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Hydration of *n*-Butenes Using Zeolite Catalysts. Influence of the Aluminium Content on Activity

FRANÇOIS FAJULA, RAFAEL IBARRA, FRANÇOIS FIGUERAS, AND CLAUDE GUEGUEN*

*Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquées, E.R.A. 954, E.N.S.C.M., 8 Rue de l'Ecole Normale, 34075 Montpellier Cedex, France and *Centre de Recherche de Solaize ELF France, B.P. 22, 69360 St. Symphorien d'Ozon, France*

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The hydration of *n*-butene over various protonic zeolites has been investigated in a batch reactor. At 523 K and 65 atm, and with a water/olefin ratio of 4.4, the alcohol yields per gram of catalyst followed the pattern mordenite > ZSM-5 > offretite ≅ omega ≅ Y. In particular, mordenites with intermediate Al contents ($7 < Si/Al < 9$) enabled 75% of the thermodynamic equilibrium to be reached with 100% selectivity. Overdealumination of mordenite as well as more severe experimental conditions led to the formation of dimer by-products. Zeolites exhibiting a hydrophobic character had a very good activity but hydrophobicity does not appear to play a determining role in the process. It is found that the activities per protonic site are correlated with the aluminium content of the catalyst regardless of its framework structure. It is proposed that, as in aqueous acid media, the hydration activity of zeolites is a direct and single function of their protonic acid strength.

INTRODUCTION

The hydration of olefins is a typical acid-catalyzed reaction (*1*). It is exothermic, being limited by the reverse reaction at high temperature and favored by pressure.

The industrial production of aliphatic alcohols by hydration of olefins in the presence of aqueous sulfuric acid is an old and widely used process. It nevertheless suffers from several disadvantages, the two major ones being the corrosiveness of the acid and the necessity of diluting the acid to recover the alcohol product.

The handling problems associated with sulfuric acid can be obviated by using solid catalysts such as phosphoric acid deposited on silica gel or clays, tungsten oxide, molybdenum-promoted silica-alumina, and organic ion-exchange resins. However, these materials give rise to new complications. In particular, with phosphoric acid based catalysts an undesirable polymer by-product is formed and acid is eluted during the process, while the ion exchange resins are unstable at temperatures above 423 K.

It has been claimed recently that chromium and rare-earth exchanged type Y zeolites (*2, 3*) and highly siliceous zeolites of the ZSM series (*4*) can be used advantageously for direct hydration of C_2–C_5 olefins under moderate pressure. Since zeolites combine cation-exchange properties, high surface acidity, and good thermal stability they could permit an updating of the industrial hydration processes.

The aim of our work has been to investigate the behavior of protonic zeolites having different structures and aluminium contents. The hydration of *n*-butenes has been chosen as a model reaction.

EXPERIMENTAL

Reactants. n-Butene (*cis*-but-2-ene, 45%; *trans*-but-2-ene, 55%) of 99.2% purity obtained from the Société Air Liquide and deionized water were used as reactants.

Catalysts. Three batches of synthetic mordenite were used, namely two hydrogen mordenites (Alite 180, H-M_1, Si/Al = 5 from the Société Chimique Grande Paroisse and Zeolon 100-H, H-M_2, Si/Al = 6.9 from Norton) and an ammonium mordenite (Si/Al = 9.2, supplied by Union Carbide). The

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latter was transformed into the protonic form (H-M_3) by calcination in air at 773 K.

Dealuminated mordenites were prepared from Zeolon 100-H(H-M_2) by treatment in 1 *N* HCl solution at 343 K for 3 h or refluxing in 3 *N* HCl solution for 6 h. The resulting powders, washed, oven dried, and calcined at 773 K had Si/Al atomic ratios of 11.1 (H-M-deal-1) and 15.3 (H-M-deal-2), respectively.

An H-ZSM-5 zeolite with a Si/Al ratio of 49 was furnished by the Institut Français du Pétrole.

A sample of potassium offretite with a Si/Al atomic ratio of 3.7 was obtained from Grace Davison. Two additional offretite samples with Si/Al ratios of 3 and 3.9 were synthesized as described elsewhere (*5*). The H form offretites (H-O) were obtained by repeated treatment in 1 *N* NH_4Cl solution at 333 K followed by calcination in air at 773 K.

An H-Ω catalyst (H-Ω_1, Si/Al = 3.5) was prepared by calcining in air at 773 K an ammonium omega zeolite supplied by Union Carbide. A second omega zeolite sample (H-Ω_2, Si/Al = 6.4) was synthesized according to Perrotta *et al.* (*6*). It was exchanged twice in 1 *N* NH_4Cl at 333 K and then calcined in air at 773 K.

The H-Y catalyst was obtained by treating at 773 K in air a sample of commercial ammonium Y zeolite (SK 41, Linde, Si/Al = 2.5).

In all cases retention of crystallinity by the fresh and used zeolite catalysts was checked by X-ray diffraction.

The chemical composition of the samples was determined by atomic absorption after dissolution.

Procedures. The hydration of *n*-butene was carried out at 473–573 K and 44–100 atm. pressure in a 110-ml stainless steel batch autoclave reactor. In a typical run, 17 ml of water (0.94 mol) and 0.3 to 0.4 g of zeolite in the form of powder were placed into the reactor. The autoclave reactor was sealed, cooled in liquid nitrogen, evacuated, and the olefin (0.21 mol) introduced. The autoclave was then heated to the desired temperature under vigorous shaking and the pressure recorded. After 2.5 to 17 h the reactor was rapidly cooled to room temperature and the gaseous and liquid phases collected.

Reaction mixtures were analysed by gas–liquid chromatography using a Porapak Q column (80-100 mesh, $\frac{1}{8}$ in., 2 m long, 343 K) with a katharometer detector and a silicone SE 30 column (15% on Chromosorb W, $\frac{1}{8}$ in., 6 m long, 298 K) with flame ionization detection.

Measurement of acid strength. The acid strength of the catalysts in water was qualitatively measured using the Benesi method (*7*) as modified by Namba *et al.* (*8*). Ten to 30 mg of zeolite in 10 ml of water were contacted for 12 h at room temperature with 2 drops of 2% ethanol solutions of Hammett indicators (H_0 = +4, +1.5, −3, −5.6, and −8.2). The acid strength was determined visually from the color of the adsorbed indicator.

Measurement of the water sorption capacity. Sorption measurements were made at 298 K using a Setaram B 60 balance. A sample of 0.2 to 0.5 g was first heated in flowing nitrogen at 673 K to constant weight and cooled to room temperature before the water vapor was admitted. The sorption capacity of the ZSM-5, offretite, and mordenite catalysts was determined by the weight gain at a partial pressure of 12 Torr (P/P_0 = 0.6). The samples were contacted with water for 12 h which permitted the equilibrium to be reached.

RESULTS AND DISCUSSION

Acid Strength and Water Sorption Behavior

Table 1 summarizes the main characteristics of the various catalysts and the qualitative determination of their acid strength in water. As already reported by Namba *et al.* (*8*), the zeolites do not show in water the high acidities ($H_0 \leq -8.2$ or acidity ≥90 wt% H_2SO_4) generally encountered in non-

TABLE 1

Acid Strength of Various Zeolites in Water Determined from the Color of the Adsorbed Indicators[a]

Zeolite[b]	Cation exchange degree (%)	Si/Al atomic ratio	pK_a of the indicator = H_0				
			+4	+1.5	−3	−5.6	−8.2
H-ZSM-5	99	49	+	+	+	+	−
H-M_1	85	5	+	+	−	−	−
H-M_2	98	6.9	+	+	−	−	−
H-M_3	99	9.2	+	+	+	±	−
H-M-deal-1	100	11.1	+	+	+	+	−
H-M-deal-2	100	15.3	+	+	+	+	−
H-O_1	70	3	+	−	−	−	−
H-O_2	67	3.7	+	±	−	−	−
H-O_3	70	3.9	+	±	−	−	−
H-Ω_1	95	3.5	+	−	−	−	−
H-Ω_2	60	6.4	+	+	−	−	−
H-Y	80	2.5	+	−	−	−	−

[a] +, Acidic color; ±, slightly acidic color; −, basic color.

[b] M, Mordenite; O, offretite.

polar solvents. The data nevertheless indicate that the acid strength in water is strongly dependent on zeolite composition. Silicon-rich zeolites (Si/Al $\geq$ 9.2) have strong acid sites ($-8.2 < H_0 \leq -5.6$) while aluminium-rich zeolites (Si/Al < 3.5) and zeolites with an intermediate Al content (6.9 > Si/Al > 3.7) exhibit weak ($H_0 > +1.5$) or moderate ($H_0 > -3$) acidities. At first glance, this result is not surprising; it is indeed well known that the acidity of a zeolite increases when the aluminium content is decreased. However, the measurements being made in water, another parameter, namely the zeolite hydrophobicity, has also to be considered.

The hydrophobic nature of highly siliceous zeolites has been first pointed out by Chen (*9, 10*). His demonstration was principally based on the observation that, in contrast with common zeolites for which the available intracrystalline void space becomes completely filled even at very low partial pressures of water, H-ZSM-5, beta- and dealuminated mordenites sorbed little or no water while exhibiting normal sorption capacities for hydrocarbons. Moreover, because the volume of sorbed water in these solids was smaller than the pore capacity, Chen was able to show (*10*) that there was a linear dependence of the amount of sorbed water on aluminium content corresponding to four water molecules per tetrahedrally coordinated aluminium atom. Checking the stoichiometry of water adsorption can thus provide a simple and rapid method of determining whether or not a zeolite is hydrophobic. Our sorption measurements were made for this purpose and results are given in Fig. 1. The left-hand plot shows actual experimental values and no assumptions are involved. The right-hand plot (suggested by a referee) has the merit of showing directly the relationship between water sorption capacity and Al content, but requires the assumption to be made that the total number of T-atoms per unit cell remains constant upon dealumination.

Among the zeolites studied, the four to one stoichiometric relationship between water and aluminium held, within experimental error, for the H-ZSM-5 sample and the H-mordenites having Si/Al atomic ratios of 9.2, 11.1, and 15.3. These solids can thus be considered as hydrophobic.

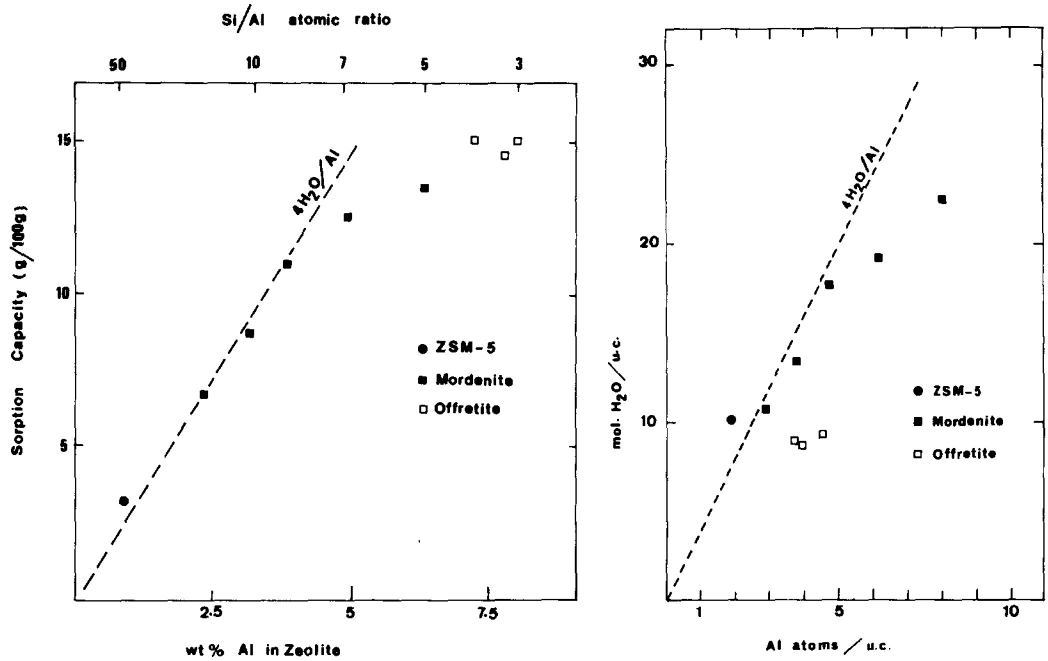

FIG. 1. Water sorption at 298 K and 12 Torr water vapor pressure. The two plots are alternative presentations of the same data (see text).

By contrast, for the other two mordenites and for the offretites the accessible pore capacity was not sufficient with respect to alumina content to accommodate four water molecules per aluminium site. These zeolites exhibited what we may call a normal sorption behavior in the sense that they were hydrophilic.

Returning now to Table 1 it is clear that as soon as the zeolitic surface became hydrophobic, the acid strength in water was greatly enhanced. This means that the zeolites with high Si/Al ratios behave like strong acids in water not only because they are highly acidic but also and mainly because their surface has a better affinity for the organic indicator than for water.

Catalytic Activity

Preliminary runs were conducted at different temperatures and pressures over H-M_2 and H-O_1 in order to determine the most suitable experimental conditions. In all our studies the amounts of water and olefin charged into the autoclave were kept constant which implied that the pressure was controlled by the reaction temperature. Since at the temperatures used a portion of the water remained in the liquid phase the maximum allowed conversions could not be calculated from the thermodynamic data of the gaseous products. These were determined experimentally by studying the sec-butanol dehydration under the corresponding conditions.

The effect of temperature and pressure on activity is shown in Table 2. H-mordenite showed a very good activity at the three temperatures and pressures investigated. At 473 and 523 K (and 44 and 65 atm of pressure, respectively) the conversions reached 54 and 75% of equilibrium, respectively. In both cases the sole product formed was sec-butyl alcohol. Hydrocarbons and oxygenated by-products could not be detected. Under more severe conditions (573 K, 100 atm) the alcohol production remained high when compared to thermodynamic equilibrium (66%) while the absolute value of the conversion decreased. Moreover, some hydrocarbons, consisting of a mixture of dimethylhexenes, were formed.

TABLE 2

Hydration of *n*-Butene over Mordenite and Offretite: Influence of the Experimental Conditions

Catalyst	H-M$_2$ (0.4 g)			H-O$_1$ (0.33 g)	
Temperature (K)	473	523	573	473	523
Pressure (atm)	44	65	100	45	65
Reaction time (h)	2.5	2.5	2.5	3	3
Conversion (mol%)	1.78	3.29	2.11	Trace	0.88
Thermodynamic equilibrium[a] (mol%)	3.28	4.39	3.21	3.29	4.39
Thermodynamic equil. (%)	54	75	66	—	20
Selectivity (mol%)[b] sec-butyl alcohol	100	100	~98	—	100
Dimers	—	—	~2	—	—

[a] Determined in the alcohol dehydration.

[b] Selectivity defined by the ratio (moles of product formed)/(conversion in moles).

The offretite did not show such a behaviour. At 473 K and 45 atm it was almost inactive. Even longer reaction times (up to 17 h) did not lead to appreciable conversion levels under these conditions. At 523 K and 65 atm the zeolite became active for alcohol formation but the conversion was low (20% of the limit).

The above study led us to evaluate the activity of the various protonic zeolites under the following standard conditions: 523 K and 65 atm, 0.4 g of catalyst and a reaction time of 2.5 h. Results are reported in Table 3, where the last column gives the integrated alcohol yields after 2.5 h reaction expressed in millimoles of alcohol produced per hour and per gram of zeolite. Such an evaluation of the activity gives only a time-averaged picture of the process since it does not yield information on the

TABLE 3

Hydration of *n*-Butene at 523 K and 65 atm (H_2O/Olefin Molar Ratio = 4.4; Catalyst Weight = 0.4 g; Reaction Time = 2.5 h): Activity of the Various Catalysts

Zeolite	Si/Al	*n*-Butene converted (mol%)			Selectivity (%)	Integrated alcohol yield (mmol h^{-1} g^{-1})
		in s-BuOH	(%eq)[a]	in C_8H_{16}		
H-ZSM-5	49	2.68	(61)	—	100	5.73
H-M$_1$	5	2.92	(66)	—	100	6.25
H-M$_2$	6.9	3.29	(75)	—	100	7.05
H-M$_3$	9.2	3.29	(75)	—	100	7.05
H-M-deal-1	11.1	3.12	(71)	0.6	84.3	6.67
H-M-deal-2	15.3	2.77	(63)	8.8	23.9	5.9
H-O$_1$	3	0.8	(18)	—	100	1.7
H-O$_2$	3.7	1.23	(28)	—	100	2.63
H-O$_3$	3.9	1.45	(33)	—	100	3.1
H-Ω$_1$	3.5	1.23	(28)	—	100	2.63
H-Ω$_2$	6.4	1.54	(35)	—	100	3.29
H-Y	2.5	0.51	(12)	—	100	1.1

[a] Percentage of the thermodynamic equilibrium.

instantaneous reaction rates and deactivation characteristics. It is nevertheless convenient to compare the different catalysts from a practical point of view.

On this basis, the twelve zeolites investigated can be divided into two groups. In the first one we find the offretite, omega and Y zeolites. Their activities were low or moderate. With these zeolites the conversions attained under our standard conditions did not exceed 35% of the thermodynamic limit.

The second group contains the ZSM-5 and mordenite catalysts. They all permitted high conversion levels (60 to 75% of the thermodynamic limit) and consequently good alcohol yields.

In a recent patent, Chang and Morgan (*4*) stated that the hydrophobic character of the highly siliceous zeolites was advantageous in the olefin hydration process. To some extent our results agree with this proposal since the four zeolites exhibiting some hydrophobicity, i.e., H-ZSM-5, H-M_3, H-M-deal-1, and H-M-deal-2 stand among the most active catalysts. It should be emphasized, however, that zeolites such as H-M_1 and H-M_2, while showing a normal water sorption behaviour, are more active than the strongly hydrophobic H-ZSM-5.

A further analysis of Table 3 reveals some additional interesting features. For offretite and omega zeolites, increasing the Si/Al ratio increased the activity. A similar trend has been noticed previously with respect to the acidity strength in water. Since these zeolites are not hydrophobic, at least the offretite samples, it is quite probable that a correlation exists between acidity and hydration activity.

Mordenite catalysts showed a more complex behaviour and the results obtained on them are presented in more detail in Figs. 2 and 3. When increasing the Si/Al ratio two regions were distinguishable. On the one hand, up to Si/Al = 9.2, the only reaction taking place was the olefin hydration. The activity increased first in a way analogous to that observed for offretite and omega, and then levelled off. On the other hand, over the dealuminated samples, a dimerization reaction producing dimethylhexene by-

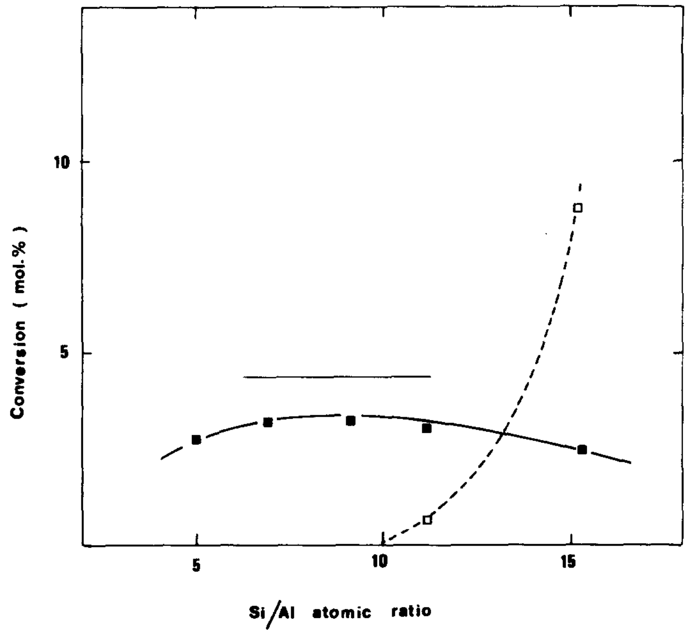

FIG. 2. Hydration and dimerization activity of mordenites as a function of the Si/Al atomic ratio. (■, sec-butyl alcohol; □, C_8H_{16}.) The line shows the alcohol thermodynamically limited conversion.

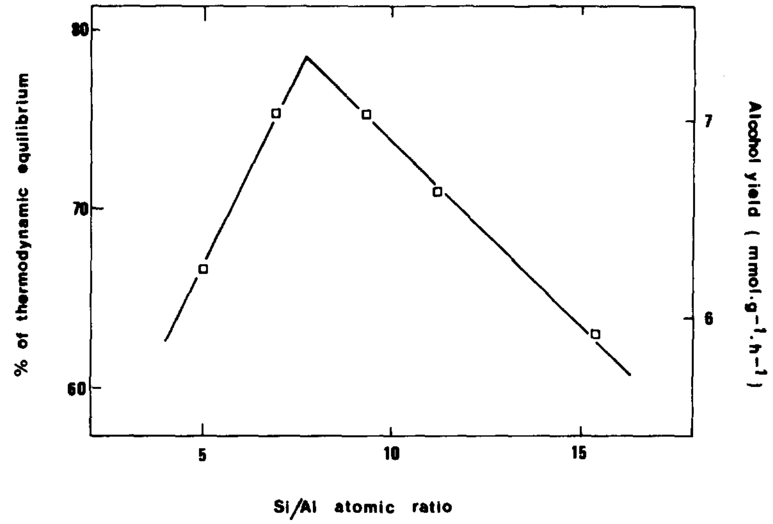

FIG. 3. Effect of the Si/Al atomic ratio on alcohol yields over mordenite.

products occurred and the alcohol conversion decreased slightly. The dimerization reaction was particularly important over H-M-deal-2 (Si/Al = 15.3), accounting for more than 75% of the *n*-butene converted.

The above results can be explained by considering that decreasing the alumina content of the mordenite increases the zeolite acidity (the implications of acidity on activity will be discussed more thoroughly later on) but decreases the number of hydrophilic centers. Upon dealumination a point is reached where the latter effect is no longer balanced by the former. The alcohol production therefore goes through a maximum, then decreases with the water sorption capacity of the zeolite. Concomitant with this, the olefin concentration within the pores increases favouring dimerization.

The data in Fig. 3 show that on mordenite, the hydration activity, although remaining fairly high when compared to the thermodynamics, was definitely maximized for a Si/Al atomic ratio ranging between 7 and 9. A very similar result has been reported by Namba *et al.* (*8*). When studying the hydrolysis of ethyl acetate in 5% aqueous solutions over a series of acid leached mordenites they observed a sharp maximum in activity for a Si/Al atomic ratio of 8.7. At this stage, the absolute value of this optimum ratio is not well understood. However, it seems to be characteristic of the mordenite structure and independent of the mode of preparation, whether synthesis or acid leaching.

Contrary to the dealuminated mordenites the H-ZSM-5 sample, despite a low aluminium content (and accordingly a low water sorption capacity), did not produce *n*-butene dimers. Taking into account the fact that each proton interacts with four water molecules (*10*) we may tentatively attribute the high selectivity of the ZSM-5 structure for alcohol production to a restricted transition state shape selective effect (*11*) which would prevent dimethylhexene formation.

Correlation between Hydration Activity and Aluminium Content

It is obvious from our data that the activity of zeolites for *n*-butene hydration depends on their aluminium content. However, on the basis of the alcohol yields per gram of catalyst it is difficult to draw general conclusions on the exact correlations existing between activity and zeolite composition. In effect, aluminium-rich zeolites such as offretite or Y are less active than mordenites having intermediate aluminium

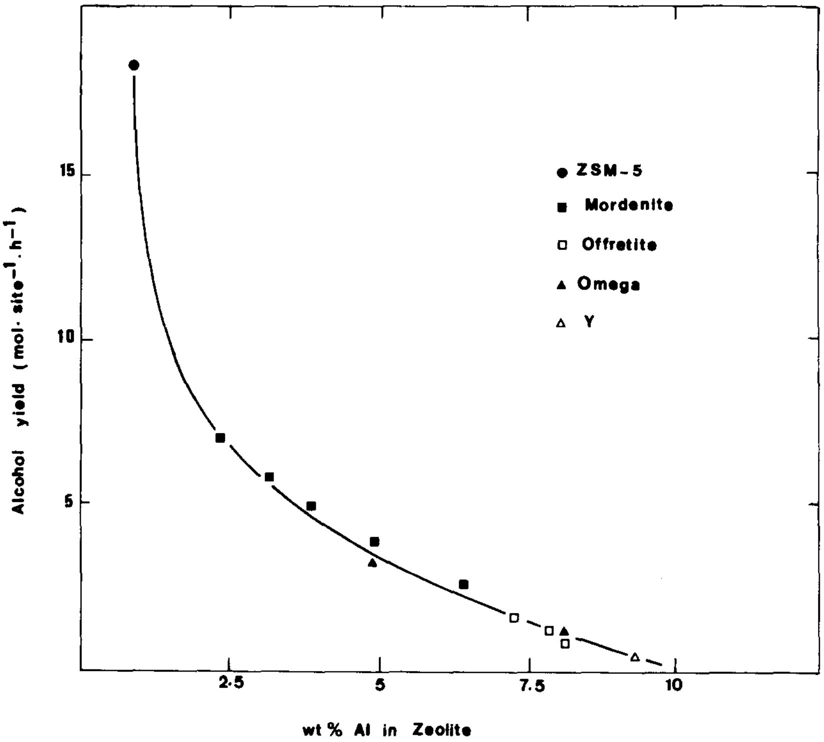

FIG. 4. Correlation between the hydration activity per protonic site and aluminium content in the various zeolites.

contents but the same is true for silicon-rich samples (H-ZSM-5, H-M-deal-2).

A more fruitful approach is to compare the activity of the different zeolites on a per site basis. In Fig. 4 the alcohol yields per protonic site (in mol site^{-1} h^{-1}) have been plotted against the concentration of aluminium in the zeolite. One can see that, regardless of the zeolite structure, all the data fit the same curve, indicating that the correlation between the two parameters is unique.

The enhancement of zeolite acidity with increasing Si/Al ratio was recognized a long time ago (*12*). More recently, CNDO/2 (*13*) and Sanderson electronegativity equalization (*14*) type calculations on various structures have shown that the charge on the proton increases as the aluminium content decreases. The correlation shown by Fig. 4 therefore suggests strongly that the hydration activity of zeolites is a direct and single function of the acid strength of the protons attached to the framework.

The existence of a direct relationship between the acidity function H_0 and the reaction rate has been demonstrated several times (*15, 16*) for olefin hydration in sulfuric acid. As mentioned earlier, the activities (per gram or per site) determined here do not correspond strictly to actual reaction rates. In spite of this, a clear analogy seems to exist between the two systems. The behaviour of zeolites during hydration can thus be related to that of conventional acid solutions as proposed by Barthomeuf (*17, 18*).

Activity coefficients would exist at high aluminium contents and would reduce the reaction rate. By contrast, at low aluminium levels, as in dilute solution, the acid centers would behave as if they were fully isolated. The activity coefficient would then be equal to unity and each site would become fully efficient in catalysis.

In such a scheme the zeolite framework would not play any specific role. Studies by

Jacobs (*19*) on isopropanol dehydration and *n*-decane hydroconversion have led to a similar conclusion.

CONCLUSIONS

The hydration of *n*-butenes has been investigated over protonic zeolites having different structures and aluminium contents. At 523 K and 65 atm pressure sec-butanol yields were high with mordenite and ZSM-5, while they were low or moderate with offretite, omega, and Y-type zeolites. Mordenites with intermediate aluminium contents ($7 < \mathrm{Si/Al} < \mathrm{Al} < 9$) enabled 75% of the thermodynamic equilibrium to be reached with 100% selectivity. Overdealumination of mordenite led to the formation of dimer by-products.

Silica-rich zeolites were hydrophobic and had strong acid sites ($-8.2 < H_0 \leq -5.6$) in water. They showed a high activity for alcohol formation but the hydrophobicity of the zeolitic surface did not appear as a determining factor in the reaction.

Comparison of the various catalysts on the basis of their activity per protonic site reveals a unique relationship between activity and aluminium content. From this, and by analogy with what is observed in sulfuric acid, it is suggested that the hydration activity of zeolites is a direct function of the acid strength of the protons attached to the framework.

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