Gas-phase Hydration of Ethylene over a Proton-exchanged Ferrierite-type Zeolite Catalyst

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The gas-phase hydration of ethylene over a proton-exchanged ferrierite-type catalyst attains approximate equilibrium at 473—673 K, contact time 3.0—6.0 g s ml^{-1}, space velocity 571—286 h^{-1}, with a molar ratio of H_2O to C_2H_4 of 1 : 1, under 1 atmosphere pressure.

Although supported phosphoric acid is the preferred industrial catalyst for gas-phase ethanol synthesis from ethylene and water, it has the disadvantage that the phosphoric acid may vapourize 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. We here report that proton-

Table 1. Catalytic hydration of ethylene over proton-exchanged zeolites.[a]

Catalyst	H^+ (%)[b]	Cat. wt. (g)	% Conversion of C_2H_4 into: EtOH	MeCHO	Me_2CO	MeCOEt	% Equil.[c]
H-Y	99	1.0	0.51	0.05	0.01	0.01	41.1
H-M	98	1.0	0.67	0.01	0.01	0	54.7
H-F	94	0.5	0.99	0.01	0	0	80.2
		1.0	0.99 ± 0.08	0.03 ± 0.02	0.02 ± 0.01	0.01	80.2 ± 6.0
H-ZSM-5	99	1.0	0.31	0	0	0	25.4
K-F	0	1.0	0.01	0	0.01	0	1.0
No cat.	—	0	0.09	0	0	0	7.5

[a] Reaction conditions: C_2H_4 and H_2O, 5.0 ml/min; 473 K. [b] Exchange level of H^+. [c] % Attainment of equilibrium.

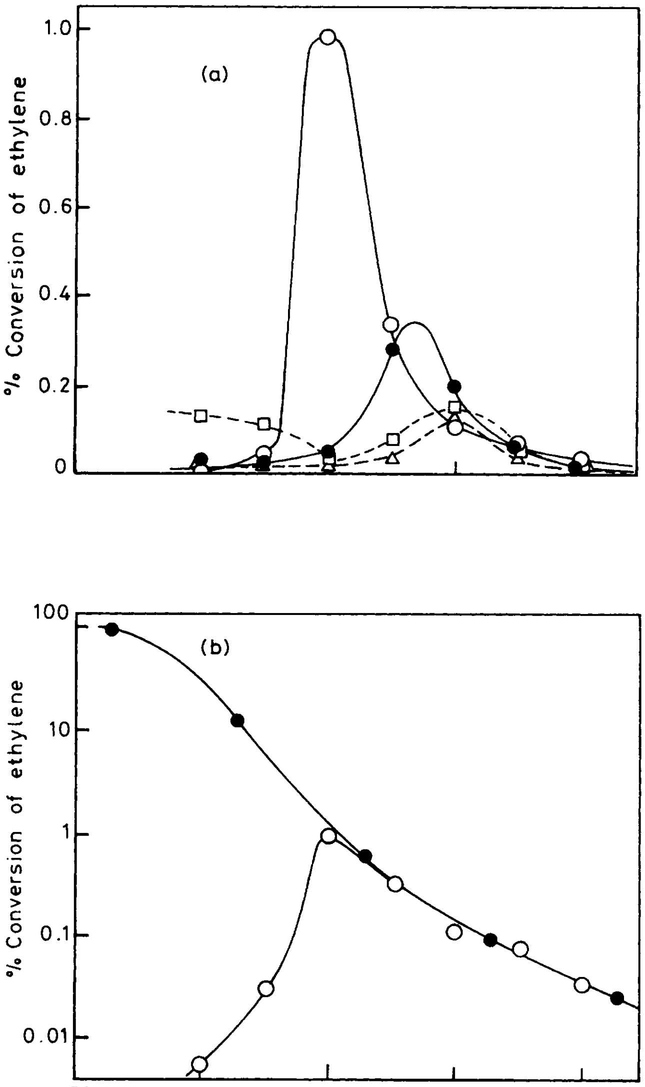

Figure 1. Temperature dependence of hydration of ethylene over a proton-exchanged ferrierite-type zeolite. (a) Composition of products: ○, EtOH; ●, MeCHO; □, Me_2CO; △, MeCOEt. (b) Comparison between computed equilibrium conversion of ethanol (●), and experimental conversion (○).

exchanged zeolites, especially a ferrierite-type zeolite, are highly effective in this reaction at a temperature as low as 473 K.

NH_4^+-exchanged zeolites were prepared by a conventional method and calcined at 673 K in air for 2 h to yield proton-exchanged zeolites; the parent zeolites ferrierite (denoted as F, SiO_2/Al_2O_3 molar ratio 17.0) and ZSM-5 (23.3) were supplied by Toyo Soda Mfg. Co. Ltd., and Y-type (Y, 4.8) and mordenite (M, 9.9) were obtained from the Catalysis Society of Japan (JRC-Z-HM 10 and JRC-Z-HY 4.8). The catalytic reaction was carried out in a continuous flow reactor at atmospheric pressure. Unless otherwise stated, flow rates of ethylene and water vapour were both 5 ml/min, and 1.0 g or *ca.* 2.1 ml of catalyst was used. The liquid- and gas-phase reactants and products were analysed by gas chromatography using PEG-1000 and Porapak-Q columns.

Steady formation of ethanol was attained within 1 h and afterwards there was no change of conversion level of ethylene into ethanol with reaction time. 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 potassium-ferrierite (K-F) zeolite was low, indicating that the presence of protons in the zeolite structure is essential for the hydration reaction. The order of activity was H-Y < H-M < H-F > H-ZSM-5. Tanabe and Nitta found that the order of catalytic activity of metal ion-exchanged zeolites for this reaction was roughly A-type < Y-type,[7] which is consistent with the present order H-Y < H-M < H-F with regard to the silica–alumina molar ratio. The low activity of H-ZSM-5 may indicate that strongly acidic sites are not so effective for the reaction.

The extent of conversion into ethanol on the H-F zeolite was not lowered even when 0.5 g of catalyst was used instead of 1.0 g, as shown in Table 1. Since the H-F zeolite was the most active among the zeolites used here, we examined the dependence of products on temperature for this catalyst, Figure 1(a). The yield of ethanol was a maximum at 473 K. 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,[8] respectively. Figure 1(b) shows a comparison between the computed equilibrium conversion of ethylene into ethanol and the experimental results. The approximate agreement of both values above 473 K indicates that the H-F zeolite is more active than the catalysts reported by other workers.[1—4] The apparent activation energy was 46 kJ/mol on the present H-F zeolite, compared with 126 kJ/mol on zirconium tungstate.[3]

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