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EVIDENCE FOR "PSEUDO-LIQUID PHASE" IN THE DEHYDRATION OF ISOPROPANOL OVER $H_3PW_{12}O_{40}$

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Transient response method using isotopically labeled isopropanol was applied to confirm the "pseudo-liquid phase" behavior of the dehydration of isopropanol over $H_3PW_{12}O_{40}$. Results were treated by moment analysis. Under the stationary state of catalytic reaction at 80-90°C, a large amount of isopropanol was present in the bulk and the absorption-desorption process of isopropanol in the whole bulk was much more rapid than its dehydration to propene, demonstrating the "pseudo-liquid phase" behavior.

In contrast with ordinary solid catalysts, the secondary structure of heteropoly acids in the solid state is variable. Due to this nature, heteropoly acids readily absorb polar molecules like alcohols into the bulk, and it is probable under certain conditions, heteropoly acids behave like solution and catalytic reactions proceed in the bulk ("pseudo-liquid phase").[1-3)]

In this communication, we wish to report evidence to show the behavior of the "pseudo-liquid phase" in the case of the dehydration of isopropanol. The rate of absorption-desorption and the amount of isopropanol absorbed in the bulk under the reaction conditions were determined, by applying transient response method (see below).[4)]

$H_3PW_{12}O_{40}$ (abrreviated as PW_{12}) was the same as before[2)]. The catalytic dehydration of isopropanol was carried out under continuous flow conditions in a tubular glass-made reactor at 80-90°C at atmospheric pressure. The catalysts were pretreated at 150°C for 0.5 h in a helium stream. The concentration of isopropanol in the helium carrier was 3.4 % and the total flow rate was 100 cm^3/min. After a stationary state was obtained the feed was replaced instaneously from isopropanol-d_0 to d_8, and the isotopic composition of isopropanol and propene was measured at a regular time intervals by use of a mass spectrometer which was directly connected to the outlet of the reactor.

Transient response upon the replacement of isopropanol-d_0 by d_8. Figure 1 illustrates a typical result. The conversion at the stationary state was 1.8 % at 80°C. When the feed was changed to isopropanol-d_8 (at t=0), the conversion gradually decreased to 1.2 %, due to isotope effect, and isopropanol-d_0 at the outlet was slowly replaced by isopropanol-d_8 (solid line in Fig. 1). The replacement took a much shorter time in the absence of PW_{12} (blank test; dotted line). The isotopic composition of propene was changed in a similar way as isopropanol.

From the decay curve of isopropanol-d_0 (or the appearance of d_8-species), the amount of isopropanol absorbed in the bulk at the stationary state was estimated to be about 7 molecules/anion. Almost the same result was obtained upon the change for isopropanol-d_8 to d_0. This amount corresponds to

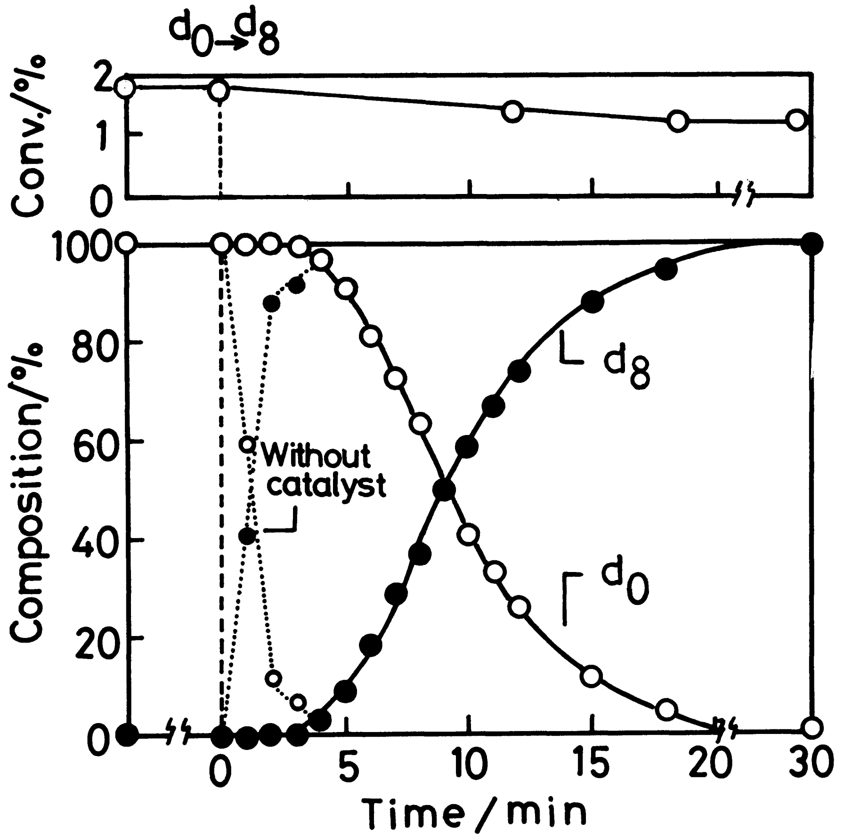

Fig. 1 Transient response in the gas phase composition upon the change of feed from isopropanol-d_0 to -d_8 in the dehydration catalyzed by PW_{12} at 80°C (Isopropanol : 3.4 %, Total flow rate 100 ml/min, PW_{12} : 500 mg)

● : Isopropanol-d_8 ○ : -d_0

about 100 layers adsorbed on the surface (the surface area; 5 m^2/g, the cross section of isopropanol; 31 A^2). Therefore, most of these of isopropanol molecules must be present in the bulk under these conditions. The concentration of isopropanol (calculated to be 6.1×10^{-3} mol/cm^3) is rather close to that of liquid isopropanol (1.3×10^{-2} mol/cm^3 at 25°C). Note that isopropanol-d_8 did not appear for at least 3 min after it was supplied. So, the rate of absorption or desorption of isopropanol at this stage is estimated to be not less than 2.9×10^{-4} mol/g•min. Since the rate of dehydration was 5.2×10^{-6} mol/g•min, the absorption-desorption is 50 times more rapid than the dehydration of isopropanol.

At 90°C, about 4 molecules of isopropanol per PW_{12} anion were present in the bulk. In the case of PMo_{12} and Cu salt of PW_{12}, the numbers of isopropanol in the bulk were 0.5 and 1.4 molecules/anion at 80°C, respectively. Even 0.5 molecules/anion cannot be explained in terms of only the adsorption on the surface, so that the "pseudo-liquid phase" model may also be applied to PMo_{12} and Cu salt of PW_{12}.

As has been reported$^{5)}$, the catalytic activity of heteropoly compounds for the dehydration of isopropanol was well correlated with bulk acidity. Moreover, increase of the surface area of PW_{12} by supporting on SiO_2 enhances 20 times the activity for the isomerization of butene (which occurs on the surface), while the activity for the dehydration of isopropanol increased 4 times at 100°C$^{5)}$. This fact indicates that a considerable part of the bulk protons takes part in the case of alcohol dehydration at this temperature. All of these results are well understood by the concept of the "pseudo-liquid phase".

Moment analyses of transient response data. Basic equations which describe the change of gaseous and intraparticle concentration in the catalyst bed are written,

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial Z} + \frac{3}{R}\,\frac{1-\alpha}{\alpha}\,D\frac{\partial Ci}{\partial r}/_{r=R} = 0 \qquad (1)$$

$$\frac{\partial Ci}{\partial t} - D(\frac{\partial^2 Ci}{\partial r^2} + \frac{2}{r}\,\frac{\partial Ci}{\partial r}) = 0 \qquad (2)$$

$$Ci/_{r=R} = HC \qquad (3)$$

These equations are similar to the conventional description[6)] of the porous materials-packed bed except that the intraparticle space through which sorbed species diffuse is not the "pores" but "pseudo-liquid phase". The difference appears in Eq. 3, which interrelates the gas phase and intraparticle concentration of isotope. H in Eq. 3 is a ratio of gaseous and intraparticle concentration of alcohols which is a constant throughout the analysis because alcohol concentration (C_3H_7OH + C_3D_7OD) is constant. The other assumptions for the derivation of Eq. 1 to 3 are that (1) axial dispersion can be neglected, (2) absorption-desorption, or exchange between gas phase and pseudo-liquid phase, is fast, and (3) the reaction rate is small in comparison with the rate of replacement, d_0 to d_8.

Instead of solving the equations analytically, "moment" expressions are derived for breakthrough curves[6,7)]. That is,

$$(\mu_1' \equiv)\ \frac{1}{C_0}\int_0^\infty (C_0 - C)dt = \frac{L}{v}(1 + H\frac{1-\alpha}{\alpha}) \qquad (4)$$

$$(\mu_2 \equiv)\ \frac{2}{C_0}\int_0^\infty (C_0 - C)tdt - \mu_1'^2 = \frac{2}{15}H\frac{L}{v}\frac{1-\alpha}{\alpha}h^2 \qquad (5)$$

where $h = R^2/D$. In the equations, the left hands are used to calculate the actual values of "moments" from the experimentally obtained curves, while the right hand equations are theoretically derived one for "ideal" breakthrough curves. Deviation from "ideal" breakthrough curves can be easily corrected by subtracting the moments of the blank test curve from that of total response.[7)]

1) Analysis of the first absolute moment. The first absolute moment calculated from Fig. 1 by using Eq. 4 are,

$$\mu_1',\ \text{with catalyst} = 593\ (s) \qquad (6)$$

$$\mu_1',\ \text{without catalyst} = 79\ (s) \qquad (7)$$

The error in these estimation due to uncertain tail of response curve amounted to 15 s, which is sufficiently small. Difference of Eqs. (6) and (7) is 514 s which is equated with the right hand of Eq. 4. With the knowledge of L=0.33 cm, α=0.5, and v=3.3 s, we can obtain, H=5.2 x 10^3. Accordingly, the concentration of isopropanol in the catalyst is given as $C_{i,A} = HC_A = 6 \times 10^{-3}$ mol/cm³.

2) Analysis of the second moment data. Similar procedure as for the first moments reveals,

$$\mu_2',\text{with catalyst} \quad \mu_2\,\text{without catalyst} = 56700\ (s^2) = \frac{2}{15}H\frac{L}{v}\frac{1-\alpha}{\alpha}\frac{R^2}{D} \qquad (8)$$

The uncertainty due to "tailing" is greater (ca. 10% of the total), but is still small. With the knowledge of H and other predetermined values,

$$R^2/D = 830\ (s) \qquad (9)$$

It is difficult to separate D values from the product R^2/D, because particle radius, R, is sensitive to the presence of polar substances[2]. We could imagine, however, R is in the order of 10^{-2} cm (or 60 - 80 mesh). If R is assumed to be 10^{-2} cm, D becomes 1.2×10^{-7} cm^2/s which is very small as a gas phase diffusional constant, but is close to effective diffusivity in liquid filled pores. The latter value, in many cases is around 10^{-6} cm^2/s.

3) Effectiveness factor. Stationary conversion of alcohols during the run in Fig. 1 is 1.8 %, from which we can obtain the rate of reaction, $r = 5.2 \times 10^{-6}$ mol/g·min = 0.26×10^{-6} $mol/cm^3 \cdot s$. The latter is the rate per unit volume of "pseudo-liquid phase". Generalized Thiele modulus, $\phi \equiv R\sqrt{k/D}$ is 0.19, where k is rate constant for first-order reactions, or R/C for other possible kinetic expressions. The relation of ϕ versus effectiveness factor for several types of kinetics were summarized by Satterfield[8], who suggested that effectiveness factor is practically unity when ϕ is smaller than 1. Accordingly, it is concluded that the reaction occurs homogeneously throughout the intraparticle pseudo-liquid phase. It should be emphasized here that for the calculation of ϕ we did not use the separate values of D and R which may contain large uncertainties, but we needed only the product, R^2/D, which was directly obtained from the moment analyses.

Nomenclature

C, C_i : Transient concentration of labeled alcohol in the gas phase and pseudo-liquid phase, respectively

C_0 : Stationary concentration of labeled alcohol in the gas phase (mol/cm^3)

D : Diffusion constant (cm^2/s)

L : Length of catalyst bed (cm)

Q : Volumetric flow rate (cm^3/s)

R : Particle radius (cm)

r : Radial coordinate in the particle (cm)

v : Linear gas velocity (cm/s)

z : Coordinate along the bed axis (cm)

α : Bed porosity (-)

μ_1', μ_2 : First absolute and second central moments, respectively (s and s^2)

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