# Catalysis by Heteropoly Compounds. 32. Synthesis of Methyl *tert*-Butyl Ether Catalyzed by Heteropolyacids Supported on Silica[1]

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**Gas phase synthesis of methyl *tert*-butyl ether (MTBE) from methanol and isobutylene has been studied by using silica-supported heteropolyacids. The activity of a Dawson-type tungstophosphoric acid, $H_6P_2W_{18}O_{62}/SiO_2$, was comparable to that of a sulfonated polymer resin, Amberlyst 15, and the selectivity was higher than that of Amberlyst 15. A Keggin-type heteropolyacid, $H_3PW_{12}O_{40}/SiO_2$, was also efficient for this reaction, while unsupported $H_3PW_{12}O_{40}$ was much less active than unsupported $H_6P_2W_{18}O_{62}$. Calorimetry of $NH_3$ absorption revealed that the difference in acid strength between $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$ was large, but the difference between the two became smaller when they were supported. This partly explains the similar activities of the two supported heteropolyacids. By supporting $H_6P_2W_{18}O_{62}$ on $SiO_2$, the MTBE selectivity on the basis of methanol increased, but the selectivity on the basis of isobutylene decreased, which was reasonably explained by the decrease of the relative contribution of pseudoliquid phase reaction to the surface reaction by supporting. The pressure dependency on methanol for $H_6P_2W_{18}O_{62}/SiO_2$ was close to that of unsupported $H_6P_2W_{18}O_{62}$, but it much differed from those of ordinary solid acids like $SO_4^{2-}/ZrO_2$ and H-ZSM-5, showing that MTBE synthesis proceeds in the pseudoliquid phase of $H_6P_2W_{18}O_{62}/SiO_2$.** © 1997 Academic Press

## INTRODUCTION

Methyl *tert*-butyl ether (MTBE) is regarded to be a nonpolluting gasoline additive and a good octane-number enhancer (1). At present, MTBE is commercially produced by a liquid phase reaction from methanol and isobutylene (2-methylpropene) catalyzed by sulfonated poly (styrene-divinylbenzene), Amberlyst 15 (1–4). But this catalyst is not stable above 373 K, and the acid groups are gradually lost from the polymer network to decrease the activity. Hence,

a new acid catalyst having high thermal stability is desirable (5). There are several reports about MTBE synthesis using various solid catalysts (6–10), but they do not have enough activity for the practical use.

Heteropolyacids are efficient catalysts for various acid-catalyzed reactions and are useful in practical application (11–17). There are some reports about MTBE synthesis from methanol and isobutylene using heteropoly compounds (18–23). In the homogeneous liquid-phase reaction of methanol and isobutylene, Maksimov and Kozhevnikov (18) reported that a Dawson-type heteropolyacid, $H_6P_2W_{18}O_{62}$, was 2.7 times more active (per unit weight) than Keggin-type heteropolyacid, $H_3PW_{12}O_{40}$.

In the gas phase synthesis, $SiO_2$-supported heteropolyacids such as 20 wt% $H_4SiMo_{12}O_{40}/SiO_2$ were reported to be active and selective, as compared with mixed metal oxides, fluorinated oxides, and mounted mineral acids (19). Ono and Baba claimed that carbon-supported $Ag_3PW_{12}O_{40}$ catalyzed this reaction (20). Recently, Yadav and Kirthivasan (21) found that $H_3PW_{12}O_{40}$ supported on K-10 (a modified clay) was active. Heteropolyacids were also used for MTBE synthesis from methanol and *tert*-butyl alcohol (24–26). The conversion of *tert*-butyl alcohol was correlated with the acidity measured by pyridine absorption (24).

The authors previously reported that the activity of the Dawson-type heteropolyacid ($H_6P_2W_{18}O_{62}$) for the gas phase synthesis was at least 13 times greater than those of Keggin-type heteropolyacids ($H_nXW_{12}O_{40}$, $X$ = P, Si, Ge, B, and Co), and more than 170 times those of $SO_4^{2-}/ZrO_2$, H-ZSM-5, and $SiO_2$–$Al_2O_3$ (22). We also found that the activity of $H_6P_2W_{18}O_{62}$ was greatly enhanced by supporting it on $SiO_2$ (23).

In the present study, it has been attempted to elucidate the catalytic features of silica-supported heteropolyacids by comparing them with Amberlyst 15 and other solid catalysts. For this purpose, the pressure dependency, the effects of the loading amount, and the change in the acidity of these catalysts caused by the supporting have been examined.

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## EXPERIMENTAL

### Materials

H₆P₂W₁₈O₆₂ · nH₂O (Dawson-type heteropolyacid) and H$_n$XW$_{12}$O$_{40}$ · nH₂O (X = P, Si, Ge, B, and Co) (Keggin-type heteropolyacids) were synthesized according to the literature (22, 27). The structures of these heteropoly-acids were confirmed by IR spectroscopy (27) and NMR spectroscopy (28). Silica-supported heteropolyacids (abbreviated as, e.g., $P_2W_{18}/SiO_2$ and $PW_{12}/SiO_2$ for $H_6P_2 \cdot W_{18}O_{62}$ and $H_3PW_{12}O_{40}$, respectively) were prepared by an impregnation of $SiO_2$ (Davison Chemical, G-62, 253 m² · g⁻¹) with an aqueous solution of heteropoly-acid (0.1 mol · dm⁻³). The loading amounts were changed from 20 to 75 wt%. 20 wt% $P_2W_{18}/SiO_2$, for example, means $H_6P_2W_{18}O_{40}/(H_6P_2W_{18}O_{40} + SiO_2) = 0.2$ in weight. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5-salt) was prepared from an aqueous solution of $Cs_2CO_3$ and the aqueous solution of $H_3PW_{12}O_{40}$ (29). $SO_4^{2-}/ZrO_2$, H-ZSM-5, and $SiO_2$– $Al_2O_3$ were obtained according to the previous report (22).

### Other Measurements

Acid strength of catalyst was measured by calorimetry of NH₃ absorption with a microcalorimeter (Tokyo Rikou Co., Ltd., HAC-450G). The catalysts (about 1.5 g) were pretreated in vacuum at 473 K for 4 h prior to the absorption of NH₃ (Sumitomo Seika Chemicals Co., Ltd. >99.99%) and the heat of absorption was measured at 423 K. The NH₃ gas was successively dosed to the catalyst with the pulse size of about 40 $\mu$mol.

### Catalytic Reactions

The reaction was performed in a flow reactor (Pyrex tube, 12 mm inside diameter) at atmospheric pressure in the temperature range from 303 to 383 K. Methanol which was dried with molecular sieve 3A was supplied from a saturator kept at 313 K. Prior to the reaction, the heteropolyacid catalysts were pretreated at 423 K in a flow of N₂ for 1 h. $SiO_2$–$Al_2O_3$, H-ZSM-5, and $SO_4^{2-}/ZrO_2$ were pretreated at 673, 723, and 723 K, respectively, in the N₂ flow. Usually, a mixture of methanol and isobutylene and N₂ (balance) (90 ml · min⁻¹) with a volume ratio of 1 : 1 : 3 was fed to 0.1 g (at 323 K) and 0.5 g (at 383 K) of catalyst (W/F = 0.46 and 2.31 g · h · (mol of feed)⁻¹, respectively). The flow rate of each gas was precisely controlled by mass flow controllers (MODEL DPM-3, KOFLOC). The gas at the outlet of the reactor was 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)). Yield and selectivity of MTBE are defined as follows in the present study:

### Yield of MTBE,

$$100 \times \{(\text{flow rate of MTBE at the outlet})\}/$$
$$\{(\text{flow rate of methanol at the inlet})\}/\%. \quad [1]$$

### Selectivity of MTBE on the basis of methanol,

$$100 \times \{(\text{flow rate of MTBE at the outlet})\}/$$
$$\{(\text{flow rate of MTBE at the outlet})$$
$$+ 2 \times (\text{flow rate of dimethyl ether at the outlet})\}/\%. \quad [2]$$

### Selectivity of MTBE on the basis of isobutylene,

$$100 \times \{(\text{flow rate of MTBE at the outlet})\}/$$
$$\{(\text{flow rate of MTBE at the outlet})$$
$$+ 2 \times (\text{flow rate of isooctene at the outlet})\}/\%. \quad [3]$$

Ordinarily, the data of yields and selectivities were collected at the stationary state which was usually attained after 2 h of the reaction.

## RESULTS

Figure 1 shows the changes of yield and selectivity as a function of the reaction temperature for 20 wt% $P_2W_{18}/SiO_2$ and Amberlyst 15. Broken line in Fig. 1a indicates the equilibrium (30). 20 wt% $P_2W_{18}/SiO_2$ gave a yield comparable to that of Amberlyst 15. The selectivity (isobutylene basis) (Fig. 1b) and selectivity (methanol basis) (Fig. 1c) were nearly 100% below 343 K for the two catalysts. On the other hand, above 363 K, both selectivities were higher for 20 wt% $P_2W_{18}/SiO_2$ than for Amberlyst 15. It is noted that the selectivity (methanol basis) reached about 99% at 383 K for 20 wt% $P_2W_{18}/SiO_2$.

The time courses of yield and selectivity (isobutylene basis) are given in Fig. 2. After 2 h at 323 K, both catalysts showed stationary yields. The selectivity at 323 K was about 100% from the initial stage of the reaction. On the other hand, the selectivity at 383 K increased with time at the initial stage of the reaction. As for the selectivity on the basis of methanol, both catalysts showed about 100% selectivity.

The yields and selectivities for various solid catalysts are summarized in Table 1. At 323 K, 20 wt% $P_2W_{18}/SiO_2$, 20 wt% $PW_{12}/SiO_2$, 20 wt% $SiW_{12}/SiO_2$, and 20 wt% $GeW_{12}/SiO_2$ exhibited more than 25% yields, which are comparable to that observed for Amberlyst 15. The yields of supported heteropolyacids were much higher than those of unsupported heteropolyacids. $SO_4^{2-}/ZrO_2$, $SiO_2$–$Al_2O_3$, and H-ZSM-5 were inactive at 323 K. No dimethyl ether was detected for all heteropolyacids and Amberlyst 15, which is consistent with the near 100% -selectivity on the basis of methanol (Table 1) at 323 K. At 383 K, 20 wt% $P_2W_{18}/SiO_2$, 20 wt% $GeW_{12}/SiO_2$, and 20 wt% $CoW_{12}/SiO_2$ showed more than 13% yields. Selectivities on the basis of
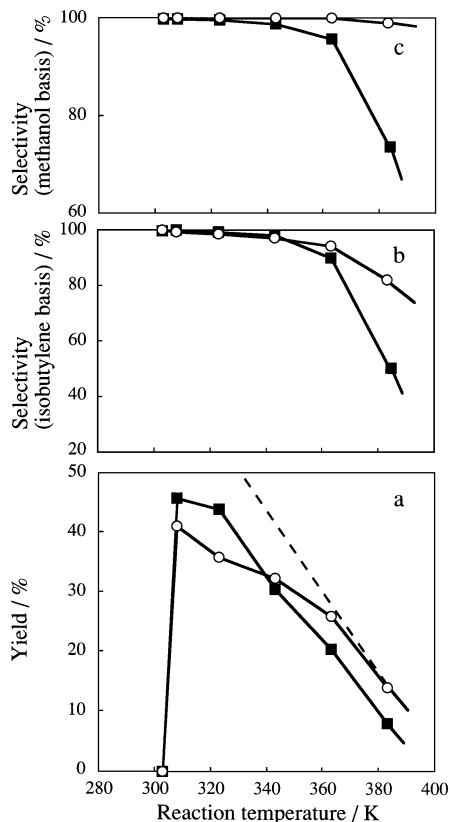
**FIG. 1.** Dependencies of yield and selectivity on reaction temperature for MTBE synthesis: (a) yield of MTBE; (b) selectivity of MTBE on the basis of isobutylene; (c) selectivity of MTBE on the basis of methanol. ○, 20 wt% $H_6P_2W_{18}O_{62}/SiO_2$; ■, Amberlyst 15. Catalyst weight: 0.5 g, methanol : isobutylene : $N_2 = 1 : 1 : 3$, total flow rate: 90 ml · $min^{-1}$. Broken line shows the equilibrium value (30).

methanol for silica-supported heteropolyacids were slightly lower at 383 K as compared with those at 323 K, and selectivities on the basis of isobutylene were 52–94% at 383 K. Mass balances on the basis of methanol were about 100% for all catalysts at both temperatures. On the other hand, mass balances on the basis of isobutylene were above 90% for the supported heteropolyacids at 323 K as shown in Table 1.

Figure 3 shows the yields and reaction rates, together with the selectivities, as a function of the loading amount of $H_6P_2W_{18}O_{62}$ or $H_3PW_{12}O_{40}$ on $SiO_2$ at 323 K. Figure 4 shows those data for $H_6P_2W_{18}O_{62}$ at 383 K. It was confirmed that the yield increased with the catalyst weight for 20 wt% $P_2W_{18}/SiO_2$. As shown in Fig. 3, when the feed gas composition was methanol : isobutylene : $N_2 = 1 : 1 : 3$, the yields were almost constant, about 30% at 20–50 wt% $P_2W_{18}/SiO_2$, $PW_{12}/SiO_2$ and then decreased at higher loading levels. In contrast, with the composition of methanol : isobutylene : $N_2 = 0.5 : 1 : 3.5$, the rate further increased for 50–75 wt% $P_2W_{18}/SiO_2$. In the case of $PW_{12}/SiO_2$, the yield started to decrease at 75 wt%. The

selectivity (isobutylene basis) was high (98–100%). The selectivity on the methanol basis was also high (about 100%) for both catalysts (not shown in Fig. 3). At 383 K (Fig. 4), the yield of $P_2W_{18}/SiO_2$ was low, independent of the loading amount. This is because the conversion level was close to the equilibrium. It is noteworthy that the selectivity on the basis of methanol decreased, while the selectivity on the basis of isobutylene tended to increase as the loading amount increased.

Effects of the pretreatment temperature for $H_6P_2W_{18}O_{62}$ and 20 wt% $P_2W_{18}/SiO_2$ are provided in Fig. 5. The yield decreased remarkably when the catalysts were pretreated above 573 K. The selectivities (methanol basis) for both catalysts were 100% and those on the basis of isobutylene were 100% and 93–100% for $H_6P_2W_{18}O_{62}$ and 20 wt% $P_2W_{18}/SiO_2$, respectively. The changes in the yields for $H_6P_2W_{18}O_{62}$ were consistent with the changes of IR spectra. As shown in Fig. 6, four characteristic IR bands of $H_6P_2W_{18}O_{62}$ were observed at 1091, 962, 914, and 780 $cm^{-1}$ after the treatment below 523 K. These bands are in agreement with those in the literature (27). At 573 K, these IR bands disappeared or became broad, showing that the Dawson structure was mostly destroyed.

In Fig. 7, the dependencies of the reaction rate on methanol pressure are given, where the reaction was
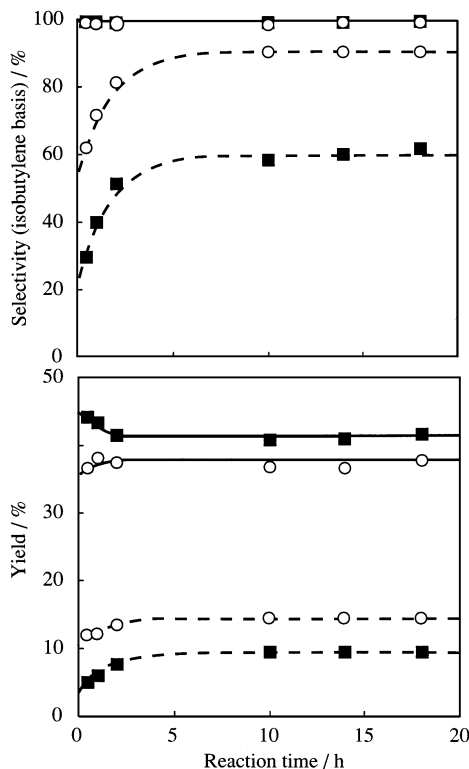


**FIG. 2.** Time courses of yields and selectivities at 323 and 383 K. ○, 20 wt% $H_6P_2W_{18}O_{62}/SiO_2$; ■, Amberlyst 15; solid lines, at 323 K; broken lines, at 383 K. Catalyst weight: 0.5 g, methanol : isobutylene : $N_2 = 1 : 1 : 3$, total flow rate: 90 ml · $min^{-1}$.

## TABLE 1

### Yield and Selectivity of Methyl *tert*-Butyl Ether for Solid Acids

| Catalyst | Yield and selectivity / % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 323 K[a] | | | | 383 K[a] | | | |
| | $Y^b$ | $S_1{}^c$ | $S_2{}^d$ | $MB^e$ | $Y^b$ | $S_1{}^c$ | $S_2{}^d$ | $MB^e$ |
| $20wt\%H_6P_2W_{18}O_{62}/SiO_2$ | 27.0(12) | 100 | 99.5(80.3) | 93.5 | 14.2(1.2) | 99.0 | 82.0(51.3) | 89.7 |
| $20wt\%H_3PW_{12}O_{40}/SiO_2$ | 27.2(12) | 100 | 99.1(74.0) | 90.6 | 7.7(0.7) | 95.8 | 52.2(27.3) | 86.5 |
| $20wt\%H_4SiW_{12}O_{40}/SiO_2$ | 27.4(12) | 100 | 99.0(82.5) | 94.5 | 7.0(0.6) | 97.9 | 69.9(29.7) | 85.2 |
| $20wt\%H_4GeW_{12}O_{40}/SiO_2$ | 25.2(11) | 100 | 99.1(79.4) | 93.7 | 13.4(1.2) | 99.4 | 69.0(55.1) | 95.1 |
| $20wt\%H_5BW_{12}O_{40}/SiO_2$ | 1.3(0.6) | 100 | 100 | 100 | 10.0(0.9) | 98.8 | 75.7(48.7) | 92.7 |
| $20wt\%H_6CoW_{12}O_{40}/SiO_2$ | 0.2(0.1) | 100 | 100 | 100 | 13.7(1.2) | 100 | 93.5(74.1) | 96.2 |
| $H_6P_2W_{18}O_{62}$ | 4.5(2) | 100 | 100 | 100 | 7.2(0.6) | 80.0 | 97.8(58.9) | 95.2 |
| $H_3PW_{12}O_{40}$ | <0.1(0) | 100 | 100 | 100 | 6.6(0.6) | 100 | 96.2(96.2) | 100 |
| $H_4SiW_{12}O_{40}$ | 0.2(0.1) | 100 | 100 | 100 | 4.6(0.4) | 100 | 97.0(48.8) | 95.4 |
| $H_4GeW_{12}O_{40}$ | 0.1(0) | 100 | 100 | 100 | 11.2(1.0) | 100 | 99.0(99.0) | 100 |
| $H_5BW_{12}O_{40}$ | <0.1(0) | 100 | 100 | 100 | 7.2(0.6) | 100 | 100 | 100 |
| $H_6CoW_{12}O_{40}$ | <0.1(0) | 100 | 100 | 100 | 5.7(0.5) | 100 | 97.8(97.8) | 100 |
| Amberlyst 15 | 24.2(11) | 100 | 100(84.1) | 95.4 | 8.1(0.7) | 69.1 | 50.0(28.9) | 88.0 |
| $SO_4{}^{2-}/ZrO_2$ | 0.1(0) | – | – | 100 | 12.7(1.1) | 25.3 | 80.3(55.4) | 96.1 |
| $SiO_2-Al_2O_3$ | <0.1(0) | – | – | 100 | 11.5(1.0) | 54.8 | 79.6(47.9) | 93.4 |
| H-ZSM-5 | <0.1(0) | – | – | 100 | 8.9(0.8) | 20.6 | 100 | 100 |

[a] 323 K: Catalyst weight : 0.1 g , W/F = 0.46 g·h·mol⁻¹, methanol:isobutylene:$N_2$ = 1:1:3,

    383 K: Catalyst weight : 0.5 g , W/F = 2.31 g·h·mol⁻¹, methanol:isobutylene:$N_2$ = 1:1:3.

[b] Yield / %. The figures in the parentheses are the reaction rates in the unit of $10^{-2}$ mol·g⁻¹·h⁻¹.

[c] $S_1$: Selectivity on the basis of methanol (eq.(2)) at 2h / %.

[d] $S_2$: Selectivity on the basis of isobutylene (eq.(3)) at 2h / %. The figures in the parentheses are 100 x (flow rate of MTBE at the outlet) / {(flow rate of isobutylene at the inlet)-(flow rate of isobutylene at the outlet)} / %.

[e] Mass balance on the basis of isobutylene = 100 x (total flow rate of MTBE, isobutylene and 2 x isooctene at the outlet) / (flow rate of isobutylene at the inlet)/ %. Mass balance on the basis of methanol was nearly 100 % for all cases.

performed at 323 K. In the cases of 20 wt% $P_2W_{18}/SiO_2$ and Amberlyst 15 (Fig. 7a), the reaction order was about zero at the low pressure region, and then changed to negative above 0.3 atm. A similar change was observed for unsupported $H_6P_2W_{18}O_{62}$ as reported previously (22). Contrary to this, Cs2.5-salt, $SO_4^{2-}/ZrO_2$ and H-ZSM-5 gave negative orders (−2, −1.5, and −1, respectively) (Fig. 7).

The results of calorimetry of $NH_3$ absorption applied for 20 wt% $P_2W_{18}/SiO_2$, 20 wt% $PW_{12}/SiO_2$, $H_6P_2W_{18}O_{62}$, and $H_3PW_{12}O_{40}$ are shown in Fig. 8. Initial heats of $NH_3$ absorption for $H_6P_2W_{18}O_{62}$ and $H_3PW_{12}O_{40}$ were 150 and 190 kJ·mol⁻¹, respectively, which are close to those

reported in the literature (31). The initial heat of absorption for 20 wt% $PW_{12}/SiO_2$ was 170 kJ·mol⁻¹, which is smaller by 20 kJ·mol⁻¹ than for $H_3PW_{12}O_{40}$. The heat of absorption for 20 wt% $P_2W_{18}/SiO_2$ was 150 kJ·mol⁻¹, which is the same as the value for $H_6P_2W_{18}O_{62}$. Thus, the difference of the acid strength of both silica-supported heteropolyacids became smaller, when they were supported. Most of the protons (1.0 mmol·g⁻¹) of $H_3PW_{12}O_{40}$ showed a high heat of absorption (>160 kJ·mol⁻¹). On the other hand, the heat of absorption for $H_6P_2W_{18}O_{62}$ decreased gradually as the $NH_3$ absorption increased. From Fig. 8, the amounts of $NH_3$ absorption having the heat of absorption more than
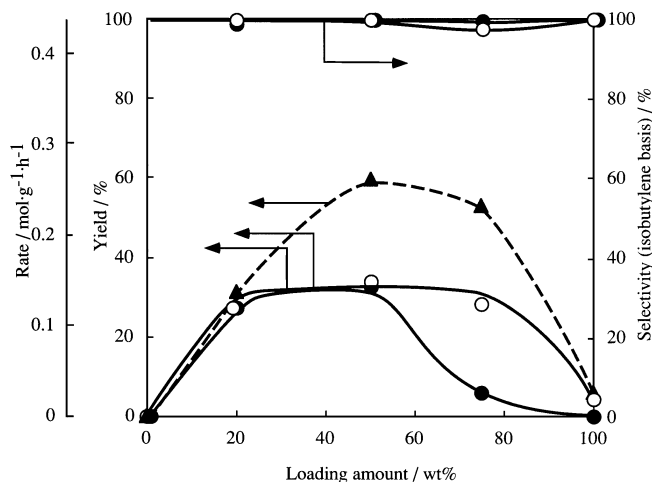
**FIG. 3.** The effect of loading amount of heteropolyacids on yield (for solid lines) or on reaction rate (for all lines) and selectivity (isobutylene basis) at 323 K. ○, Yield (and reaction rate) and selectivity; ▲, Reaction rate of $H_6P_2W_{18}O_{62}/SiO_2$; ●, Yield (and reaction rate) and selectivity of $H_3PW_{12}O_{40}/SiO_2$. Catalyst weight: 0.05–0.1 g, methanol : isobutylene : $N_2 = 1 : 1 : 3$ for ○,●; $= 0.5 : 1 : 3.5$ for ▲. Total flow rate: 90 ml · $min^{-1}$.

50 kJ · $mol^{-1}$ were estimated to be 1.05 and 1.27 mmol · $g^{-1}$ for $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$, respectively. The former value approximately agreed with the number of whole protons of the solid $H_3PW_{12}O_{40}$, in accordance with our earlier results (32). The latter value was also close to the number of whole protons of $H_6P_2W_{18}O_{62}$. When the amount of $NH_3$ absorbed in $H_6P_2W_{18}O_{62}$ exceeded about 0.85 mmol · $g^{-1}$, the heat of absorption declined rapidly. The amounts of
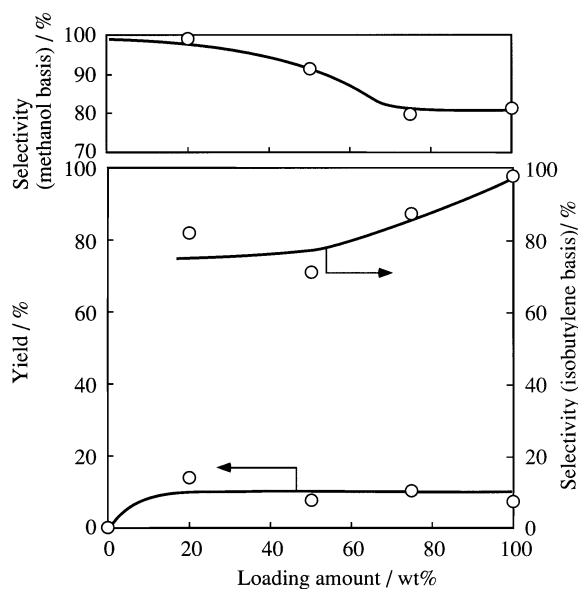


**FIG. 4.** Effects of loading amount of $H_6P_2W_{18}O_{62}$ on $SiO_2$ on yield and selectivities (methanol and isobutylene basis) at 383 K. Catalyst weight: 0.5 g, methanol : isobutylene : $N_2 = 1 : 1 : 3$, total flow rate: 90 ml · $min^{-1}$.
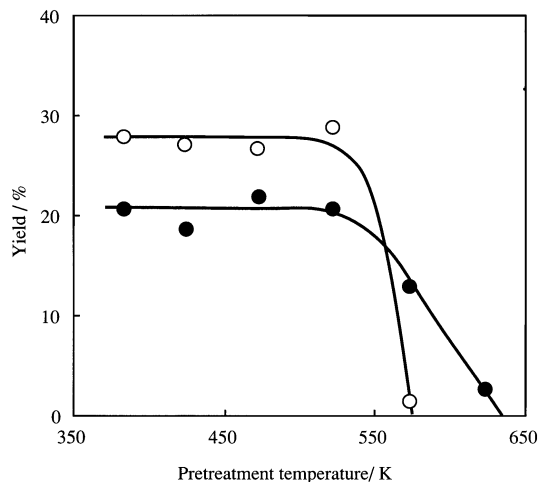


**FIG. 5.** Effects of pretreatment temperature on yield at 323 K. ○, 20 wt% $H_6P_2W_{18}O_{62}/SiO_2$ (0.1 g); ●, $H_6P_2W_{18}O_{62}$ (0.5 g). Methanol : isobutylene : $N_2 = 1 : 1 : 3$, total flow rate: 90 ml · $min^{-1}$.

acid sites of the supported catalysts were about one-fifth those of unsupported ones, the amounts of acid sites per heteropolyacids being almost unchanged. Between the supported catalysts, the acid amount of 20 wt% $PW_{12}/SiO_2$ was slightly larger than 20 wt% $P_2W_{18}/SiO_2$.

## DISCUSSION

### MTBE Synthesis by Supported Heteropolyacids

Figure 1 and Table 1 demonstrate the high catalytic performance of 20 wt% $P_2W_{18}/SiO_2$ for this reaction. The activity was comparable to that of Amberlyst 15 and selectivities on the basis of both methanol and isobutylene were higher than those of Amberlyst 15 especially at 383 K.
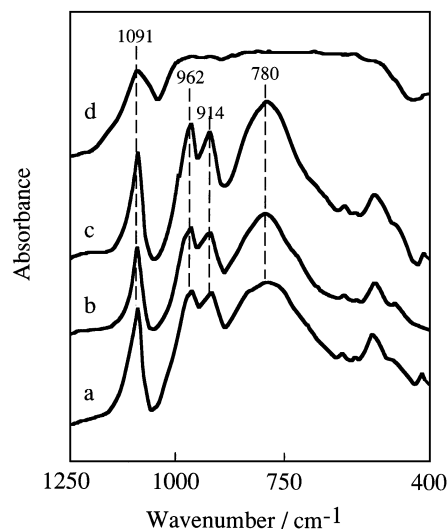


**FIG. 6.** Infrared spectra of $H_6P_2W_{18}O_{62}$ after pretreatment at various temperatures: (a) 423; (b) 473; (c) 523; and (d) 573 K.
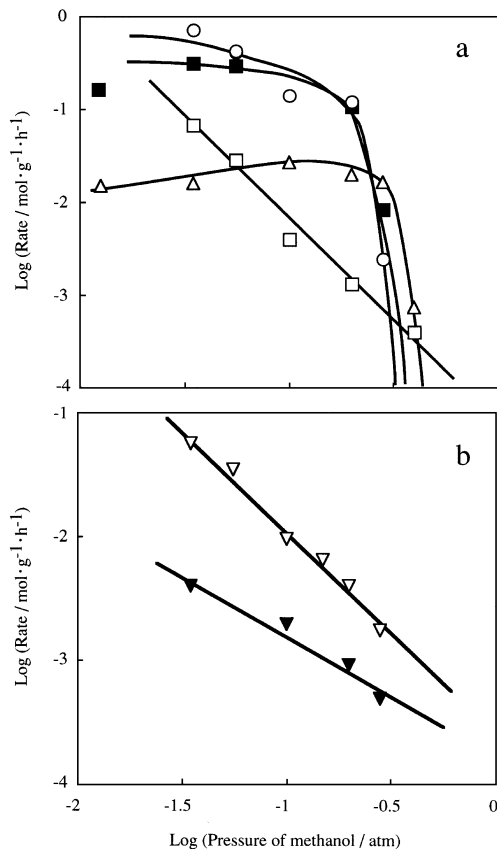
**FIG. 7.** Pressure dependency on methanol for MTBE synthesis: (a) 323 K: $\bigcirc$, 20 wt% $H_6P_2W_{18}O_{62}/SiO_2$; $\triangle$, $H_6P_2W_{18}O_{62}$; $\square$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$; $\blacksquare$, Amberlyst 15. (b) 343 K: $\triangledown$, $SO_4^{2-}/ZrO_2$; $\blacktriangledown$, H-ZSM-5. Catalyst weight: 0.01–0.3 g, flow rate: 90 ml · $min^{-1}$.

No deactivation was observed at least for 20 h at 383 K for 20 wt% $P_2W_{18}/SiO_2$ (Fig. 2). Interestingly, supported-heteropolyacids exhibited very high selectivity of more than 96% on the basis of methanol, but the selectivity on the basis of isobutylene was 52–94% at 383 K. Note that, both selectivities were almost 100% at 323 K.

We previously reported that the MTBE synthesis took place in the pseudoliquid phase of unsupported $H_6P_2W_{18}O_{62}$ (22). The pseudoliquid behavior is a unique phenomenon of heteropolyacid found by us. Polar or basic molecules are rapidly absorbed into the solid lattice and react there, the solid catalyst behaving in a sense like a concentrated solution (11, 12) and giving high activities (36). As for the supported heterpolyacids, the effects of the dispersion of heteropolyacids on the support which influences the surface area of heteropolyacids and therefore pseudoliquid behavior should be considered for the factor governing the catalytic activity and selectivity. Besides, the change in the acid strength of heteropolyacids caused by the support needs to be examined.

(i) *Effects of dispersion of heteropolyacids on $SiO_2$.* As demonstrated in Fig. 7a, the reaction orders to methanol

pressure were nearly zero in the lower pressure region and became negative at higher pressures for 20 wt% $P_2W_{18}/SiO_2$, $H_6P_2W_{18}O_{62}$, and Amberlyst 15. Contrary to this, the reaction orders for Cs2.5-salt (Fig. 7a), $SO_4^{2-}/ZrO_2$, and H-ZSM-5 (Fig. 7b) were negative ($-2$, $-1.5$, and $-1$ for Cs2.5-salt, $SO_4^{2-}/ZrO_2$, and H-ZSM-5, respectively) and nearly constant. This sharp contrast between the two groups of catalysts in the pressure dependency indicates that the two groups are different in the pseudoliquid behavior as discussed below.

The pressure dependences of 20 wt% $P_2W_{18}/SiO_2$ and $H_6P_2W_{18}O_{62}$ for MTBE synthesis (Fig. 7a) were very similar to that for ethanol dehydration over $H_3PW_{12}O_{40}$ (33) that will proceed in the pseudoliquid phase. Furthermore, MTBE synthesis over $H_6P_2W_{18}O_{62}$ has also been concluded to be the pseudoliquid phase reaction (22). On the other hand, the rate of ethanol dehydration over Cs2.5-salt showed zeroth-order dependency (34), which is very different from the case of $H_3PW_{12}O_{40}$. Since Cs2.5-salt has little absorption capability for polar molecules and does not show the pseudoliquid behavior for dehydration of ethanol (34), MTBE synthesis is also considered to take place on the surface of Cs2.5-salt (surface type reaction). Similar pressure dependence of Cs2.5-salt to $SO_4^{2-}/ZrO_2$ and H-ZSM-5 (Fig. 7) supports this idea. Therefore, the pressure dependency of 20 wt% $P_2W_{18}/SiO_2$ which shows similarity to that of unsupported $H_6P_2W_{18}O_{62}$ and a marked difference with that of Cs2.5-salt suggest that the reaction proceeds in the pseudoliquid phase in the case of 20 wt% $P_2W_{18}/SiO_2$. Probably, $H_6P_2W_{18}O_{62}$ exists as aggregates on $SiO_2$ (35) and the pseudoliquid is realized in the aggregates.

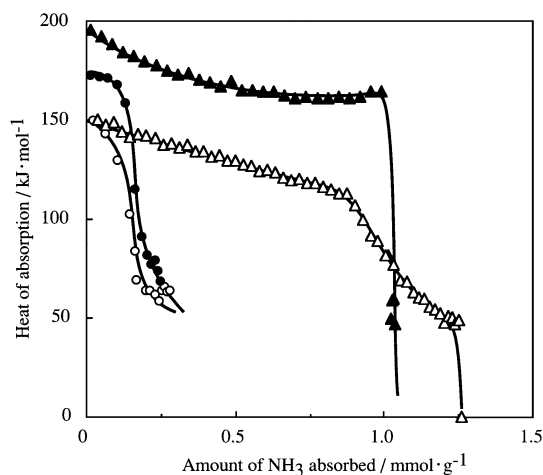As for the unsupported heteropolyacids, there are differences in the pressure dependence between the MTBE



**FIG. 8.** Heat of $NH_3$ absorption for unsupported and supported heteropolyacids: $\bigcirc$, 20 wt% $H_6P_2W_{18}O_{62}/SiO_2$; $\bullet$, 20 wt% $H_3PW_{12}O_{40}/SiO_2$; $\triangle$, $H_6P_2W_{18}O_{62}$; $\blacktriangle$, $H_3PW_{12}O_{40}$. Catalysts were pretreated at 473 K in vacuum. The heat of $NH_3$ absorption was measured at 423 K.

synthesis (Fig. 7) and dehydration of ethanol (33), while both reactions are assumed to proceed in the pseudoliquid phases. That is, the reaction orders in the lower pressure range were about zero for the MTBE synthesis and positive for dehydration of ethanol. A possible reason for the difference may be the different reaction temperature. It has been reported that there are two or more stable states of pseudoliquid phases having different amounts of reactant absorbed (11, 36). Since the temperature of MTBE synthesis was lower than that of dehydration of ethanol, a stable pseudoliquid phase might be formed in MTBE synthesis at lower pressure region. This idea explains the zeroth-order dependence for MTBE synthesis in the lower pressure region. On the other hand, the amount of absorbed ethanol increased as the pressure increased in this pressure range (33), which is responsible for the positive-order dependence.

Another possible reason is the difference in the reaction type, i.e., bimolecular (for MTBE synthesis) or monomolecular (for ethanol dehydration) reaction. As will be discussed below, if the reaction takes place only on the surface, the pressure dependency must be influenced by whether the reaction is bimolecular or monomolecular through competitive adsorption of reactants. However, isobutylene may be absorbed into the pseudoliquid phase by the organophilic interaction assisted by the methanol absorbed. So the absorption of these reactants is not necessarily competitive and it is less likely that the difference in the reaction type is the main reason for the difference in the pressure dependence.

As for the pressure dependence for Cs2.5-salt, a difference between the MTBE synthesis (the order; −2) and ethanol dehydration (the order; about zero) is also noted. This difference may be due to whether the reaction is bimolecular or monomolecular, since both reactions take place on the surface of Cs2.5-salt (11, 34), not in the pseudoliquid. The zeroth-order dependence for ethanol dehydration over Cs2.5-salt (34) indicates that the surface is fully covered by ethanol. On the other hand, in the case of MTBE synthesis, methanol and isobutylene are adsorbed competitively on the surface. Considering the lower temperature of the MTBE synthesis, the coverage of methanol is possibly close to unity. If so, it is reasonable that the reaction rate is negatively dependent on the methanol pressure; an increase in methanol pressure would suppress the isobutylene adsorption.

The pressure dependence for Amberlyst 15 is also unique (Fig. 7a). The reported pressure dependencies for dehydration of n-butyl alcohol (37) and gas phase MTBE synthesis (38) over Amberlyst 15 are similar to the result of the present study. Since polar molecules can be absorbed in the bulk of Amberlyst 15 (39, 40), the unusual pressure dependency observed for Amberlyst 15 (Fig. 7) may also be explained by "pseudoliquid phase behavior."

(ii) *Effects of acid strength of heteropolyacids.* Next, the influence of the acid strength will be discussed. The order of the acid strength of unsupported heteropolyacids measured by indicator test was $H_3PW_{12}O_{40}$ [−3.6] > $H_4SiW_{12}O_{40}$ [−3.4] > $H_4GeW_{12}O_{40}$ [−2.9], $H_6P_2W_{18}O_{62}$ [−2.9] > $H_5BW_{12}O_{40}$ [−1.3] > $H_6CoW_{12}O_{40}$ [−0.6], where the figures in the parentheses are the values of $H_0$ of the acetonitrile solutions (23). The order obtained by calorimetry of $NH_3$ absorption (31), $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ > $H_6P_2W_{18}O_{62}$, is consistent with the above. As shown in Fig. 8, the acid strength of $H_3PW_{12}O_{40}$ became apparently weaker by supporting. This result is also consistent with the literature data (41). On the other hand, the acid strength of $H_6P_2W_{18}O_{62}$ was almost unchanged when it was supported on silica (Fig. 8). Due to this different behavior, the acid strength of $P_2W_{18}/SiO_2$ and $PW_{12}/SiO_2$ became closer. This may be responsible at least in part for the comparable activity between $P_2W_{18}/SiO_2$ and $PW_{12}/SiO_2$ (Table 1), since the difference in the amount of acid sites between the supported catalysts was small. Another reason for the smaller difference of catalytic activity is that the absorption–desorption was easier due to presumably smaller particle sizes for supported heteropolyacids, and hence, the rate of absorption–desorption which is faster for $H_6P_2W_{18}O_{62}$ became less influential.

### Effects of Loading Amounts of Heteropolyacids

As shown in Fig. 3, the supporting the heteropolyacids on $SiO_2$ enhanced greatly the yield. The dependences were similar for $P_2W_{18}/SiO_2$ and $PW_{12}/SiO_2$ below 50 wt% (solid lines). The yield showed saturation at high loading levels in Fig. 4, too. The reason of the saturation in Fig. 4 is due to the limitation from the equilibrium, since the equilibrium conversion is 9%.

But, as for the results given in Fig. 3 (solid lines), the possibility of the equilibrium limitation is excluded, as the equilibrium conversion is 66% and the higher conversions than those in Fig. 3 were obtained when the catalyst amount was increased. The possibility that the diffusion in the pores of the silica gel is rate-limiting is also excluded, because when the methanol partial pressure was low (the high-activity state in Fig. 7), the rate of MTBE formation became two times greater for 50–75 wt% $P_2W_{18}/SiO_2$ (broken line in Fig. 3).

Hence, the changes of the yield observed in Fig. 3 are closely related to the unusual pressure dependencies shown in Fig. 7. The dependencies are explained by the pseudoliquid behavior as discussed before, where the rate of reaction depends on the state of the pseudoliquid (high-activity or low-activity state), the depth of the phase determined by the relative rate of diffusion in the phase to the rate of reaction, and the particle size of heteropolyacid. As seen in Fig. 7, the reaction conditions for the data of $P_2W_{18}/SiO_2$ shown by

the solid line in Fig. 3 are the transient region between the high-activity state and the low-activity state (log $P = -0.7$). Unusual behavior may be observed in the transient region. On the other hand, the data shown by the broken line were obtained at the high-activity state (log $P = -1$). The decrease in the activity at high loading levels for the high activity state may be understood by too large crystallites of heteropolyacids, where the diffusion in the heteropolyacid particles influences the overall rate. Then, it is reasonable that the activity of $PW_{12}/SiO_2$ decreased at a lower loading level, since $H_3PW_{12}O_{40}$ shows slower absorption (22).

As for the selectivity, significant changes were found with the loading level of $H_6P_2W_{18}O_{62}$ (Fig. 4). The selectivity on the basis of isobutylene tended to increase, but the selectivity on the basis of methanol decreased as the loading level increased. This different behavior may be explained as described below. The decrease in the selectivity on the basis of methanol is due to the formation of dimethyl ether by dehydration of methanol. Since the dehydration of methanol proceeds preferably in the pseudoliquid phase of heteropolyacids as methanol is a polar molecule (22, 33), it is possible that as the loading level increases, the size and amount of aggregates of heteropolyacids on $SiO_2$ increase and this side reaction would be enhanced. On the other hand, oligomerization of isobutylene which is a nonpolar molecule proceeds favorably on the surface of the heteropolyacid. As the loading level increases, the ratio of the surface polyanion to the bulk polyanion decreases, and hence, the selectivity on the basis of isobutylene would increase, suppressing relatively the oligomerization.

As mentioned above, the mass transport effects in the pseudoliquid phase on the rate need to be considered. Dehydration of 2-propanol over $H_3PW_{12}O_{40}$ is a typical example of pseudoliquid phase reaction. For this system, evidence that the catalytic reaction takes place in the pseudoliquid phase has been obtained by a transient response analysis using isotopically labeled reactants (42). It was confirmed by this experiment that the rates of absorption and desorption were 50 times larger than the reaction rate under the reaction conditions. In the case of MTBE synthesis over unsupported $H_6P_2W_{18}O_{62}$, the rate of methanol absorption measured in a separate experiment was 3.3 mol $(\text{catalyst-mol})^{-1} \cdot \text{min}^{-1}$, which is still higher than that of the reaction rate, 1.6 mol $\cdot (\text{catalyst-mol})^{-1} \cdot \text{min}^{-1}$ at 323 K (22). However, the difference is not very large in this case, so that under certain reaction conditions, the mass transfer in the pseudoliquid may influence the overall rate. Here, it is to be noted that the diffusion in the pores of the catalyst support is not limiting the rate, as discussed above.

## CONCLUSIONS

$P_2W_{18}/SiO_2$ as well as $PW_2/SiO_2$, $SiW_{12}/SiO_2$, and $GeW_{12}/SiO_2$ exhibited high catalytic performance for gas-

phase synthesis of MTBE , and the activities were comparable to that of Amberlyst 15. It is concluded that the MTBE synthesis mainly takes place in the bulk phase of the supported heteropolyacids, similarly to the case of the unsupported heteropolyacids. $P_2W_{18}/SiO_2$ was thermally stable up to 523 K.

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