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HIGH-PRESSURE CATALYTIC HYDRATION OF OLEFINS OVER VARIOUS PROTON-EXCHANGED ZEOLITES

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Catalytic hydration of ethylene, propylene, and 1-butene to alcohol was investigated at high pressures using proton-exchanged zeolites. All the zeolites more or less exhibited the hydration activities. Pentasil- and ferrierite-type zeolites were the most active among the zeolite catalysts. The activities of zeolite catalysts are correlated with the amount of adsorbed water, indicating that hydrophobic acid sites are effective for olefin hydration.

The synthesis of aliphatic alcohols by vapor phase hydration of olefins has been industrialized using solid phosphoric acid as a catalyst.1) However, this process has disadvantages such as the corrosion of reactor and the deactivation of catalyst due to elimination of phosphoric acid during operation. There have been some attempts to improve the hydration catalyst using tungsten oxide, molybdenum-promoted silica-alumina and cation-exchange resins; however, their activities are not satisfactory to be replaced with the solid phosphoric acid.2,3) Iwamoto et al.4) have investigated activities of zeolites for hydration of ethylene at atmospheric pressure and pointed out high alcohol yield over H-ferrierite. In this communication, catalytic activities of various proton-exchanged zeolites for hydration of ethylene, propylene, and 1-butene were investigated in a high pressure reactor and discussed in relation to their adsorption properties.

Zeolite catalysts used in the study are abbreviated hereafter as shown in Table 1. Commercial zeolite samples, pentasil, mordenite, ferrierite and erionite-offretite (Toyo Soda Mfg. Co. Ltd.) and Y (Shokubai Kasei Kogyo) were suspended in NH_4NO_3 solution and washed with water. Only in the case of pentasil-type zeolites, hydrochloric acid was used for protonation. Amounts of water and ethanol adsorbed on zeolite samples were measured in a vacuum system. Catalytic hydration of olefins was performed in a high pressure flow reactor at 150-200 °C and 1-8 atm. A gaseous mixture of water and olefin (water/olefin=1-4) was fed to the catalyst at 7.5·g-cat.·h/mol. Products were analyzed by gas chromatography (PEG 400 column).

Hydration of olefin,

$$CH_2{=}CHR \quad + \quad H_2O \rightleftharpoons CH_3CH(OH)R \qquad (R{=}H,\ CH_3,\ C_2H_5) \qquad (1)$$

is one of the acid catalyzed reactions. The thermodynamic equilibrium in Eq. 1 proceeds to the forward direction by operating the reaction at low temperatures and high pressures. Catalytic activities of P1 catalyst for hydration of ethylene, propylene, and 1-butene were tested as functions of temperture and pressure as

Table 1. Catalytic hydration of olefins over various zeolites

Zeolite	Si/Al atomic ratio	Surface area m^2/g	Hydration of ethylene (200 °C)				Hydration of propylene (150 °C)				Hydration of 1-butene (150 °C)			
			1 atm		5 atm		1 atm		5 atm		1 atm		5 atm	
			Y_e	S_e	Y_e	S_e	Y_p	S_p	Y_p	S_p	Y_b	S_b	Y_b	S_b
P1	11.7	320	0.59	81.3	2.16	72.8	1.38	90.2	3.53	94.4	0.33	72.6	2.10	95.7
P2	20.2	307	0.56	96.2	1.53	81.3	0.61	99.8	0.50	99.9	0.22	75.5	1.17	97.3
P3	24.9	331	0.56	80.8	1.44	81.1	0.49	99.9	0.30	100	0.03	100	0.39	84.6
M1	5.1	382	0.37	93.0	0.26	100	0.18	99.1	0.10	93.0	0.33	95.0	0.44	95.6
M2	7.5	440	0.37	97.1	0.42	98.3	0.16	98.5	0.10	92.8	0.05	85.4	0.12	86.7
M3	10.1	373	0.44	90.8	0.61	95.4	0.25	97.4	0.19	94.6	0.32	91.4	0.84	78.0
F	8.4	289	0.64	72.9	1.68	84.5	1.59	95.2	4.10	98.1	0.36	87.5	1.27	99.2
E-O	3.7	474	0.53	97.7	0.57	95.7	0.93	99.6	0.23	94.6	0.29	96.0	1.09	96.6
Y	2.6	677	0.10	100	0.04	100	1.21	82.9	0.13	100	0.31	100	1.08	92.0
Equilibrium conv./%			0.86		4.04		1.71		7.58		0.46		2.21	

P1,P2,P3 pentasil; M1,M2,M3 mordenite; F ferrierite; E-O erionite-offretite.

Y_e, Y_p, and Y_b = Yield/% of ethanol, 2-propanol, and 2-butanol, respectively;

S_e, S_p, and S_b = Selectivity/% to ethanol, 2-propanol, and 2-butanol, respectively

Water/Olefin=1.0; Catalyst weight=1.0 g; W/F=7.5 g-cat·h/mol.

Equilibrium conversion of ethylene at 150 °C = 2.81% (1 atm), 12.8% (5 atm).

preliminary runs. With an increase in reaction temperature, the catalytic activities for hydration of olefin increased initially followed by maxima as shown in Fig. 1. The decreases in conversion at elevated temperatures correspond to those in equilibrium conversions which are expressed by broken lines in this figure. Temperatures at the maximum conversions were about 190 °C, 160 °C, and 150 °C for hydration of ethylene, propylene, and 1-butene, respectively. Dependence of product selectivities on temperature over the P1 catalyst is shown in Fig. 2. In the hydration of ethylene and propylene, the main products were ethanol and 2-propanol but their selectivities decreased gradually with increasing reaction temperature. Small amounts of ether, acetaldehyde, and acetone were produced

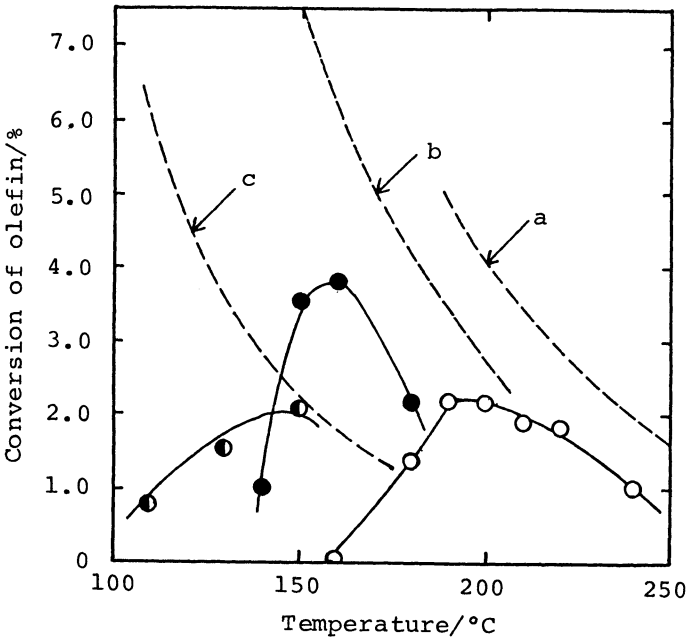

Fig. 1. Temperature dependence of the activities of H-pentasil (P1) catalyst for hydration of ○ :ethylene, ● :propylene, and ◐ :1-butene. Equilibrium conversion of a :ethylene, b :propylene, and c :1-butene. Pressure =5 atm; Water/olefin=1.0; W/F=7.5 g-cat.·h/mol

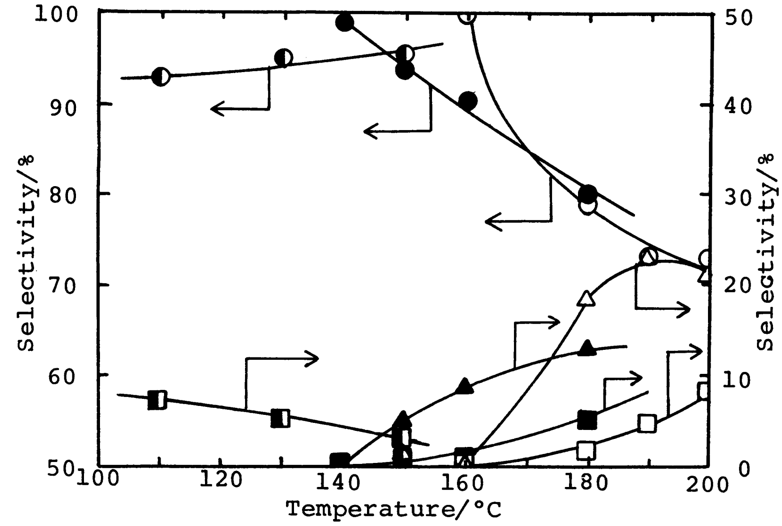

Fig. 2. Dependence of selectivity on temperature over H-pentasil (P1) catalyst.

○:ethanol, △:diethyl ether, □:acetaldehyde,
●:2-propanol, ▲:diisopropyl ether, ■:acetone
◐:2-butanol, ▲:diisobutyl ether,
◧:ethyl methyl ketone.

Pressure =5 atm; Water/olefin=1.0;
W/F=7.5 g-cat.·h/mol

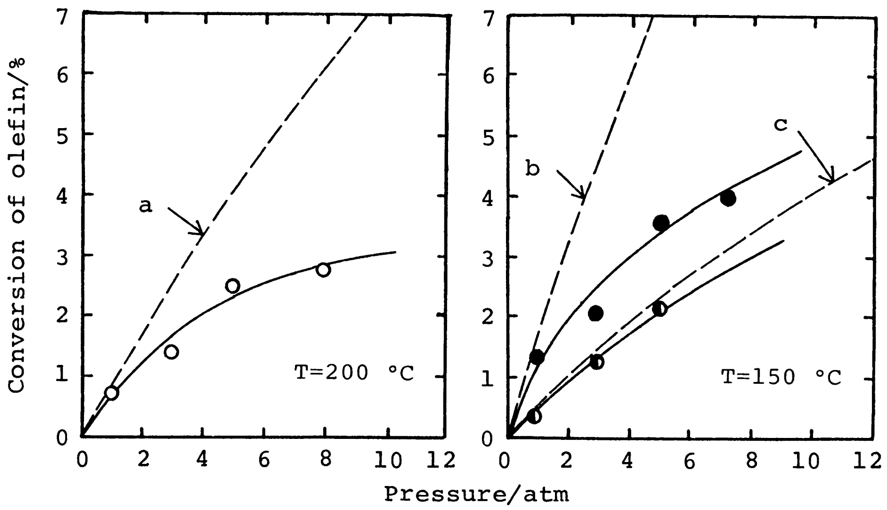

Fig. 3. Effect of total pressure on the activities of H-pentasil (P1) catalyst for hydration of ○ :ethylene, ●:propylene, and ◐:1-butene.

Equilibrium conversion of
a :ethylene, b :propylene, and c :1-butene.

Pressure =5 atm; Water/olefin=1.0;
W/F=7.5 g-cat.·h/mol

by condensation and dehydrogenation of alcohol. The selectivity to 2-butanol from 1-butene, however, was almost constant at about 90%. Dependence of olefin conversion on total pressure of water and olefin mixture over P1 catalyst is shown in Fig. 3. The space time yield of alcohol monotonously increased with increasing the total pressure, however, the observed increase is more gradual than that of equilibrium conversion. The pressure dependence of hydration is basically the same as that reported for the zirconium phosphate catalyst.[3)] The ratio of observed alcohol yield to the equilibrium hydration conversion is introduced to evaluate the catalyst activity and is denoted as R-value. The R-value is the highest in the hydration of 1-butene, however, those for the hydration of ethylene and propylene are only less than 40% at 7 atm. Table 1 summarizes the hydration activities and selectivities of various proton-exchanged zeolites together with their Si/Al ratios and surface areas. Following sequence for the equilibrium hydration conversions of olefins is reported:

ethylene > propylene > 1-butene. (2)

on the other hand, the order of R-values was generally measured to be

etyhlene < propylene < 1-butene. (3)

This sequence of R-values, which well reflects the relative stabilities of their carbonium cations, confirms that the reaction proceeds via the carbonium intermediates adsorbed on the acid sites of zeolites. Since the catalytic activity is given by the product of equilibrium conversion and R-value, the hydration reactivity of propylene is the highest among the three olefins. On the zeolite investigated in this study, the pentasil (Pl) and ferrierite (F) catalysts were most active for hydration of olefins. The proton-exchanged ferrierite is the candidate of hydration catalyst, since the 2-propanol yield is comparable to that of solid phosphoric acid. Not only the effect of zeolite structure but that of Si/Al ratio on the variation of hydration activity was obvious in pentasil-type (Pl-P3) and mordenite-type (Ml-M3) zeolites. But the difference in activity among the zeolites could not be simply explained in terms of number of acid site or acid strength. After various attempts, it has become apparent that the activities for ethylene and propylene hydration over zeolite catalysts decrease with an increase in the amount of adsorbed water per acid site (N) as shown in Fig. 4. To take the difference in reaction temperature into account (150 and 200 °C), the amounts of adsorbed water were obtained at two different pressures where the adsorption potentials are close to those of reaction conditions. The number of acid site in this case was experimentally estimated as the number of chemisorbed ethanol molecules on zeolite surface at 70 °C. These correlations in Fig. 4 suggest that adsorption of olefin molecules on the acid site is competitive with that of water molecules, being inhibited by the large amount of preadsorbed water. Thus, the hydrophobic nature of the acid site promotes the hydration of olefins on zeolite catalysts. In the case of hydration of 1-butene, however, the correlation between activity and N-value is unclear probably because of the close approach to equilibrium.

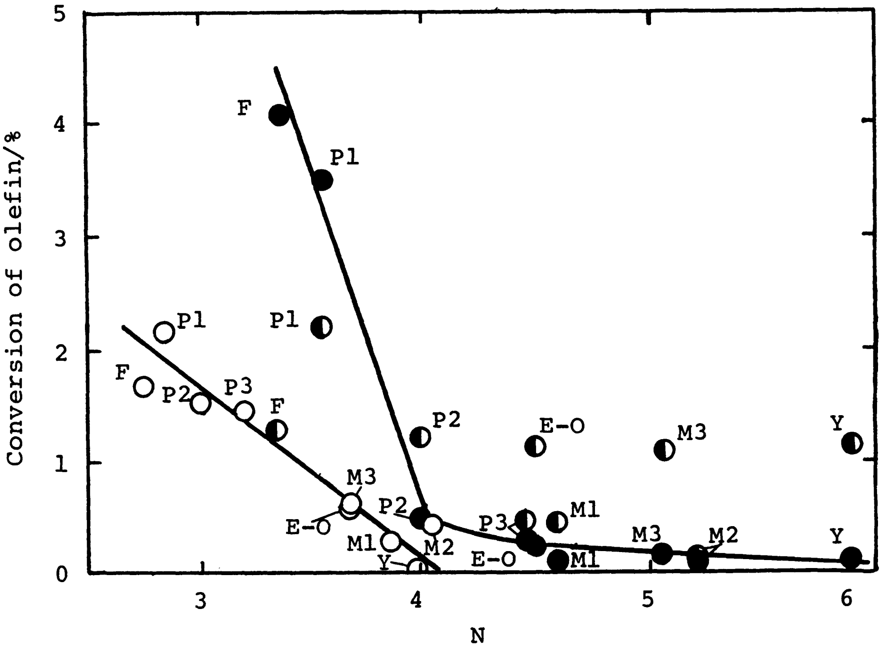

Fig. 4. Correlation between conversion of olefin and amount of adsorbed water over various zeolite catalysts for hydraton of ○:ethylene, ●:propylene, and ◐:1-butene.

$$N=\frac{\text{Adsorbed } H_2O\ [70\ °C,\ P_{H_2O}=19\ \text{Torr}(○)\ \text{and}\ 50\ \text{Torr}(●,◐)]}{\text{Chemisorbed } C_2H_5OH\ (70\ °C)}$$

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