

Strong influence of the polyanion structure on the secondary structure of solid heteropolyacids and their catalytic activity; methyl *tert*-butyl ether synthesis in the pseudo-liquid phase of heteropolyacids

Sawami Shikata and Makoto Misono*†

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

It has been shown that the high catalytic activity of a Dawson-type heteropolyacid for gas-phase methyl *tert*-butyl ether synthesis at low temperatures is attributable to its amorphous secondary structure, which brings about a flexible pseudo-liquid phase and facilitates rapid absorption and desorption of molecules.

High catalytic activities of Keggin-type heteropolyacids for gas-phase synthesis of methyl *tert*-butyl ether (MTBE) have already been reported.¹ We recently found that a Dawson-type heteropolyacid ($H_6P_2W_{18}O_{62}$) was more than ten times more active than Keggin-type heteropolyacids ($H_nXW_{12}O_{40}$, X = P, Si, Ge, B, Co) at a low temperature that is favorable for the equilibrium of this reaction.^{2,3} In the present study, it has been deduced that the high catalytic activity of $H_6P_2W_{18}O_{62}$ is due to its amorphous and flexible pseudo-liquid phase that is very probably brought about by the elliptical shape of the primary structure (polyanion) of $P_2W_{18}O_{62}^{6-}$. As described below, both heteropolyacids were nearly anhydrous, so that the water content was not regarded to be the main factor controlling the activities.

Pseudo-liquid phase behaviour is a unique phenomenon of heteropolyacids.⁴ Polar and basic molecules are rapidly absorbed into the solid lattice and react there, the solid catalyst behaving in a sense like a concentrated solution.⁵ This behaviour often brings about high catalytic activities and unique selectivities. MTBE synthesis catalyzed by the heteropolyacids has already been inferred to take place in the pseudo-liquid phase based on the following facts;³ (i) the relative catalytic activities of various heteropolyacids can not be explained by the acidity, but are well correlated with the absorption behavior, (ii) the dependence of the rate on methanol pressure was very similar to that for the pseudo-liquid phase observed previously, and (iii) the catalytic activity of $CS_{2.5}H_{0.5}PW_{12}O_{40}$ for which the reaction takes place on the surface was lower than that of $H_6P_2W_{18}O_{62}$, although the acid site concentration on the surface was more than ten times greater for $CS_{2.5}H_{0.5}PW_{12}O_{40}$ than for $H_6P_2W_{18}O_{62}$.⁶

MTBE synthesis was carried out in a flow reactor at atmospheric pressure at 323 K as reported previously.³ Prior to the reaction, catalysts were treated in a flow of N_2 at 423 or 523 K. In ordinary experiments, the feed gas was a mixture of methanol, isobutylene and N_2 with a volume ratio of 1 : 1 : 3 and the total flow rate was $90 \text{ cm}^3 \text{ min}^{-1}$. In *ex situ* XRD measurements, the samples after pretreatment or reaction were quickly transferred onto a sample holder and sealed by polyethylene film to avoid contact with moisture. This was performed in an N_2 flow in the case of thermal pretreatment.

Fig. 1 shows the time courses of MTBE synthesis over $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$, after pretreatments at 423 and 523 K. Just after the start of the reaction, rapid increases in the MTBE yields were observed (0–10 min). These are due to the rapid absorption of reactants and formation of MTBE in the solid bulk as discussed previously.³ Here the MTBE yields at 10–15 min are regarded to relate to the initial activities. For

$H_3PW_{12}O_{40}$, the initial activity was strongly influenced by the pretreatment temperature and the activities at the stationary stage (after 2 h) were very low because of excessive absorption, as reported previously.³ On the other hand, for $H_6P_2W_{18}O_{62}$, irrespective of the pretreatment temperature, after the absorption progressed in the initial stage and MTBE yield increased rapidly, high stationary catalytic activities were maintained.

Powder XRD patterns for the two kinds of heteropolyacids just after two different pretreatments and after the stationary states of reaction are shown in Fig. 2. The peak intensities in Fig. 2 are normalized on the basis of the peak area of polyethylene film used to cover the samples (marked by solid circles). The Keggin-type heteropolyacid after pretreatment at 423 K [Fig. 2(a)(i)] showed an ordinary cubic bcc pattern. It was noted that the lattice constant was slightly smaller ($d = 11.7 \text{ \AA}$) than that of $H_3PW_{12}O_{40} \cdot 6H_2O$ ($d = 12.1 \text{ \AA}$).⁷ After reaction [Fig. 2(a)(ii)], the cubic pattern was essentially retained, while the lines became broader with a small increase in the lattice constant ($d = 12.1 \text{ \AA}$) and additional weak lines appeared. After the Keggin-type heteropolyacid was treated at 523 K, the lines were much weaker [Fig. 2(a)(iii)], indicating that the secondary structure was almost amorphous. It is remarkable that after the reaction, the XRD pattern which was very like that after the reaction of the 423 K-treated sample, appeared again [Fig. 2(a)(iv)]. According to IR spectra, the primary structures were intact for all of these samples.^{6,8}

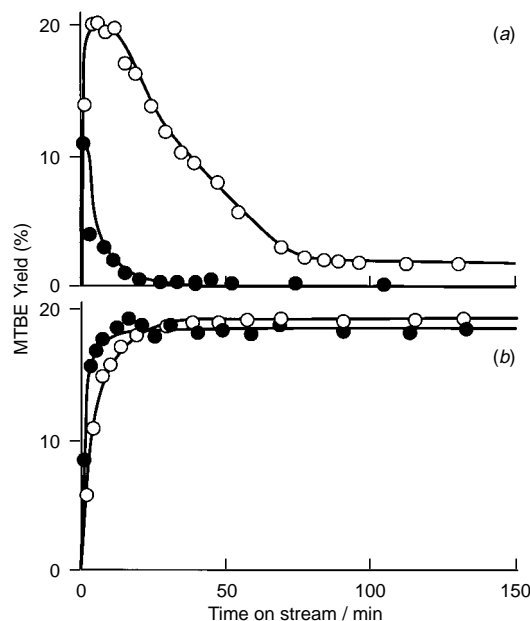


Fig. 1 Effects of pretreatment temperature on MTBE synthesis catalyzed by $H_3PW_{12}O_{40}$ (a) and $H_6P_2W_{18}O_{62}$ (b) pretreated at 423 K (●), 523 K (○) in an N_2 flow. Catalyst mass: 0.5 g, reaction temperature: 323 K, methanol : iso- C_4H_8 : $N_2 = 1 : 1 : 3$, flow rate: $90 \text{ cm}^3 \text{ min}^{-1}$.

Table 1 The secondary structures and the catalytic activities of MTBE synthesis over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$

Primary structure	Pretreatment temperature/K	Secondary structure		Catalytic activity ^a	
		Before reaction	After reaction	Initial	Stationary
$\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Keggin type)	423	Cubic	Cubic	2	>0
	523	Amorphous	Cubic	20	<2
$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ (Dawson type)	423	} Amorphous	Amorphous	17	18
	523				

^a MTBE yields (%) at the initial (10–15 min) and stationary (after 2 h) stages.

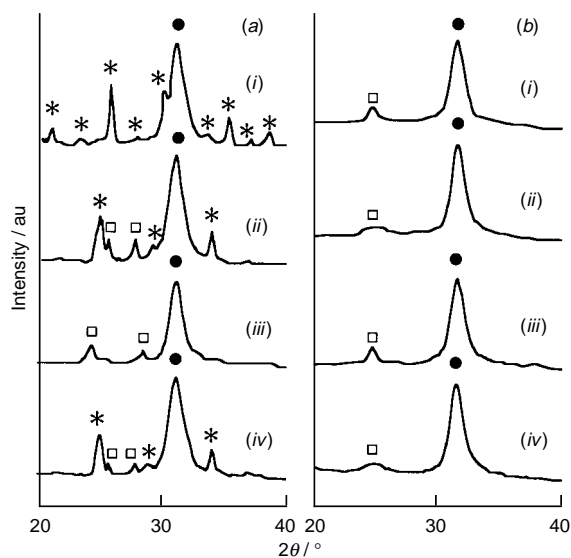


Fig. 2 Powder XRD patterns of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (a) and of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ (b), before and after MTBE synthesis reaction. (i) After pretreatment at 423 K, (ii) after reaction at 323 K of the sample (i), (iii) after pretreatment at 523 K, and (iv) after reaction of the sample (iii). (●) Peaks of polyethylene film, (*) peaks due to cubic structure and (□) unknown structures.

In contrast, for the Dawson-type heteropolyacid, the XRD lines were weak and broad before and after the reaction for both treatments [Fig. 2(b)(i)–(iv)], indicating that the secondary structure was always mostly amorphous. IR spectra showed that the primary structure (heteropolyanion) was retained. Although there remain unidentified structures, it is evident that the samples of Fig. 2(a)(i), (ii) and (iv) are mostly crystalline and those of Fig. 2(b)(i)–(iv) and Fig. 2(a)(iii) are mostly amorphous.

These structural data are compared with the results of catalytic activity in Table 1. A close correspondence was noted in Table 1 between the secondary structures and the reaction rates observed for the eight cases; two heteropolyacids with two different pretreatments for the initial and stationary states. A high rate was always observed when the secondary structure was amorphous, and a low rate was observed for crystalline cubic structures. For example, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ treated at 523 K showed high activity at first, but the activity declined to a very low level at the steady state, accompanying the change of the secondary structure from amorphous to crystalline (cubic), while $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ always showed a high activity and amorphous XRD pattern. It was confirmed experimentally that surface areas and pore volumes of the two heteropolyacids little changed with the change of the pretreatment temperature (423 or 523 K). The acid strength also remains constant.⁹ According to the DTA–TG analyses, although the water desorbs more

easily for the Dawson-type at low temperatures, both heteropolyacids were nearly anhydrous after treatment at 523 K. Moreover, the differences in the water content between the pretreatments at 423 and 523 K were smaller for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.3 H_2O /heteropolyanion) than for $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ (ca. 1 H_2O /heteropolyanion). This is in contrast to the fact that the catalytic behaviour differed more for the Keggin-type [Fig. 1(a)] than the Dawson-type [Fig. 1(b)] between the 423 and 523 K treatments. Hence, the water content is not the main factor controlling these activities.

We previously indicated³ that the high catalytic activity of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is brought about by a high-activity state of the pseudo-liquid phase in which moderate amounts of molecules are absorbed and the absorption–desorption is rapid, while the pseudo-liquid phase of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is in a low-activity state where the absorption is excessive and slow. The transformation between active and less active pseudo-liquid phases with partial pressure was reported previously.¹⁰ If this conclusion is combined with the present results summarized in Table 1, an interesting correlation is deduced between the nature of the pseudo-liquid phase (secondary structure) and the polyanion structure (primary structure). That is, the elliptical shape of the Dawson anion is not suitable for the formation of a stable crystalline structure and leads to an amorphous and flexible structure, the absorption–desorption being easier and catalytic activity high, while the spherical shape of the Keggin anion favors a crystalline cubic structure, where absorption–desorption is slow and catalytic activity is low.

A part of the present study was presented at the Symposium of Catalysis Society of Japan.¹¹

Notes and References

† E-mail: tmisono@hongo.ecc.u-tokyo.ac.jp

- A. Igarashi, T. Matsuda and Y. Ogino, *J. Jpn. Petrol. Inst.*, 1979, **22**, 331.
- S. Shikata, T. Okuhara and M. Misono, *Sekiyu Gakkaishi*, 1994, **37**, 632.
- S. Shikata, T. Okuhara and M. Misono, *J. Mol. Catal.*, 1995, **100**, 49.
- M. Misono, *Catal. Rev., -Sci. Eng.*, 1987, **29**, 269; K. Y. Lee, T. Arai, S. Nakata, S. Asaoka, T. Okuhara and M. Misono, *J. Am. Chem. Soc.*, 1992, **114**, 2836.
- T. Okuhara, T. Hashimoto, M. Misono, Y. Yoneda, H. Niiyama, Y. Saito and E. Echigoya, *Chem. Lett.*, 1983, 573.
- S. Shikata, S. Nakata, T. Okuhara and M. Misono, *J. Catal.*, 1997, **166**, 263.
- G. M. Brown, M.-R. Noe-Spirlet, W. R. Busing and H. A. Levy, *Acta Crystallogr., Sect. B*, 1977, **33**, 1038.
- K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Faraday. Trans.*, 1995, **91**, 367.
- F. Lefebvre, F. X. Liu-Cai and A. Auroux, *J. Mater. Chem.*, 1994, **4**, 125.
- K. Takahashi, T. Okuhara and M. Misono, *Chem. Lett.*, 1985, 841.
- S. Shikata and M. Misono, *Shokubai*, 1997, **39**, 174.

Received in Cambridge, UK, 18th March 1998; 8/02138D