of catalyst is similar.

Table 3

Turn over frequencies and  $h$  values for hydration of phenylacetylene and hydroxymethylation of furfuryl alcohol as a function of Si/Al ratio of mordenites

Zeolite	Si/Al	Site number g <sup>-1</sup> (× 10 <sup>-20</sup> )	$h$	TOF (s <sup>-1</sup> ) × 10 <sup>3</sup> hydration	TOF (s <sup>-1</sup> ) × 10 <sup>3</sup> hydroxymethylation
H-M 1	6.9	12.5	0.3	1	–
H-M 2	11	8.45	0.49	19	0.9
H-M 3	49	1.99	0.78	196	31
H-M 4	100	0.98	0.87	266	220

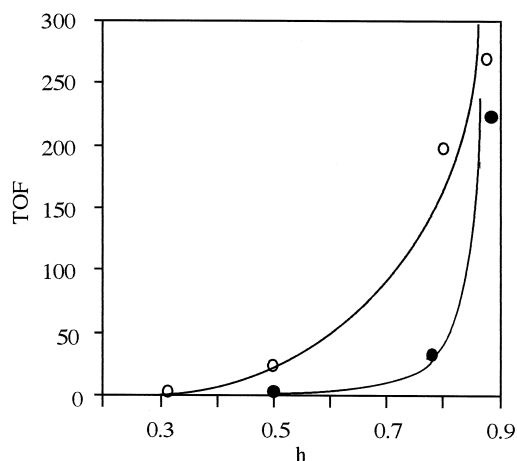


Fig. 2. TOF for hydration (○) and hydroxymethylation (●) against the hydrophobicity values of mordenites used in the reactions.

Furthermore, the influence of the framework Si/Al ratio of a zeolite on the softness of a given acid site has been recently studied by Corma et al. [20] and Corma [21]. These authors found, by means of quantum chemical calculations, that the higher the framework Si/Al ratio of the zeolite, the softer should be the acid sites and, consequently, that the local softness is a measure of activity of sites for reactions where orbital control may exist. As suggested in our previous paper on hydrophobicity concept [22], we can assume that the hydrophobic character of a zeolite has an effect on the softness of Brönsted sites and thus on their activity.

Thus, the increase of the framework Si/Al ratio of the zeolite leads not only to an increase of the hydrophobic interactions between organic substrates and the siliceous surface of the zeolite but also to a corresponding increase of the activity of the acidic sites. Moreover, as discussed in our previous paper [22], the rate is a function of both adsorption constants  $\lambda$  and  $K$ , which are respectively the adsorption coefficient on protonic site and the affinity constant of the substrate for hydrophobic surface, and concentrations of reactants:  $r = f(\lambda, K, [\text{reactants}])$ . The hydrophobic character of a zeolite influences all these parameters and thus leads to an increase of the reaction rate. The more hydrophobic is the catalyst, the more active is the catalytic site and the stronger is the adsorption of the substrate (furfuryl alcohol or phenylacetylene) upon the hydrophobic surface of the catalyst. Although the mechanisms for the two reactions considered are different (electrophilic addition for hydration and electrophilic substitution for hydroxymethylation), it is obvious that both reactions are very sensitive to the hydrophobic character of the catalyst. Such a behaviour was also found in the reaction of hydroxymethylation of guaiacol to vanillic alcohols in aqueous solution and in the presence of the same series of mordenites [23]. This increase of activity is generally not observed for dealuminated zeolites in organic media.

Moreover, another manner to account for the influence of the hydrophobicity parameter on the reactivity is to express the rates of reaction in terms of LFER (linear free energy relationship) [24], i.e.,  $\log \text{TOF} = \rho h + C$ , in which the slope  $\rho$  would be representative of the sensitivity of the reaction to the hydrophobic character of the catalysts.

For the two reactions considered in this work, such a LFER transformation leads to linear plots (correlation coefficient  $> 0.97$ ) as illustrated in Fig. 3.

The values of the slopes appear also to be closely dependent upon the operating conditions: (1) slope  $\approx +7$  for the hydroxymethylation which is performed in a large excess of water, (2) slope  $\approx +4$

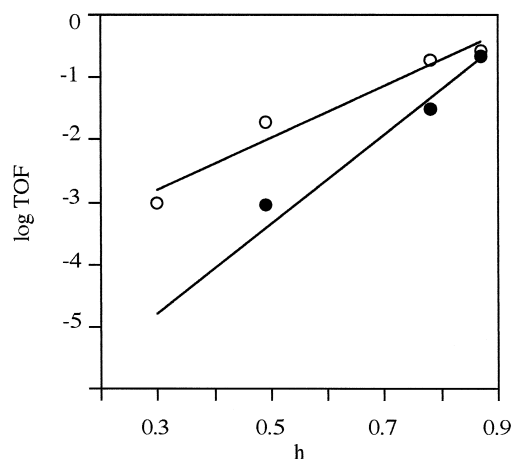


Fig. 3. Log TOF for hydration (○) and hydroxymethylation (●) vs. hydrophobicity  $h$ .

for the hydration which is carried out in an alcohol-rich mixture. It is thus logic to find, in the case of an organic solvent, a slope near zero, expressing that the hydrophobicity has no effect on the activity in this organic medium.

#### 4. Conclusion

Hydroxymethylation of furfuryl alcohol with aqueous formaldehyde and hydration of phenylacetylene in alcoholic medium carried out in the presence of mordenites with increasing Si/Al ratios (from 7 to 100), have been chosen as model reactions in order to depict the relationship between the hydrophobic character of zeolites of same structure and activity of these catalysts in aqueous media. For both reactions, initial rates and TOF increase in a significant extent with increasing Si/Al ratios. A corresponding increase is observed for the hydrophobicity parameter  $h$ , determined from thermogravimetric analysis. The differences observed in the TOF values are characteristic of variations in hydrophobicity of the various dealuminated mordenites, taking into account that these samples present the same strong acidity. These hydrophobic effects can be also discussed in terms of the softness and activity of the corresponding Brønsted acid sites. For these reactions carried out in aqueous media, the more efficient catalyst is a highly dealuminated mordenite, due to the more hydrophobic character of such a zeolite and consequently to the strong adsorption of the substrate upon the catalyst, increasing its reactivity.

This constitutes another important step in attempting quantification of hydrophobicity in zeolite-catalyzed organic reactions.

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