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The Conversion of Methanol into Hydrocarbons over Dodecatungstophosphoric Acid

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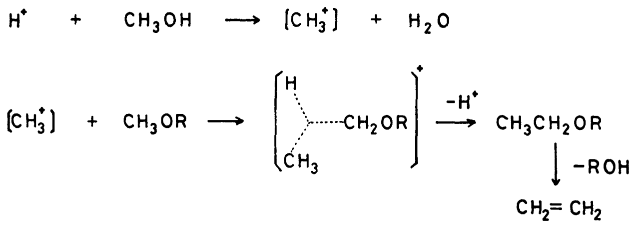
Dodecatungstophosphoric acid (TPA) is a very effective catalyst for the conversion of methanol into hydrocarbons. The effects of the reaction parameters, such as the temperature or the methanol partial pressure, were therefore examined. The kinetic features of the conversion over TPA are quite different from those over ZSM-5 zeolites. This difference is caused by the unique nature of the conversion over TPA; methanol molecules are sorbed and undergo the conversion in the bulk of solid TPA.

Zeolites, especially ZSM-5, are very effective catalysts for converting methanol into hydrocarbons.[1–3] Ono and Mori[4] have studied the mechnism of the conversion in detail and have concluded that Brönsted acid sites are responsible for the conversion, refuting the mechanism which involves a carbene-like intermediate.[1] According to this mechanism,[4] the first carbon-carbon bond is formed in the following manner:



The subsequent fast reactions of lower olefins and methanol lead to the formation of a higher molecular weight. The overall reaction proceeds autocatalytically.[4–6] Thus, the yield of the hydrocarbons shows an abrupt increase with a small increase in the reaction temperature,[6] or the rate of hydrocarbon formation is accelerated as the reaction proceeds.[4,5]

Judging from the above mechanism, it seems that the methanol conversion should proceed over solid substances other than zeolites, if they are highly acidic. In fact, Ono *et al.* have reported that heteropolyacids such as dodecatungstophosphoric acid (TPA) are quite effective catalysts for the conversion.[4,7,8] Some heteropolyacids are known to have a high solid acidity and to be very active catalysts for various acid-catalyzed reactions.[9] Thus, TPA has a much higher activity than hydrogen-Y zeolite for the dehydration of 2-propanol.[9] In this work, the influences of the various reaction variables on the methanol conversion over TPA will be described, and the mechanistic characteristics will be discussed with reference to those of the conversion over zeolites.

Experimental

Dodecatungstophosphoric acid (TPA), obtained from Wako Pure Chemicals Ind., was made into pellets, crushed, and sorted into 9—16 mesh. The reaction was carried out with a continuous-flow reactor operating at atmospheric pressure. The catalyst was packed into a reactor of silica-tubing (10 mm i.d.) and placed in a vertical furnace. Methanol was delivered by means of a motor-driven syringe and vaporized in the preheating zone of the reactor, containing 10 cm^3 of quartz. The gas from the outlet of the reactor was analyzed by means of a gaschromatograph equipped with a flame-ionization detector. A 2-m Porapak Q column separated the hydrocarbon products efficiently. The yield or distribution of the products was calculated on a carbon-number basis.

Results and Discussion

Table 1 shows the product and hydrocarbon distribution in the conversion of methanol and dimethyl ether over TPA. The reaction conditions were as follows: reaction temperature, 573 K; methanol pressure, 50.7 kPa, and contact time $(W/F) = 72.0$ g h mol^{-1}, where W and F denote the catalyst weight (g) and the total molar flow rate (mol h^{-1}) respectively. As is shown in Table 1, the two reactants gave similar hydrocarbon distributions except that a higher propylene/propane ratio was obtained when dimethyl ether was used as the starting material. At this temperature, the main products are lower aliphatic hydrocarbons, among which isobutane is most predominant. The formation of carbon monoxide

TABLE 1. PRODUCT DISTRIBUTION IN THE CONVERSION OF METHANOL AND DIMETHYL ETHER

	Reactant	
	CH_3OH	CH_3OCH_3
Reaction conditions		
Reaction temperature/K	573	573
(W/F)/ g mol^{-1} h	72	75
Pressure/kPa	50.7	50.7
Product distribution/%		
CH_3OH	Trace	0.0
CH_3OCH_3	55.1	55.8
Hydrocarbons	44.9	44.2
Hydrocarbon distribution/%		
CH_4	2.6	1.9
C_2H_4	11.9	12.5
C_2H_6	0.6	0.4
C_3H_6	8.3	11.9
C_3H_8	17.9	10.6
C_4	40.0	39.8
C_5	11.9	12.6
C_6	5.3	6.2
C_7^+ a)	1.5	4.1

a) C_7^+ shows the hydrocarbons with more than six carbon atoms.

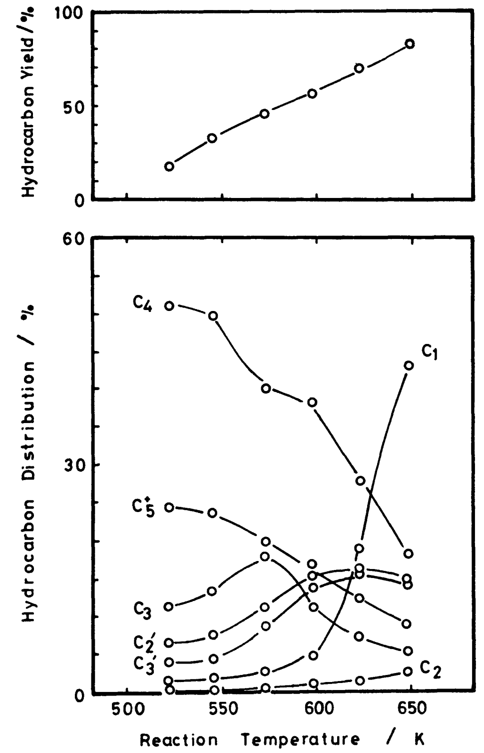


Fig. 1. Effect of the reaction temperature on the total hydrocarbon yield and the distribution of produced hydrocarbons.
Reaction conditions: methanol pressure 50.7 kPa, $W/F = 72$ g h mol^{-1}.

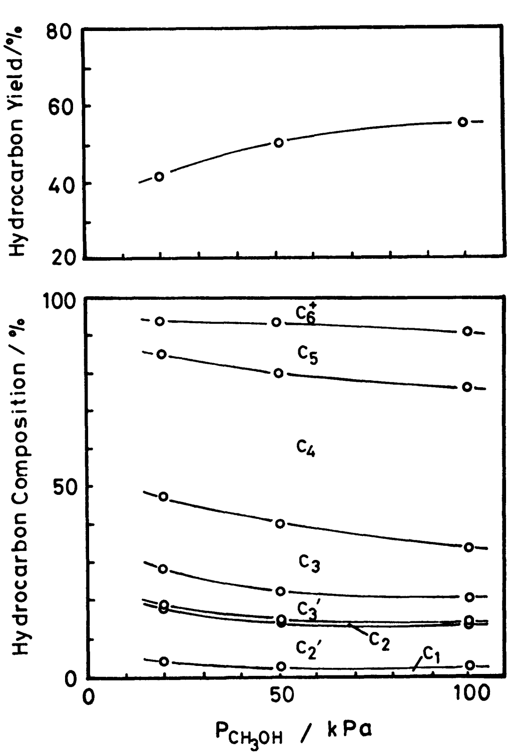


Fig. 2. Effect of the partial pressure of methanol on the total hydrocarbon yield and the composition of the produced hydrocarbons.
Reaction conditions: 573 K, $W/F = 71$ g h mol^{-1}.

and carbon dioxide is negligible. In contrast to the conversion over ZSM-5, only a small amount of aromatic compounds is produced. The loss of the catalytic activity with the process time was small in spite of the accumulation of coke. Thus, under the conditions of 573 K, $W/F = 140$ g h mol^{-1}, and a methanol pressure of 101 kPa, the hydrocarbon yields were 62.8 and 50.2% at 1 and 15 h of process time respectively.

Figure 1 shows the temperature dependence of the yield of hydrocarbons and their distribution in methanol conversion. The hydrocarbon yield increased gradually with the reaction temperature. In contrast to the conversion over ZSM-5,[6] no abrupt increase in the hydrocarbon yield was observed; that is, the reaction seems not to be an autocatalytic one. Among the products, C_4 (hydrocarbons with four carbon atoms) and C_5 hydrocarbons were the predominant products at lower temperatures, and their fractions decreased with the reaction temperature. The fractions of lower olefins (ethylene+propylene) increased with the reaction temperature up to 623 K and decreased at higher temperatures. The fraction of methane was small below 570 K, but increased sharply over 620 K. The optimum temperature for the conversion lies around 570—600 K.

Figure 2 shows the effect of the methanol partial pressure on the hydrocarbon yield and the hydrocarbon

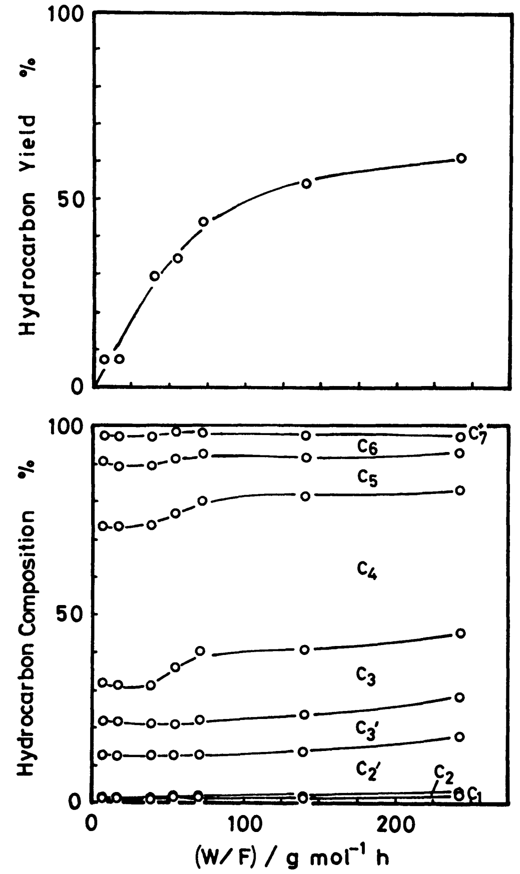


Fig. 3. Effect of the contact time (W/F) on the total hydrocarbon yield and the composition of the produced hydrocarbons.
Reaction conditions: 573 K, methanol pressure 50.7 kPa.

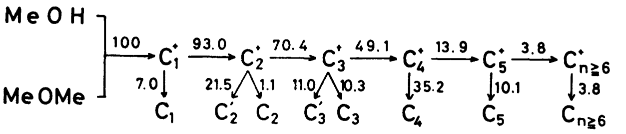
distribution. The yield of hydrocarbons increased only slightly with the methanol partial pressure, indicating that the overall rate of methanol conversion has a slightly higher order than one with respect to the methanol pressure. By lowering the methanol partial pressure, the fraction of lower hydrocarbons in the hydrocarbon products increased slightly.

Figure 3 shows the effect of the contact time (W/F) on the yield of hydrocarbons and their distribution at 573 K. The hydrocarbon yield increased gradually with the increase in the contact time. No acceleration in the rate of hydrocarbon formation was observed, in contrast to the conversion over ZSM-5.[4,5] This again indicates that the methanol conversion over TPA is not an autocatalytic reaction. For the conversion over ZMS-5, the autocatalytic phenomena were explained by assuming that Reaction 2 proceeds much faster than Reaction 1, according to the following reaction scheme:[4,5]

$$CH_3OH \longrightarrow \text{olefins (ethylene)} \qquad (1)$$

$$CH_3OH + \text{olefins} \longrightarrow \text{olefins} + \text{paraffins}. \qquad (2)$$

The lack of autocatalytic phenomena suggests that this assumption is not valid for the conversion over TPA. In conformity with this, the hydrocarbon distribution does not change appreciably with the total hydrocarbon yield. This is more clearly illustrated in Figs. 4—6, where the yield of each hydrocarbon species is plotted against the total hydrocarbon yield. The yield of each hydrocarbon species increases proportionally with the total hydrocarbon yield until the latter reaches *ca.* 50%, implying that all the hydrocarbon species are produced concurrently. Therefore, the following reaction scheme is plausible, assuming carbonium-ion intermediates.



The numbers in the scheme represent the relative rates of the individual steps, which were calculated from the initial distribution of hydrocarbons.

The distinct difference between the mechanism over heteropolyacids and that over ZSM-5 is that olefins once desorbed from the catalyst surface hardly react at all with methanol in the former catalyst, while over ZSM-5 olefins react with methanol rapidly, as has been described above.

The high catalytic activity of TPA seems to be rather unusual, considering the small surface area of TPA ($\approx 2\ m^2\ g^{-1}$). To determine the effective number of active sites of TPA, the effect of pyridine sorption was examined. The reaction was started by feeding methanol and nitrogen at 573 K. After 2 h, pyridine was added to the feed, and then finally the feed was changed back to the starting mixture. Most of the pyridine introduced was retained by the catalyst. As

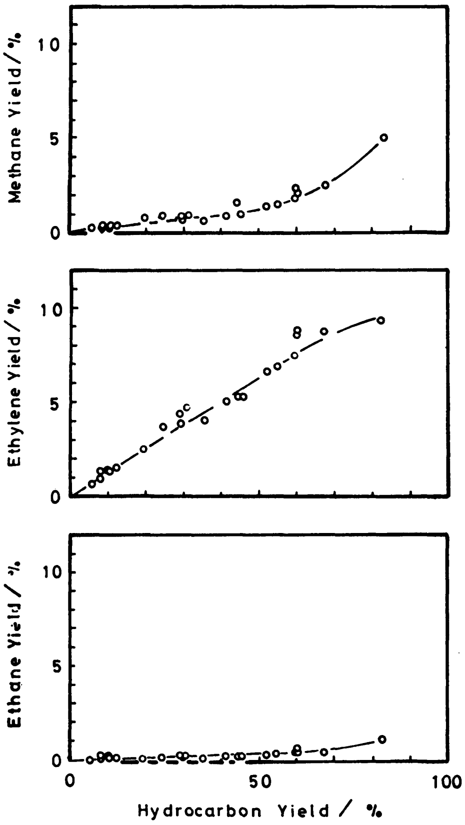


Fig. 4. Yields of methane, ethylene, and ethane as a function of the total hydrocarbon yield.
Reaction conditions: 573 K, methanol pressure 50.7 kPa.

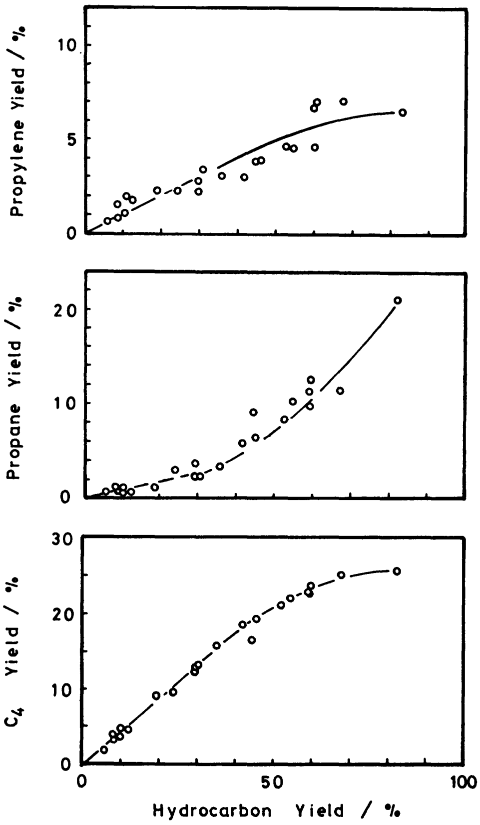


Fig. 5. Yields of propylene, propane and C_4-hydrocarbons as a function of the total hydrocarbon yield.
Reaction conditions, see Fig. 4.

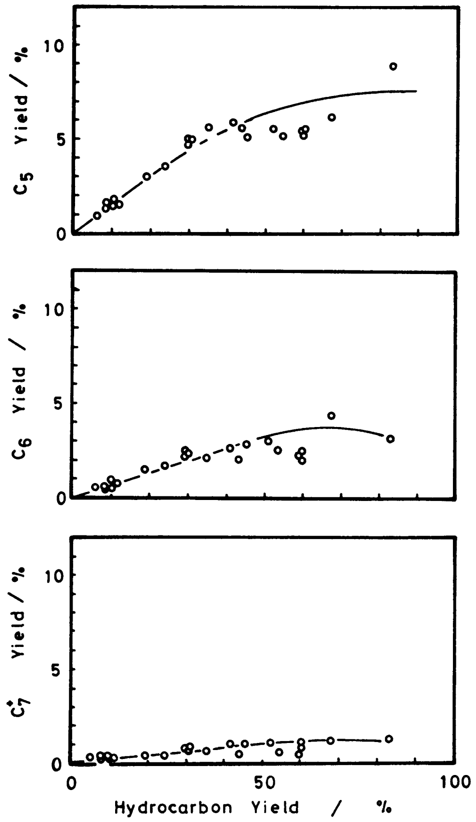


Fig. 6. Yields of C_5-, C_6-, and $C_7{}^+$-hydrocarbons as a function of the total hydrocarbon yield.
Reaction conditions, see Fig. 4.

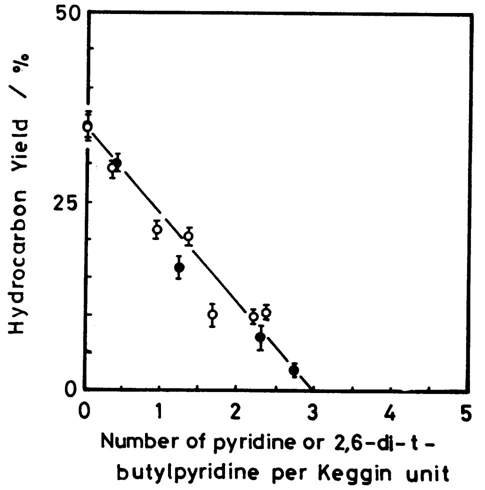


Fig. 7. Change in the hydrocarbon yield with the amount of the sorbed pyridine (○) and 2,6-di-*t*-butylpyridine (●).
Reaction conditions: 573 K, methanol pressure 50.7 kPa, W/F=55.0 g h mol^{-1}.

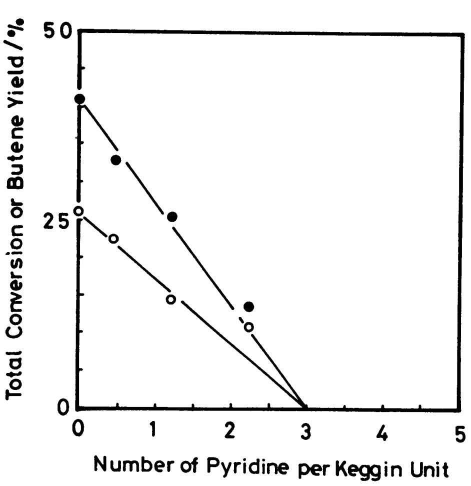


Fig. 8. Change in the conversion of 1-butanol (●) and the yield of butenes (○) in the dehydration of 1-butanol over TPA. The difference between the conversion and butene yield corresponds the formation of dibutyl ether. Reaction conditions: 433 K, 1-butanol pressure, 24.3 kPa, W/F=24.0 g $hmol^{-1}$.

is shown in Fig. 7, the catalytic activity after pyridine sorption decreased linearly with the amount of the sorbed pyridine, a complete loss of the activity being attained when the molar ratio of the sorbed pyridine and the TPA used as a catalyst was three. The use of 2,6-di-*t*-butylpyridine instead of pyridine as a base has the same effect, as is shown in Fig. 7. Since the former poisons Brönsted-acid sites, but not Lewis-acid sites, the type of acid responsible for the conversion is Brönsted acid.

The amount of acid thus estimated indicates that all the protons in the solid TPA are accessible to pyridine molecules. The stoichiometric absorption of pyridine by heteropolyacids at 573 K was reported earlier.[10–12] Since methanol and other polar molecules are known to be absorbed by TPA, even at room temperature,[13,14] we presume that methanol molecules penetrate into the bulk of the solid TPA at the reaction temperature and react in the bulk. This explains the high activity of TPA, irrespective of its small surface area. Okuhara *et al.*,[12] on the basis of the correlation of the activity with the bulk acidity, recently proposed that the conversion of methanol occurred also in the bulk.

Methanol conversion was carried out with TPA (50 wt%) supported on three kinds of silica-gel with surface areas of 14.6, 37.5, and 80.9 $m^2\,g^{-1}$. The yield of hydrocarbons depended only slightly on the surface area of the silica-gel. Thus, under the conditions of 573 K, W/F=48.0 g mol^{-1} h and a methanol pressure of 101 kPa, the hydrocarbon yields were 10.0, 9.1, and 10.6%. This again indicates that the reaction proceeds in the bulk; otherwise, the yield would depend on the surface area of silica-gel.

To confirm that the phenomenon is not specific to the conversion of methanol, the number of acid sites for the dehydration of 1-butanol to dibutyl ether and butenes was determined in a similar manner. As is shown in Fig. 8, the amount of acid sites responsible for the dehydration of 1-butanol is again three times as large as the amount of TPA used as a catalyst. Thus, the dehydration of 1-butanol is also presumed to proceed in the bulk of the solid. It has been reported that the dehydration of ethanol[13] and 2-propanol proceeds in the bulk of heteropolyacids.

Olefins, nonpolar molecules, cannot penetrate into the bulk of the solid TPA. Therefore, the reaction of olefins with methanol occurs only on the surface of the solid, while the reaction between methanol molecules can proceed even in the bulk of the solid. This explains why Reaction 2 is not much faster than Reaction 1, and why the autocatalytic phenomena are not observed in the conversion of methanol over TPA.

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