Vapour Phase Carbonylation of Methanol or Dimethyl Ether with Metal-ion Exchanged Heteropoly Acid Catalysts

Richard W. Wegman

Union Carbide Corporation, PO Box 8361, South Charleston, WV 25303, USA

Metal-ion exchanged heteropoly acids of the general formula $M[W_{12}PO_{40}]$ (M = a group VIII metal) supported on SiO_2 have been found to be excellent catalysts for the vapour phase carbonylation of methanol or dimethyl ether to methyl acetate at 225 °C and 1 atm total operating pressure.

Heteropoly acids (HPA) of the formula $H_3M_{12}PO_{40}$ (M = Cr, Mo, W) are known to catalyse many types of reactions.[1] Examples include dehydration of alcohols, Friedel–Crafts type reaction, oxidative dehydrogenation and partial oxidation of organic compounds.[2–5] Recently, much attention has been given to $H_3W_{12}PO_{40}$ as a catalyst for the conversion of methanol into hydrocarbons.[6–10] This reaction is carried out in the vapour phase (300–375 °C) and the products include ethylene, propylene and saturated C_1–C_5 hydrocarbons. It is postulated that carbonium ions are intermediates in the reaction mechanism.[11]

Surprisingly, there has been little work directed toward exploring the possibility of carbonylating carbonium ions generated in the vapour phase by HPAs. This approach is reminiscent of the Koch reaction which is traditionally carried out in the liquid phase with a strong acid catalyst.[12] For example, BF_3 will catalyse the carbonylation of methanol (liquid phase) at 160–200 °C and 10 000 psi CO in low yield *via* Koch chemistry, eqns. (1)–(3).

$$\mathrm{MeOH + H^+ \longrightarrow Me^+ + H_2O} \quad (1)$$

$$\mathrm{Me^+ + CO \longrightarrow MeC(O)^+} \quad (2)$$

$$\mathrm{MeC(O)^+ + MeOH \longrightarrow MeC(O)OMe + H^+} \quad (3)$$

It seemed plausible to us that HPAs might catalyse the carbonylation reaction in the gas phase according to eqns. (1)–(3). Experiments with $H_3M_{12}PO_{40}$ (M = Mo, W) were carried out in a conventional flow reactor at 1 atm CO, GHSV = 900 h^{-1}, MeOH LHSV = 0.15 h^{-1}, and 200–275 °C. Reaction products were analysed by gas chromatography. At these conditions methanol is converted into dimethyl ether (DME) and small amounts of C_1–C_5 saturated hydrocarbons and C_2–C_4 olefins (this product mixture will be referred to as HC). Increasing the temperature to 300–350 °C resulted in a substantial increase in HC although a trace amount of methyl acetate was observed with $H_3Mo_{12}PO_{40}$ at 350 °C. Supporting $H_3Mo_{12}PO_{40}$ on SiO_2 slightly increased the amount of methyl acetate formed.

The acidic protons of $H_3M_{12}PO_{40}$ were exchanged with various group VIII metal cations capable of satisfying the HPA valence requirements according to the idealized reaction shown below for Rh^{3+} [13]

$$\mathrm{H_3M_{12}PO_{40} + Rh^{3+} \longrightarrow RhM_{12}PO_{40} + 3H^+} \quad (4)$$

This idealized exchange process may be more complex than indicated by eqn. (4).[14] The materials reported here were not thoroughly characterized and may, in fact, be metal-doped HPAs and not truly ion exchanged. The exchanged HPAs were supported on SiO_2 (*via* incipient wetness) with a loading of 1.75 wt% and tested for carbonylation activity as noted above. The results are given in Table 1. Interestingly, we found that while $RhMo_{12}PO_{40}$ is not an overly active catalyst, the corresponding W-based compound is active. For example, with $RhMo_{12}PO_{40}/SiO_2$ at 250 °C, the methyl acetate yield is very low, whereas, with $RhW_{12}PO_{40}/SiO_2$, the methyl acetate yield is 44% with the other observed product yields being MeOH = 3, DME = 48 and HC = 5% (yields are on a water-free basis). At this temperature the methyl acetate yield dropped rapidly to <1% over 6 h with DME, MeOH, and HC increasing. Decreasing the temperature to 220 °C lowered the methyl acetate yield to 34% but the catalyst activity remained constant over 6 h. In this case, only trace amounts of HC were formed and the methyl acetate selectivity (excluding DME and MeOH) was >95%. Replacing CO with N_2 during the course of an experiment results in the immediate loss of methyl acetate and concurrent formation of HC. Similar results were obtained if the $RhW_{12}PO_{40}/SiO_2$ catalyst was prepared with $Rh(NO_3)_3$ or $RhCl_3 \cdot 3H_2O$.

The $RhW_{12}PO_{40}$ catalyst was prepared with alumina (acidic and neutral), Florisil and Alundum supports. All of these were significantly inferior to the SiO_2-supported catalysts.[15] Alumina- and Alundum-based catalysts resulted in the coproduction of methyl acetate and HC. The Florisil-supported catalyst was inactive. A Rh/SiO_2 catalyst was prepared and tested under conditions identical to $RhW_{12}PO_{40}/SiO_2$. DME was the only observed product; methyl acetate and HC were not formed. These results indicate that Rh, $H_3W_{12}PO_{40}$, and SiO_2 are necessary components of the Rh–W based catalyst. The preference for SiO_2 as a support for HPAs used in various catalytic reactions has been reported previously.[16]

DME is the main component of the product mixture demonstrating the acidic character of the $RhW_{12}PO_{40}$ catalyst.[17] Dehydration of methanol to DME is a well known reaction and occurs readily in the presence of a HPA.[18,19] It is generally accepted that in the conversion of MeOH to HC, the preliminary step is formation of DME and that it is converted to HC.[20,21] We found that the reaction of DME and CO (1 : 3 molar ratio) with the $RhW_{12}PO_{40}/SiO_2$ catalyst (225 °C, 1 atm CO and GHSV = 900 h^{-1}, and no MeOH feed) resulted in the formation of methyl acetate. The DME conversion was 16% and methyl acetate was the only product, there was no MeOH or HC detected in the product mixture.

In this work we have demonstrated that in the presence of metal exchanged HPAs methanol or dimethyl ether are carbonylated with CO in lieu of being converted to HCs. Based on the above results the overall reaction can be expressed as shown in eqns. (5) and (6).

$$\mathrm{2MeOH \rightleftharpoons MeOMe + H_2O} \quad (5)$$

$$\mathrm{MeOMe + CO \longrightarrow MeC(O)OMe} \quad (6)$$

Table 1 Metal exchanged $H_3W_{12}PO_{40}$ catalysts supported on SiO_2

	Product yield (%)[a]		
Catalyst[b]	MeOH	DME	MeC(O)OMe
$IrW_{12}PO_{40}$	8	52	40
$RhW_{12}PO_{40}$	17	49	34
$HPdW_{12}PO_{40}$	0	92	8
$HMnW_{12}PO_{40}$	0	96	4
$HCoW_{12}PO_{40}$	5	92	3
$HNiW_{12}PO_{40}$	7	90	3
$FeW_{12}PO_{40}$	7	92	1

[a] MeOH, DME, and MeC(O)OMe were the only products observed with these catalysts during the 6 h reaction. [b] Idealized stoichiometries based on eqn. (4). All reactions carried out at 225 °C, 1 atm CO, GHSV = 900 h^{-1}, MeOH LHSV = 0.15 h^{-1}.

Although the detailed mechanism of this carbonylation reaction is not known, the intermediacy of carbocations and their reaction with CO cannot be ruled out. Eqn. (1) has been postulated to occur in the dehydration of methanol to DME. The role of CO in the zeolite catalysed methanol to HC reaction is unclear.[22] It is possible that Rh coordinates CO and increases its effective concentration within the catalyst. In many ways this is similar to the liquid phase Koch catalysts where Cu^+ and Ag^+ are utilized to solubilize CO. It is also possible that MeOH or DME reacts directly with Rh to form a Rh–Me intermediate that undergoes carbonylation to methyl acetate. This is similar to the well established mechanism in the homogeneous process catalysed by Rh and an iodide promoter. Compared to the known liquid phase methanol carbonylation processes, some advantages of this gas phase reaction are: (*i*) halide promoters (iodide) are not required, (*ii*) product separation is very simple and (*iii*) the reaction conditions are mild.

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