Conversion of Methanol into Hydrocarbons Catalysed by Metal Salts of Heteropolyacids

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Summary Metal salts of dodecatungstophosphoric acid and dodecatungstosilicic acid, especially the copper(II) and silver(I) salts, convert methanol into hydrocarbons in high yield.

ONO *et al.*[1] have reported that heteropolyacids such as dodecatungstophosphoric acid (HTP) are active catalysts for the conversion of methanol into hydrocarbons. Since metal salts of heteropolyacids are often active catalysts of acid-catalysed reactions, we have examined the catalytic activities of various metal salts of HTP and dodecatungstosilicic acid (HTS) for this methanol conversion. Herein we report that copper(II) and silver(I) salts of the heteropolyacids are more active than the acids.

The metal salts of heteropolyacids were prepared as follows. Silver salts were obtained as precipitates by adding silver carbonate to an aqueous solution of the heteropolyacids; copper(II) salts were obtained by adding the stoicheiometric amount of copper(II) hydroxide carbonate to an aqueous solution of heteropolyacids and drying the resultant solution over a water-bath. Salts thus obtained were made into pellets and sorted into grains of diameter 1·6—2·8 mm. The reaction was carried out at 573 K with a continuous-flow reactor operating at atmospheric pressure. The catalyst (3 g) was packed into a reactor of silica tubing (10 mm i.d.) and placed in a vertical furnace. The feed rate of methanol was $2{\cdot}12 \times 10^{-2}$ mol h^{-1} The results are given in the Table in which the product

TABLE. Product distribution of the conversion of methanol into hydrocarbons

	Catalyst					
	HTP[a]	CuTP	AgTP	HTS[a]	CuTS	AgTS
Product distribution (%)[b]						
MeOH	1·3	1·2	0	3·9	4·7	0
MeOMe	38·6	37·3	2·0	57·5	35·5	20·1
Hydrocarbons	60·1	61·5	98·0	38·6	50·8	79·9
Hydrocarbon distribution (%)[b]						
CH_4	3·7	5·2	9·0	1·6	7·3	3·2
C_2H_4	11·3	9·5	9·0	10·3	11·2	10·3
C_2H_6	0·9	0·8	5·2	0·5	0·5	1·2
C_3H_6	8·3	8·5	3·8	8·3	8·7	8·3
C_3H_8	16·1	13·4	34·0	9·8	14·5	21·9
C_4	39·3	39·2	26·1	41·8	35·1	36·4
C_5	12·5	13·7	7·2	15·8	15·1	13·3
C_6	7·9	9·7	5·7	11·9	7·6	5·4

[a] TP and TS indicate dodecatungstophosphate and dodecatungstosilicate, respectively. [b] Calculated on a carbon-number basis.

distribution and the hydrocarbon distribution are expressed on a carbon-number basis, exclusive of the coke remaining in the reactor. In every case, methanol was converted into dimethyl ether and hydrocarbons and the formation of carbon monoxide or carbon dioxide was negligible. The main products were the C(2)—C(5) aliphatic hydrocarbons; the fraction of aromatic hydrocarbons in the products was very low ($< 2{\cdot}5\%$), in contrast with the conversion over zeolites.[2-4] The catalytic activities of silver and copper salts were much higher than those of the corresponding acids. There was no appreciable change in the activity after 30 h for copper(II) dodecatungstophosphate [Cu(II)–TP] at 573 K. Silver(I) dodecatungstophosphate had a high activity, even at 523 K, and gave a hydrocarbon yield of 37·6%. At 673 K, the main product was methane for all the catalysts examined.

Since the conversion of methanol is caused by a Brönsted-acid site,[5] the high activities of copper(II) and silver(I) salts of the heteropolyacids suggest that these salts have high acidity close, or superior, to that of the acids. In fact, the presence of Brönsted-acid sites in Cu(II)–TP was confirmed by a band at ν 1532 cm^{-1} due to the pyridinium ion, produced when pyridine was adsorbed. It is not clear, however, what causes Brönsted acidity in the salts. Studies to determine this and the factors affecting product selectivity are now in progress.

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[1] Y. Ono, T. Mori, and T. Keii, Preprints of 7th International Congress on Catalysis, C 12 1980, Tokyo.
[2] C. D. Chang and A. J. Silvestri, *J. Catal.*, 1977, **47**, 249.
[3] E. G. Derouane, J. B. Nagy, P. Dejaifve, J. H. C. van Hooff, B. P. Spekman, J. C. Vedrine, and E. Naccache, *J. Catal.*, 1978, **53**, 40.
[4] Y. Ono, E. Imai, and T. Mori, *Z. Phys. Chem. Neue Folge*, 1979, **115**, 99.
[5] Y. Ono, T. Mori, and T. Keii, *J. Chem. Soc., Faraday Trans.* 1, in the press.