

# Determination of the acid strength of solid catalysts in water by means of a kinetic tracer

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## Abstract

The kinetic analysis of the hydrolysis of acetals in the presence of various solid acid catalysts, dealuminated H-form mordenites, H-montmorillonite and strong ion exchange resins has been carried out. Experiments performed in water as the solvent at different agitation speeds, catalyst weights and acetal concentrations show that the reaction is not controlled by external diffusion, nor by internal diffusion as resulting from the calculation of the Thiele modulus. From the standard plots of the logarithms of the rate constants against the Hammett acidity function  $H_0$  established in homogeneous catalyzed reactions, it is possible to calculate such an acidity function for solid catalysts from the measurement of the reaction rates and extrapolation on the previously established standardization plot. Kinetic analysis of the experimental results allows the determination of the maximum reaction rates in the absence of diffusional limitations and, as a consequence, the determination of the maximum acidity of solids under working reaction conditions. The influence of the dealumination of mordenites is as expected, a maximum of acidity being found for Si/Al ratios around 10–15. In a similar way, the perfluorinated sulfonic resin referred to as Nafion is by far the most acidic catalyst. Nevertheless, a leveling effect of the acidity of solids is observed in water as the solvent, the strongest acid being the hydroxonium ion  $H_3O^+$  with a  $H_0$  limit value of  $-1.74$ . For dealuminated mordenites, the relationship found between the measured maximum acidity function and the protonic acidity calculated from the number of protons in the lattice would mean that only 20% of the protons present on the solid are efficient for the catalytic reaction. As in homogeneous catalysis, it is then possible to establish compared acidity scales of solid acids in solvents, water in this work.

*Keywords:* Zeolites; Resins; Acidity; Hydrolysis; Acetals

## 1. Introduction

The use of heterogeneous catalysis for the production of organics is receiving more and more interest. The large majority of data pub-

lished up to date concerns acid-catalyzed reactions [1,2]. The acid properties of solid catalysts such as clays or amorphous and crystalline aluminosilicates are related to surface acidity, the nature of which being either of Brønsted or Lewis type. The complete characterization of the acidity of a surface requires the determination of the nature, the density and the strength of the sites. Several physical methods exist for

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the characterization of acidic catalysts, but few methods exist for the characterization of those catalysts under working reaction conditions, and particularly in water as the solvent. The research of acidity vs activity correlations is thus particularly relevant. This latter approach was made for example by Karge et al. for cyclohexanol dehydration [3], by Namba et al. for ester hydrolysis [4], Lopez et al. for trioxane depolymerization [5], Corma et al. for esterification reactions [6].

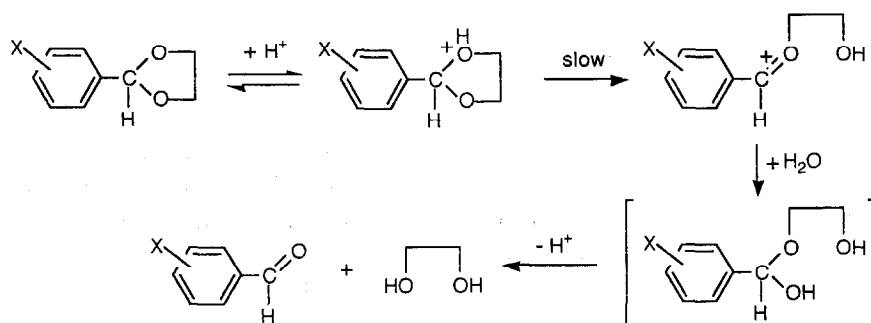
The aim of our work was to develop a simple and accurate method to measure acidities in aqueous media where a large majority of organic reactions is performed. Little was known in this field. In the presence of water, the acidity is essentially of the Brønsted type. In a previous paper [7], we have reported on the possibility of such measurements by using hydrolysis of acetals derived from benzaldehyde, a reaction known to be submitted to a specific acid catalysis in solution [8]. This reaction was further investigated with the study of the hydrolysis of *meta*- and *para*-substituted 2-phenyl-1,3-dioxolanes in the presence of representative solid acid samples such as clays, zeolites and ion exchange resins.

In a homogeneous medium [8], the rate determining step for hydrolysis of this acetal is the decomposition of the protonated acetal, and is

catalyzed by protons only (Scheme 1). The rate of the reaction,  $r$ , is expressed by the following equation,  $r = k_{H^+}[H^+][S]$ , in which  $k_{H^+}$  is the bimolecular rate constant, and  $[H^+]$  and  $[S]$  are the concentrations in protons and acetal, respectively. The product  $k_{H^+}[H^+]$  is the observed rate constant  $k_{obs}$ .

It is then possible to correlate the acidity of the medium to the observed rate constant through the equation  $\log k_{obs} = \log k_{H^+} + \log [H^+]$  for several tracers [7]. This equation is valid for diluted strong acids only, where pH and the Hammett acidity function,  $H_0$ , are equivalent.

The determination of the acidity of a solid according to this method is carried out in two steps. In the first step, the rate of hydrolysis of acetals is measured for different concentrations of hydrochloric acid, and the correlations between the logarithm of the observed rate constants  $k_{obs}$  are plotted against pH or the Hammett acidity function,  $H_0$ . Linear relationships are obtained, with a slope equal to  $-1$ , characteristic of a specific acid catalyzed reaction [9]. In the second step, hydrochloric acid is replaced by a solid acid catalyst and a reaction rate is measured. It is then possible to estimate the corresponding acid strength from the standardization diagram previously established for hydrochloric acid.



X = H, m-OCH<sub>3</sub>, p-OCH<sub>3</sub>, m-CH<sub>3</sub>, p-CH<sub>3</sub>, m-Cl, p-Cl, p-NO<sub>2</sub>

Scheme 1. Kinetic reaction scheme for acid catalyzed hydrolysis of 2-phenyl-1,3-dioxolanes.

## 2. Experimental

### 2.1. Materials

The various acetals were synthesized from the corresponding aldehydes available commercially (Aldrich), and according to standard procedures reported in the literature [8].

H-form Montmorillonite K10, Amberlyst 15 and Nafion 117 ion exchange resins were commercial products. Parent samples of mordenite were obtained from the Société Chimique Grande Paroisse (Alite 180, Si/Al = 5.5), and from the Norton Cie (Zeolon 100 H, Si/Al = 6.9). Two dealuminated mordenites with Si/Al ratios equal to 8.7 and 11.1 were prepared from the Zeolon 100 H sample using combined steam and acid treatments as described elsewhere [10]. Two additional dealuminated mordenites with Si/Al ratios of 15 and 40 were supplied by the Institut Français du Pétrole.

### 2.2. Kinetic measurements

Reaction kinetics were followed by UV spectrophotometry (Gilford 250) by recording the increase in optical density due to the formation of the aldehyde at the corresponding  $\lambda_{\max}$  as a function of time.

In aqueous solution, the measurements were performed by mixing rapidly in quartz cells 20  $\mu\text{l}$  of a  $0.7 \times 10^{-2}$  M solution of acetal in dioxane to 2 ml of a solution of titrated hydrochloric acid.

With the solid catalysts, the procedure was as follows: a weighted amount of powder was dispersed in 40 ml of deionized water in thermostated flask (25°C) under stirring and 10  $\mu\text{l}$  of pure acetal were added to this solution. An aliquot of filtered solution was continuously fed into a 100  $\mu\text{l}$  recirculating UV cell using a volumetric pump and the optical density was recorded versus time.

In both cases the rate constants were deduced from the experimental plots by curve fitting and simulation using a pseudo-first order kinetic

model:  $D = D_{\text{inf}} + (D_{\text{inf}} - D)e^{-kt}$ , where  $D_{\text{inf}}$  and  $D$  are the optical densities at infinite and  $t$  times, respectively, and  $k$  is the observed rate constant.

## 3. Results and discussion

### 3.1. Standardization in homogeneous medium

The reference curves have been established for hydrolysis of *meta*- and *para*-substituted 2-phenyl-1,3-dioxolanes (substituents = H, *m*-OCH<sub>3</sub>, *p*-OCH<sub>3</sub>, *m*-CH<sub>3</sub>, *p*-CH<sub>3</sub>, *m*-Cl, *p*-Cl and *p*-NO<sub>2</sub>) for various hydrochloric acid dilutions (Table 1). The logarithms of the observed rate constants obtained versus  $H_0$  are given in Fig. 1. Linear correlations with a slope equal to  $-1$ , characteristic of a specific acid catalyzed reaction, have been obtained.

### 3.2. Reaction on solid catalysts

Before measuring the acidity of the solid catalysts, a series of experiments was performed aiming at the determination of the kinetic parameters of the reaction, kinetic law, reaction orders, diffusional limitations.

#### 3.2.1. external diffusion

**3.2.1.1. Influence of agitation speed.** The variation of observed rates constants as a function of agitation speed is illustrated in Fig. 2 for hydrolysis of 2-phenyl-1,3-dioxolane over H-mordenite (Si/Al = 5.5) with an initial concen-

Table 1  
Observed rate constants ( $\times 10^3 \text{ s}^{-1}$ ) for hydrolysis of substituted 2-phenyl-1,3-dioxolanes in hydrochloric acid at 25°C

$H_0$	<i>p</i> -OCH <sub>3</sub>	<i>m</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>m</i> -CH <sub>3</sub>	H	<i>p</i> -Cl	<i>m</i> -Cl	<i>p</i> -NO <sub>2</sub>
-0.9	-	-	-	-	-	-	-	49
0	-	439	-	-	1122	169	50	7
1	1140	49	454	235	126	19	6	0.7
2	126	6	48	24	14	2	0.7	-
3	14	0.6	5	3	1.4	-	-	-

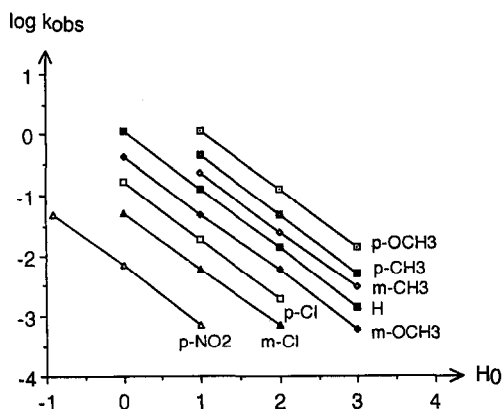


Fig. 1. Standardization plot of logarithms of the observed reaction rate constants against  $H_0$  acidity function for hydrolysis of substituted 2-phenyl-1,3-dioxolanes in hydrochloric acid at 25°C.

tration in acetal of  $1.66 \times 10^{-3}$  M. It is seen that no mass transfer limitation occurs at agitation speed over 700 rpm.

**3.2.1.2. Influence of catalyst weight.** Plots of initial reaction rates as a function of the catalyst weight was studied in the presence of H-montmorillonite K10 and H-mordenite (Si/Al = 6.9) using different concentrations in 2-phenyl-1,3-dioxolane.

With H-montmorillonite K10 as catalyst, it can be seen that at low concentration in acetal (Fig. 3), the reaction obeys a classical Langmuir–Hinshelwood mechanism with a maxi-

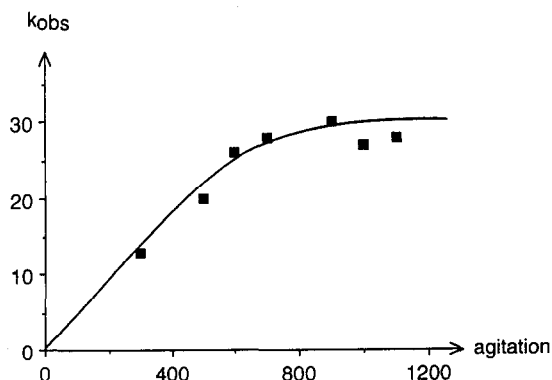


Fig. 2. Plot of observed reaction rate constants ( $\times 10^4 \text{ s}^{-1}$ ) against agitation speed (rpm) for hydrolysis of 2-phenyl-1,3-dioxolane over 200 mg of H-mordenite (Si/Al = 5.5), and  $1.66 \times 10^{-3}$  M initial acetal concentration at 25°C.

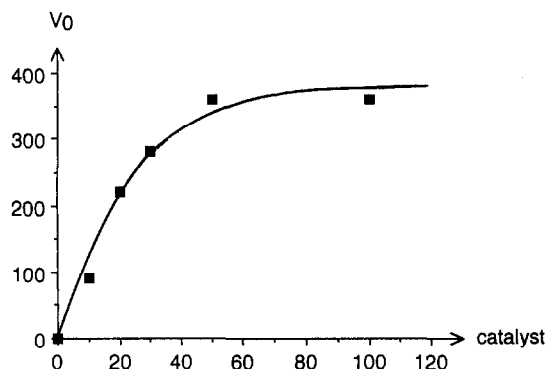


Fig. 3. Plot of initial reaction rates ( $\times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$ ) against catalyst weight (mg) for hydrolysis of 2-phenyl-1,3-dioxolane over H-montmorillonite K10, and  $1.3 \times 10^{-4}$  M initial acetal concentration at 25°C.

imum of about  $350 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$  for the reaction rate. At higher concentration in acetal, a similar behavior is observed, with a maximum rate of the same order of magnitude.

With H-mordenite (Si/Al = 6.9), a similar behavior is again obtained (Fig. 4). The maximum rate, around  $420 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ , is obtained at higher catalyst weight compared to H-montmorillonite clay K10, thus confirming the low acidity of this weakly dealuminated mordenite.

**3.2.1.3. Influence of acetal concentration.** The variation of the initial reaction rates as a function of the initial concentration in acetal is

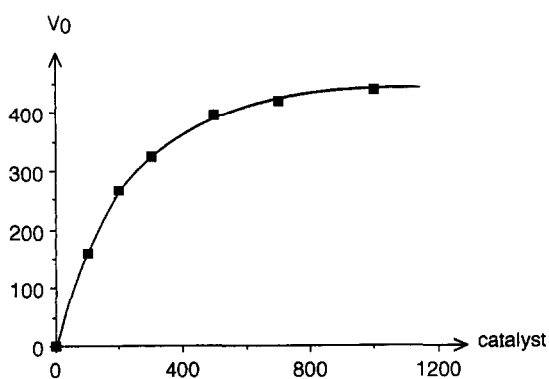


Fig. 4. Plot of initial reaction rates ( $\times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$ ) against catalyst weight (mg) for hydrolysis of 2-phenyl-1,3-dioxolane over H-mordenite (Si/Al = 6.9), and  $2.6 \times 10^{-4}$  M initial acetal concentration at 25°C.

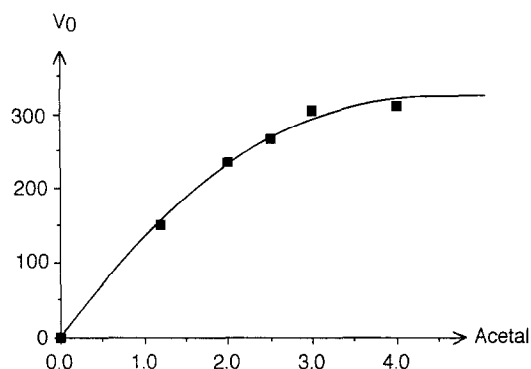


Fig. 5. Plot of initial reaction rates ( $\times 10^7$  mol  $l^{-1}$  s $^{-1}$ ) against acetal concentration ( $\times 10^4$  M) for hydrolysis of 2-phenyl-1,3-dioxolane over 200 mg of H-mordenite (Si/Al = 6.9), at 25°C.

illustrated in Fig. 5 for hydrolysis of 2-phenyl-1,3-dioxolane over H-mordenite (Si/Al = 6.9). The maximum reaction rate, around  $300 \times 10^{-7}$  mol  $l^{-1}$  s $^{-1}$ , is close to that observed when plotting initial reaction rates as a function of the catalyst weight. It is thus observed a Langmuir–Hinshelwood mechanism in which the products and the solvent are not involved in the rate equation,  $V_0 = k\lambda_{Acetal}[Acetal]/1 + \lambda_{Acetal}[Acetal]$ . As shown in the plot of the initial reaction rates against the catalyst weight (Fig. 4), at low coverage of the catalyst, an apparent kinetic first order is observed. At high coverage, the saturation of the substrate occurs and a zero order is then observed. These kinetic orders are confirmed in the plot of the initial reaction rates against acetal weight (Fig. 5), and from both figures it is possible to calculate the maximum value of the reaction rate, i.e. about  $400 \times 10^{-7}$  mol  $l^{-1}$  s $^{-1}$ .

Such a behavior observed when plotting the initial reaction rates against catalyst weight or initial reactant concentration has been already considered by Tanabe and Aramata [11] in depolymerization of paraldehyde in terms of close analogy with the Michaelis–Menten mechanism operating in enzymatic reactions with the formation of an enzyme-substrate complex.

Confirmation of the validity of the kinetic model is also obtained by plotting the reciprocal of the initial reaction rates against the reciprocal

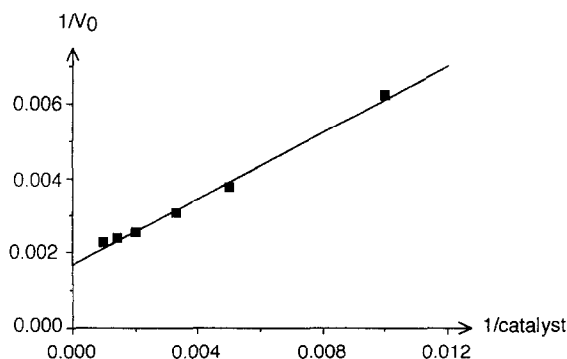


Fig. 6. Plot of reciprocal of initial reaction rates ( $\times 10^{-7}$  l s mol $^{-1}$ ) against reciprocal of catalyst weight ( $mg^{-1}$ ) for hydrolysis of 2-phenyl-1,3-dioxolane over H-mordenite (Si/Al = 6.9), and  $2.6 \times 10^{-4}$  M initial acetal concentration at 25°C.

of the catalyst weight (Fig. 6) and acetal concentration (Fig. 7). From both plots and their intercepts with the y-axis, it is thus possible to calculate the reaction rate constant,  $6-7 \times 10^{-5}$  mol $^{-1}$  s $^{-1}$  g $^{-1}$  for the mordenite Si/Al = 6.9.

### 3.2.2. internal diffusion

The importance of internal diffusion can be estimated from the equation proposed by Weisz and Swegler [12]:  $dN/dt \times 1/C_0 \times R^2/D_{eff} < 0.1$ , in which  $dN/dt$  is the reaction rate (mol/s/g),  $C_0$  is the initial reactant concentration (mol/cm $^3$ ),  $R$  is the particle radius (cm) and  $D_{eff}$  is the effective diffusivity coefficient (cm $^2$ /s). With a maximum reaction rate of  $5 \times 10^{-2}$  mol/s/g, an initial concentration of 1.66

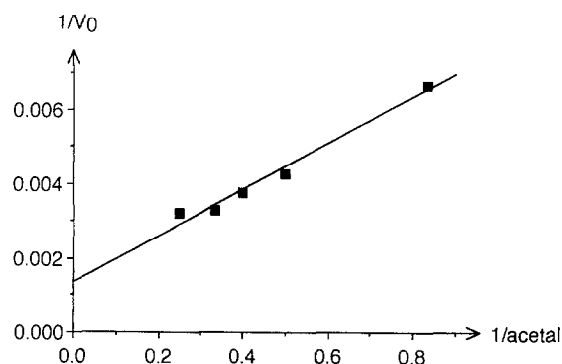


Fig. 7. Plot of reciprocal of initial reaction rates ( $\times 10^{-7}$  l s mol $^{-1}$ ) against reciprocal of acetal concentration ( $\times 10^{-4}$  M $^{-1}$ ) for hydrolysis of 2-phenyl-1,3-dioxolane over 200 mg of H-mordenite (Si/Al = 6.9) at 25°C.

$\times 10^{-6}$  mol/cm<sup>3</sup> and a mean particle radius of  $15 \times 10^{-4}$  cm, there is no limitation by internal diffusion if  $D_{\text{eff}}$  is larger than  $6.7 \times 10^{-7}$  cm<sup>2</sup>/s, a reasonable value for the diffusivity coefficient of liquids in microporous systems.

### 3.3. Reaction mechanism

In a recent work [13], we have reported on the increasing use of Hammett relationships to assess reaction mechanisms in heterogeneous catalyzed reactions, in particular for acid catalyzed reactions. As far as the kinetic parameters show that the reaction is working under chemical regime, the use of such relationships becomes of particular interest.

For substituted 2-phenyl-1,3-dioxolanes hydrolysis, the rate determining step is the cleavage of the protonated C–O bond of the acetal (Scheme 1) in a water/dioxane (50/50 by volume) mixture. When plotting the logarithms of the rate constants of *meta*- and *para*-substituted 2-phenyl-1,3-dioxolanes against the substituent constants,  $\sigma$ , a linear plot is observed [8] with a negative slope value of  $-3.35$ , indicative of the formation of a positive charge on the reaction center.

Over heterogeneous catalysts, namely H-montmorillonite K10 and H-mordenite (Si/Al = 6.9), similar correlations are obtained as shown in Fig. 8 and Fig. 9, respectively. Slope values of  $-2.75$  ( $r^2 = 0.92$ ) and  $-3.18$  ( $r^2 =$

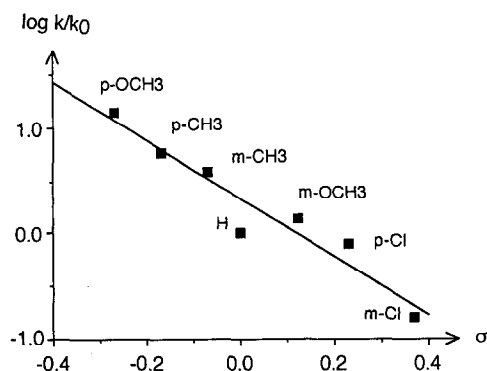


Fig. 8. Hammett plot for hydrolysis of substituted 2-phenyl-1,3-dioxolanes over H-montmorillonite K10 at 25°C.

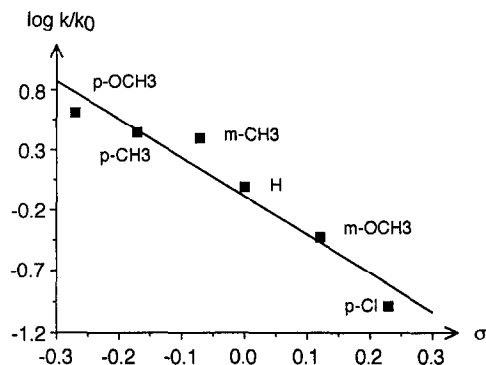


Fig. 9. Hammett plot for hydrolysis of substituted 2-phenyl-1,3-dioxolanes over H-mordenite (Si/Al = 6.9) at 25°C.

0.93) have been calculated for H-montmorillonite K10 and H-mordenite (Si/Al = 6.9), respectively. The slightly lower values would result from an increase in the polarity of the solvent [14].

All these aspects, kinetics, reaction mechanisms, seem to indicate that the reaction is not controlled by external diffusion. Internal diffusion can also be ruled out from the Weisz criterion and absence of difference in the reactivity of *meta*- and *para*-substituted acetals which could have occurred due to the pore dimensions of the mordenites used. The possibility for the reaction to occur within the mesopores of dealuminated mordenites at the outer surface was also ruled out from other series of experiments. In a recent work on the dehydration of another relatively bulky molecule such as fructose [15], in the presence of a series of dealuminated mordenites, we had already assumed that the presence of mesopores might lead to an increase in the acid strength as due to the formation of  $\text{H}_3\text{O}^+$  species within the mesopores as it was observed with macropores of ion-exchange resins. No significant difference in the catalytic activity was observed. On the other hand, an important drop in the selectivity of the reaction was observed. In addition, in closely related reactions of substituted aromatics over the same series of catalysts [16], passivation of the outer surface does no longer lead to significant differences in the catalytic activity.

In the present work, except in the case of the most dealuminated mordenite (Si/Al = 40) which has an external surface area of 82 m<sup>2</sup>/g, all other mordenites have external surface areas ranging between 36 and 58 m<sup>2</sup>/g as calculated from nitrogen adsorption isotherms. As a consequence, this slight change in the outer surface, compared to the inner surface, cannot account for a large increase in the catalytic activity by a factor of about 100.

Thus, assuming that the reaction takes place mainly in the micropores of the catalysts, it is then possible to see what kind of information we can get on the acidity of solid catalysts in water from such structure-activity relationships.

#### 4. Determination of the acid properties of solid catalysts in water

Under the operating conditions used avoiding external and internal diffusional limitations, it is possible to determine the maximum of activity for any solid acid catalyst in water as the solvent, and the corresponding acidity function. Two tracers, 2-phenyl-1,3-dioxolane and its *para*-methyl derivative have been used for this purpose depending on the expected activity of the catalysts. After measurement of the reaction rates and calculation of the corresponding acidity function from the standardization curve, a classification was established for various solid acid catalysts such as zeolites, clays and resins. This classification is given in Table 2.

From Table 2, it can be seen that the order of acidity in water is in accordance with what could be expected from studies in other solvents. Sulfonic ion exchange resins are given as strong acid catalysts with a pK<sub>a</sub> value of about 1 for Amberlyst 15 and an increased acidity in the perfluorinated resin referred to as Nafion. In the series of dealuminated mordenites, a classical behavior is observed, the acidity increasing with the decreased aluminum content.

Nevertheless, it is worth mentioning that all the solids studied are less acidic in character

Table 2

Observed rate constants (s<sup>-1</sup>) and corresponding acidity function H<sub>0</sub> for hydrolysis of substituted 2-phenyl-1,3-dioxolanes (X = H, CH<sub>3</sub>) in the presence of various solid acid catalysts at 25°C

Catalysts	k <sub>obs</sub>	Tracer (X)	H <sub>0</sub>
HCl (0.68 M)	1.23	H	0.04
H-mordenite (Si/Al = 4.5)	0.005	<i>p</i> -CH <sub>3</sub>	3.05
H-mordenite (Si/Al = 5.5)	0.013	<i>p</i> -CH <sub>3</sub>	2.60
H-mordenite (Si/Al = 6.9)	0.11	<i>p</i> -CH <sub>3</sub>	1.70
	0.04	H	1.60
H-mordenite (Si/Al = 8.7)	0.31	<i>p</i> -CH <sub>3</sub>	1.24
H-mordenite (Si/Al = 11.1)	0.16	H	0.90
H-mordenite (Si/Al = 15)	1.83	<i>p</i> -CH <sub>3</sub>	0.50
H-mordenite (Si/Al = 40)	3.20	<i>p</i> -CH <sub>3</sub>	0.25
H-montmorillonite K10	0.23	H	0.80
Amberlyst 15	0.39	H	0.60
Nafion 117	1.15	H	0.08

than the hydrochloric reference solution with H<sub>0</sub> close to zero. That could result either from the hydrophilic character of the solids [4] or from the leveling effect of the solvent [17]. Concerning the hydrophilic character, water covers the surface of the solid and retards adsorption of organic molecules. It was shown by Kerr [18] that a loss of Brønsted acidity, by about 25%, is observed by contacting a H-Y zeolite with water for some minutes. Concerning the leveling effect, the use of a protic solvent could lead to a limitation of the available acidity by the conjugated acid of the solvent. In this way, the acid strength in water would be limited to the strongest acid present in the medium, i.e. hydroxonium ion H<sub>3</sub>O<sup>+</sup> with a pK<sub>a</sub> of -1.74.

#### 5. Effect of the dealumination of mordenites

In Table 3, the results concerning the determination of the acidity function H<sub>0</sub> for the

Table 3

Acidity function determined from kinetic experiments and H<sup>+</sup> (meq/g) calculated from unit cell over a series of dealuminated H-mordenites

Si/Al	4.5	5.5	6.9	8.7	11.1	15	40
H <sub>0</sub> kin	3.05	2.60	1.70	1.24	0.90	0.50	0.25
H <sub>calc</sub> <sup>+</sup>	2.65	2.16	1.72	1.36	1.07	0.79	0.29

series of dealuminated mordenites, and the corresponding number of protons, in meq/g, calculated from the zeolite structure [19] are summarized. The effect of the dealumination of mordenites on the catalytic activity in water is close to that reported in the literature for non-aqueous as well as for aqueous solvents. A maximum of activity is generally observed for mordenites with a Si/Al ratio from 10 to 15. Those results are explained in terms of a balance between the reduced number of protonic sites as due to the dealumination, and reinforcement of their strength.

For acetal hydrolysis, reaction rates are still increasing with the Si/Al ratio. From Table 3, a linear relationship ( $r^2 = 0.97$ ) between  $H_0$  and  $H_{\text{calc}}^+$  (Fig. 10) is observed which would appear as fortuitous because of the logarithmic dimension of the acidity function  $H_0 = -\log H_0$  or  $H_0 = -\log H^+$  for dilute solutions. By plotting  $H_0$  as a function of  $-\log H_{\text{calc}}^+$ , we obtain a fairly good linear correlation ( $r^2 = 0.96$ ), as illustrated in Fig. 11, if we except the data for H-mordenite Si/Al = 40. This linear plot is thought to reflect nearly exactly the correspondence between activity and the acidic properties of the catalyst, whereas for highly dealuminated mordenites the activity should include another parameter due to the hydrophobic character of the zeolite and this phenomenon was also shown to appear in other reactions performed in water as the solvent [20].

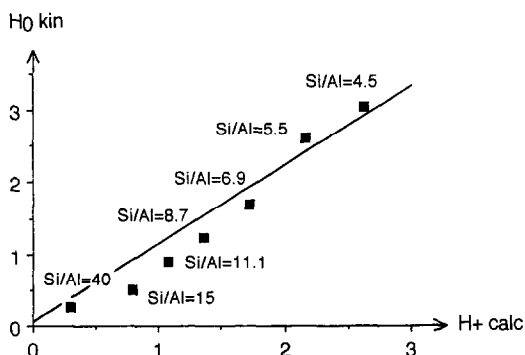


Fig. 10. Plot of  $H_0$  acidity function determined from kinetics against proton concentration (meq g) calculated from the dealuminated mordenites framework.

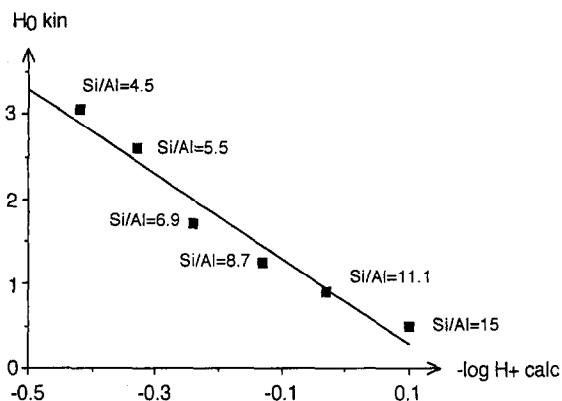


Fig. 11. Plot of  $H_0$  acidity function determined from kinetics against the logarithm of calculated proton concentration (meq g).

Another important feature resulting from the relationship shown in Fig. 11 is the value of the slope,  $-5$  instead of  $-1$  in the case of the homogeneous catalyzed reaction. If  $H_0_{\text{kin}}$  is representative of the acidity function obtained from the standardization in solution, this would mean that, to obtain the same solid acidity in the presence of a solvent, five catalytic sites are required. In other words, it would mean that only 20% of the protonic sites present on the surface of the mordenites are capable of performing hydrolysis of acetals.

## 6. Conclusion

In water as solvent, acetals readily hydrolyze to their corresponding aldehydes over solid catalysts through a mechanism similar to that already proposed for the homogeneous catalyzed reaction.

The determination of the maximum hydrolysis rates then allows, in the absence of diffusional limitations, to set up a scale of acidity for different solid acids in water. In such a manner, it is possible to compare the acidity of more or less dealuminated mordenites with sulfonic resins. Nearly similar acidities are obtained when the Si/Al ratio is higher than 15. For strongly dealuminated mordenites, the acidity is no longer increasing as due, probably, to a kind of com-



pensating effect resulting from the increasing hydrophobic effect of the catalyst in water.

It should also be noted that solvent effects may also apply for reactions catalyzed by heterogeneous catalysts, the acidity being limited by the strongest acid present in the reaction medium,  $\text{H}_3\text{O}^+$  in the case of water.

Finally, from the different relationships found between the acidity measured kinetically after homogeneous standardization and the calculated number of protonic sites present on H-mordenites, only 20% of those protonic sites would be available for the reaction to occur.

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