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Reactions of H_2-D_2 and H_2-O_2 over $H_3PW_{12}O_{40}$

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Isotopic equilibration of H_2-D_2 in the gas and the whole bulk phases of $H_3PW_{12}O_{40}$ proceeded very rapidly, as compared with its reduction and H_2O-evolution. It was demonstrated that the formation of H_2O in the bulk phase was the rate-determining step for the reduction.

We previously reported that catalytic oxidation over 12-molybdophosphates can be classified into two groups; the surface-type and bulk-type (II) catalysis.[1,2] Dehydrogenation of isobutyric acid or cyclohexene as well as the oxidation of H_2 is the example of the bulk-type (II) catalysis. We tentatively proposed for the bulk-type (II) catalysis a hypothesis that protons and electrons, the redox carriers, migrate rapidly into the catalyst bulk, so that the whole catalyst bulk participates in the catalysis, although the transformation of reactants proceeds on the surface. However, to explain the independency of the rate on the surface area, it is necessary that a reaction in the bulk is the rate-determining step. It has been an essential question what kind of bulk reaction can be the rate-determining step.

Here, we wish to report a novel phenomenon found in the reactions of H_2-D_2 and H_2-O_2 over $H_3PW_{12}O_{40}$, which provides an example of bulk-type (II) catalysis, in which a bulk reaction is rate-determining.

$H_3PW_{12}O_{40}\cdot nH_2O$ was commercially obtained and used after recrystallization. Reactions were carried out in a closed circulation system. The solid samples (1 g, 3.3×10^{-4} mol) were treated for 2 h at 300 °C in circulating O_2 (53 Torr; 1 Torr = 133.3 Pa), prior to the reaction. Initial pressure for H_2-D_2 reaction was

H_2: 11.5 Torr (1.46 x 10^{-4} mol) and D_2: 19.9 Torr (2.53 x 10^{-4} mol). Isotopic composition was determined by a quadrupole mass spectrometer connected to the reaction system. The uptake of H_2 and D_2 caused by the reduction of catalysts was followed by the pressure decrease. Water evolved was trapped by a dry ice-ethanol trap and the volume was measured after vaporization. The rate of H_2-O_2 reaction (H_2: 99.5 Torr, O_2: 52.5 Torr) was followed by the pressure decrease, while H_2O formed was condensed by the cold trap.

Figure 1 shows the H_2-D_2 isotopic equilibration in the gas phase (Eq. 1) and the exchange between the gas and solid phases (Eq. 2) over $H_3PW_{12}O_{40}$ at 300 °C, as well as the H_2, D_2-uptake.

$$H_2 + D_2 \rightleftharpoons 2HD \qquad \text{(equilibration)} \qquad (1)$$

$$D_2 + H_3PW_{12}O_{40} \rightleftharpoons HD,\ H_2 + (H,\ D)_3PW_{12}O_{40} \qquad \text{(exchange)} \qquad (2)$$

It is notable in Fig. 1 that not only the equilibration but also the exchange proceeded much faster than the reduction, so that the content of H in the gas phase much increased at first. Within 1 h the whole hydrogen atoms (H, D) in the gas and bulk phases reached isotopic equilibrium; $\left\{ p(HD)^2 / p(H_2)\cdot p(D_2) \right\} = 3.79$ and the D content in the gas phase = 28 ± 1 %. The rapid exchange and equilibration was rather surprising, since the dissociation of H_2 was believed to be the slow step of the reduction by H_2 of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, the latter being reduced

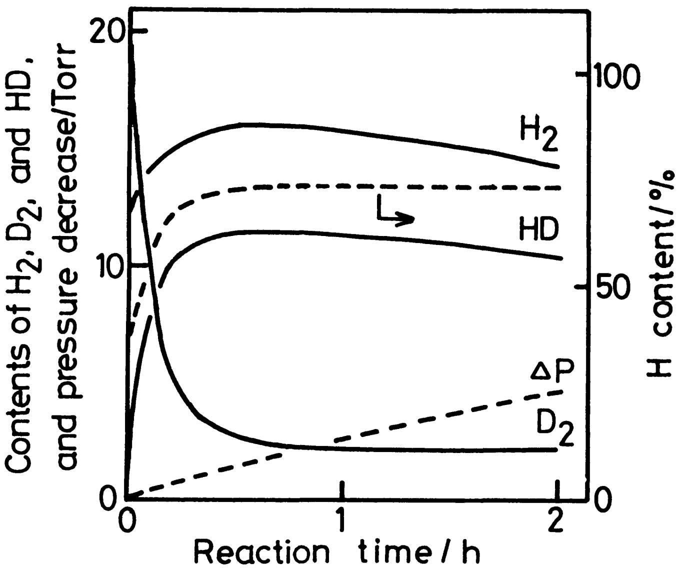

Fig. 1. Reaction of a H_2 and D_2 mixture over $H_3PW_{12}O_{40}$ at 300 °C.

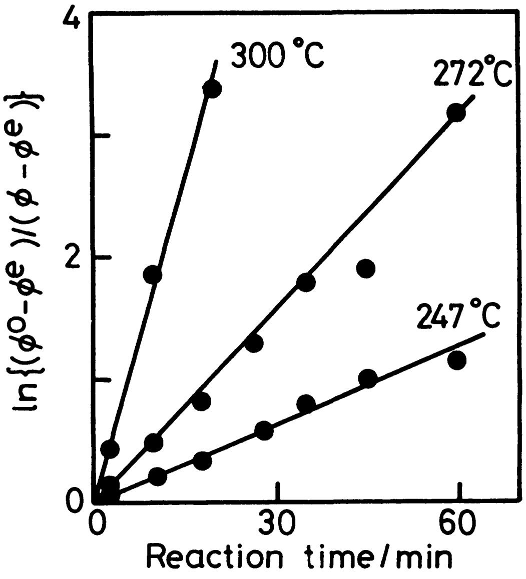

Fig. 2. First-order plots of H-D exchange reaction over $H_3PW_{12}O_{40}$.

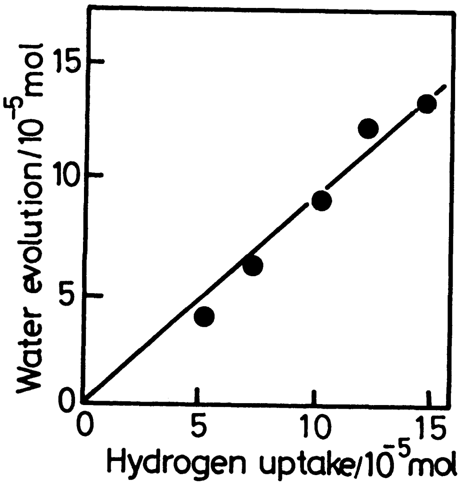

Fig. 3. Water evolution during the reduction of $H_3PW_{12}O_{40}$ by H_2 at 300 °C.

Table 1. First-order Rate Constants of the Reactions of H_2-D_2 and H_2-O_2 ($min^{-1} \cdot g^{-1}$)

	Temp /°C	Equilibration $\times 10^2$	Exchange $\times 10^2$	Reduction[a] (uptake) $\times 10^4$
H_2-D_2	247	2.7	2.0	3.2
	272	4.8	5.2	7.6
	300	13	18	25
	300[b]	19[b]	19[b]	—
H_2-O_2	300	—	—	29[c]

a) Average for the initial 5 min.
b) In the presence of oxygen (13 Torr).
c) Rate of $H_2 + 1/2O_2 \rightarrow H_2O$.

much more slowly at 200 - 300 °C.4)

First-order plots for the exchange reaction at 247 - 300 °C, according to $\ln(\phi^o - \phi^e)/(\phi - \phi^e) = kt$, where ϕ^o, ϕ^e, and ϕ are the D fractions in the gas phase at t = 0, ∞, and t, are shown in Fig. 2. The rates of HD production were approximately expressed also by first-order rate equations. Since the rates of reduction were ca. 0.9th order in hydrogen pressure, the rate constants were approximately obtained by dividing the initial rate of reduction by the pressure of H_2 plus D_2. Those rate constants are given in Table 1. The much greater rate constants of the isotopic exchange for the whole system than those of reduction indicate that the migration of protons and electrons is rapid in the bulk, and that the reduction proceeds in the whole bulk.

Reduction of $H_3PW_{12}O_{40}$ by H_2 may formally be represented by Eq. 3.5)

$$H_2 + H_3PW_{12}O_{40} \rightleftharpoons H_5PW_{12}O_{40} \xrightarrow{\Lambda} H_3PW_{12}O_{39} + H_2O \qquad (3)$$

It is obvious from Fig. 1 that the first step in Eq. 3 is reversible and rapid,6) and hence the last step is rate-determining. Figure 3 confirms this idea, since the rate of H_2-uptake agreed with the rate of H_2O-evolution. In other words, one mole of H_2 was consumed only after one mole of H_2O evolved. This result also indicates that the equilibrium constant of the first step is very small. Removal of an oxygen atom from the polyanion structure (the last step of Eq. 3) probably stabilizes the reduced state and causes the H_2 uptake to proceed further.

According to the present result, the very low reducibility of $H_3PW_{12}O_{40}$ observed previously5) was due to the slow rate of the last step. Thus the reduction of $H_3PW_{12}O_{40}$ takes place in the whole bulk (including the surface) and the rate-determining step of the reduction is a "bulk reaction". As a result, the rate becomes proportional to the weight of $H_3PW_{12}O_{40}$, and not to the surface area.

The catalytic oxidation of hydrogen (H_2-O_2 reaction) very likely proceeds by the reduction-oxidation cycle of $H_3PW_{12}O_{40}$ (redox mechanism), since the rate of H_2-O_2 reaction was comparable with the rate of stoichiometric reduction (Table 1), and close to the rate of reduction of a slightly reduced $H_3PW_{12}O_{40}$. By the similar comparison of the rates, the redox mechanism has already been proved in the case of H_2-O_2 reaction over $H_3PMo_{12}O_{40}$.1) It was further confirmed that the rates of isotopic reactions did not change in the presence of O_2 (Table 1). If the redox mechanism is operative in the present case, the H_2-O_2 reaction over $H_3PW_{12}O_{40}$ will show the bulk-type behavior and be the first example of bulk-type (II) catalysis in which the "bulk reaction" is specified.

References

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2) The bulk-type (II) catalysis is different from the bulk-type (I) catalysis observed for acid-catalysis at relatively low temperature. In the latter case the reactant molecules are absorbed in the bulk and react there.3)

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6) The first step of Eq. 3 is not exactly the same as Eq. 2. H_2 and D_2 dissociate probably accompanying partial reduction of polyanions as in Eq. 3, and exchange with the H^+, D^+ in the whole bulk, that is, Eq. 2.

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