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Catalytic Synthesis of 2-Propanol from a Propylene–Oxygen–Water Mixture over Pd–Cu Zeolite

Lower alcohols have been commercially produced by vapor-phase hydration of olefins using a solid phosphoric acid catalyst (*1*); however, this process has disadvantages such as corrosion of the reactor and deactivation of the catalyst during operation. As reported previously (*2, 3*), H-pentasil and H-ferrierite are also active for hydration of olefins. But the conversion of olefin hydration is below the equilibrium value, which is only 1.71% at 150°C and at atmospheric pressure. In this note, we report a high catalytic activity of cation-exchanged pentasil-type zeolite for production of 2-propanol from C_3H_6–O_2–H_2O mixture.

The zeolite powders used here are pentasil (P1, Si/Al = 11.7) and ferrierite (F, Si/Al = 8.4) obtained from Tosoh Mfg. Co., Ltd. The zeolite powder was suspended in water at 90°C. Then, an aqueous solution of Pd $(NH_3)_4Cl_2$ was added to the suspension. After filtration, the amount of Pd^{2+} in the powder was estimated by a chemical analysis of the filtrate solution. Palladium-exchanged zeolite thus obtained was calcined at 300°C and reduced with H_2 at the same temperature. Cation exchange with Cu was performed by soaking the Pd zeolite or original zeolite powder in water and adding $CuCl_2$ solution (0.1 *M*). The subsequent procedure and chemical analysis were the same as those for Pd-exchanged sample. Reaction of C_3H_6–O_2–H_2O was carried out in a flow system at 110–180°C and at 2 atm. All the products were analyzed by gas chromatography.

The reaction of C_3H_6–O_2–H_2O over Pd^{2+}- and Cu^{2+}-exchanged pentasil zeolite, which is abbreviated hereafter as Pd–Cu–Na–P1, was carried out as a function of temperature (Fig. 1). The conversion of propylene increased with a rise in reaction temperature. Acrolein and propionaldehyde were produced mainly below 120°C, but their selectivities decreased significantly above 140°C. The selectivity to 2-propanol increased with rising temperature followed by a maximum at 150°C. The yield of 2-propanol was maximum (10.7%) at 150°C, but decreased gradually due to consecutive oxidation at elevated temperatures. The maximum yield far exceeded that obtained in hydration of C_3H_6 using H-pentasil at the same temperature, $P_{C_3H_6}$, and P_{H_2O}, due to the low equilibrium conversion (2.91%) of the latter reaction.

Table 1 summarizes the effect of cation and type of zeolite on the product distribution of the reaction of C_3H_6–O_2–H_2O. It is evident that both Pd^{2+} and Cu^{2+} ions are

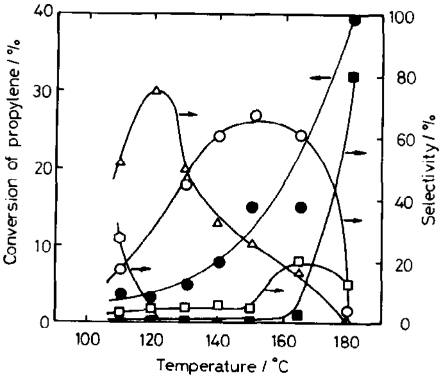

FIG. 1. Temperature dependence of catalytic reaction of $C_3H_6:H_2O:O_2$ (2:4:1) on Pd–Cu–Na–P1. Pressure, 2 atm; W/F, 10.0 g-cat. h/mol. (○) 2-propanol, (△) acrolein, (□) acetone, (Ọ) propionaldehyde, (■) carbon dioxide, (●) conversion

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TABLE 1

Reaction Results for a Mixture of C_3H_6, H_2O, and O_2 over Various Ion-Exchanged Zeolite Catalysts

Catalyst	Conversion (%)	Selectivity (%) (formation rate[a])		
		2-Propanol	Acetone	Acrolein
Pd–Cu–Na–P1	16.0	67.0 (3.06)	5.8 (0.27)	14.5 (0.16)
Pd–Cu–H–P1	15.5	78.2 (3.46)	10.7 (0.47)	9.0 (0.40)
Pd–Cu–Na–F	2.1	56.6 (0.34)	14.3 (0.09)	29.3 (0.18)
Pd–Cu–H–F	3.7	74.0 (0.78)	9.0 (0.10)	17.0 (0.18)
Pd–Na–P1	4.0	33.2 (0.38)	46.7 (0.53)	16.0 (0.18)
Pd–H–P1	4.8	64.6 (0.89)	8.9 (0.12)	25.1 (0.34)
Cu–Na–P1	1.2	96.9 (0.33)	3.0 (0.01)	tr (tr)
Cu–H–P1	2.2	94.7 (0.60)	4.3 (0.03)	1.0 (0.01)
Na–P1	0	0 (0)	0 (0)	0 (0)
H–P1[b]	1.4	90.2 (0.36)	3.9 (0.02)	0 (0)
H–F[b]	1.6	95.2 (0.44)	0.1 (tr)	0 (0)

Note. Catalyst: Pd 1.0 wt%, Cu 4.0 wt%. Reaction conditions: 150°C, 2.0 atm, W/F = 10.0 g-cat./h mol. Feed ratio, $C_3H_6:H_2O:O_2 = 2:4:1$.

[a] mmol/g-cat. h.

[b] Hydration of propylene: 150°C, 1.0 atm, W/F = 7.5 g-cat. h/mol. Feed ratio, $C_3H_6:H_2O = 1:1$.

indispensable in deriving a high conversion of propylene. The catalytic activity was also greatly influenced by the type of zeolite; i.e., Pd^{2+}- and Cu^{2+}-exchanged ferrierite (Pd–Cu–Na–F) was far less active than Pd–Cu–Na–P1. The main product over Pd–Cu–Na–P1 was 2-propanol as mentioned, and acetone and acrolein were by-products. The formation of acetone is sometimes observed in other cation-exchanged zeolites, such as Cu–Y. In this reaction, only a small amount of 2-propanol was produced as an intermediate (*4*). Acrolein, which was obtained only over the catalysts containing Pd, appeared to be produced by allylic oxidation of C_3H_6.

TABLE 2

Reaction Results over Pd–Cu–NaP1 Catalyst

Reactant	Conversion (%)	Selectivity (%)			
		2-PrOH	ACE	ACR	CO_2
$C_3H_6:H_2O:O_2$ (2:4:1)	16.0	67.0	5.8	14.5	tr
$C_3H_6:H_2O$ (2:4)	0.9	97.0	3.0	0	0
$C_3H_6:O_2$ (2:1)	1.0	0	40.0	60.0	tr

Note. Temperature, 150°C; pressure, 2.0 atm. 2-PrOH, 2-propanol; ACE, acetone; ACR, acrolein.

Table 2 shows the effect of water and oxygen on formation of 2-propanol over Pd–Cu–Na–P1 catalyst. The high conversion of propylene was obtained only when both water and oxygen were supplied with propylene. The conversion of propylene was significantly lowered in the absence of either water or oxygen. In the reaction of C_3H_6 and H_2O, hydration appears to be catalyzed by a small number of acid sites, as has been suggested for Cu–Y catalyst (*4*). But the conversion did not exceed that of equilibrium. As for the reaction between C_3H_6 and O_2, the main products were acrolein and acetone, but 2-propanol was scarcely formed.

In order to investigate the reaction mechanism over cation-exchanged zeolite the mixture of C_3H_6, O_2, and H_2O (molar ratio, 2 : 4 : 1) was pulsed repeatedly onto the catalysts at 150°C, as shown in Fig. 2. 2-Propanol was not formed on Cu^{2+}-exchanged

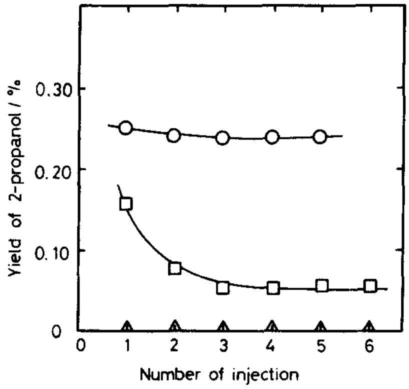

FIG. 2. Pulse reaction of a C_3H_6, H_2O, and O_2 mixture over Pd-, Cu-, and Pd–Cu–Na–P1 catalysts. Temperature, 150°C; pressure, 2.0 atm; feed ratio, $C_3H_6 : H_2O : O_2 = 2 : 4 : 1$. (○) Pd–Cu–Na–P1, (△) Pd–Na–P1, (□) Cu–Na–P1.

pentasil zeolite from the first pulse. Although the initial activity for 2-propanol formation was high over Pd^{2+}-exchanged pentasil zeolite, the yield decreased significantly with repeated pulses. The activity of Pd–Cu–Na–P1 catalyst was the highest and was unchanged in the course of the pulse experiment. Judging from the above results, the active component for 2-propanol production is Pd^{2+} ions, but after reduction palladium cannot be reoxidized by gaseous oxygen without Cu^{2+} ions. Therefore, the Pd–Na–P1 catalyst is soon deactivated in the course of reaction. Copper ions appear to promote reoxidation of Pd. The role of each component resembles that in the Wacker-type olefin oxidation in the liquid phase (*5*). Although acetone is produced by oxidation of propylene in the Wacker-type reaction, a high activity for 2-propanol formation is characteristic of the present system.

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