The Conversion of Methanol into Hydrocarbons over Metal Salts of Heteropolyacids

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Synopsis. Metal salts of heteropolyacids are active catalysts for the conversion of methanol into hydrocarbons. Though the activity depends on the kind of metal salt, the reaction mechanism for the conversion is common to most of the metal salts, and the active centers are probably Brönsted acid centers.

Heteropolyacids such as dodecatungstophosphoric acid (TPA) have a high catalytic activity for the conversion of methanol into hydrocarbons.[1,2] This high activity is caused by the high Brönsted acidity of the heteropolyacids.[2,3] The metal salts of heteropolyacids are effective catalysts for many reactions, for which Brönsted acid sites are supposed to be responsible.[4–8] In this paper, the catalytic activities of various metal salts of TPA and dodecatungstosilicic acid (TSiA) for the conversion of methanol into hydrocarbons will be examined. The mechanistic features of the conversion over the salts will also be discussed.

Metal salts of heteropolyacids were prepared as follows. To the aqueous solution of TPA or TSiA, a stoichiometric amount of metal carbonate in the powder form was added slowly. For metals of which carbonates were not available, metal nitrates in an aqueous solution were used instead. When the metal salts of the heteropolyacids were obtained as precipitates (metal salts of TPA: Al, K, Ag, Cd, Cs, La, and Tl; metal salts of TSiA: Rb, Ag, Cs, La, and Tl), they were filtered, washed with water and dried. To obtain metal salts of heteropolyacid soluble in water, the aqueous solutions were heated to dryness over a water-bath.

The metal salts thus prepared were made into pellets, crushed, and sorted into grains of 9—16 mesh. The reaction was carried out at 573 K with a continuous-flow reactor at atmospheric pressure. The catalyst (3 g) was packed in a reactor of silica tubing (10 mm i.d.), placed in a vertical furnace, and then heated under a nitrogen stream at the reaction temperature. Methanol was delivered at the rate of 2.12×10^{-2} mol h^{-1} by means of a motor-driven syringe; it was vaporized by 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 gas chromatography.

TABLE 1. PRODUCT DISTRIBUTION OF THE CONVERSION OF METHANOL INTO HYDROCARBONS

	Catalyst					
	Cu–TPA[a)]	Fe–TPA	Al–TPA	Cu–TSiA[a)]	Fe–TSiA	Al–TSiA
Product distribution/%[b)]						
CH_3OH	1.4	0	0	4.6	1.8	2.1
CH_3OCH_3	37.3	51.7	64.2	34.7	74.0	83.4
Hydrocarbons	61.3	48.3	35.8	60.7	24.2	14.5
Hydrocarbon distribution/%[b)]						
CH_4	5.2	2.3	5.6	8.2	3.2	4.3
C_2H_4	9.5	9.5	8.4	14.8	10.3	12.4
C_2H_6	0.8	0.5	0.8	0.4	0.4	0.6
C_3H_6	8.5	7.5	7.1	7.9	9.5	13.8
C_3H_8	13.4	13.0	16.0	12.2	12.4	13.1
C_4	39.2	41.4	38.7	36.0	36.1	32.4
C_5	13.7	14.3	11.0	14.3	16.1	14.5
C_6^+	9.7	11.5	12.4	6.2	12.0	8.9

a) TPA and TSiA indicate dodecatungstophosphate and dodecatungstosilicate respectively. b) Calculated on a carbon-number basis.

In Table 1, the product and the hydrocarbon distribution for several metal salts of TPA and TSiA are listed. In every case, methanol is converted into dimethyl ether and hydrocarbons, the formation of carbon monoxide and carbon dioxide being negligible. The main hydrocarbon products are lower aliphatic hydrocarbons; the fraction of aromatic hydrocarbons in the products was very low. The catalytic activities of most of the metal salts did not change appreciably with the running time, though the rather high fraction of paraffins in the products indicates coke deposition in the catalyst bed. Thus, in the case of the conversion over copper(II) salts of TPA, the hydrocarbon yields were 63.1% and 62.4% at the running times of 2.5 h and 32 h respectively.

The activities of the series of metal salts of TPA and TSiA are listed as follows:

For salts of TPA:

$$\begin{array}{ccccccccccccc} \text{Ag} & > & \text{Cu} & > & \text{Cd} & > & \text{H} & > & \text{Fe} & > & \text{Tl} & > & \text{Al} \\ (98.0) & & (61.3) & & (61.0) & & (60.1) & & (48.3) & & (37.3) & & (35.8) \end{array}$$

$$\begin{array}{ccccccccccccc} \text{Cs} & > & \text{Pb} & > & \text{La} & > & \text{Na} & > & \text{K} & > & \text{Cr} & > & \text{Zn} \\ (35.4) & & (25.6) & & (23.6) & & (23.5) & & (20.9) & & (20.4) & & (12.8) \end{array}$$

$$\begin{array}{ccccccccccccc} \text{Li} & > & \text{Ni} & > & \text{Mn} & > & \text{Co} & > & \text{Mg} & > & \text{Ca} & > & \text{NH}_4 \\ (12.0) & & (11.8) & & (10.7) & & (7.7) & & (6.9) & & (4.1) & & (2.6) \end{array}$$

For salts of TSiA

$$\begin{array}{ccccccccccccc} \text{Ag} & > & \text{Cu} & > & \text{H} & > & \text{Cs}^* & > & \text{Rb} & > & \text{Fe} & > & \text{Na} \\ (78.9) & & (60.7) & & (38.6) & & (38.4) & & (28.7) & & (24.2) & & (22.2) \end{array}$$

$$\begin{array}{ccccccccc} \text{Al} & > & \text{Zn} & > & \text{Tl} & > & \text{La} & > & \text{Mg} \\ (14.5) & & (7.3) & & (5.5) & & (2.4) & & (1.2) \end{array}$$

* $HCs_3SiW_{12}O_{40}$[9)]

The numbers in parentheses indicate the hydrocarbon yield at a running time of 2—6 h except for the cadmium salt of TPA, for which the yield at 1 h was adopted because of the rapid deactivation. In general, the metal salt of TPA is more active than the same metal salt of TSiA. As has been reported previously,[10)] silver and copper salts are most active among the metal salts; they are even more active than the protonic forms.

In Figs. 1 and 2, the yields of specific hydrocarbons over metal salts are plotted against the total hydrocarbon yield. It is worthy of note that the points obtained for a variety of catalysts fall onto one common line for each hydrocarbon species. Moreover, when the hydrocarbon yield over Cu(II) salt of TPA was reduced by decreasing the contact time, the yield of each hydrocarbon species was decreased, as was to be expected from the lines

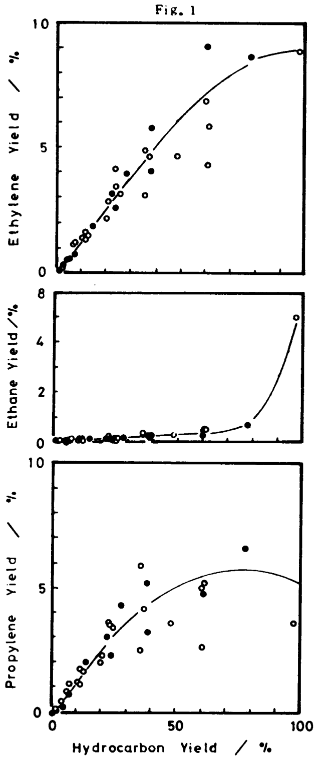
Fig. 1


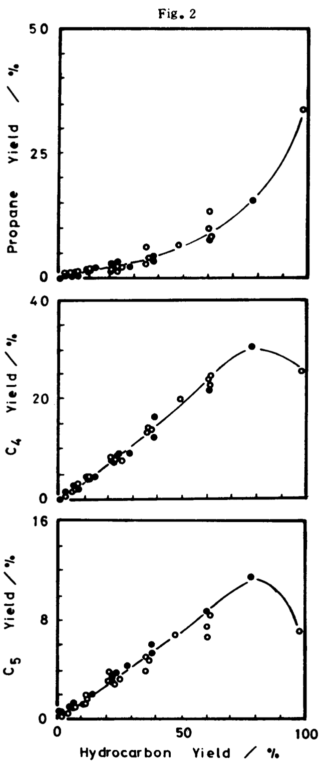
Fig. 2


Fig. 1. The yields of ethylene, ethane, and propylene, as a function of the total yields of hydrocarbons obtained over metal salts of dodecatungstophosphoric acid (○) and dodecatungstosilicic acid (●).

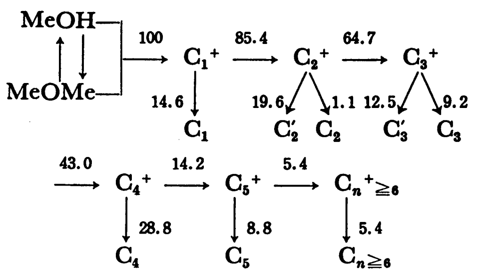
Fig. 2. The yields of propane, C_4-, and C_5-hydrocarbons, as a function of the total yields of hydrocarbons obtained over metal salts of dodecatungstophosphoric acid (○) and dodecatungstosilicic acid (●).

drawn in Figs. 1 and 2. These facts strongly suggest that the reaction mechanism is common for most of the metal salts, although the activity depends on the kind of metal salt. Thus, the active centers for the methanol conversion should be common, and they are presumably Brönsted acid sites. In fact, the activities of copper and silver salts of TPA were poisoned by the addition of pyridine under the present reaction conditions. Presumably, Brönsted acid is produced by the reduction of metal cations by hydrogen molecules or atoms formed by the decomposition of methanol:

$$Ag^+ + 1/2H_2(H) \longrightarrow Ag^0 + H^+.$$

This explains why the salts with highly reducible metal cations, like Ag(I) or Cu(II), have high catalytic activities. The formation of Brönsted acid by the dissociation of water[5] could also be operative for salts with less reducible metals.

Figures 1 and 2 also show that the yield of each hydrocarbon is nearly proportional to the total hydrocarbon yield until the latter reaches 30%, indicating that the hydrocarbon products are formed concurrently at the first stage of the reaction; the products once desorbed from the catalysts do not react easily with methanol or other products. Thus, the reaction scheme of the reaction may be expressed as follows:



Furthermore, one can estimate the relative rate of each reaction step from the initial distribution of hydrocarbons given in the above scheme.

Figures 1 and 2 indicate that the situation is different at the later stage of the conversion. The fraction of propane in the product hydrocarbons increases at the expense of the fractions of light olefins, especially propylene. This change in the product distribution is apparently caused by the presence of water, one of the products, since the addition of water to the starting methanol has a similar effect on the product distribution. Thus, when the feed was composed of methanol (20.2 kPa) and nitrogen (80.8 kPa), the conversion of methanol over copper(II) salt of TPA gave the propane/propylene and butanes/butenes ratio of 0.99 and 2.9 respectively, while the ratios were 4.8 and 8.7 when water (80.8 kPa) was added to the feed instead of nitrogen.

The great difference in the conversion over heteropolyacids from that over zeolites is that olefins, once formed, react with methanol only slowly,[3] while, over zeolites, the reaction of olefins with methanol is so fast that the overall reaction proceeds autocatalytically.[11,12]

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