

Attempt to quantify the hydrophobic character of highly dealuminated H-mordenites in hydroxymethylation of furfuryl alcohol with aqueous formaldehyde

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Abstract

The hydrophobic character of three dealuminated mordenites has been investigated and quantified from the kinetic study of the hydroxymethylation of furfuryl alcohol with aqueous formaldehyde. The affinity constant of the substrate for the siliceous framework of the zeolite reflects this hydrophobic character and increases with the Si/Al ratio. These results are in agreement with adsorption measurements of furfuryl alcohol from aqueous solutions on dealuminated mordenites. © 1999 Elsevier Science B.V. All rights reserved.

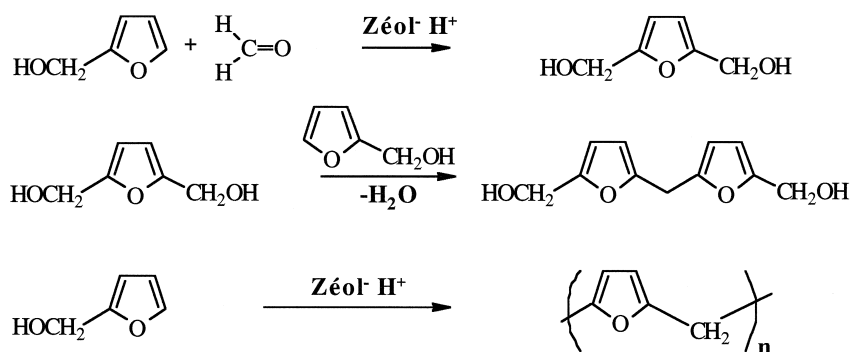
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1. Introduction

In a previous work, we have reported on hydroxymethylation of furfuryl alcohol with aqueous formaldehyde leading to 2,5-bis(hydroxymethyl)furan (BHMF) in the presence of a highly hydrophobic H-mordenite as catalyst with a Si/Al ratio of 100 [1] (Scheme 1). An original kinetic law involving two types of sites was described. It was suggested, in particular, that the surface reaction occurred between formol hydrate adsorbed on Brönsted sites and furfuryl alcohol adsorbed on the hydrophobic framework of that dealuminated mordenite. However, furfuryl alcohol molecules could also be adsorbed on acidic sites competitively with formol hydrate, leading to an inhibition of the reaction at high furfuryl alcohol concentrations. The consequence of this behavior was that the reaction rate went through a maximum at an optimum furfuryl alcohol concentration. The proposed kinetic law satisfactorily accounted for the experimentally observed kinetics.

The aim of the present work was to compare the kinetic behavior of three dealuminated mordenites with Si/Al ratios of 100, 49 and 11 in the title reaction in order to determine the relative adsorption

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Scheme 1. Overall reaction scheme for hydroxymethylation of furfuryl alcohol with formalin in the presence of zeolites.

constants of the reactants on the solid surface and to estimate the hydrophobic character of these zeolites.

2. Experimental

2.1. Catalysts

The three mordenites used in this work were supplied by Zeocat. Typical properties of these catalysts are shown in Table 1.

2.2. Hydroxymethylation procedure

Reactions were carried out in a glass reactor using 37% aqueous formaldehyde (6 ml of formalin), at 338 K, in the presence of 250 mg of dealuminated mordenite. The resulting suspension was magnetically stirred at 338 K for 0.5 h before adding furfuryl alcohol (from 0.06 to 1 ml). Samples were withdrawn periodically and analyzed by high performance liquid chromatography (HPLC), using a Shimadzu pump LC-6A with a 0.5 ml min⁻¹ constant flow, a Shimadzu UV spectrophotometer detector SPD-6A at 230 nm and controlled by a PC with a software package (ICS). A Kromasil C18 column (15 cm, 5 μm) was used and the mobile phase was acetonitrile/water (30/70 by volume).

2.3. Adsorption procedure

Adsorption experiments were carried out at 338 K with a 0.1 M initial concentration in furfuryl alcohol. The beginning of the kinetic study corresponded to the addition of the zeolite to the aqueous

Table 1
Catalysts properties

Catalyst	Composition (wt.%)			Si/Al atomic ratio ^a	Number of sites/ g × 10 ⁻²⁰	Porosity (cm ³ g ⁻¹)		Specific surface area (m ² g ⁻¹)
	SiO ₂	Al ₂ O ₃	Na ₂ O			Micro	Meso	
H-MOR	92.79	7.17	0.01	11	8.45	0.192	0.056	486
H-MOR	98.29	1.70	0.01	49	1.99	0.178	0.132	485
H-MOR	99.15	0.84	0.005	100	0.98	0.183	0.144	522

^aTotal and framework Si/Al ratio are identical.

solution of furfuryl alcohol. Aliquots were sampled time to time and analyzed as a function of time by HPLC.

3. Results and discussion

Hydroxymethylation of furfuryl alcohol was studied over mordenites having different framework Si/Al ratios. The corresponding conversion and selectivity data are given in a previous paper [2]. The present one is essentially devoted to kinetic results.

3.1. Influence of the framework Si / Al ratio on reaction rates

It is well established that highly siliceous materials show a marked hydrophobicity on their surfaces [3]. Therefore, high-silica zeolites are expected to have a high activity as solid acid catalysts in aqueous solution [4–6]. As shown in Fig. 1, the highest activity is obtained when H-MOR(100) catalyst is used. The volcano-shape plots of r_0 against the initial concentrations in furfuryl alcohol obtained for the three mordenites show that the maximum initial rate is drastically reduced and shifted towards higher initial furfuryl alcohol concentrations when the Si/Al ratio decreases.

3.2. Influence of the framework Si / Al ratio on turn-over frequencies (TOF)

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, the results are expressed in terms of turn-over frequencies which are obtained by dividing the initial rates by the number of acid sites (or aluminum atoms) per gram (Fig. 2).

Taking into account that an increase in the Si/Al ratio of a zeolite leads not only to an increase of the acid strength of the protonic site [7] but also to an increase of the hydrophobicity of the surface, i.e., to a better affinity for the organic substrate than for water [3], the high activity observed for dealuminated mordenites may reflect the effect of both factors. However, Barthomeuf [8] calculated a Si/Al ratio of 9.4 as the maximum acid strength of mordenites, i.e., when no Al atom has another Al atom as a next-nearest neighbor. Specially for H-MOR(49) and H-MOR(100), the number of acidic sites is low, so that these are very isolated from each other in the zeolite lattice, but the remaining

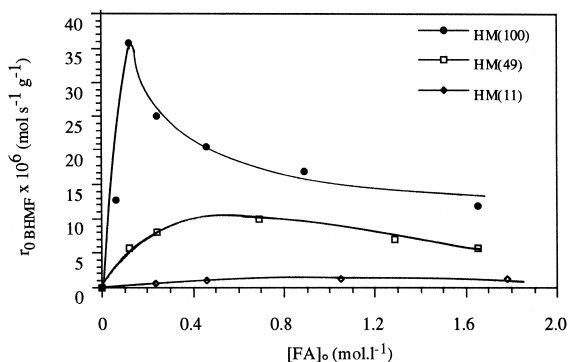


Fig. 1. Initial rates of BHMF formation from furfuryl alcohol: formol mixtures as a function of initial concentration in furfuryl alcohol, at constant formaldehyde concentration, in the presence of H-MOR(100), H-MOR(49) and H-MOR(11).

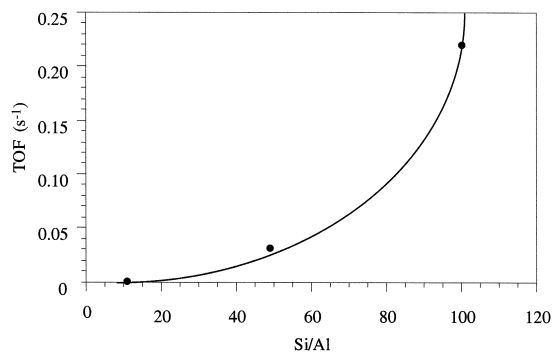


Fig. 2. Influence of Si/Al ratio on TOF for hydroxymethylation of furfuryl alcohol by aqueous formaldehyde at 338 K.

sites are assumed to be very strong. Differences in the TOF values are certainly due to variations of the hydrophobic character of zeolites (Fig. 2).

3.3. Determination of kinetic parameters

From the kinetic law proposed in our previous paper for the initial reaction rate [1]:

$$r_0 = k \frac{\lambda_F [F]_0 \cdot K [FA]_0}{(\lambda_{FA} [FA]_0 + 3 \lambda_F [F]_0)(1 + K [FA]_0)} \quad (1)$$

with λ_{FA} : adsorption coefficient of furfuryl alcohol on protonic site; λ_F : adsorption coefficient of formol hydrate on protonic site; $[FA]$: concentration in furfuryl alcohol; $[F]$: concentration in formol hydrate; K : affinity constant of furfuryl alcohol for hydrophobic surface, it is possible to calculate the parameters λ_F , λ_{FA} and K .

The fully developed Eq. (1) is:

$$\Leftrightarrow r_0 = k \frac{\lambda_F [F]_0 \cdot K [FA]_0}{\lambda_{FA} [FA]_0 + K \lambda_{FA} [FA]_0^2 + 3 \lambda_F [F]_0 + 3 K \lambda_F [F]_0 [FA]_0}$$

from which the following equation for the reverse of the initial reaction rate is obtained:

$$\frac{1}{r_0} = \frac{\lambda_{FA} [FA]_0}{k K \lambda_F [F]_0} + \frac{\lambda_{FA} [FA]_0}{k \lambda_F [F]_0} + \frac{3}{k K [FA]_0} + \frac{3}{k}$$

Multiplying the above expression by $[FA]_0/[F]_0$, the following equation is obtained:

$$\frac{1}{r_0} \frac{[FA]_0}{[F]_0} = \left(\frac{[FA]_0}{[F]_0} \right)^2 \frac{\lambda_{FA}}{k \lambda_F} + \frac{[FA]_0}{[F]_0} \left(\frac{3 K \lambda_F [F]_0 + \lambda_{FA}}{k K \lambda_F [F]_0} \right) + \frac{3}{k K [F]_0} \quad (2)$$

It is not possible to obtain a linear form from the rate law (Eq. (1)). A fairly complex expression is obtained which is a two-order polynomial equation (Eq. (2)) with the following coefficients:

$$\begin{aligned} \text{-- order 2: } a &= \frac{\lambda_{FA}}{k \lambda_F} \\ \text{-- order 1: } b &= \frac{3 k \lambda_F [F]_0 + \lambda_{FA}}{K k \lambda_F [F]_0} \\ \text{-- order 0: } c &= \frac{3}{k K [F]_0} \end{aligned}$$

Table 2
Determination of coefficients a , b , c

Zeolite	a	b	c
H-MOR(100)	350 031	33 042	57
H-MOR(49)	1 008 458	19 143	1441
H-MOR(11)	3 470 889	135 083	24 674

Table 3
Determination of λ_{FA}/λ_F and K for the three mordenites

Zeolite	λ_{FA}/λ_F	K
H-MOR(100)	38	37.5
H-MOR(49)	31	5.4
H-MOR(11)	14	2.4

Coefficients a , b , c were estimated by smoothing down the polynomial curves. From the coefficients' values (Table 2), the determination of the parameters λ_{FA}/λ_F and K was possible for the three zeolites, taking into account that $K = 3/kc[F]_0$ and $\lambda_{FA}/\lambda_F = ak$ (Table 3).

As expected, K increases with dealumination as illustrated in Fig. 3 depicting the relationship between K and the Si/Al ratio.

The more hydrophobic the zeolite, the more important K (which represents the affinity of furfuryl alcohol for the siliceous framework). The evolutions of TOF and K against the Si/Al ratio are similar (Figs. 2 and 3) and there is a linear relationship between TOF and K (Fig. 4). For zeolites with very low Al content, adsorption of organic substrates on the hydrophobic surface becomes the predominant factor in the catalyst activity. This conclusion might be related to the results of Mirth et al. [9].

Hydrophobicity of a solid is usually measured by sorption capacity for water and hydrocarbon molecules [3] or by the partition coefficient of a tracer between the catalyst and the bulk solution [10]. Another experimental method for characterizing the hydrophobic surface properties of zeolites is to measure, by thermogravimetric analysis, the weight loss of samples as a function of temperature [11]. In the present work, K , the affinity constant of furfuryl alcohol for hydrophobic surface, is determined under working reaction conditions and is thought to characterize the hydrophobicity of the catalyst in situ. Investigations are being performed to correlate these values and those obtained

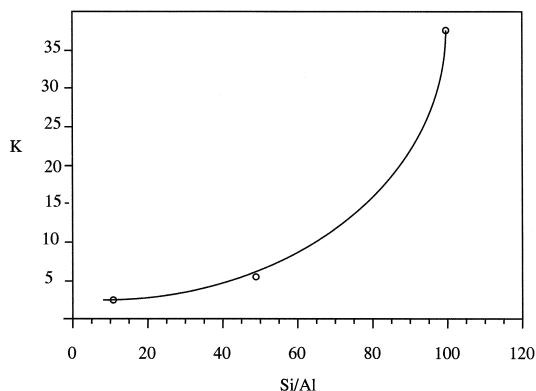


Fig. 3. Influence of Si/Al ratio on the adsorption constant K .

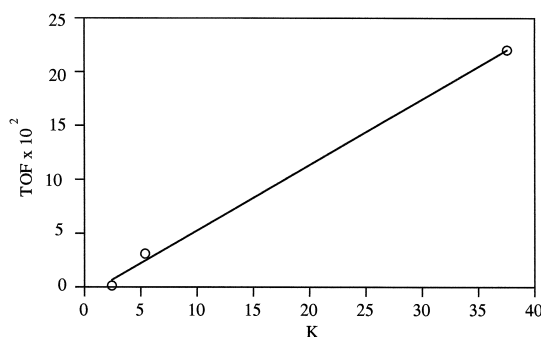


Fig. 4. Linear relationship between TOF and K .

according to the Anderson and Klinowski's method [11] with the TOF obtained in different aqueous reactions using mordenites with various Si/Al ratio as catalysts [12].

The ratio λ_{FA}/λ_F which represents the competitive adsorption of furfuryl alcohol and formaldehyde on the protonic site, is also increasing with dealumination. At high concentration, furfuryl alcohol is approximately 38 times more strongly held by the acid sites of H-MOR(100) than formaldehyde. Consequently, the dealumination of the zeolite has an influence on Brönsted sites. This result is not yet clearly explained and seems to be linked with the ones of Mirth et al. [9], Corma [13] and Corma et al. [14].

3.4. Adsorption

Adsorption measurements of furfuryl alcohol in aqueous solution at 338 K have been performed on the three dealuminated mordenites (H-MOR 100, 49 and 11) (Fig. 5). After 15 min, the amounts of alcohol adsorbed on H-MOR(100), H-MOR(49) and H-MOR(11) are 1.1, 0.5 and 0.2 mmol g⁻¹, respectively, corresponding to 0.095, 0.043 and 0.017 cm³ of furfuryl alcohol per gram of zeolite. The concentration of furfuryl alcohol within the pores has been estimated to about 3.3 M, whereas the bulk concentration is 0.1 M, showing the preferential adsorption of organic substrate on highly siliceous zeolite. Moreover, the smaller the Al content of the zeolite, the more important the adsorption.

Adsorption of organics on zeolites, either from aqueous solutions or from a mixture of organic molecules, all individually capable of penetrating the entire adsorbent, has already been reported [15,16]. Narita et al. [15] have investigated adsorption of phenols from aqueous solution on siliceous

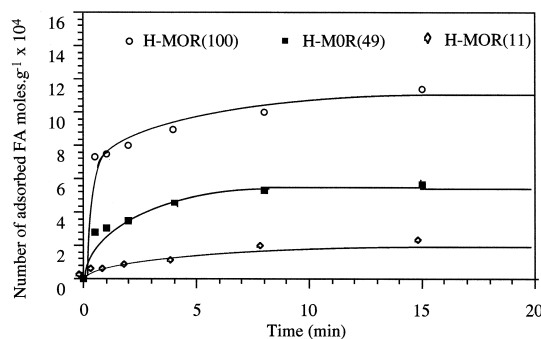


Fig. 5. Adsorption of furfuryl alcohol from aqueous solution on H-MOR(100), H-MOR(49) and H-MOR(11) at 338 K.

zeolites. For example, the high hydrophobicity of ZSM-5 permits the selective sorption of organic compounds dissolved in water. Dessau [16] has found that a dealuminated mordenite with a Si/Al of 30 can adsorb 29 mg/g of xylene isomers at equilibrium. Two effects should be taken into account: the affinity and the capacity for compound to adsorb. The capacity is directly related to micropore filling, the affinity to specific interactions with the surface (polarity, dispersion forces, etc.). As concerns H-MOR(100) and H-MOR(49), Table 1 reveals that microporous and mesoporous volumes are the same for these two dealuminated zeolites ($\sim 0.32 \text{ cm}^3 \text{ g}^{-1}$). However, adsorption of furfuryl alcohol is higher for H-MOR(100) by a factor of 2. This result clearly illustrates the affinity of organic compounds for hydrophobic zeolites. We suggest that adsorption occurs via the dispersive interaction of the furanic ring with the zeolite surface both in the meso- and micropores.

4. Conclusion

From the activity of dealuminated mordenites in hydroxymethylation of furfuryl alcohol by aqueous formaldehyde, the kinetic approach has allowed us to quantify the hydrophobicity of these mordenites by way of the affinity constant (K) of furfuryl alcohol for the zeolite hydrophobic surface. The K values determined in this study confirm that the hydrophobic character increases with dealumination and reveal the importance of this factor on the activity of acidic catalysts in water as solvent. Preferential adsorption of furfuryl alcohol from aqueous solutions on dealuminated mordenites are in agreement with these results.

Acknowledgements

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