



ELSEVIER

Journal of Molecular Catalysis A: Chemical 100 (1995) 49–59

**JOURNAL OF
MOLECULAR
CATALYSIS**
A: CHEMICAL

Catalysis by heteropoly compounds. Part XXVI¹. Gas phase synthesis of methyl *tert*-butyl ether over heteropolyacids

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Received 1 June 1995

Abstract

Gas phase synthesis of methyl *tert*-butyl ether (MTBE) from methanol and isobutylene has been studied with several heteropolyacids at 303–383 K. It was found that a Dawson-type heteropolyacid, $H_6P_2W_{18}O_{62}$, was much more active than Keggin-type heteropolyacids, $H_nXW_{12}O_{40}$ ($X = P, Si, Ge, B,$ and Co), and other solid acids such as SO_4^{2-}/ZrO_2 , $SiO_2-Al_2O_3$ and H-ZSM-5 at 323 K. Since the acid strength of $H_6P_2W_{18}O_{62}$ was weaker than $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, factors other than the acid strength are important for the catalytic activity. Pseudoliquid phase behavior was demonstrated for $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$ by the measurements of the absorption of methanol during the reaction and by the unique pressure dependencies of the rate of synthesis. From the absorption data (the amount and rate), it is concluded that the high catalytic activity of $H_6P_2W_{18}O_{62}$ is brought about by a high-activity state of the pseudoliquid phase in which controlled amounts of molecule are absorbed and the absorption–desorption is rapid. On the other hand, the pseudoliquid phase of $H_3PW_{12}O_{40}$ is in a low-activity state absorbing excessive amounts of molecule.

Keywords: Methyl *tert*-butyl ether; Gas phase; Heteropolyacids; Pseudoligand phase; Tungsten

1. Introduction

Methyl *tert*-butyl ether (abbreviated as MTBE) is regarded to be a clean and non-polluting gasoline additive and a good enhancer of octane number. The world production of MTBE is increasing [1]. At present, MTBE is commercially produced by a liquid-phase reaction from methanol and isobutylene (2-methylpropene) with ion-exchange resins such as Amberlyst [1–4]. The resin catalyst

is unstable above 373 K, where the acid groups are lost from the resin polymer network. A new acid catalyst having a high thermal stability is desirable in order to combine the MTBE synthesis with the methanol synthesis from syngas [5].

Because of high thermal stability, zeolites are possible candidates. There are several reports about the MTBE synthesis from methanol and isobutylene using zeolites [5–9]. Chu and Kühl [7] reported that ZSM-5 and ZSM-11 are more selective than Amberlyst 15, while the activity is comparable in liquid phase synthesis from methanol and isobutylene. For the gas phase synthesis, Nikolopoulos et al. studied the effects of acid strength using a series of alkali-exchanged HY zeolites [8]. They found that the initial activity

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¹ For Part XXV see: K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Faraday Trans.*, 99 (1995) 367.

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was independent of the acid strength and attributed this to a strong mediating effect of adsorbed methanol on the acid strength. HY zeolites were less active than Amberlyst 15 [8]. A titanium–silicalite also showed catalytic activity, but was less active than H-ZSM-5 [9].

Heteropolyacids are efficient catalysts for various kinds of acid-catalyzed reactions [10–15] and are useful in practical application [16]. Heteropoly compounds are also active for the MTBE synthesis [17–24]. In homogeneous liquid-phase reaction of methanol and isobutylene, a Dawson-type heteropolyacid, $H_6P_2W_{18}O_{62}$, showed a higher activity than typical Keggin-type heteropolyacids such as $H_3PW_{12}O_{40}$ as well as H-ZSM-5 [17].

In the gas phase synthesis, SiO_2 -supported heteropolyacids were reported to be more active and selective than mixed metal oxides, fluorinated oxides, and mounted mineral acids [18]. Ono and Baba showed that carbon-supported $Ag_3PW_{12}O_{40}$ was efficient for this reaction after H_2 pretreatment [19]. The authors examined preliminarily the effects of the kind of heteropolyanions and of supporting them onto SiO_2 for the gas phase synthesis [20]. The activity order was $H_6P_2W_{18}O_{62} \gg H_4SiW_{12}O_{40} \approx H_4GeW_{12}O_{40} \approx H_3PW_{12}O_{40} > H_5BW_{12}O_{40} \approx H_6CoW_{12}O_{40}$ at 323 K. By supporting $H_6P_2W_{18}O_{62}$ or $H_3PW_{12}O_{40}$ on SiO_2 , the yield of MTBE became comparable to that of Amberlyst 15 [20]. Reaction of *tert*-butyl alcohol and methanol to MTBE is also catalyzed by heteropoly compounds [22–24]. The %-conversion of *tert*-butyl alcohol correlated with the amount of pyridine absorbed in heteropoly compounds [22]. Dependence of the rate on the methanol pressure resembled that of the absorption of methanol in the bulk, suggesting the presence of pseudoliquid phase behavior [23], which was proposed by us and shown for several reactions (e.g., see [10]).

In the present study, it has been attempted to elucidate the reasons of the unique catalytic behavior of the Dawson-type heteropolyacid for the MTBE synthesis. Effects of the acid strength, the absorption properties of these heteropolyacids,

and pressure dependencies were examined. On the basis of these data, the high catalytic activity of $H_6P_2W_{18}O_{62}$ for this reaction will be discussed, in relation to the pseudoliquid phase behavior.

2. Experimental

2.1. Materials

$H_6P_2W_{18}O_{62} \cdot nH_2O$ was synthesized according to the literature [25,26]. $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were supplied from Nippon Inorganic Colour and Chemical, Co., Ltd. $H_4GeW_{12}O_{40} \cdot nH_2O$ was prepared from $Na_2WO_4 \cdot 2H_2O$ and GeO_2 by the same method as in the literature [26,27]. $H_5BW_{12}O_{40}$ was synthesized from $Na_2WO_4 \cdot 2H_2O$ and H_3BO_3 [26,28]. $H_6CoW_{12}O_{40} \cdot nH_2O$ was obtained from $Na_2WO_4 \cdot 2H_2O$ and $Co(OCOCH_3)_2 \cdot 4H_2O$ [26,29]. These heteropolyacids were extracted with diethyl ether and then recrystallized from water. These heteropolyacids were characterized by IR spectroscopy (Shimadzu FT-IR 8500) and NMR spectroscopy (JEOL, JNM-GXM270). For reference, $SiO_2-Al_2O_3$ ((13% Al_2O_3), Catalyst and Chemical Industries), H-ZSM-5 (obtained from Na-ZSM-5, which was supplied from Tosoh Co. (HSZ-820 NAA)), SO_4^{2-}/ZrO_2 [30], and $\gamma-Al_2O_3$ (Reference Catalyst JRC-ALO-4, The Catalysis Society of Japan) were used.

2.2. Measurement of acid strength

The acid strength of heteropolyacids in acetonitrile solution was determined by UV spectroscopy using a Hammett indicator [31]. After the heteropolyacids were pretreated in an N_2 flow at 423 K to remove the water of crystallization, they were added into acetonitrile which was dried in advance with a molecular sieve 3A, where the concentration of the nominal proton is $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. Dicinnamylidene acetone ($pK_a = -3.0$) ($3.5 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ in acetonitrile) was used as an indicator, where K_a is the dissociation constant of the protonated indicator

($\text{p}K_{\text{a}} = -\log K_{\text{a}}$). The UV spectra were measured with a quartz cell ($L = 1$ cm) by use of a Hitachi 340 spectrophotometer in 190–850 nm region. The sample cell was sealed with a polymer film to avoid being exposed to moisture during the measurement.

2.3. Water content and surface area

The surface area was determined with N_2 adsorption by BET method at 77 K after the samples were pretreated at 423 K in vacuum for 1 h. The content of the crystallization of water of the heteropolyacid was measured with a microbalance (Seiko Instruments, TG/DTA 220) [26].

2.4. Catalytic reactions

Synthesis of MTBE from methanol and isobutylene was performed in a flow reactor (Pyrex tube, 12 mm of inside diameter) at an atmospheric pressure in the temperature range from 303 to 383 K. Methanol which was dried with molecular sieve 3A was fed by bubbling N_2 through an isothermal saturator kept at 313 K. Prior to the reaction, the heteropolyacids were pretreated at 423 K in the N_2 flow for 1 h. $\text{SiO}_2\text{-Al}_2\text{O}_3$, H-ZSM-5, and $\text{SO}_4^{2-}/\text{ZrO}_2$ were also pretreated at 673, 723, and 723 K, respectively. For the standard reaction conditions, a mixture of methanol and isobutylene and N_2 (balance) ($90 \text{ ml} \cdot \text{min}^{-1}$) was fed at the ratio of 1:1:3 over 0.5 g of the catalyst ($W/F = 2.3 \text{ g} \cdot \text{h} \cdot (\text{mol of feed})^{-1}$). The partial pressure of methanol was controlled by changing the ratio of the feed rate when the pressure dependence of the reaction rate was measured.

Dehydration of methanol was carried out in the same flow reactor at 423 K and one atmospheric pressure. After the heteropolyacids and $\gamma\text{-Al}_2\text{O}_3$ were pretreated in the N_2 flow at 423 and 673 K, respectively, methanol was supplied from the saturator. The pressure of methanol was changed by changing the ratio of methanol to N_2 in the feed. Gas flow rates were kept constant using mass flow controllers. Gases at the outlet of the reactor were analyzed with a gas chromatograph (Shimadzu

GC-6A, TCD) equipped with a capillary column (directly connected DB-5 (60 m), OV-101 (25 m), and OV-1701 (25 m)).

2.5. Absorption of methanol or MTBE

The absorption (or adsorption) measurements were performed in the flow reactor system. After the heteropolyacids were pretreated at 423 K for 1 h in the N_2 flow, methanol or MTBE were supplied to the catalyst by the operation of a 4-way valve at 323 or 313 K, respectively. The concentration of each gas at the outlet of the reactor was monitored as a function of time with the gas chromatograph at a time interval of about 1.5 min. By comparing the concentration vs. time curve of the feed gas (methanol or MTBE) in the presence of catalyst with that of the blank experiment (in the absence of catalyst), the initial rate and the amount of absorption were estimated.

3. Results

3.1. Surface area and acid strength

Infrared spectra of these heteropolyacids were in good agreement with the literature data [26,27,32]. ^{31}P NMR of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ in D_2O gave a single peak at 12.9 ppm (with respect to 85% H_3PO_4 as an external standard), of which chemical shift is very close to that (12.7 ppm) of $\alpha\text{-H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ reported previously [33]. Furthermore, the NMR peak (in D_2O) remained unchanged after the MTBE synthesis at 323 K, indicating that the structure was retained during the reaction.

In Table 1, the surface areas of the catalysts and acid strength of the acetonitrile solution of heteropolyacids are summarized. Heteropolyacids have surface areas from 0.8 to $9 \text{ m}^2 \cdot \text{g}^{-1}$ after evacuation at 423 K, which are much lower than those of $\text{SiO}_2\text{-Al}_2\text{O}_3$, H-ZSM-5, and $\text{SO}_4^{2-}/\text{ZrO}_2$ (Table 1) [34]. The values of H_0 (Hammett acidity function) of the acetonitrile solution of heteropolyacids differ depending on the kind of

Table 1
Surface area and acid strength for various heteropolyacids

Catalyst	Surface area ^a m ² ·g ⁻¹	Acid strength ^b <i>H</i> ₀	MTBE yield ^c %
H ₆ P ₂ W ₁₈ O ₆₂	2.1	-3.6	17.5
H ₃ PW ₁₂ O ₄₀	9.0	-3.4	0.2
H ₄ SiW ₁₂ O ₄₀	9.0	-2.9	1.3
H ₄ GeW ₁₂ O ₄₀	5.3	-2.9	0.6
H ₃ BW ₁₂ O ₄₀	0.8	-1.3	<0.1
H ₅ CoW ₁₂ O ₄₀	3.4	-0.6	<0.1
SO ₄ ²⁻ /ZrO ₂	93	-	<0.1
SiO ₂ -Al ₂ O ₃	546	-	<0.1
H-ZSM5	332	-	<0.1

^a Measured after pretreatment at 423 K.

^b In acetonitrile solution. The proton concentration of the acid in the solution was 1×10^{-4} mol·dm⁻³. The concentration of dicinnamylideneacetone ($pK_a = -3.0$) was 3.5×10^{-5} mol·dm⁻³.

^c Reaction temperature: 323 K, catalyst weight: 0.5 g, total flow rate: 90 ml·min⁻¹, methanol:isobutylene:N₂ = 1:1:3.

heteropolyacids. *H*₀, a measure of the acidity, is defined by

$$H_0 = pK_a - \log \{ [BH^+] / [B] \} \quad (1)$$

when equilibrium given by



is maintained. [B] and [BH⁺] are the concentrations of the neutral and protonated forms of the indicator, respectively. Results in Table 1 show that the *H*₀ values of the heteropolyacids having the Keggin structure increase as the valency of the central atom increases from 2+ (Co) to 5+ (P) as reported previously [31]. In spite of the same valency, Si⁴⁺ and Ge⁴⁺ gave slightly different acidity. The acidity of H₆P₂W₁₈O₆₂ was close to

that of H₄GeW₁₂O₄₀, which has a moderate acidity among these heteropolyacids.

3.2. Catalytic reactions

Fig. 1 shows the time courses of the total conversion of methanol (Fig. 1a) and the yield of MTBE (Fig. 1b) at 323 K over the heteropolyacid catalysts. The total conversion of methanol is defined by $\{ (\text{flow rate of methanol at the outlet}) / (\text{flow rate of methanol at the inlet}) \} \times 100 / \%$ and the yield of MTBE by $\{ (\text{flow rate of MTBE at the outlet}) / (\text{flow rate of methanol at the inlet}) \} \times 100 / \%$. Since the selectivity to MTBE (based on methanol) was nearly 100% for all catalysts under these reaction conditions, the yield of MTBE is almost equal to the conversion of methanol to MTBE. The selectivity on the basis of isobutylene was also about 100% at the stationary state. As shown in Fig. 1a, the changes of the total conversion with the reaction time for some Keggin-type heteropolyacids are complicated. For example, for H₄SiW₁₂O₄₀ it increased once at the initial stage, and then decreased gradually with time. The stationary conversions for the Keggin-type heteropolyacids were less than 1.3%. In the case of H₆P₂W₁₈O₆₂, while the total conversion decreased rapidly at the initial stage, it was about 18% at the stationary state.

The trends of the changes in the MTBE yield with time were similar to those of the total conversions for each of the Keggin-type heteropolyacids. On the other hand, in the case of

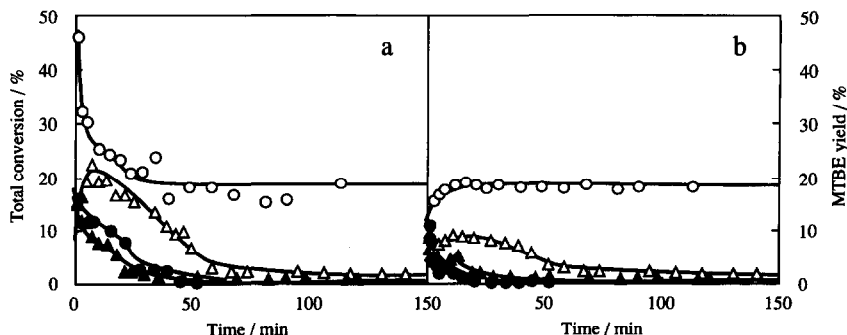


Fig. 1. Time courses of MTBE synthesis from methanol and isobutylene over heteropolyacids at 323 K; (a) total conversion of methanol, (b) yield of MTBE. (○); H₆P₂W₁₈O₆₂, (●); H₃PW₁₂O₄₀, (△); H₄SiW₁₂O₄₀, (▲); H₄GeW₁₂O₄₀. Catalyst weight: 0.5 g, methanol:isobutylene:N₂ = 1:1:3 (total flow rate: 90 ml·min⁻¹), W/F = 2.3 g·h·(mol of total feed)⁻¹.

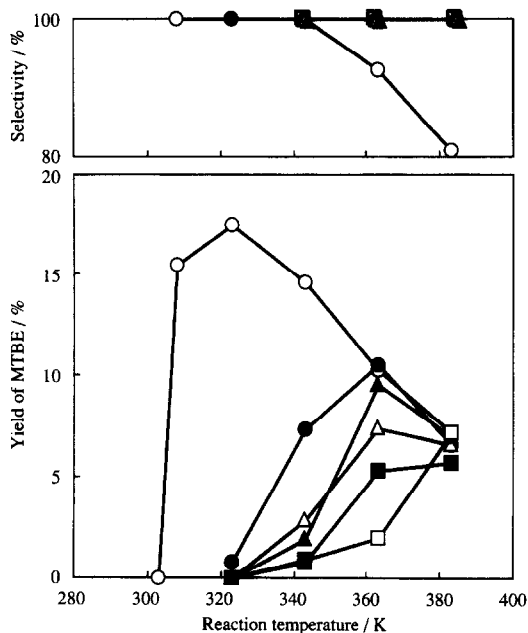


Fig. 2. Dependence of MTBE yield and selectivity on reaction temperature of MTBE synthesis; (○); $H_6P_2W_{18}O_{62}$, (●); $H_3PW_{12}O_{40}$, (△); $H_4SiW_{12}O_{40}$, (▲); $H_4GeW_{12}O_{40}$, (□); $H_3BW_{12}O_{40}$, (■); $H_6CoW_{12}O_{40}$. Catalyst weight: 0.5 g, methanol:isobutylene: $N_2 = 1:1:3$ (total flow rate: 90 ml min^{-1}).

$H_6P_2W_{18}O_{62}$, the yield was nearly independent of time after the increase at the initial stage. It was appreciable that at the initial stage of the reaction the yields were significantly low as compared with the total conversions for all cases. Since the selectivities (for both methanol and isobutylene) were nearly 100% for all cases, the difference between the total conversion and yield is due to the uptake of methanol by the catalyst. As will be discussed below in detail, methanol is readily absorbed into the bulk phase of these heteropolyacids.

In Fig. 2, temperature dependency of the MTBE yield is given. In these experiments, the reaction was first performed at 383 K and then the temperature was decreased after the reaction reached the stationary state (after about 1 h) at each temperature. All data were collected after 1 h of the reaction. The Keggin-type heteropolyacids showed appreciable activities only above 343 K. On the other hand, $H_6P_2W_{18}O_{62}$ gave a high MTBE yield even at 308 K. Equilibrium conversions under these reaction conditions are estimated by the equilibrium constant [35] and the

partial pressures to be 66, 43, 22, and 9% for 323, 343, 363, and 383 K, respectively. Thus the reaction reached the equilibrium only at 383 K in this catalytic system. The selectivity based on methanol was about 100% for Keggin-type heteropolyacids at these temperatures, while that for $H_6P_2W_{18}O_{62}$ decreased above 363 K. The selectivity on the basis of isobutylene was about 100% for all catalysts at the stationary state. In the cases of other solid acids such as $SiO_2-Al_2O_3$, H-ZSM-5, and SO_4^{2-}/ZrO_2 , the conversions were less than 0.1% at 323 K from the initial stage of the reaction (Table 1) [20].

Fig. 3 shows the changes in the total conversion for $H_6P_2W_{18}O_{62}$ upon the variation of the reaction temperature. In these experiments the data were collected after the reaction reached approximately the stationary state at each temperature. The MTBE yield gave a nearly constant value at each temperature, irrespective of the reaction history. Fig. 4 gives the W/F dependence of total conversion (based on methanol) at the stationary state for $H_6P_2W_{18}O_{62}$ at 323 K, where W is the catalyst weight and F is the total flow rate. The conversion increased linearly as W/F increased up to about $4 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$. Hence, the comparison of the catalytic activity was made in this range of the W/F . For $W/F > 4 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$, the conversion increased only slightly. Since the equilibrium conversion was estimated to be 66% at 323 K [35],

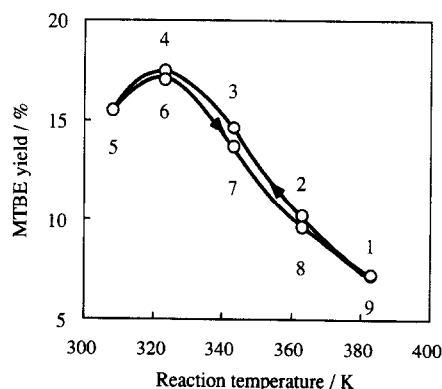


Fig. 3. Changes in the conversion of methanol for MTBE synthesis over $H_6P_2W_{18}O_{62}$ upon variation of reaction temperature; Catalyst weight: 0.5 g, methanol:isobutylene: $N_2 = 1:1:3$ (total flow rate: $90 \text{ ml} \cdot \text{min}^{-1}$). The sequence of the run is shown by the number in the figure.

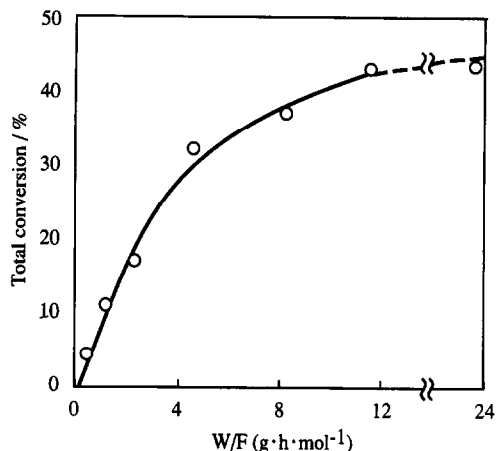


Fig. 4. W/F dependence of the conversion of methanol for MTBE synthesis over $H_6P_2W_{18}O_{62}$ at 323 K; Catalyst weight: 0.1–2.0 g, flow rate: 30–180 ml·min⁻¹, methanol:isobutylene: N_2 = 1:1:3.

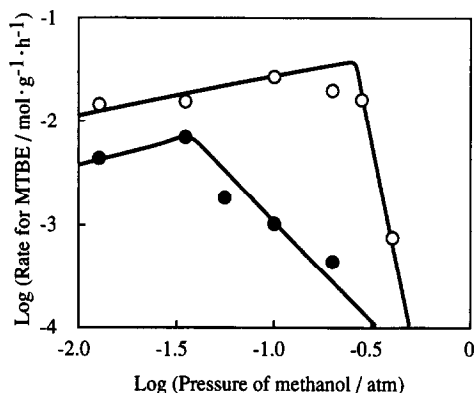


Fig. 5. Dependence of rate for MTBE synthesis on methanol pressure at 323 K; (○); $H_6P_2W_{18}O_{62}$, (●); $H_3PW_{12}O_{40}$. Catalyst weight: 0.1 g, total flow rate: 90 ml·min⁻¹.

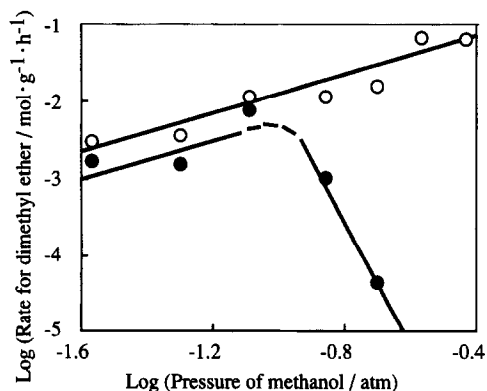


Fig. 6. Pressure dependence for dehydration of methanol at 423 K; (○); $H_6P_2W_{18}O_{62}$, (●); $H_3PW_{12}O_{40}$. Catalyst weight: 0.5 g, total flow rate: 100 ml·min⁻¹.

the slight increase in the conversion at the higher W/F is not only due to the limitation by the thermodynamic equilibrium.

Dependence of the reaction rate on the methanol partial pressure is shown in Fig. 5. For both $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$, the rates increased at first, and then decreased rapidly with increasing the methanol pressure. However, the maximum rate was observed at a higher pressure for $H_6P_2W_{18}O_{62}$ than for $H_3PW_{12}O_{40}$. In addition, $H_6P_2W_{18}O_{62}$ was always more active than $H_3PW_{12}O_{40}$ in this pressure range. Fig. 6 shows the pressure dependence for methanol dehydration at 423 K. For $H_3PW_{12}O_{40}$, as the partial pressure increased, the rate increased at first, and then decreased greatly. This change is similar to that of the MTBE synthesis shown in Fig. 5. On the other hand, the reaction rate over $H_6P_2W_{18}O_{62}$ continued to increase with the partial pressure in this pressure range. It is also noted that $H_6P_2W_{18}O_{62}$ was much more active than $H_3PW_{12}O_{40}$ at higher pressures. It was confirmed that the activity of $H_6P_2W_{18}O_{62}$ was more than 100 times that of $\gamma-Al_2O_3$ at 423 K and 0.2 atm of methanol.

3.3. Absorption of methanol or MTBE

The typical transient behavior observed for the absorption of methanol by $H_6P_2W_{18}O_{62}$ and

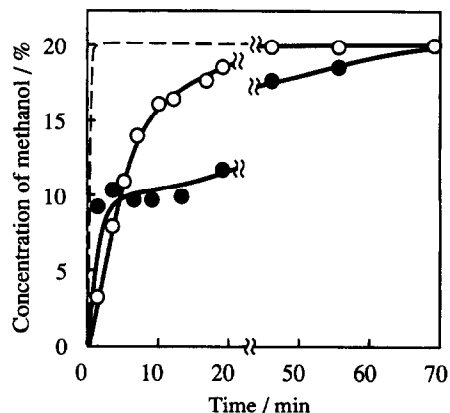


Fig. 7. Typical transient behavior of methanol concentration during absorption of methanol in heteropolyacids at 323 K; (○); $H_6P_2W_{18}O_{62}$ (1.8 g), (●); $H_3PW_{12}O_{40}$ (2.6 g). Methanol: N_2 = 1:4, flow rate: 100 ml·min⁻¹. The broken line shows the transient behavior of methanol concentration at the outlet of the reactor when methanol was fed in the absence of catalyst (blank experiment).

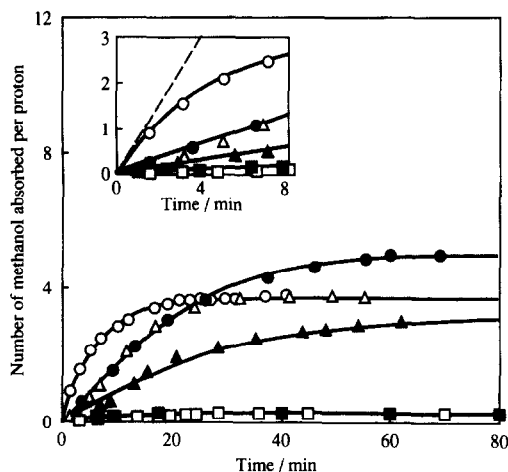


Fig. 8. Time courses of methanol absorption (or adsorption) in (or on) heteropolyacids at 323 K; (○); $H_6P_2W_{18}O_{62}$, (●); $H_3PW_{12}O_{40}$, (△); $H_4SiW_{12}O_{40}$, (▲); $H_4GeW_{12}O_{40}$, (□); $H_3BW_{12}O_{40}$, (■); $H_6CoW_{12}O_{40}$. Methanol: N_2 = 1:4, flow rate: $100 \text{ ml} \cdot \text{min}^{-1}$. The broken straight line shows the amount of methanol absorption expected when 100% of methanol was absorbed in $H_6P_2W_{18}O_{62}$.

Table 2
Amounts and rate of absorption of methanol and MTBE for various heteropolyacids

Catalyst	Amounts ^a		Rate ^b	
	MeOH	MTBE	MeOH	MTBE
$H_6P_2W_{18}O_{62}$	3.8 (270)	1.5 (190)	3.3	1.30
$H_3PW_{12}O_{40}$	5.0 (66)	2.5 (62)	0.6	0.08
$H_4SiW_{12}O_{40}$	3.7 (63)	0.03 (1)	0.5	<0.01
$H_4GeW_{12}O_{40}$	3.0 (84)	0.05 (3)	0.3	0.06
$H_3BW_{12}O_{40}$	0.3 (76)	0.03 (13)	0.1	<0.01
$H_6CoW_{12}O_{40}$	0.3 (17)	<0.01	0.2	<0.01

^a Numbers of the molecules absorbed per proton in the presence of methanol (152 Torr at 323 K) or MTBE (100 Torr at 313 K). The figures in the parentheses are the numbers of surface layer (see text).

^b Absorption rate ($\text{mol} \cdot (\text{cat} \cdot \text{mol})^{-1} \cdot \text{min}^{-1}$) after 1.5 min for methanol or for MTBE.

Table 3
Absorption amounts of methanol for various heteropolyacids during MTBE synthesis at 323 K

Catalyst	Amounts of methanol ^a
$H_6P_2W_{18}O_{62}$	1.0
$H_3PW_{12}O_{40}$	3.5
$H_4SiW_{12}O_{40}$	3.6
$H_4GeW_{12}O_{40}$	2.7

^a Numbers of methanol absorbed (as methanol or MTBE) per proton. Methanol:isobutylene: N_2 = 1:1:3.

$H_3PW_{12}O_{40}$ is given in Fig. 7. The concentration of methanol at the outlet is plotted against the feed time. The lower concentration for $H_6P_2W_{18}O_{62}$ than for $H_3PW_{12}O_{40}$ at the initial stage shows that the initial absorption rate is greater for $H_6P_2W_{18}O_{62}$. The area between the blank curve and the curve obtained in the presence of catalyst corresponds to the absorption amount. The absorption amounts calculated from data as in Fig. 7 are plotted in Fig. 8 as a function of the feed time. The ordinate is the amount expressed by the unit of the number of molecule per proton of the whole bulk of heteropolyacid. Except for $H_5BW_{12}O_{40}$ and $H_6CoW_{12}O_{40}$, large amounts of methanol were absorbed. For example, the amount absorbed in $H_3PW_{12}O_{40}$ at 70 min was about five methanol molecules per proton, which corresponds to about 70 surface layers [20,36]. The initial rate of absorption, which is defined by the amount of methanol absorbed in the initial 1.5 min, depends greatly on the kind of heteropolyacid (the inset of Fig. 8). The initial rate of absorption for $H_6P_2W_{18}O_{62}$ was the highest.

In Table 2, the amounts of absorption and the initial rate are summarized. The absorption of methanol or MTBE for $H_6P_2W_{18}O_{62}$ was at least 5 times more rapid than those for the Keggin-type heteropolyacids. Absorption of MTBE was also appreciable for $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$. The absorption amounts of methanol under the reaction conditions (Fig. 1) are given in Table 3, which were calculated from the differences between the total conversion and the MTBE yield. In this case, whether methanol exists as methanol itself or MTBE in the bulk cannot be differentiated. The amount of methanol absorbed in $H_6P_2W_{18}O_{62}$ was about one molecule per proton. This value was smaller than that observed when only methanol was introduced. In the latter case the value was about four molecules per proton (Table 2). On the other hand, $H_3PW_{12}O_{40}$ absorbed about four molecules per proton during the reaction (Table 3), which is close to that observed with methanol only (about five molecules per proton) (Table 2).

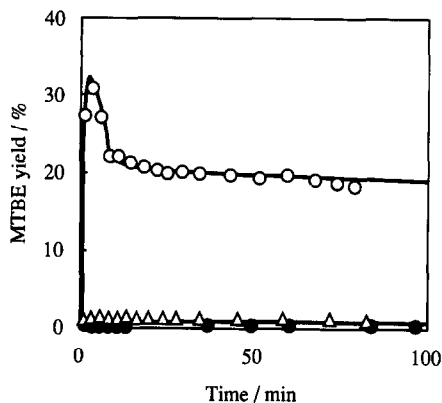


Fig. 9. Time courses of MTBE yield for the reaction of methanol with isobutylene at 323 K over heteropolyacids preabsorbing about three molecules of methanol per proton; (\circ); $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 18\text{CH}_3\text{OH}$, (\bullet); $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 9\text{CH}_3\text{OH}$, (\triangle); $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 12\text{CH}_3\text{OH}$. Catalyst weight: 0.5 g, methanol:isobutylene: $\text{N}_2 = 1:1:3$ (total flow rate: 90 ml min^{-1}).

In order to examine the influence of methanol absorbed in the bulk on the catalytic behavior, the MTBE synthesis was carried out using typical heteropolyacids preabsorbing about three methanol molecules per anion. At the first stage, only methanol (0.2 atm with N_2 balance) was fed at 323 K to obtain heteropolyacids absorbing about three molecules of methanol per proton. Then the feed gas was switched to the reactant mixture. The time courses of the reaction are shown in Fig. 9. Clear difference between the Dawson and the Keggin-type heteropolyacids in the formation of MTBE was found. $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ showed as usual the high MTBE yield after the slight decrease at the initial stage of the reaction. The stationary activity was very close to that in Fig. 1. Desorption of methanol from the bulk was evidenced at the initial stage from the carbon balance in the gas phase. That is, the reaction in this case reached the stationary state after a part of preabsorbed methanol was desorbed. Contrary to this, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ gave less than about 1% of the MTBE yield from the initial stage of the reaction without such desorption of preabsorbed methanol.

4. Discussion

4.1. Effect of acid strength

Fig. 1 and Table 1 demonstrate that the Dawson-type heteropolyacid, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, is an effi-

cient catalyst for this reaction at 323 K; the stationary catalytic activity (per unit weight) of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ at 323 K was 13, 90 and 170 times those of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and $\text{H}_5\text{BW}_{12}\text{O}_{40}$. Furthermore, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ was far superior to H-ZSM-5, $\text{SO}_4^{2-}/\text{ZrO}_2$, and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Table 1). The low activity of H-ZSM-5 at 323 K is consistent with the data in the literature [5,6]. The superiority of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ to Keggin-type heteropolyacids has already been reported by Kozhevnikov et al. in homogeneous liquid-phase synthesis [17]. However, in this case the difference in the activity between Dawson-type and Keggin-type was small (less than 2.7 times per weight). For the decomposition of isobutyl propionate in homogeneous liquid-phase, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ was reported to be much less active than $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [26]. Hence much higher activity of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ found in this study is remarkable.

It is generally accepted in acid-catalyzed reactions that the acid strength is an important factor in determining the catalytic activity. The acid strength of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ measured in acetonitrile solution was lower than those of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (Table 1). The order of the acid strength obtained in the present study is in good agreement with that in the solid state measured by absorption calorimetry of NH_3 : $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ [37]. Therefore, the activity for this reaction is not governed only by the acid strength. The surface area of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is $2 \text{ m}^2 \cdot \text{g}^{-1}$, which is less than those of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (Table 1), showing that the high activity of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is not due to the surface area. Another acidic property to be considered is the acid amount. This is closely related to the reaction field, i.e., pseudoliquid phase as will be described below. If the bulk phase is the reaction field, there is not large difference in the acid amount among these heteropolyacids.

4.2. Pseudoliquid phase behavior

'Pseudoliquid phase behavior' is a unique concept for heteropolyacid proposed by us in 1979

and the behavior often brings about high catalytic activity of heteropolyacid [10,11]. Polar molecules like alcohols are readily absorbed into the solid bulk expanding the distance between the polyanions. By this, solid heteropoly compounds absorbing a significant amount of polar molecules behave in a sense like a concentrated solution, and the reaction takes place in the solid bulk. We called this state 'pseudoliquid phase'. Since methanol is known to be readily absorbed into the bulk of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [36,38], it is plausible that these heteropolyacids work in the state of pseudoliquid phase. As a matter of fact, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, etc. absorb large amounts of methanol under the reaction conditions (Table 3), indicating that the reaction takes place in the pseudoliquid phase.

The unique pressure dependency for the MTBE synthesis (Fig. 5), which is very similar to that observed for dehydration of ethanol [39], strongly supports the involvement of the pseudoliquid phase behavior. This pressure dependence is unique and not observed for this reaction over ordinary solid acids. In the case of $\text{TiO}_2\text{-SiO}_2$, the pressure dependence of methanol for this reaction was explained by Langmuir-type adsorption of methanol [9]. Therefore, the unique pressure dependencies are very probably brought about by the pseudoliquid phase. As stated above, the change in the rate upon the methanol pressure (Fig. 5) resembles those of the dehydration of ethanol over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the solid bulk [39]. The essential trend in the ethanol dehydration was explained by the changes in the concentration of the intermediates, the protonated ethanols [39]. Thus in this case, the decreases in the rate at the higher pressures are probably due to the formation of inactive protonated methanol oligomers $[(\text{CH}_3\text{OH})_n\text{H}^+ (n > 3)]$, which is a proton solvated by excess methanol.

One question may arise that isobutylene is a non-polar molecule, and ordinarily such a molecule is not absorbed into the bulk [36,38]. If one considers that isobutylene is absorbed into the aqueous solutions of heteropolyacid [40], it may be possible that isobutylene is absorbed into the

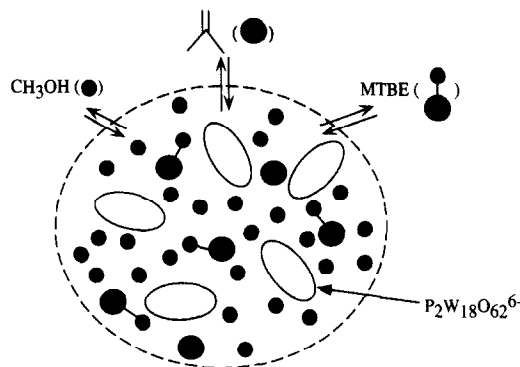


Fig. 10. Model of pseudoliquid phase for MTBE synthesis with $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$.

pseudoliquid phase. The pseudoliquid phase containing a significant amount of methanol may enhance the absorption due to the organophilic interaction. A model of the pseudoliquid phase for this reaction system is illustrated in Fig. 10.

The difference in the activity between $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can be explained on the basis of the pseudoliquid phase behavior. In the dehydration of 2-propanol at 353 K, there are at least two discrete pseudoliquid phases of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ differing in the amount of 2-propanol absorbed and also in the catalytic activity [10,41]. The high-activity state corresponds to the pseudoliquid phase having a small amount of the reactant molecule (about one molecule of 2-propanol per proton) and the low-activity state absorbing a large amount of the molecules (about three molecules per proton). As shown in Table 3, during the MTBE synthesis at 323 K, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ absorbs about four molecules of methanol per proton, while the absorption amounts of methanol for $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ was only one molecule per proton. Therefore under the reaction conditions (323 K and 0.2 atm of methanol), it is considered that $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is in the high-activity state, but $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the low-activity state. The pressure dependencies in Fig. 5 indicate that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is in the low-activity state and $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is still in the high-activity state at 0.2 atm ($\log(0.2 \text{ atm}) = -0.7$) of methanol. It is also shown in Fig. 5 that the high-activity state transforms to the low-activity state by the increase in the methanol pressure to 0.4 atm ($\log(0.4 \text{ atm}) = -0.4$). The

different pseudoliquid phases are also suggested for the dehydration of methanol which is shown in Fig. 6. The rapid decrease in the rate occurred at about 0.1 atm over $\text{H}_3\text{PW}_{12}\text{O}_{40}$, while the rate over $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ continued to increase. This indicates that the high-activity state of the pseudoliquid phase is kept for $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ throughout this pressure range.

Characteristic time courses of the reaction (Fig. 1) presumably reflect the transient periods until stationary pseudoliquid phases are reached. This is mainly caused by the absorption of methanol as described below. For example, in the case of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, the formation of pseudoliquid phase absorbing mainly methanol occurs at the initial stage and accelerates the reaction. Then it transforms into the low-activity state at the later stage of the reaction by absorbing a large amount of methanol. In the case of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, the high-activity state is formed at the initial stage by the rapid absorption of methanol. But it does not transform into the low-activity state. The absorption amount of methanol is in the order, $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} \approx \text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} > \text{H}_4\text{GeW}_{12}\text{O}_{40} \gg \text{H}_5\text{BW}_{12}\text{O}_{40} \approx \text{H}_6\text{CoW}_{12}\text{O}_{40}$ (Table 2). This is consistent with that of the acid strength. As already reported [36], the acid strength governs the amount of methanol absorbed. The low amount of methanol absorbed keeps the high-activity state for $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$.

Another remarkable characteristic of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is that the absorption rate was the highest among the heteropolyacids (Table 2). Since the absorption rate in the bulk of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is primarily determined by the basicity (or polarity) of molecule [36], the rate of methanol into heteropolyacids may also be governed by their acid strength. However, the order of the rate was $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \gg \text{H}_3\text{PW}_{12}\text{O}_{40} \approx \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_4\text{GeW}_{12}\text{O}_{40} > \text{H}_6\text{CoW}_{12}\text{O}_{40} > \text{H}_5\text{BW}_{12}\text{O}_{40}$ (Table 2), which is different from that of the acid strength. The results of MTBE absorption was essentially the same as that of methanol. If one considers that methanol is absorbed by changing the secondary structure to some extent or the distance between the polyanion lattice

[10,11,36,38], the strength of the interaction between the polyanions or the flexibility of the secondary structure may be another factor in determining the absorption rate. The shape of Dawson-type heteropolyanion is not spherical as that of Keggin-type, so that the secondary structure of Dawson may be less ordered and rigid, although evidence to confirm this is necessary. Nonetheless, it can be concluded that the high-activity state of pseudoliquid and the rapid absorption–desorption are the reasons for the high activity of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$.

Recently, Kogelbauer et al. observed that about 2.5 molecules of methanol were adsorbed per acid site on HZSM-5 and HY zeolites, while isobutylene formed a 1:1 adsorption complex. They attributed the high selectivity of zeolites to the excess methanol adsorption on acid sites [42]. Therefore, it is very probable that the pseudoliquid phase behavior of these heteropolyacids, in which the protons are solvated by methanol, plays a key role in the high selectivity for MTBE suppressing the dimerization of isobutylene, and the adequate amount of methanol absorption for the Dawson-type heteropolyacid brings about its high catalytic activity.

Acknowledgements

The present work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

- [1] K.W. Otto, *Oil Gas J.*, 37, Jan. 11 (1993).
- [2] A. Rehfinger and U. Hoffmann, *Chem. Eng. Sci.*, 45 (1990) 1605.
- [3] T. Nishina, *Shokubai (Catalyst)*, 36 (1994) 186.
- [4] T. Deguchi, *Petrotech*, 15 (1992) 874.
- [5] A.A. Nikolopoulos, A. Kogelbauer, J.G. Goodwin, Jr. and G. Marcelin, *Appl. Catal. A*, 119 (1994) 69.
- [6] R. Le Van Mao, R. Carli, H. Ahlafi and V. Ragaini, *Catal. Lett.*, 6 (1990) 321.
- [7] P. Chu and G.H. K uhl, *Ind. Eng. Chem. Res.*, 26 (1987) 365.

- [8] A. Kogelbauer, M. Ocal, A.A. Nikolopoulos, J.G. Goodwin, Jr. and G. Marcelin, *J. Catal.*, 148 (1994) 157.
- [9] K.H. Chang, G.J. Kim and W.S. Ahn, *Ind. Eng. Chem. Res.*, 31 (1992) 125.
- [10] M. Misono, *Catal. Rev.-Sci. Eng.*, 29 (1987) 269; 30 (1988) 339.
- [11] M. Misono, *Proc. 10th Int. Congr. Catal.*, 1992, Budapest, Akademiai Kiado, 1993, Part A, p. 69.
- [12] I.V. Kozhevnikov, *Russ. Chem. Rev.*, 56 (1987) 811.
- [13] Y. Ono, in J.M. Thomas and K.I. Zamaraev (Eds.), *Perspectives in Catalysis*, Blackwell, London, 1992, p. 431.
- [14] Y. Izumi, K. Urabe and M. Onaka, *Zeolite, Clay and Heteropolyacid in Organic Reactions*, Kodansha-VCH, Tokyo-Weinheim, 1992.
- [15] J.B. Moffat, in J. Fraissard and L. Petrakis (Eds.), *Acidity and Basicity of Solids*, Kluwer Academic Publishers, 1994, p. 217.
- [16] M. Misono and N. Nojiri, *Appl. Catal.*, 64 (1990) 1.
- [17] G.M. Maksimov and I.V. Kozhevnikov, *React. Kinet. Catal. Lett.*, 39 (1989) 317.
- [18] A. Igarashi, T. Matsuda and Y. Ogino, *Sekiyu Gakkaishi*, 22 (1979) 331.
- [19] Y. Ono and T. Baba, *Proc. 8th Int. Congr. Catal.*, Berlin, 1984, Vol. 5, Verlag Chemie-Dechema, Weinheim, 1984, p. 405.
- [20] S. Shikata, T. Okuhara and M. Misono, *Sekiyu Gakkaishi*, 37 (1994) 632.
- [21] G.D. Yadav and N. Kirthivasan, *J. Chem. Soc., Chem. Commun.*, 1995, 203.
- [22] J.S. Kim, J.M. Kim, G. Seo, N.C. Park and H. Niiyama, *Appl. Catal.*, 37 (1988) 45.
- [23] Y. Saito, H. Niiyama and E. Echigoya, *Nippon Kagaku Kaishi*, 1984, 391.
- [24] K. Sugiyama, K. Kato, H. Miura and T. Matsuda, *Sekiyu Gakkaishi*, 26 (1983) 243.
- [25] H. Wu, *J. Biol. Chem.*, 43 (1920) 189.
- [26] C. Hu, M. Hashimoto, T. Okuhara and M. Misono, *J. Catal.*, 143 (1993) 437.
- [27] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, 22 (1983) 207.
- [28] P. Souchay, *Bull. Soc. Chim. Fr.*, 18 (1951) 365.
- [29] L.C.W. Baker and T.P. McCutcheon, *J. Am. Chem. Soc.*, 78 (1956) 4503.
- [30] M. Hino and K. Arata, *React. Kinet. Catal. Lett.*, 19 (1982) 101.
- [31] T. Okuhara, C. Hu, M. Hashimoto and M. Misono, *Bull. Chem. Soc. Jpn.*, 67 (1994) 1186.
- [32] C. Rocchiccioli-Deltcheff and R. Thouvenot, *Spectrosc. Lett.*, 12 (1979) 127.
- [33] R. Massart, R. Contant, J.M. Fruchart, J.P. Ciabrini and M. Fournier, *Inorg. Chem.*, 16 (1977) 2916.
- [34] T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, *J. Mol. Catal.*, 74 (1992) 247.
- [35] J. Tejero, F. Cunill and J.F. Izquierdo, *Ind. Eng. Chem. Res.*, 27 (1988) 338.
- [36] T. Okuhara, S. Tatematsu, K.Y. Lee and M. Misono, *Bull. Chem. Soc. Jpn.*, 62 (1989) 717.
- [37] F. Lefebvre, F.X. Liu-Cai and A. Auroux, *J. Mater. Chem.*, 4 (1994) 125.
- [38] M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, 55 (1982) 400.
- [39] K.Y. Lee, T. Arai, S. Nakata, S. Asaoka, T. Okuhara and M. Misono, *J. Am. Chem. Soc.*, 114 (1992) 2836.
- [40] A. Aoshima, S. Yamamatsu and T. Yamaguchi, *Nippon Kagaku Kaishi*, 1987, 976.
- [41] K. Takahashi, T. Okuhara and M. Misono, *Chem. Lett.*, 1985, 841.
- [42] A. Kogelbauer, A.A. Nikolopoulos, J.G. Goodwin, Jr. and G. Marcelin, *J. Catal.*, 152 (1995) 122.