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Gas-Phase Direct Hydration of Ethylene over Proton-Exchanged Zeolite Catalysts at Atmospheric Pressure[1]

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Gas-phase hydration of ethylene over proton-exchanged zeolites with various Si/Al ratios and structures such as ZSM-5, mordenite, ferrierite, and Y type has been studied. It was found that the catalytic activity of the zeolites was not influenced by the framework structure but showed a volcano-shaped dependence on Al content. There was a linear correlation between activity and amount of acid on the zeolite. A proton–ferrierite zeolite with a SiO_2/Al_2O_3 molar ratio of 16.3 (HF-16) was the best catalyst among the zeolites examined here. Conversion of ethylene to ethanol reached 1.4% at 463 K and atmospheric pressure. The catalytic activity of HF-16 exhibited a bell-shaped dependence on calcination temperature for preparing HF from a parent NH_4F zeolite. It was clarified that this phenomenon resulted from a change in the amount of Brønsted acid sites.

INTRODUCTION

Although supported phosphoric acid is the preferred industrial catalyst for gas-phase ethanol synthesis from ethylene and water, it has the disadvantage that it may vaporize or be eluted during the reaction, resulting in a decrease in catalytic activity and corrosion of equipment. Tungstosilicic acid on silica gel (*1*), $ZnO–TiO_2$ (*2*), zirconium tungstate (*3*), and niobic acid (*4*) have been proposed as alternative effective catalysts (excluding patent references), but they also have problems of acid depletion (*5*), reproducibility of the catalyst (*6*), and lower catalytic activity.

The hydration of olefins is a typical acid-catalyzed reaction (*7*). It is well known that zeolites have cation-exchange properties, high surface acidity, and good thermal stability, which could make possible the updating of industrial hydration processes. Fajula *et al.* (*8*) have indeed reported high activity for mordenite in the hydration of *n*-butenes; however, they performed the reaction in a batch reactor at 65 atm. We report here that first, proton-exchanged zeolites, especially a ferrierite-type zeolite, are highly effective in this reaction at a temperature as low as 463 K in a flow system at atmospheric pressure; second, catalytic activity showed a volcano-shaped dependence on Al content and was correlated with the amount of acid sites; and third, calcination temperature of zeolites was an important factor in the determination of catalytic activity.

EXPERIMENTAL

NH_4^+-exchanged zeolites were prepared by a conventional method and calcined at 673–523 K in air for 2 h to yield proton-exchanged zeolites, unless otherwise stated. The parent zeolites ferrierite (denoted as F) and ZSM-5 (Z) were supplied by Toyo Soda Manufacturing Company Ltd., and mordenite (M) and Y type were obtained from the Catalysis Society of Japan (JRC-Z-HM-10, -15, and -20, and JRC-Z-HY-4.8 and -5.6). The number in the sample name represents the SiO_2/Al_2O_3 mo-

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TABLE 1

Properties of Proton-Exchanged Zeolites Used and Their Catalytic Activities for Hydration of Ethylene[a]

Catalyst	$\frac{Al}{Al + Si}$	S_{BET}[b] (m^2/g)	H^+[c] (%)	Acid amount (mmol/g)	% Conversion of C_2H_4 into EtOH	MeCHO	% Equil.[d]
JRC-Z-HY4.8	0.278	646	99	0.80	0.51	0.05	32
JRC-Z-HY5.6	0.263	634	72	0.57	0.21	tr.	13
JRC-Z-HM10	0.168	187	98	1.13	0.67	0.01	42
JRC-Z-HM15	0.118	309	99	1.20	0.86	0.01	54
JRC-Z-HM20	0.091	299	99	1.23	0.77	0.02	48
HF-12	0.141	245	99	1.02	0.99	0.01	62
HF-16	0.109	280	94	1.14	1.05	tr.	66
HZ-23N[e]	0.079	248	99	0.36	0.31	tr.	19
HZ-23C[f]	0.079	248	99	0.28	0.18	tr.	11
HZ-40	0.047	255	99	0.35	0.40	tr.	25
KF-17	0.105		0		0.01	0	1
No cat.	—	—	—	—	0.09	0	6

[a] Reaction conditions: C_2H_4 5 cm^3/min, H_2O 12.1 cm^3/min, catalyst 1.0 g, 473 K, 1 atm.

[b] Surface area determined by N_2 adsorption.

[c] Exchange level of H^+.

[d] Percentage attainment of equilibrium.

[e] Prepared by using HNO_3 solution.

[f] Prepared by using HCl solution.

lar ratio.[3] Proton exchange levels, surface areas, and SiO_2/Al_2O_3 molar ratios determined by chemical analysis are summarized in Table 1.

The catalytic reaction was carried out in a continuous flow reactor at atmospheric pressure. Unless otherwise stated, flow rates of ethylene and water vapor were 5 and 12.1 cm^3 min^{-1}, respectively, and 1.0 g or ca. 2.1 cm^3 of catalyst was used. The liquid- and gas-phase reactants and products were analyzed by gas chromatography using PEG-1000 and Porapak-Q columns. IR spectra were measured by using JASCO IR-810. A self-supporting zeolite wafer was placed parallel in a sample holder which was similar to that described elsewhere (*9*, *10*).

RESULTS AND DISCUSSION

Catalytic Activities of Various Proton-Exchanged Zeolites

Approximately steady formation of ethanol was attained within 1 h and afterward there was no change in the conversion level of ethylene into ethanol with reaction time, though the amounts of other products were slowly changed as will be discussed in the following section. Ethanol was the main product in all experiments, with small amounts of acetaldehyde, diethyl ether, acetone, and methyl ethyl ketone as by-products. Typical results at 473 K are summarized in Table 1. It is clear that all proton-exchanged zeolites used were active catalysts for ethanol synthesis, while the activity of a potassium ferrierite (KF) zeolite was low, indicating that the presence of protons in the zeolite structure is essential to the hydration reaction. The order of activity was HY < HM < HF > HZSM-5.

[3] In the case of JRC-Z-HY 4.8, the silica/alumina ratio of mother zeolite, NaY, was 4.8 but was changed to 5.2 during the proton exchange probably due to the dealumination. The "4.8" was used in the sample name, though the numerical value is not correct.

Tanabe and Nitta found that the order of catalytic activity of metal ion-exchanged zeolites for this reaction was roughly A type < Y type (*11*), which is consistent with the present order HY < HM < HF with regard to the silica–alumina molar ratio.

The catalytic activities at 473 K were plotted in Fig. 1 as a function of Al content, Al/(Si + Al). Figure 1 clearly shows that the catalytic activity was principally dependent on Al content and definitely maximized for a Al/(Si + Al) value of 0.11 or a Si/Al atomic ratio of 8.2. Note that the exchange level of HY-5.6 was as low as 72%, which is presumably the reason that the activity of HY-5.6 was lower than that of HY-4.8. Results very similar to those in Fig. 1 have been reported by Namba *et al.* (*12*) and Fajula *et al.* (*8*), independently. When studying the hydrolysis of ethyl acetate in 5% aqueous solutions over a series of acid-leached mordenites, Namba *et al.* observed a maximum in activity for a Si/Al atomic ratio of 8.7 (*12*). In addition, a maximum activity of proton–mordenites for the hydration reaction of *n*-butenes in aqueous phase was observed around Si/Al = 8 by Fajula *et al.* (*8*). The good agreement of the ratios is worth noting. At this stage, the absolute value of this optimum ratio is not well understood. However, it seems likely that the channel structure of each zeolite did not essentially affect the catalytic activity.

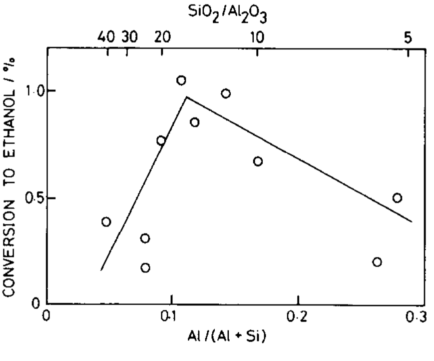

FIG. 1. Correlation between extent of conversions of ethylene to ethanol at 473 K and Al content of the zeolites, Al/(Si + Al).

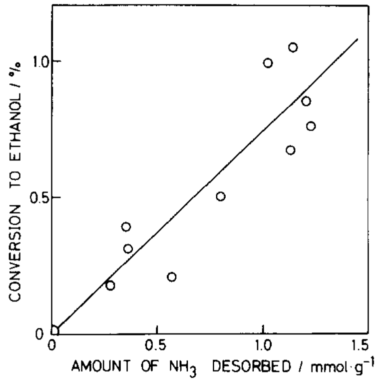

FIG. 2. Dependence of catalytic activity of proton-exchanged zeolites on amount of acid sites determined by temperature-programmed desorption of ammonia. The ordinate is the degree of conversion of ethylene to ethanol at 473 K and the abscissa is the amount of NH_3 desorbed, i.e., the amount of acid.

It is obvious from our data that the activity of zeolites for ethylene hydration depends on their Al contents. Taking into consideration that the hydration of olefins is an acid-catalyzed reaction, a more fruitful approach would be to compare the activity of the zeolites with their acid amounts or acid strengths. In Fig. 2 the conversions to alcohol per gram of catalyst have been plotted against the amounts of acid sites and it was found that, regardless of the zeolite structure, there is a linear correlation between the activities and the acid amounts. The latter values were determined by temperature-programmed desorption (TPD) profiles of ammonia adsorbed on the zeolites[4] and are listed in Table 1. It was recognized that the amounts of acid sites roughly show a volcano-shaped dependence on the Al/(Si + Al) value. This corresponds well with the results in Fig. 1 and is the reason for the linear correlation in Fig. 2. It follows therefore that the hydration

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[4] TPD spectra were measured after adsorption of NH_3 at 298 K and 13.3 kPa for 30 min and subsequent evacuation at 373 K for 60 min. Although two desorption peaks of NH_3 (α and β peaks) were always observed in the range 373–973 K, only the desorption peaks observed at higher temperatures (β peak) were concluded to be related to the acidic sites. The amounts of β peak are summarized in Table 1. See (*13*).

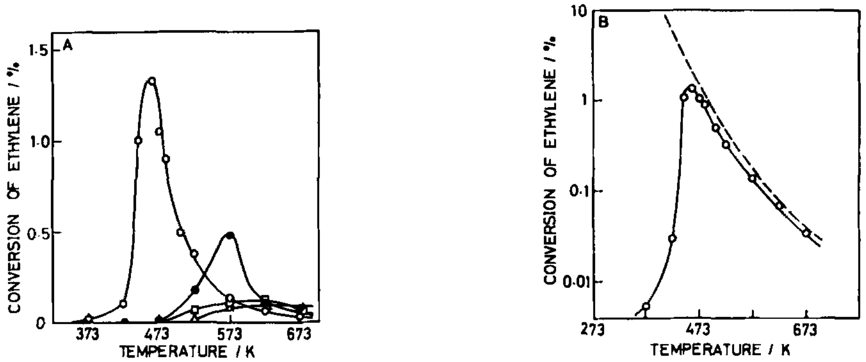

FIG. 3. Temperature dependence of hydration of ethylene over the HF-16 zeolite. (A) Composition of products: ○, EtOH; ●, MeCHO; □, Me_2CO; △, MeCOEt. (B) Comparison between computed equilibrium conversion of ethylene into ethanol (broken line) and experimental conversion (solid line).

activity of zeolite is a direct and single function of the acid amount in the framework.

In the TPD experiments with adsorbed ammonia the desorption temperatures were varied with the zeolites,[4] indicating a change in the acid strength of the protons attached to the framework. On the other hand, the enhancement of zeolite acidity with increasing Si/Al ratio was recognized a long time ago (*14*). More recently, CNDO/2 (*15*) and Sanderson electronegativity equalization (*16*) types of calculations on various structures have shown that the charge on the proton increases as the aluminum content decreases. However, we could not obtain correlation line between acid strength and catalytic activity better than that in Fig. 2. This fact and the correlation shown in Fig. 2 suggest that the acid sites with acid strength above a certain level would all be effective for the reaction.

Catalytic Behavior of a Proton-Exchanged Ferrierite Zeolite

Since the HF-16 zeolite was the most active among the zeolites used here, we examined the dependence of product distribution on catalyst weight and reaction temperature. The extents of conversion into ethanol on the HF-16 zeolite were 0.99, 0.89, and 0.70%, respectively, when 0.5, 0.4, and 0.25 g of catalyst were used at flow rates, pressures, and temperatures similar to those in Table 1. It is clear that little or no change in the conversion of ethylene to ethanol with contact time was observed at or above 3.0 $g \cdot s \cdot cm^{-3}$ in this case.

The temperature dependence of the products was depicted in Fig. 3A. The yield of ethanol was a maximum at 463 K, 1.4%. Above 523 K, acetaldehyde and acetone were the major products. These products probably resulted from dehydrogenation of ethanol and reaction of a dimeric product of ethylene (*17*), respectively. Figure 3B shows a comparison between the computed equilibrium conversion of ethylene into ethanol and the experimental results. The conversion to ethanol increased with increasing reaction temperature, reached approximately 70% of equilibrium at 463–473 K, and then decreased owing to equilibrium limitation. This fact and the above contact time dependence of conversion indicate that the HF-16 zeolite is better than catalysts previously reported (*1–4*). The degree of attainment of equilibrium on each catalyst is listed in Table 1.

The change in the product distribution with reaction time, i.e., time course, has been briefly examined. Results of 473 K are plotted in Fig. 4. It is clear that the yield of ethanol was roughly constant, while the amount of acetaldehyde increased slightly with reaction time. Although the reason for increasing acetaldehyde is unknown, we

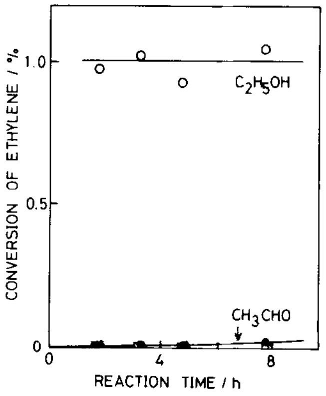

FIG. 4. Time course of ethylene hydration over the HF-16 zeolite at 473 K. The symbols in the figure are the same as those in Fig. 3.

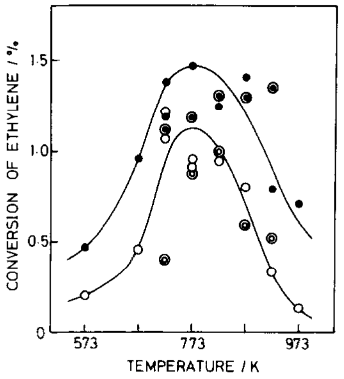

FIG. 5. Catalytic activity at 443 K (○, ◎) and 463 K (○, ◉) of HF-16 zeolites as a function of calcination temperature in air (○, ●) or dynamic vacuum (◎, •).

suggest one possibility: that coke produced in the reaction would be an active center to extract hydrogen atoms from an ethanol molecule. In fact, important roles of surface carbon atoms have been claimed in several reactions such as the Fischer–Tropsch reaction.[5]

Dependence of catalytic activity on calcination temperature in preparing HF-16 from the parent NH_4^+-exchanged ferrierite-type zeolite (NH_4F) was studied. The NH_4F zeolite was heated in air or in a dynamic vacuum at a desired temperature for 2 h. Catalytic activities at 443 and 463 K of the zeolites obtained are shown in Fig. 5. It was clearly demonstrated that the maximum activity of the HF-16 zeolite was obtained by decomposition of the NH_4F zeolite around 773 K, and lower or higher temperatures for decomposition caused a decrease in catalytic activity. It was also worth noting that the difference in the calcination atmospheres around the NH_4F zeolite, that is, air and dynamic vacuum, induces little distinction between the catalytic activities of the HF zeolites produced.

To reveal the reason for the phenomenon depicted in Fig. 5, X-ray powder diffraction patterns, TG-DTA curves, and IR spectra were measured. X-Ray analysis showed that there occurred no gross crystallinity changes even after the NH_4F zeolite was calcined at 973 K for 2 h. This indicated that the activity change shown in Fig. 5 is not attributable to the crystallinity change in the zeolite. The TG-DTA curve of the NH_4F zeolite revealed the presence of two processes at 300–453 and 573–773 K where weight loss of the NH_4F zeolite and heat transfer were both observed at the same time.

IR spectra were recorded at ambient temperature in a static vacuum after evacuation of a self-standing NH_4F zeolite wafer at elevated temperatures. With increasing evacuation temperature, we could recognize a diminution in the absorption bands attributable to the NH_4^+ group (3240–3360 and 1400–1450 cm^{-1}), and the appearance and subsequent disappearance of a zeolite-proton band (3600 cm^{-1}). The TG-DTA and IR data concluded that adsorbed water was desorbed around 373 K and conversion of the NH_4F zeolite to the HF zeolite started around 573 K and finished around 773 K.[6] It was also demonstrated by IR spectra that heating of the HF zeolite at 823 K or higher temperatures resulted in desorption of hy-

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[5] For example, see Ref. (*18*).

[6] Similar results on the other zeolites have been summarized in a review (*19*).

droxyl groups from the zeolite structure. This indicates that Brønsted acid sites were changed into Lewis acid sites.

It was confirmed in a separate IR experiment that, after evacuation of the NH_4F zeolite at 873 K, introduction of water vapor onto the zeolite sample at 298 K for 1 h did not cause regeneration of the OH band at 3600 cm^{-1}. This indicates that there is no reversibility between Brønsted and Lewis acid sites on the ferrierite zeolite under these experimental conditions, and is not consistent with the widely accepted concept that water would convert Lewis sites into Brønsted sites; the reason for this phenomenon is a problem to be solved in the future. We have shown in the previous section that the presence of protons in the zeolite structure is essential to the hydration reaction. All findings in the present work lead to the conclusions that the ethylene hydration reaction proceeds on a Brønsted acid site and not on a Lewis site, and that the bell-shaped dependence of the activity on calcination temperature (Fig. 5) is due to a change in the amount of Brønsted acid sites on the catalyst.

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