

EVALUATION OF DIFFUSIVITY AND SOLUBILITY OF ALCOHOL AND WATER IN HETEROPOLY ACID CATALYST BY USE OF ISOTOPE-REPLACEMENT TECHNIQUE

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A transient response method using the isotope replacement technique was used to verify "pseudo-liquid phase" behavior of 12-tungstophosphoric acid and to investigate the solubility and mobility of polar substances such as alcohols and ethers. The relationship between the concentration of labeled molecules in gas phase and that in bulk phase can reasonably be assumed as linear in this technique, regardless of intrinsic non-linear relationships of diffusion and absorption. It was found that the polar molecules can be absorbed into the bulk phase of catalyst under these experimental conditions. The small values of effective diffusivities, which are on the order of $10^{-10} \text{ m}^2 \text{ s}^{-1}$, are observed to be close to that in liquid-filled pores. The amount of absorbed molecules of alcohols, determined by polarity, tend to have a unique stoichiometry corresponding to the number of protons in $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and the mobility depends on either polarity or molecular size.

Introduction

Recently, a considerable number of reports which describing the structure and characterization of heteropoly compounds have appeared. Since their secondary structures are flexible¹⁾, polar molecules such as alcohols, ethers and nitrogen-containing bases are readily absorbed and diffuse into solid bulk, whereas non-polar molecules like hydrocarbons are not absorbed but only adsorbed on the surface. Based on these unique properties, known as "pseudo-liquid phase (PLP)^{4,9,10)}" catalysis, a new concept of catalysis in which heteropoly compounds discriminate among reactant molecules depending on their polar or non-polar properties, analogously to the shape-selective catalysis of zeolite, has been anticipated. This PLP catalytic function was found to relate closely to the higher catalytic activity of heteropoly acids against polar reactants compared to conventional solid acids.

The transport phenomena, particularly the rate of absorption and diffusion of polar molecules, in PLP have been observed to play an important role in the catalytic functions of these compounds and to have a remarkable effect on rate of reaction and selectivity. For instances, Niiyama *et al.*⁸⁾ suggested that the dehydration reactivity sequence of alcohols relate to their absorption rate and equilibrium at higher pressure. Unusual pressure dependencies of the rate

and selectivity of ethanol dehydration was also reported by Misono *et al.*⁵⁾ Although the relation of catalytic behavior of heteropoly acids to the mobility and solubility of polar molecules in the PLP has been qualitatively described, no quantitative analyses of catalytic performances have been made because of lack of quantitative data for these properties^{1,7,11)}. More information is required.

In the present study an investigations of the solubilities and diffusivities of polar substances such as water and alcohols in PLP of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, abbreviated as HPW, was carried out by means of the isotope replacement transient-response technique.

1. Theory

In principle, a simple and rapid means of studying adsorption kinetics and equilibria can be provided by elution chromatographic experiments in which a small packed adsorption column is subjected to a perturbation of the inlet concentration, for instance a step increase in an adsorbable species, and the dynamic response at the column outlet is measured. In the interpretation and analysis of this method, the critical point is that all processes involved must be described by linear equation for easier mathematical treatment. For chemisorption this requirement is often limited inevitably to sufficiently dilute concentration range over which the response is measured. These difficulties, however, can be overcome by using the isotope replacement technique. By this technique, the

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linear relationship between the concentration of labeled species in gas phase (C) and that in PLP (C_i) can be established from Eq. (1), even over a high concentration range of practical interest, inasmuch as the sum of the concentration of unlabeled molecule (C_H) and that of labeled molecule (C_i) in PLP is constant during a given experiment.

$$\frac{dC_i}{dt} = r_a - r_d = k_a C(n_0 - (C_H + C_i)) - k_d C_i \quad (1)$$

Similarly, the diffusivity, which may depend on the concentration, also becomes a constant throughout the experiment.

It is clear that the above-mentioned isotope replacement technique is strictly applicable to the evaluation of parameters. However, pseudolinear relationships hold in a variety of bimolecular counter-diffusion systems. Let us consider next the H_2O -polar substances replacement method. This method assumes that the exchange process is similar to bimolecular counter-diffusion in the sense that the number of molecules transported in is the same as that transported out, keeping the total concentration in PLP constant throughout the analysis:

$$C_A + C_w = C_T \quad (2)$$

If the system is for two species in PLP absorbed simultaneously and without dissociation, absorption of the species could be expressed by the Langmuir isotherm, Eq. (3).

$$\theta_A = \frac{K_a C_A}{1 + K_a C_A + K_w C_w} \quad (3)$$

From Eqs. (2) and (3):

$$\theta_A = \frac{K_a C_A}{(1 + K_a C_T) + (K_w - K_a) C_w} \quad (4)$$

It is evident from Eq. (4) that if the term $1 + K_a C_T$ is much larger than $(K_w - K_a) C_w$, a pseudo-linear relationship of the isotherm is obtainable. It should be pointed out that a similar process happened in the isotope replacement experiment. The difference is that $(K_w - K_a)$ is assumed to be small in the present case while it is strictly zero in the isotope replacement technique, provided that isotope effects are ignored. Hence, this method has advantages in the sense that no expensive labeled species is necessary and conventional gas chromatographic analysis is applicable. Also, and more scientifically interestingly, diffusion of alcohols in the presence of water, which is of practical importance, can be studied.

Moment analysis: Assuming (1) no axial dispersion in gas phase in the column, (2) negligible isotope effect, external diffusion and adsorption resistances, (3) no reaction, and (4) simple equimolar counterdiffusion

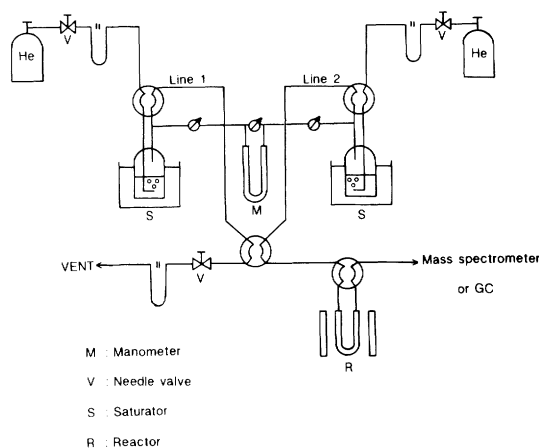


Fig. 1. Schematic flow diagram of apparatus

into account, the differential equations describing the change of gaseous and intraparticle concentrations of labeled species in a spherical catalyst particle bed with boundary and initial conditions are easily written⁷⁾. The theoretically analyzed results of the “moment” expressions which relate the first and second moment of the breakthrough curve at the exit to the solubility and diffusivity parameters are then given. The mathematical derivations were presented elsewhere⁷⁾.

The perturbations of the breakthrough curves caused by the dead volume and silica support on which polar substances may be adsorbed are corrected by subtracting the moments of the blank test curves from those of the experimentally obtained breakthrough curves. The final equations of corrected “moments” which refer to the absolute response of HPW are:

$$\frac{\Delta\mu'_1}{(1-\alpha)/\alpha} = H \frac{L}{v} \quad (5)$$

$$\frac{\Delta\mu_2}{[(1-\alpha)/\alpha][L/v]} = \frac{2}{15} H \frac{R^2}{D} \quad (6)$$

2. Experimental

2.1 Catalyst preparation

Silica (JRC-SIO-5, pore volume $1 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$) used as support was calcined at 673 K for 6 h. The catalyst, 12-tungstophosphoric acid, was obtained commercially from Merck. Three catalysts of various particle sizes (1.26, 2.24, 3.68 mm in diameter) were prepared by impregnating the calcined silica with highly-concentrated aqueous HPW, with subsequent drying at 373 K for 1 h. The loading of HPW was 70% by weight on dry basis, which is almost enough to fill up the pores of the SiO_2 support. Before commencing the study, the catalysts were pretreated in a He stream for 1 h at 573 K.

2.2 Procedure

The experiments were carried out with linear gas velocities ranging from 0.007 to 0.0225 m/s in a continuous-flow reactor, as shown in Fig. 1, at given

temperatures where any chemical reaction hardly occurs. About 0.0027 kg of supported HPW catalyst particles were packed in a Pyrex glass U-tube of 0.008 m ID, yielding a bed height of 0.05 m. First, unlabeled species of gas were introduced with helium from line 1 through the column until a steady state was established. They were then replaced by the labeled ones by operation of a 4-way valve. The pressure in both lines was kept the same in order to eliminate potential turbulence of the breakthrough curves. The effluents were periodically monitored by a mass spectrometer connected directly to the column outlet. The experiments regarded as blank tests were done by using silica without HPW to eliminate extraneous perturbation of the breakthrough curves.

For water-polar substance replacement experiments, the bed was first exposed to H₂O until a steady state was established. Then the H₂O was replaced by one of the polar substances: 1-propanol, 2-propanol, isobutanol or diethylether. The partial pressure of H₂O and the polar substances were chosen so that the amounts of absorption of both species were the same. The effluents were analyzed by gas chromatography rather than mass spectroscopy.

3. Results

Figure 2 shows a transient response curve of labeled ethanol for columns packed with HPW/SiO₂ and with SiO₂. It is evident that the response curves differ significantly enough to evaluate the corrected "moment" precisely. The broadening of the response curve is mainly caused by the effect of mass transfer resistance, particularly diffusion in PLP of heteropoly acid. The breakthrough curves of other polar substances show the same result as that for ethanol.

The plot of $\Delta\mu'_1/[1-\alpha]/\alpha$ versus L/v according to Eq. (5) should yield a straight line with a slope of H . The result for methanol, as an example, is shown in **Fig. 3**. The first moment's lack of dependence on particle size implies that the linear relationship for the diffusion rate process and sorptive properties holds. The H values are evaluated and summarized in Table 1.

Figure 4 shows a plot of $\Delta\mu_2/[(L/v)(1-\alpha)/\alpha]$ against velocity for methanol at given particle sizes. The negligible axial dispersion effect under these experimental conditions was corroborated by the independence from velocity of the second moment.

Figure 5 illustrates the plot of $\Delta\mu_2/[(L/v)(1-\alpha)/\alpha]$ versus R^2 for methanol at each temperature. The term $\Delta\mu_2/[(L/v)(1-\alpha)/\alpha]$ is directly proportional to R^2 . By Eq (6) the diffusion coefficients (D) were evaluated from the slope of each line coupled with the evaluated H values. The results for water and ethanol are the same as that for methanol.

Table 1 summarizes the obtained values of

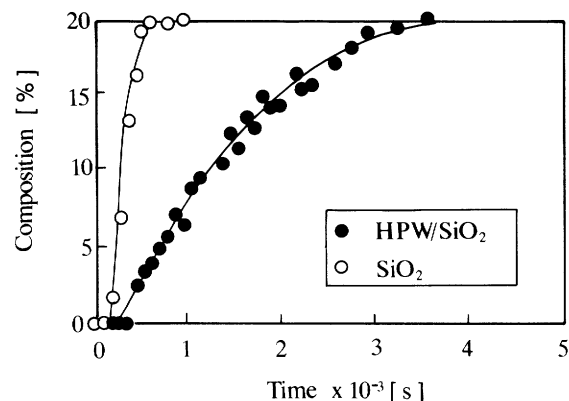


Fig. 2. Transient response in gas phase composition upon change of feed from C₂H₅OH to 20% C₂D₅OD ($T=323$ K, $v=1.72 \times 10^{-2}$ m/s)

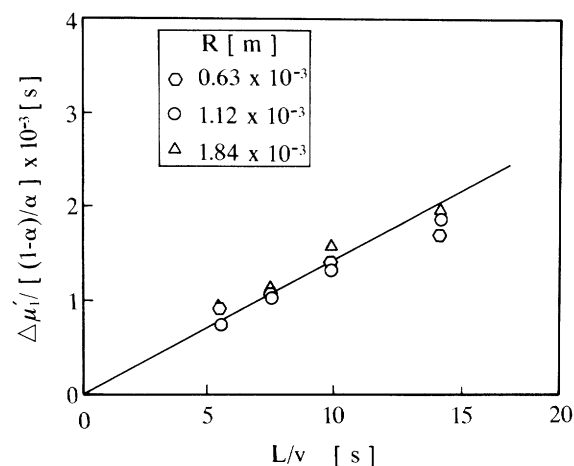


Fig. 3. Dependence of $\Delta\mu'_1/[(1-\alpha)/\alpha]$ on L/v for various particle sizes: Isotope replacement of methanol at $T=333$ K

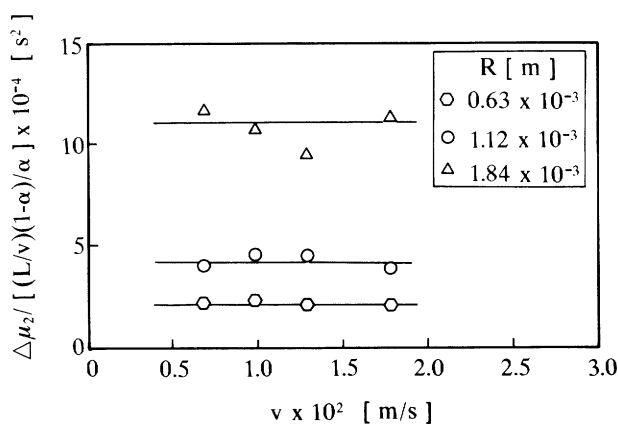


Fig. 4. Dependence of $\Delta\mu_2/[(L/v)(1-\alpha)/\alpha]$ on v for various particle sizes: Isotope replacement of methanol at $T=333$ K

solubilities (H), diffusivities (D), and amount of absorbed molecules (n) per one polyanion, that is, the Keggin unit. The Keggin unit, a polyanion structure, was proposed by J. F. Keggin²⁾, who first studied the structure of 12-heteropolyanions by X-ray diffraction. The values of n can be estimated

Table 1. Summary of values of H , n and D for the substance in saturator 1 at given conditions

	Saturator 1		Saturator 2		H (—)	T (K)	n (molecules/ polyanion)	$D \times 10^{10}$ (m ² /s)
	μ (Debye)	$P_1 \times 10^{-2}$ (kPa)		$P_2 \times 10^{-2}$ (kPa)				
H ₂ O	1.85	0.1986	D ₂ O	0.1986	663	343	12.7	1.32
		0.1834		0.1834	1368	333	10.8	1.36
		0.1834		0.1834	1120	353	9.0	1.70
CH ₃ OH	1.71	0.0821	CD ₃ OD	0.0821	718	373	5.7	2.10
		0.3733		0.3733	162	323	6.4	5.30
		0.3733		0.3733	148	333	5.5	6.00
		0.3733		0.3733	146	343	5.5	6.80
		0.3733		0.3733	127	353	4.8	7.50
C ₂ H ₅ OH	1.73	0.3733	H ₂ O	0.0759	143	323	6.4	2.70
		0.2000	C ₂ D ₅ OD	0.2000	335	323	6.4	2.53
		0.2000	H ₂ O	0.0426	380	323	6.8	2.05
		0.1866		0.0334	347	323	6.0	1.80
		0.1866		0.0334	330	333	5.7	2.06
		0.1866		0.0334	248	343	4.3	1.73
		0.3999		0.0334	138	343	5.1	2.98
1-C ₃ H ₇ OH	1.73	0.1631	H ₂ O	0.0378	607	328	8.5	2.36
		0.1600		0.1573	583	328	8.2	2.00
		0.0667		0.0405	905	323	5.3	1.00
2-C ₃ H ₇ OH	1.67	0.2939	H ₂ O	0.1573	250	328	6.4	2.00
		0.2000		0.0405	383	323	6.7	1.70
iso-C ₄ H ₉ OH	1.80	0.0733	H ₂ O	0.0759	1085	323	7.0	0.72
C ₂ H ₅ OC ₂ H ₅	1.17	0.2466	H ₂ O	0.0426	114	323	2.7	0.50
		0.2466		0.0334	80	323	2.0	0.50
		0.2466		0.0066	70	323	1.8	0.40
		0.7333		0.4653	72	323	3.3	0.64

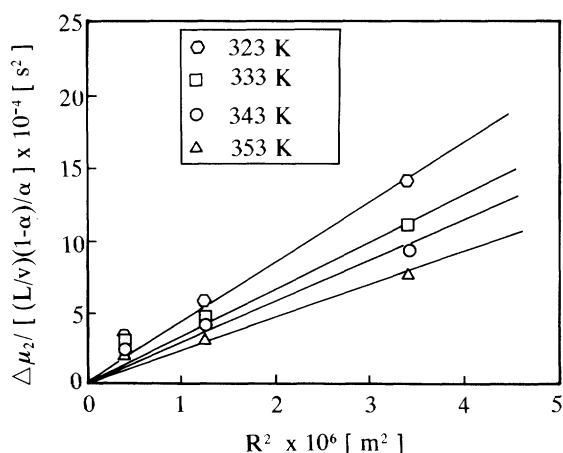


Fig. 5. Dependence of $\Delta\mu_2/[(L/v)(1-\alpha)/\alpha]$ upon particle size at various temperatures: Isotope replacement of methanol at $v = 1.3 \times 10^{-2}$ m/s

by multiplying H by the stationary gas-phase concentration (C_0). The results show that the values of n and D are seldom affected by a change in partial pressure of water, but they vary with temperature, partial pressure, and the kind of sorbed molecules. The latter factor relates closely to the polarity or dipole moment and molecular size of sorbed species.

The amount of absorption increases with decreasing temperature and with increasing partial pressure. However, in some partial pressure ranges the number

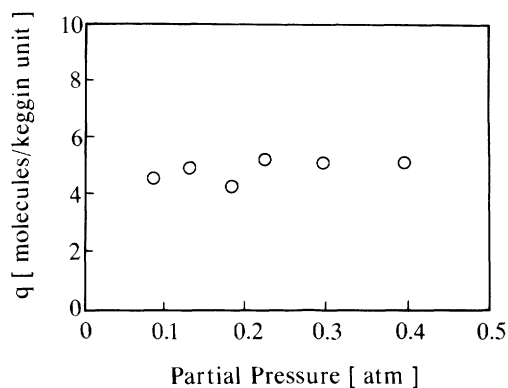


Fig. 6. Pressure dependence of amount of ethanol absorbed into $H_3PW_{12}O_{40}$ at 343 K

of absorbed molecules do not change significantly, as revealed by the result for ethanol in **Fig. 6**. The amount of absorbed molecules in the given experimental conditions decrease in the order, $H_2O > \text{isobutanol} > 1\text{-propanol} > 2\text{-propanol} = \text{ethanol} > \text{methanol} > \text{diethylether}$.

The mobilities of alcohols, which are represented by the diffusion coefficients, vary slightly with change in temperature and partial pressure and tend to decrease in the following order: $\text{methanol} > \text{ethanol} > 2\text{-propanol} = 1\text{-propanol} > \text{isobutanol} = H_2O > \text{diethylether}$.

4. Discussion

The independence of the first moment from particle size, shown in Fig. (3), manifests that the assumption of a linear relationship is reasonably valid. It is clear that the isotope replacement technique is more advantageous and can be used reliably.

For 1-propanol, 2-propanol, isobutanol, and diethylether, the isotope species of which are not commercially available, H₂O-polar substances replacement was attempted instead of isotope replacement. This may cause some error in the initial period of replacement since the partial pressure of water in this period is rather higher than that of alcohols. However, it seems to have little effect provided that step input and moment analysis are applied. This is warranted by the result for ethanol obtained by this modified method (Table 1), which agrees quite well with those from the experiment of isotope replacement. It thus allows us to say that H₂O-polar substances can also be used practically in the present work.

4.1 Amount of absorption

The experimentally estimated amounts of absorbed molecules of alcohols (Table 1) are much greater than the values calculated theoretically from the known values of surface area of HPW and of the cross section of the molecules. Accordingly, it can be suggested that these polar molecules are adsorbed not only on the surface but also absorbed into the bulk phase of catalyst, as reported previously¹¹. In addition, as the number of absorbed ethanol molecules is nearly constant in a certain range of partial pressure (Fig. 6), we may conclude that a unique stoichiometry for the sorption of alcohol is established. This means that the cation-polyanion matrix of heteropoly acids can be accommodated with a limited number of sorbed molecules so as to stabilize its secondary structure. Studies by Misono *et al.*⁶⁾ enhance this idea by suggesting some stoichiometry for sorption of pyridine established in a certain range of pressure; sorbed pyridine/Keggin unit=6, although the stoichiometry may change depending upon temperature and pressure. Moreover, owing to the strong acidity of HPW, the polarity of alcohols, represented by the dipole moment, is expected to be the crucial factor in determining their absorbability. Such anticipation concurs entirely with the experimentally obtained results, showing that the ether, the polarity of which is smaller, is absorbed to a lesser extent than the other alcohols.

4.2 The mobility of alcohols

The diffusivities of alcohols, as shown in Table 1, are on the order of $10^{-10} \text{ m}^2 \text{ s}^{-1}$, which is comparable to the theoretically calculated diffusivity in liquid-filled pores. These results confirm the significant "pseudo-

liquid phase" catalysis of heteropoly acids. The mobility of alcohols in the PLP of HPW tends to decrease with molecular size. However, a discrepant result is observed in the case of water, the diffusivity of which is relatively small in comparison with the other alcohols, although the molecular size of the former is smaller than that of the latter. This suggests that the mobility or diffusivity of polar molecules, which occur simultaneously with absorption in PLP, should be also related to the affinity to acid sites or strength of absorption. This conclusion seems reasonable since water ($\mu=1.85$ Debye) has a higher polarity than the others. Accordingly, we may postulate that the mobility of polar molecules in the PLP is determined by either molecular size or polarity of sorbed species.

In this analysis, or in any other technique¹¹⁾ in diffusion studies, some uncertainties remain in the evaluation of particle radius. We are sure that the time constant of diffusion, R^2/D , can be evaluated accurately. To separate the D value from the product R^2/D , however, the exact value of R must be known. Our model is based on the complete filling of HPW in pores of support SiO₂. The model was supported, even if partially, by the fact that the loading was so high that no more loading was possible. An attempt at further loading resulted in the deposition of HPW on the outer surface of the support particles. The loaded value was 70% in weight, while the calculated value for complete filling was 80%. Although some cleavage of supported HPW may occur during the drying and calcination pretreatments, we may imagine that they coalesce again under the experimental condition where sorbable molecules exist and expand the size of the unit lattice, to become pertinent to the relevant model.

Nomenclature

C, C_i	= transient concentration of labeled molecule in gas phase and in PLP, respectively	[mol m ⁻³]
C_0	= stationary concentration of labeled molecule in gas phase	[mol m ⁻³]
C_A, C_w	= transient concentration of alcohols and water in PLP, respectively	[mol m ⁻³]
C_H	= concentration of unlabeled species in PLP	[mol m ⁻³]
D	= effective diffusion coefficient	[m ² s ⁻¹]
H	= Pseudo-Henry's constant given by the ratio of C_i and C	[—]
k_a	= absorption rate constant	[s ⁻¹]
k_d	= desorption rate constant	[s ⁻¹]
K_a	= Langmuir constant for alcohol	[—]
K_w	= Langmuir constant for H ₂ O	[—]
L	= length of catalyst bed	[m]
n_0	= amount of saturated absorption	[mol m ⁻³]
r_a	= rate of absorption	[mol m ⁻³ s ⁻¹]
r_d	= rate of desorption	[mol m ⁻³ s ⁻¹]
R	= radius of catalyst particle	[m]

t	= time	[s]
v	= linear gas velocity in the interparticle space	[m s ⁻¹]
α	= bed porosity	[—]
θ_A	= fraction of alcohol in PLP	[—]
μ'_1, μ_2	= first absolute and second central moments, respectively	[s, s ²]

Literature Cited

- 1) Akaratiwa, S. and H. Niiyama: *J. Chem. Eng. Japan*, **23**, 143 (1990).
- 2) Kegglin, J. F.: *Proc. Roy. Soc. (London)*, **A144**, 75 (1934).
- 3) Misono, M.: *Catal. Rev.-sci. Eng.*, **29(2&3)**, 269–321 (1987).
- 4) Misono, M., K. Sakata, Y. Yoneda and W. Y. Lee: in “Proceedings, 7th International Congress on Catalysts, Tokyo, 1980”, p. 1047. Kodansha/Tokyo and Elsevier/Amsterdam, 1981.
- 5) Misono, M., T. Okuhara, T. Ichiki, T. Arai and Y. Kanda: *J. Am. Chem. Soc.*, **109**, 5535 (1987).
- 6) Misono, M., N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara and Y. Yoneda: *Bull. Chem. Soc. Jpn.*, **55**, 400 (1982).
- 7) Okuhara, T., T. Hashimoto, M. Misono, Y. Yoneda, H. Niiyama, Y. Saito and E. Echigoya: *Chem. Lett.*, 573 (1983).
- 8) Saito, Y., N. C. Park, H. Niiyama and E. Echigoya: *J. Catal.*, **95**, 49–56 (1985).
- 9) Sakata, K., M. Furuta, M. Misono and Y. Yoneda: “ACS/CSJ Chemical Congress, Honolulu, April, 1979”; *Shokubai*, **21**, 307 (1979); Misono, M., “1st Japan–France Catal. Seminar, July 1979.”
- 10) Saito, Y., N. Yoneda, H. Niiyama and E. Echigoya: “46th Symposium on Catalysis, 3P07, Sendai, 1980.”
- 11) Okuhara, T., S. Tatematsu, W. Y. Lee and M. Misono: *Bull. Chem. Soc. Jpn.*, **62**, 717 (1989).