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PHASE TRANSITION-LIKE PHENOMENON OBSERVED FOR "PSEUDO-LIQUID PHASE" OF HETEROPOLY ACID CATALYSTS

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We found for dehydration of 2-propanol over $H_3PW_{12}O_{40}$ at 80-100 °C that there were at least two pseudo-liquid phases which differed in the amount of alcohol absorbed and the catalytic activity. The transition between the two phases proceeded nearly reversibly depending on the temperature and pressure.

An important feature of heteropoly compounds, when they are used as solid catalysts, is pseudo-liquid phase behavior; some reactant molecules are readily absorbed into inner bulk of catalyst, where they are converted to products.[1-3] We reported previously for dehydration of 2-propanol over 12-tungstophosphoric acid that the absorption-desorption process was very rapid and the amount of alcohol absorbed was quite large.[3] We studied this system in detail and found novel phenomena concerning the pseudo-liquid behavior. We wish to report in this letter the facts that there are at least two pseudo-liquid phases which differ in the number of alcohol molecules absorbed, N, and the reaction rate, R, and that nearly reversible phase transition takes place between the two phases. N and R were measured by a transient response method as in the previous report.[3] The feed gas was instantaneously changed from 2-propanol-d_0 to -d_8 and vice versa and the variation of isotopic composition at the outlet of the reactor was followed by a mass spectrometer and a gas chromatograph.

Figure 1 shows R and N as functions of the partial pressure of 2-propanol at different reaction temperatures. As seen in this figure, the pressure dependency showed unusual behavior. For example, at 80 °C the reaction order was 0 (0.3 - 0.8 kPa), -1.5 (0.8 - 1.5), and -0.2 (1.5 - 7.8). Therefore, R changed rather abruptly at a certain pressure from a high activity state to a low activity state. The pressure at which the transition occurred tended to be higher as the reaction temperature increased. Close correspondence was found between N and R. N changed at the transition between the above two states. For example, at 80 °C, N was 3

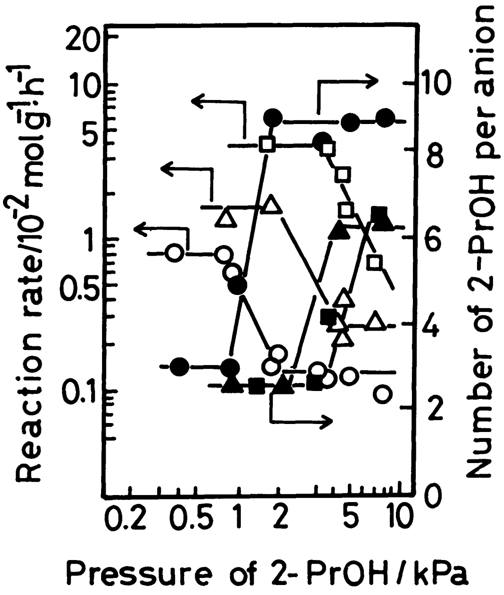

Fig. 1. Pressure dependencies of the rate of 2-propanol dehydration, R, and the number of 2-propanol absorbed, N.
○●: 80 °C, △▲: 90 °C, □■: 100 °C.

molecules/anion for the high activity state and 8-9 molecules/anion for the low activity state.

Reversibility of the transition was examined and typical results are shown in Fig. 2. At 100 °C, R as well as N varied reversibly. As the reaction temperature decreased, the transition from the high N phase (low activity state) to the low N phase (high activity state) became slower and it was very slow at 80 °C. The partial pressure of 2-propanol or the amount absorbed is likely the important factor determining these two states, while water formed may have some influence.[4] Effectiveness factor of catalysts calculated as in the previous report[3] was greater than 0.95 for the high N phase and 0.90 to 0.95 for the low N phase. It was confirmed that the rate of dehydration of 2-propanol observed for 2-propanol solution of 12-tungstophosphoric acid (6.25×10^{-2} mol/l) at 80 °C was much slower than that for the low activity state at the same temperature.

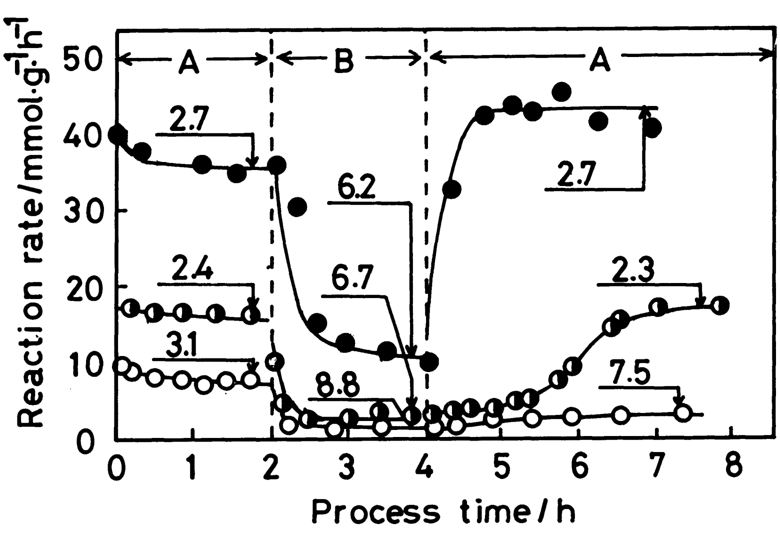

Fig. 2. Responses of the rate of 2-propanol dehydration to the changes of the partial pressure of 2-propanol.
The numbers in the figure are the amounts of 2-propanol absorbed (molecules/anion). Reaction temperature, 80 °C (○), 90 °C (◑), 100 °C (●), pressure of 2-propanol, A: 0.8 kPa (80, 90 °C), 1.3 kPa (100 °C), B: 4.8 kPa (80, 90 °C), 7.8 kPa (100 °C), conversion, A (at 2 h): 25% (80 °C), 45% (90 °C), 42% (100 °C), B (at 4 h): 0.8% (80 °C), 1.5% (90 °C), 11% (100 °C).

References
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2) T. Okuhara, A. Kasai, N. Hayakawa, Y. Yoneda, and M. Misono, J. Catal., 83, 121 (1983).
3) T. Okuhara, T. Hashimoto, M. Misono, Y. Yoneda, H. Niiyama, Y. Sato, and E. Echigoya, Chem. Lett., 1983, 573.
4) The pressure of water formed (Fig. 2) was considerably lower than that of 2-propanol. Although the water pressure was A (at 2 h) > B (at 4 h) at 80 and 90 °C, but B > A at 100 °C, R varied closely correspondingly to N at 80-100 °C.

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