

SELECTIVE FORMATION OF ETHYLENE AND PROPENE FROM  
METHANOL OVER PYRAZINIUM SALTS OF  $H_3PW_{12}O_{40}$ Atsushi KASAI, Toshio OKUHARA, Makoto MISONO,\*  
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The catalytic conversion of methanol into hydrocarbons has been studied over a variety of metal and organic salts of  $H_3PW_{12}O_{40}$ . Pyrazinium salts exhibited remarkably high selectivity to ethylene and propene.

Since aromatic-rich gasoline production from methanol was announced using new zeolite by Mobil,<sup>1)</sup> much attention has been drawn on the catalytic synthesis of hydrocarbons from methanol. The catalytic synthesis of light olefins from methanol is also an important process for chemical industry. It has been reported that  $C_2$  to  $C_4$  olefins were produced as major products on ZSM-5 modified with phosphorus compounds,<sup>2)</sup> manganese-doped aluminosilicates,<sup>3)</sup> and aluminum dihydrogenphosphate catalyst.<sup>4)</sup> Heteropoly acids such as  $H_3PW_{12}O_{40}$  and  $H_4SiW_{12}O_{40}$  catalyzed this reaction,<sup>5)</sup> but they yielded a wide range of hydrocarbons with a considerable proportion of paraffins.

In this communication, we wish to report that organic salts of  $H_3PW_{12}O_{40}$  are effective for the selective formation of ethylene and propene from methanol.

The reaction was carried out under a reduced pressure (80 mmHg) of methanol using a circulating system (188 ml) at 250-285°C. The products were analyzed by on-line gas chromatography using three columns: Porapak Q (0°C, 1 m) for  $CH_4$ , CO,  $CO_2$ ,  $C_2H_4$  and  $C_2H_6$ , Porapak Q (120°C, 2 m) for  $CH_3OH$  and  $CH_3OCH_3$ , and VZ-7 (0°C, 6m) for  $C_3$ - $C_4$  hydrocarbons.  $C_1$ - $C_6$  hydrocarbons were analyzed in more detail by temperature-programmed gas chromatography (40 to 80°C, the heating rate: 1°C/min). The metal and organic salts of  $H_3PW_{12}O_{40}$  were prepared by titrating aqueous solution of  $H_3PW_{12}O_{40}$  with pre-determined amount of aqueous solution of metal carbonates and/or organic compounds. The catalysts were evacuated at reaction temperature for 1 h prior to the introduction of methanol.

Results of the reaction by the metal salts are shown in Table. The original heteropoly acid ( $H_3PW_{12}O_{40}$ ) yielded paraffins in preference to olefins at 250°C,  $C_2$  to  $C_3$  olefins being only about 13%. Metal salts were not effective for the formation of light olefins, although a little higher selectivity was found with Ni and Na salts.

The activities and selectivities over organic salts of  $H_3PW_{12}O_{40}$  are given in the same table. The organic salts with phenazine(1), triethylenediamine(2), and piperazine(3) did not exhibit selective formation of olefins. However, pyrazinium salts(4-1, 4-2) brought about remarkable improvement in the selectivity to light

olefins, although the activity was rather depressed. In particular, the pyrazinium salt(4-2) produced ethylene in 61% selectivity(ethylene+propene:74%) based on carbon efficiency. Results with the pyrazinium salt at a higher conversion are shown in the last two lines of the table. The high selectivity to ethylene and propene was retained even at a higher conversion. Therefore, the formation of light olefins is an inherent feature of pyrazinium salts. Variation in the composition during the course of the reaction was small. The rate decreased to a half after 3 h.

Table Hydrocarbon Formation from Methanol over Metal and Organic Salts of  $H_3PW_{12}O_{40}$

Catalyst	Activity <sup>a)</sup>		Conversion <sup>b)</sup>	Product distribution(%) (carbon efficiency) <sup>c)</sup>						
	(ml/g·h)	(%)		C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> <sup>-</sup>	C <sub>3</sub>	C <sub>3</sub> <sup>-</sup>	C <sub>4</sub> (+)	C <sub>4</sub> <sup>-</sup> (+)
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	(0.1) <sup>d)</sup>	7.1	6.1(1.5)	16.8	0.9	6.0	27.5	7.0	29.0	12.8
	(1.0)	6.9	23.9(0.5)	17.5	1.9	4.9	26.8	6.5	34.3	8.2
Na <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	(0.25)	0.8 <sup>e)</sup>	6.9(4.5)	16.4	1.5	12.7	13.1	18.5	24.7	13.1
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	(1.0)	>29.0	100 (0.5)	2.4	0.2	2.2	9.6	0.1	71.2	14.3
Cu <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub>	(1.0)	1.3	25.0(3.5)	72.5	0.4	6.3	0.1	5.0	13.0	2.7
Ni <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub>	(1.0)	2.6	26.4(1.5)	21.5	0.6	14.5	6.7	17.3	23.0	16.4
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<u>1</u> (1.0)		2.9	24.4(1.5)	23.4	1.8	9.1	50.7	5.0	7.5	2.5
<u>2</u> (1.0)		8.1	27.7(0.5)	8.1	0.5	7.5	12.2	15.9	33.6	22.2
<u>3</u> (0.25)		3.7	17.2(3.5)	9.0	0.3	11.1	22.3	13.9	33.4	10.0
<u>4-1</u> (1.0)		0.6	7.2(4.5)	21.0	0.8	30.6	9.1	17.3	14.2	6.9
<u>4-2</u> (1.0)		0.3	5.2(5.5)	16.2	0.1	48.7	5.1	17.9	0.1	11.9
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<u>4-1</u> (2.0)		0.9 <sup>e)</sup>	26.6(3.0)	24.6	0.8	30.7	3.4	27.5	6.4	6.6
<u>4-2</u> (2.0)		0.4 <sup>e)</sup>	23.1(3.0)	18.7	0.4	61.0	1.4	13.1	3.5	1.9

Reaction temperature: 250°C.

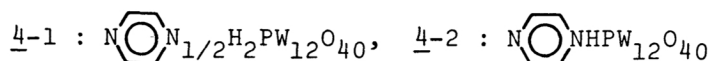
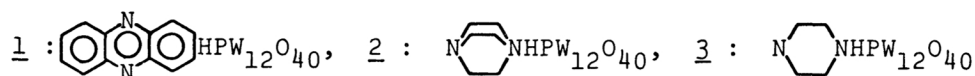
a) estimated from the amounts of hydrocarbons produced for initial 40 min.

b) at the reaction time (h) shown in the parentheses.

c)  $\frac{nC_n \text{ or } nC_n^-}{\sum(nC_n + nC_n^-)} \times 100$  (n; carbon number, C<sub>n</sub>; paraffins, C<sub>n</sub><sup>-</sup>; olefins)

d) Catalyst weight (g) in parentheses.

e) Reaction temperature: 285°C.



#### References

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