# PSEUDO-LIQUID PHASE CATALYSIS OF HETEROPOLY COMPOUND: APPLICATION OF THE EFFECTIVENESS FACTOR CONCEPT

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The "pseudo-liquid phase" catalytic behavior of 12-tungstophosphoric acid was confirmed by studying the effect of catalyst particle size on the apparent rate of t-BuOH dehydration. The apparent rate of reaction strongly depended on the particle size, indicating strong diffusional effects in the pseudo-liquid phase. Based on the theory of Thiele with some modification and extension to pseudo-liquid phase catalysis, along with a knowledge of intrinsic reaction rate, diffusivity values were evaluated. The effective diffusivity was found to lie in a range of $10^{-11}$–$10^{-10}\,m^2/s$, which are very small values for diffusivity in gas phase, but close to that in liquid-filled pores. Due to the large temperature dependency of diffusivity, the effectiveness factor is smaller in the lower-temperature region—a sharp contrast to the usual diffusion-restricted gas-solid catalytic reaction in a microporous solid.

## Introduction

In general, gas-solid heterogeneous catalysis is considered as "surface" or "contact" catalysis, which occurs at the interface of gas and solid: Reactant molecules are adsorbed on the surface and then undergo a catalytic reaction known as "surface reaction". Recently, it has become apparent[3,4,7-12] that heteropoly compounds such as 12-tungstophos-

phoric acid $(H_3PW_{12}O_{40})$ and 12-molybdophosphoric acid $(H_3PMo_{12}O_{40})$ show remarkable characteristics for *absorbing* polar substances such as alcohols, ether, and nitrogen-containing bases into their solid lattice. On the other hand, nonpolar ones like hydrocarbons are *adsorbed* only on the surface.[3,7]

For the former cases, catalytic reaction may also take place in the solid lattice and is known as "pseudo-liquid phase (PLP)" catalysis[4,11,12] or "bulk reaction".[8,9] It will be readily expected that the effectiveness of a catalyst is higher for polar reactants,

because all active sites, either on the surface or in the bulk, are potentially active for such reactants. Based on this concept, it may be said that heteropoly compounds can discriminate reactant molecules based on their polarity: A new concept of polar/nonpolar selective catalysis, analogous to the shape-selective catalysis in Zeolite, may be developed to account for this phenomenon.

Although diffusion in PLP is thought to play an important role in catalytic behavior, few values have been reported. Such a study was done by one of the present authors in collaboration with Misono for dehydration of 2-propanol.[10] A recent publication[6] also considered diffusional effect in catalysis of heteropoly compounds but, in our opinion, that analysis mainly concerned gas-phase diffusion in pores. There is no doubt that more information on mobility or diffusional rate in PLP under working condition of the catalysts are required for a better understanding of the catalytic behavior of heteropoly compounds.

In this paper a theory is developed for PLP catalysis, taking both solubility and diffusivity into account. The effect of particle size on the apparent rate of dehydration of $t$-BuOH over supported 12-tungstophosphoric acid was experimentally examined. Combining stationary reaction studies with theory and transient-response experiments[13] for evaluation of the intrinsic rate constant, it becomes possible to evaluate reaction rate constant, diffusivity and solubility, all of which may potentially effect the apparent reaction rate.

## 2. Theory

If we consider isothermal spherical particles in which diffusion and reaction take place simultaneously in pseudo-liquid phase, material balance equations for reaction species are

$$D\left(\frac{d^2C_A^*}{dr^2} + \frac{2}{r}\frac{dC_A^*}{dr}\right) + k^*C_A^* = 0 \qquad (1)$$

$$\text{at} \quad r = R, \quad C_A^* = HC_g \qquad (2)$$

$$\text{at} \quad r = 0, \quad \frac{dC_A^*}{dr} = 0 \qquad (3)$$

These equations are similar to the conventional ones[6] except that diffusion and reaction of species do not occur in "pores" but in the "pseudo-liquid phase". The difference from the usual equation appears in Eq. (2), which means that sorption equilibrium is established at the interface.

With appropriate mathematical manipulations, we then obtain the reactant concentration as a function of radial position, $r$, within the pseudo-liquid phase:

$$\frac{C_A^*}{HC_g} = \frac{\sinh 3h(r/R)}{(r/R)\sinh(3h)} \qquad (4)$$

$$h = \frac{R}{3}(k^*/D^*)^{1/2} \qquad (5)$$

Conventional procedure yields the effectiveness factor, $\eta$, as a function of the Thiele modulus.

$$\eta = \frac{1}{h}\left(\frac{1}{\tanh(3h)} - \frac{1}{3h}\right) \qquad (6)$$

$$r_{obs} = k^*\eta C_{A,r=R}^* = k^*\eta HC_g$$
$$= k\eta C_g \qquad (7)$$

Accordingly, both Thiele modulus and effectiveness factor can be evaluated from experimental examination of apparent reaction rate as a function of particle size. The procedure is called the "triangle method".[2]

In the present case, $k^*$ cannot be obtained from the conventional reaction studies because it is defined on the basis of concentrations in PLP rather than in gas phase. For such evaluation the transient response technique was applied. Its principle has already been reported.[14]

## 3. Experimental

### 3.1 Catalyst preparation

Commercially available (Merck reagent grade) 12-tungstophosphoric acid, abbreviated as HPW, was used as a catalyst. To avoid change of catalyst particle size, which may occur during the reaction by absorption of a considerable number of polar molecules, catalyst was supported on Vycor glass (Corning, code NO 7930, mean pore size 4 nm) by impregnating the support with concentrated aqueous HPW. The supported amount of 0.29 kg/kg-support on dry basis is almost comparable to that calculated from the pore volume of the Vycor glass, $0.17 \times 10^{-3}$ m³/kg, indicating that the pores are completely filled with HPW. Five catalysts of various particle sizes (1.34, 0.92, 0.65, 0.2, and 0.1 mm diameter) were used. Prior to use, catalyst was pretreated in He stream for 1 h at 423 K.

### 3.2 Procedure

Stationary reaction studies: The dehydration of $t$-BuOH was carried out in a conventional fixed-bed flow-type reactor under atmospheric pressure. Supported catalyst was packed in a straight glass reactor of 0.015 m ID. The reaction temperature was measured by a thermocouple placed in the catalyst bed. Alcohol was fed by a syringe-type microfeeder at a concentration of 3.45% by volume in helium flow. W/F, based on the total gas flow, was 75.6 kg-cat s/m³-NTP. Products were analysed by a gas chromatograph through a 6-port sampling valve. In the previous paper,[15] the acid-catalytic behavior of heteropoly acid

for the dehydration of alcohols was reported. It revealed that apparent activity increased with time on-stream and established a stationary value after a few hours. The results, which will be described later, are for stationary activity. The experimental arrangements and procedures were almost the same as reported previously.[14,15] No ether and only traces of higher hydrocarbons (oligomerized products of isobutene) were observed in the present experiments.

Transient response experiment: Catalyst of the smallest particle size (0.1 mm in diameter) was used, in order to obtain rate of reaction with negligible diffusional influence. The reaction was carried out in the same way as described above. After the stationary state had been established, the feed was stopped and effluent products leaving the catalyst bed were analysed at appropriate time intervals by a gas chromatograph connected to the effluent stream through a 6-port sampling valve.

## 4. Results

**Figure 1** shows that the apparent rate of dehydration is strongly influenced by the size of catalyst particles. For smaller catalyst particles the effect is less significant, indicating that the mass transport limitation is small.

For larger catalysts, however, the effect becomes significant. This means that diffusion into the PLP is relatively slow, so that reaction occurs mainly in the outer shell of particles. That is, the effectiveness factor, $\eta$, is small.

From the experimental data shown in Fig. 1, both the effectiveness factor, $\eta$, and Thiele modulus, $h$, for catalyst of each particle size can be detemined at the same time by the "triangle method".

This method is based on the fact that both $\log(\eta_1/\eta_2)$ and $\log(h_1/h_2)$ can be calculated from Fig. 1, simply by taking the ratio of apparent rates for catalysts of different sizes and the ratio of particle radii. When we make a right triangle of which the vertical and horizontal laterals are $\log(r_{1,obs}/r_{2,obs})$ and $\log(R_1/R_2)$ respectively, and place it on the theoretical curve of Eq. (6) so as to fit well, we can determine absolute values of both $\eta_1$ and $\eta_2$, and consequently those of $h_1$ and $h_2$. Practically, all the points were used to fit with the theoretical curve.

The data points agree reasonably well with theoretical curve, as is shown in **Fig. 2**, and give values of the effectiveness factor and Thiele modulus for different catalyst particles at each temperature.

Since values of $\eta_i$ and $h_i$ are thereby obtained (subscript $i$ refers to each catalyst of various particle size), the intrinsic rate constant, $k$, and effective diffusivity, $D$, can be calculated, in an usual analysis, by Eqs. (8) and (9):
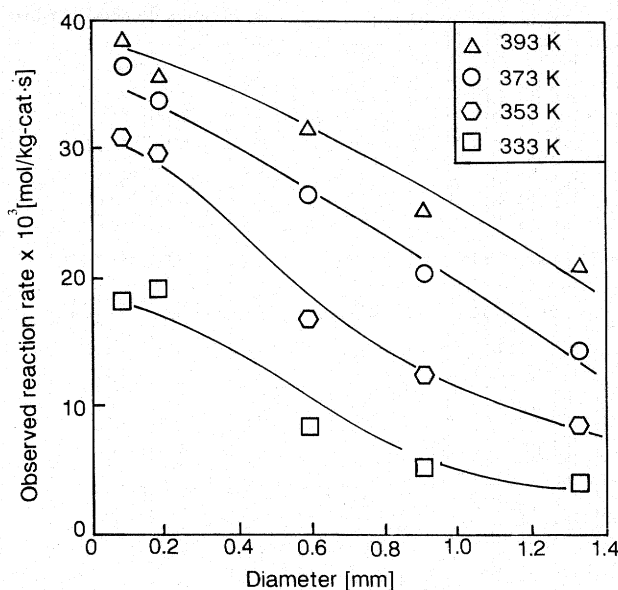


**Fig. 1.** Effect of particle size on rate of reaction
Reaction conditions: $t$-BuOH conc. $= 3.45\%$ (by volume); $W/F = 75.6$ kg-cat s/m³-NTP. Catalyst pretreated in He at 423 K, 1 h.
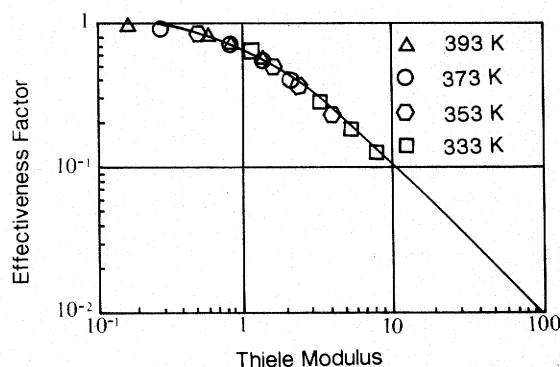


**Fig. 2.** Curve fittings of experimentally observed reaction rates for various particle sizes to the theoretical curve of effectiveness factor against Thiele modulus

$$k = (k_{obs})_i/\eta_i \qquad (8)$$

$$D = R_i^2 k/9h_i^2 \qquad (9)$$

In the present case, however, $k$ and $D$ thus obtained and listed in **Table 1** are not the intrinsic ones. This is because the basic equations were written in terms of concentrations in PLP, while $k$ was calculated on the basis of gas-phase concentration, that is, $(k_{obs})_i = $ (observed rate)$/C_g$. In other words, $k$ is the product of H and $k^*$:

$$k = k^*H \qquad (10)$$

To determine the values of $k^*$, the transient response method was applied.

An experimental result is shown in **Fig. 3**, which illustrates the effluent product of isobutene from the catalyst bed against time on-stream before and after the $t$-BuOH feed stopped. Supposing that most of the

**Table 1.** Values of $k$, $D$, $k^*$, $H$ and $D^*$ at various temperatures

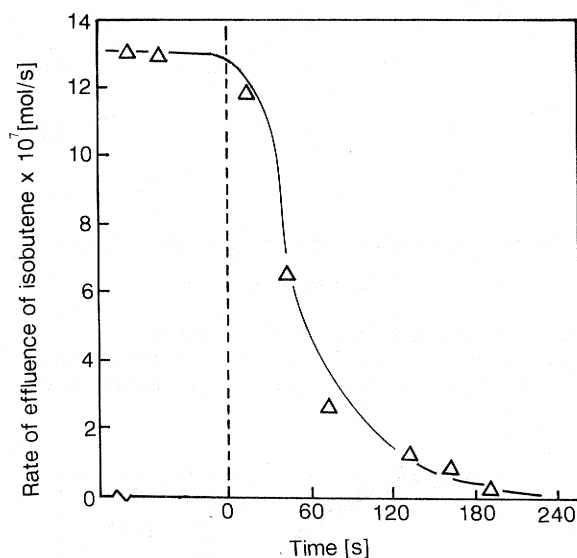| $T$ [K] | $k$ [1/s] | $D$ [m²/s] | $k^*$ [1/s] | $H$ [m²/s] | $D^*$ [—] |
|---|---|---|---|---|---|
| 333 | 47.12 | $3.82 \times 10^{-8}$ | 0.025 | $1.90 \times 10^3$ | $2.01 \times 10^{-11}$ |
| 353 | 54.60 | $1.88 \times 10^{-7}$ | 0.021 | $2.60 \times 10^3$ | $7.21 \times 10^{-11}$ |
| 373 | 58.64 | $7.07 \times 10^{-7}$ | 0.023 | $2.55 \times 10^3$ | $2.77 \times 10^{-10}$ |
| 393 | 59.56 | $1.65 \times 10^{-6}$ | 0.024 | $2.48 \times 10^3$ | $6.65 \times 10^{-10}$ |



**Fig. 3.** Transient behaviour of effluent product from catalyst bed after $t$-BuOH feed stoppage. Data points before time 0 correspond to stationary rate of reaction
Reaction temperature = 373 K, W/F = 75.6 kg-cat s/m³-NTP, catalyst $H_3PW_{12}O_{40}$, $t$-BuOH = 3.45% (by volume) → 0.



**Fig. 4.** Transient behaviour after $t$-BuOH feed stoppage, verifying of Eq. (13)

absorbed $t$-BuOH was converted to isobutene, integration of these transient response curves gives the amount of $t$-BuOH absorbed in the bulk in the stationary state. It was estimated to be about 3.25 mol $t$-BuOH/kg-HPW or 9 molecules/polyanion ($PW_{12}O_{40}^{3-}$: Keggin unit), suggesting that $t$-BuOH must be absorbed into the bulk under these conditions.

Based on these considerations, the transient response curve depicted in Fig. 3 was analysed by the same procedure as described in previous papers.[5,14] The amount of chemisorbed $t$-BuOH remaining at time $t$ is proportional to the integrated amount of isobutene produced from time $t$ to infinity:

$$C_A^* |_t = c \int_t^\infty f(t)dt \qquad (11)$$

where $f(t)$ is a function that expresses the transient response curve of isobutene formation as shown in Fig. 3, and $c$ is a proportionality constant. The observed rate is assumed to be proportional to $C_A^*$:

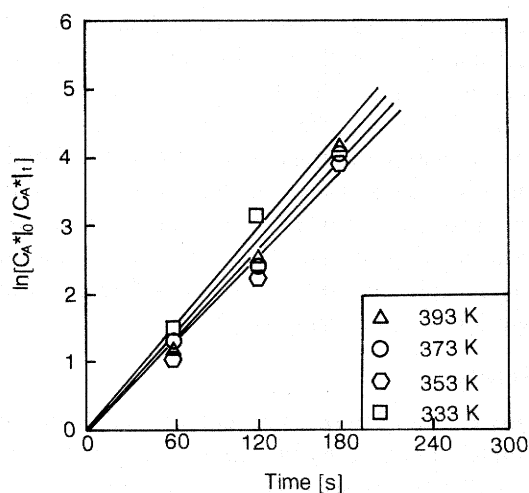$$r = -\frac{dC_A^*}{dt} = k^* C_A^* \qquad (12)$$

which on integration gives

$$\ln \frac{C_A^* |_0}{C_A^* |_t} = k^* t \qquad (13)$$

Finally, it becomes

$$\ln \left( \int_0^\infty f(t)dt \Big/ \int_t^\infty f(t)dt \right) = k^* t \qquad (14)$$

A verification of these equations is given in **Fig. 4**, which shows a fairly straight line through the origin from which $k^*$ can be evaluated.

Table 1 also summarizes the values of $k^*$, $H$, and $D^*$ for various temperatures.

From these data, the activation energy of reaction and diffusion are also estimated by the Arrhenius plot-type graph in **Fig. 5**.

The activation energy of diffusion was estimated to be 65.8 kJ/mol and is larger than that of reaction, 3.35 kJ/mol.

## 4. Discussion

The effective diffusivity, $D^*$, thus obtained lay in the range of $10^{-11}$ to $10^{-10}$ m²/s. We have no data for tortuosity and porosity of the catalyst. However, it is frequently assumed that the intrinsic diffusivity, after corrections for porosity and tortuosity, is almost 10 times larger than the experimentally obtained effective diffusivity.[13] The intrinsic diffusivity thus
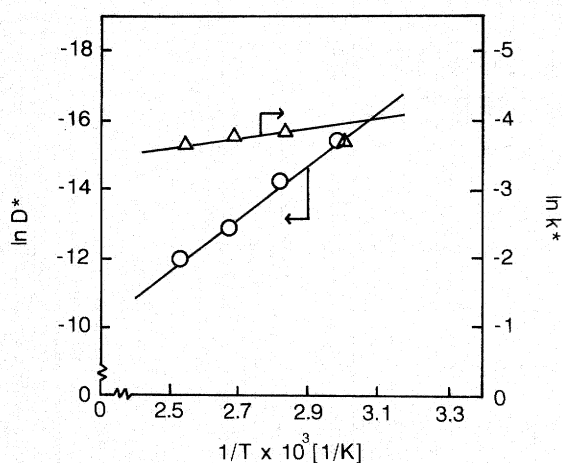
**Fig. 5.** Arrehenius-type graph for $D^*$ and $k^*$

calculated, of the order of $10^{-9}$–$10^{-10}$ m$^2$/s, should be compared with diffusivity in liquids. For example, the diffusivity of $t$-BuOH in H$_2$O and in benzene at 353 K, 1 atm can be calculated,[13] as $3.1 \times 10^{-9}$ m$^2$/s and $6.68 \times 10^{-9}$ m$^2$/s respectively. On the other hand, the gas-phase diffusivity of $t$-BuOH in He at 353 K, 1 atm was $4.6 \times 10^{-5}$ m$^2$/s and the Knudsen diffusivity in pores of 4 nm (corresponding to Vycor glass pore) at 353 K is $3.53 \times 10^{-7}$ m$^2$/s. It is clear that the diffusivity in HPW is close to that in liquid phase rather than in gas phase. The value herein obtained is of the same order of magnitude as that of 2-propanol in HPW,[10] which is obtained through physical sorption/desorption experiments (not through reaction).

Another characteristic feature of this system is the large temperature dependency of diffusivity. It is known that water in hydrated HPW exists as clusters like $3H^+[H_2O]_{29}$,[1] as revealed by X-ray examination. Water molecules in this structure may need high activation energy to move from one site to another. Alcohol may have a function similar to that of water and may have a high activation energy of diffusion.

When the effectiveness factor is far smaller than unity, the temperature dependency of effectiveness factor is expressed by

$$-\frac{d(\ln \eta)}{d(1/T)} = \frac{d(\ln h)}{d(1/T)} = \frac{-E_R + E_D}{2R} \qquad (15)$$

where $E_R$ and $E_D$ are activation energy for reaction and diffusion respectively. In the usual case, activation energy for reaction is larger than that for diffusion, while the reverse is true in the present case. As a result, the effectiveness factor is smaller in the low-temperature region—a sharp contrast to the usual gas-phase reaction, in which the diffusional effect becomes significant at higher temperatures. This may

be one of the characteristics of pseduo-liquid phase catalysis.

## Nomenclature

| | | |
|---|---|---|
| $C_A^*$ | = concentration of alcohol in pseudo-liquid phase | [mol/m$^3$] |
| $C_g$ | = concentration of alcohol in gas phase | [mol/m$^3$] |
| $D$ | = Apparent "diffusion constant", calculated from Eq. (9) | |
| $D^*$ | = Effective diffusion coefficient in pseudo-liquid phase | [m$^2$/s] |
| $E_R$ | = activation energy of reaction | [kJ/mol] |
| $E_D$ | = activation energy of diffusion | [kJ/mol] |
| $H$ | = solubility or a partition coefficient between gas and pseudo-liquid phase | [—] |
| $h$ | = Thiele modulus | [—] |
| $k^*$ | = intrinsic rate constant based on pseudo-liquid phase concentration | [1/s] |
| $k$ | = intrinsic rate constant based on gas phase | [1/s] |
| $k_{obs}$ | = apparent rate constant | [1/s] |
| $R$ | = particle radius | [m] |
| $r$ | = radial distance from center of particle | [m] |
| $r_{obs}$ | = observed rate of reaction | [mol/m$^3$ s] |
| $t$ | = time | [s] |
| $\eta$ | = effectiveness factor | [—] |

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