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Methanol Conversion over Metal Salts of 12-Tungstophosphoric Acid

HIROMU HAYASHI[1] AND J. B. MOFFAT[2]

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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The sodium, boron, calcium, magnesium, zinc, aluminum, and zirconium salts of 12-tungstophosphoric acid have been prepared and characterized using X-ray diffraction, mercury porosimetry, the chemisorption of ammonia, and Hammett indicators. Methanol conversion at 350°C and a variety of residence times produced hydrocarbons ranging from C_1 to C_5 in amounts which varied with the cation. The more strongly acidic salts produced the higher yields of hydrocarbons. The maximum yield of the major product C_4 was found with the aluminum salt. The activities were related to the partial change on the oxygen atoms in the various catalysts.

INTRODUCTION

In the last several years there has been increasing interest in the catalytic properties of heteropoly acids (*1*). This partly arises from the interesting properties, both structural and chemical, of these highly acidic solids (*2, 3*) and the increasing evidence for their catalytic flexibility (*1*). Although the metal salts of these acids have been known for many years, only recently has interest arisen in their catalytic properties. Metal salts of 12-molybdophosphoric and 12-molybdosilicic acids have been shown to be effective in hydro-desulfurization (*4*), epoxidation of olefins (*5*), alkylation (*6, 7*), preparation of saturated carbonyl compounds (*8*), direct oxidation of benzene to phenol (*9*), oxidation of methacrolein (*10*), and vapor-phase oxidative dehydrogenation of isobutyric acid (*11*).

Heteropoly acids have been shown to be active in the conversions of methanol to hydrocarbons (*1*) and very recently interest has developed in metal salts of these acids as catalysts for this process. The copper salts of 12-tungstophosphoric acid and of 12-tungstosilicic acid (12) and the copper and silver salts of dodecatungstophosphoric acid and dodecatungstosilicic acid have been shown to convert methanol to hydrocarbons (*13*). Methanol conversion has also been studied over the sodium, calcium, nickel, and copper salts of 12-tungstophosphoric acid (*14*).

The present work has been initiated to compare the catalytic activities of a number of salts of 12-tungstophosphoric acid as well as the parent acid for the methanol conversion process.

EXPERIMENTAL

Methanol conversion was carried out in a microcatalytic pulse reactor as described in the previous paper (*1*). Metal salts for Na, Ca, Mg, and Zn were obtained (*15*) from an aqueous solution of 12-tungstophosphoric acid by addition of stoichiometric quantities of the carbonates or basic carbonates given in Table 1. Salts for Al, B, and Zr were prepared by the reaction of the alkoxides given in Table 1 with the acid in ether for which the stoichiometry is:

$$H_3PW_{12}O_{40} + B(OC_3H_7)_3 \rightarrow BPW_{12}O_{40} + 3C_3H_7OH$$

The resultant salt (etherate) was washed twice with water and ether to remove by-

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[1] On leave from Department of Chemical Engineering, Tokushima University, Minamijosanjima, Tokushima, 770 Japan.

[2] To whom correspondence should be addressed.

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TABLE 1

Properties of Metal Salts of 12-Tungstophosphoric Acid[a]

Metal cation source	Hydrated salt obtained	Surface area (m^2/g)[b]	Chemisorbed NH_3 (mmol/KU)[c]	Acid strength, H_0[d]			
				+1.5	−3.0	−5.6	−8.2
$NaHCO_3$	$Na_3PW_{12}O_{40} \cdot 12H_2O$	6.2	3.7_2	+	−	−	−
$CaCO_3$	$Ca_3[PW_{12}O_{40}]_2 \cdot 26H_2O$	5.9	2.8_2	+	(+)	−	−
$ZnCO_3 \cdot 2ZnO \cdot 3H_2O$	$Zn_3[PW_{12}O_{40}]_2 \cdot 37H_2O$	4.9	6.3_7	+	+	−	−
$Mg(OH)_2 \cdot 4MgCO_3 \cdot 5H_2O$	$Mg_3[PW_{12}O_{40}]_2 \cdot 33H_2O$	5.9	3.1_2	+	+	(+)	−
$Al(OC_3H_7\text{-}i)_3$	$AlPW_{12}O_{40} \cdot 13H_2O$	5.5	3.0_2	+	+	+	−
$B(OC_3H_7\text{-}n)_3$	$BPW_{12}O_{40} \cdot 9H_2O$	5.6	3.3_5	+	+	+	−
$Zr(OC_3H_7\text{-}n)_3$	$Zr_3[PW_{12}O_{40}]_4 \cdot 44H_2O$	4.6	2.1_0	+	+	+	−
—	$H_3PW_{12}O_{40} \cdot 24H_2O$	3.2(3.1)[e]	4.3_2	+	+	+	+

[a] For metal salts calcined at 400°C in He for 2 hr.

[b] Porosimetry.

[c] KU = Keggin Unit, $PW_{12}O_{40}$.

[d] Indicator method: +, acidic color; −, basic color; (+), vague.

[e] BET.

product alcohol. Using ethanol or dioxane as a solvent, the boron salt turned black during calcination presumably due to carbonization of the strongly bound solvent. A similar reaction of tri-alkylphosphate and orthophosphoric acid has been reported to give boron phosphate (*16–18*). Carbonates of Na and Mg were obtained from Baker as analyzed reagent grade, and those of Ca and Zn, and 12-tungstophosphoric acid from BDH Chemicals as Analar analytical reagent. Aluminum *i*-propoxide and zirconium *n*-propoxide were obtained from Alfa Products, and tri-*n*-propyl-borate from K&K Inc. Apparatus and procedure for characterization of catalysts were described in the previous paper (*1*).

RESULTS

Table 1 shows some properties of the salts calcined at 400°C in helium. Anhydrous $H_3PW_{12}O_{40}$ was shown to be strongly acidic with Ho values as low as −8.2 and the acid strength of salts decreased in the order of $H > Zr \simeq Al \simeq B > Mg > Zn > Ca > Na$, as evident in Table 1. The surface areas and concentrations of acidic sites estimated from the chemisorption of ammonia at room temperature were each of the same order of magnitude, ranging around 5 m^2/g and 3 mmol/Keggin-unit, respectively. The uncalcined heteropoly salts are highly hydrated and a porous texture may be expected to form by the removal of zeolitic water (*19*). However, mercury porosimetry showed that the salts possessed negligible amounts of pore volume with radii less than 100 Å as anticipated from the relatively low surface areas. Similar areas were found by Akimoto *et al.* (*11*) for 12-molybdophosphoric acid, 12-molybdosilicic acid, and sodium and lithium salts of these acids.

Powder X-ray diffraction patterns for the sodium, boron, and zirconium salts were similar to those for the parent acid but the 2θ values were slightly shifted in the former cases from those in the latter (Fig. 1). Interestingly the calcium, magnesium, and zinc salts appeared to be amorphous, while the aluminum salt is partly crystalline. Similarly, Akimoto *et al.* (*11*) found their heteropoly compounds, with the exception of the alkaline-earth metal salts, were relatively highly crystallized.

Figure 2 compares the results for methanol conversion over metal salts of 12-tungstophosphoric acid at 350°C covering a wide range of residence times (W/F). The most weakly acidic sodium salt (a) gave exclusively dimethyl ether by dehydration of methanol for relatively low values of W/F, in good agreement with the conversion of

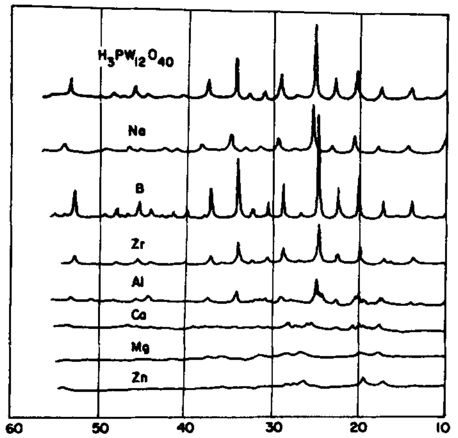

FIG. 1. Powder X-ray patterns of metal salts of 12-tungstophosphoric acid calcined at 150°C in air for 2 hr.

methanol (X_A) and the yield of ether (Y_E), both of which increased with increasing W/F. Methane and ethylene appeared in trace amounts with Y_E decreasing below X_A as W/F increased beyond 250 (mg-cat min/ml-He). The calcium salt (b) gave various hydrocarbon products ranging from C_1 to C_5. The total hydrocarbon yield increased, while Y_E decreased, with the increase in W/F. It may also be noted that the C_4 and C_5 yields pass through maxima within the range of the W/F values examined.

The more strongly acidic salts, zinc (c), magnesium (d), aluminum (e), zirconium (f), and boron (g), resulted in higher yields of hydrocarbons. The gross features of the yield pattern are similar to those of the free acid (h). Methane increased with the increase in W/F, while other hydrocarbons passed through a maximum. The distribution in carbon number was centered at C_4 and sharply dropped at C_5. The maximum yield of the major product C_4 increased with the increase in acid strength in the order of Ca < Zn < Mg < Al, and then decreased in the order of Al > Zr > B, approaching to the behavior of the free acid (h).

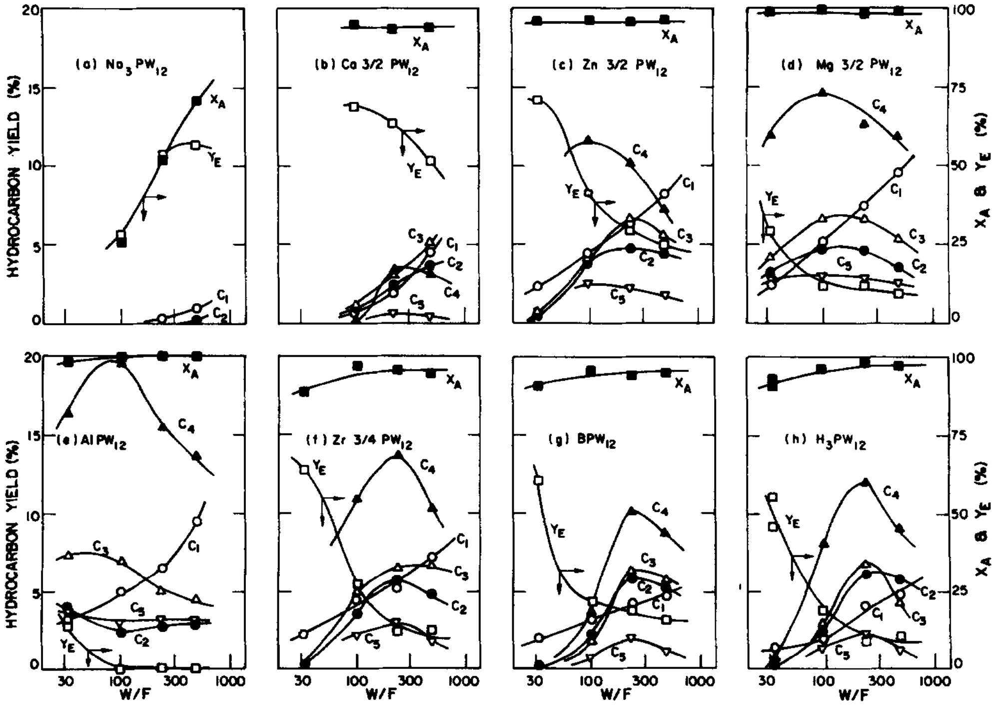

FIG. 2. Methanol conversion over metal salts of 12-tungstophosphoric acid. Reaction temperature: 350°C. Catalyst calcined at 400°C in He for 2 hr.

Ethylene was the major product in C_2, while iso-paraffins were predominant among C_4 and C_5 for all salts given in Fig. 2. It is of interest to notice that the ratio of propylene/propane in C_3 was 0.7–1.9 for strongly acidic aluminum (e), zirconium (f), and boron (g) salt, while that for weakly acidic zinc (c) and magnesium (d) salt was 4.0–6.6 and calcium salt (b) gave exclusively propylene. The production of CO and CO_2 was negligible with all the metal salts studied.

DISCUSSION

With all the catalysts examined in the present work, with the exception of the sodium salt, virtually all of the methanol is consumed for the entire range of residence times examined. In addition, the yield of dimethyl ether decreases as the concentration of hydrocarbons increases. Evidently the process by which methanol is converted to dimethyl ether occurs readily and the ether serves as the primary precursor in the subsequent formation of hydrocarbons.

Since the salts are acidic, but with a range of maximum acid strengths, it is highly probable that the most abundant reaction intermediates in the methanol conversion process are carbonium ions. Further evidence for this is seen in the distribution of hydrocarbon products. As is characteristic of the cracking pattern found with carbonium ions, the C_4 hydrocarbon dominates the reaction products. The observation of ethylene as the primary C_2 hydrocarbon and iso species as the predominant C_4 and C_5 hydrocarbons is consistent with a carbonium ion mechanism.

It is not possible with the present data to discriminate between Brønsted and Lewis acid sites as the effective centers of catalytic activity for the formation of the carbonium ions. Since water is produced in the conversion of methanol to dimethyl ether and there is no evidence of the poisoning of the catalytic activity resulting from the presence of water, Brønsted sites are expected to be the primary acidic sites. Presumably the conversion of Lewis sites would be readily facilitated by the water vapor present.

The largest concentration of C_4 hydrocarbons is produced by the aluminum salt. The aluminum salt also is the most active in total (C_1 to C_5) hydrocarbon production, although the magnesium salt shows activity very close to that of aluminum on the latter basis. The activity is seen to be approximately related to the maximum acid strengths, although boron and zirconium salts have maximum acid strengths similar to that of the aluminum salt but conversion activities somewhat smaller.

It is of interest to relate the catalytic activity to a parameter indicative of acid strength. At least for Brønsted acidic sites, the fractional charge on the oxygen atom may suffice for such purposes. Sanderson (*20*) has developed a simple semiempirical method for estimating the fractional charges on atoms found in a molecule. The partial charge

$$\delta = \frac{\Delta\chi}{\Delta\chi(1)}$$

is related to the change in electronegativity ($\Delta\chi$) of an atom in becoming part of a molecule and the corresponding change ($\Delta\chi(1)$) in gaining or losing one electron. The latter term can be related to the electronegativity, χ, of the isolated atom by

$$\Delta\chi(1) = 2.08\ \chi^{1/2}.$$

Values for $\Delta\chi$ for each of the molecules of interest are obtained from the principle of electronegativity equalization (*20*). A plot (Fig. 3) of the yield of C_4 hydrocarbons versus the fractional charge on oxygen (δ_O) in various salts shows an exponentially decreasing yield of C_4 with δ_O beginning with aluminum and ending with sodium. This is as expected if it is assumed that Brønsted sites are of primary importance as catalytic centers in the present salts. Interestingly there is a rather sharp decrease in C_4 hydrocarbon yield for salts with δ_O smaller than that in the aluminum salt. This is suggestive

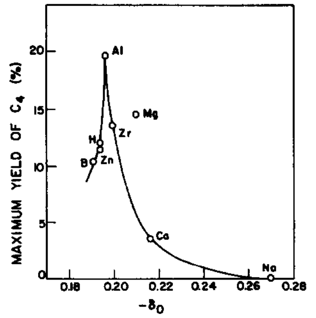

FIG. 3. Maximum yield for C_4 hydrocarbons in methanol conversion and the partial charge on oxygen (δ_O) in the metal salts of 12-tunstophosphoric acid.

of a relatively narrow range of efficiently active acidic sites. It is to be noted that irreversible chemisorption and carbon formation as evidenced in mass balances are more predominant in those salts with δ_O below that in the aluminum salt. Consequently such salts may owe their apparently decreased activity as much to a tight binding of the product hydrocarbon as to any deficiency in conversion capabilities. Total yields of C_1–C_5 hydrocarbons approximately paralleled those obtained for C_4 hydrocarbons.

As noted earlier, more propane than propylene is produced on the more acidic catalysts studied in the present work while significantly larger amounts of propylene are found with the less acidic catalysts. Such observations suggest that hydrogen transfer occurs more readily on the more acidic catalysts, a result which appears to be contrary to that found with silica–alumina and zeolite catalysts (*22*).

While no conclusions on detailed aspects of the mechanism can be drawn from the present data, it is useful to comment briefly on the process. In this regard it should be noted that, except for methane, the concentrations of all hydrocarbons show a maximum with residence time. The concentration of methane increases continuously with W/F. Two processes are apparently in competition, one of oligomerization, the other of cracking, the latter producing methane as an ultimate product. Although quite obviously dissimilar in various respects, ZSM zeolites and heteropoly acids are both acidic catalysts capable of converting methanol to hydrocarbons. A number of different mechanisms have been proposed for methanol conversion on ZSM (*23–25*). Chang and Silvestri (*23*) have suggested that both acidic and basic sites are required to produce a carbene-like intermediate. Derouane *et al.* (*24*) postulate that an ethyl carbonium ion forms an ethoxy group on the surface while Ono and Mori (*25*) suggest that the interaction of methanol and surface hydroxyl group produces methoxy groups bound to the surface. With the present salts of 12-tunstophosphoric acid it appears probable that dimethyl ether interacts with a Brønsted site, initially forming a surface methoxy group. The reaction of the latter group with a second ether molecule can then produce a surface ethoxy group. The process of oligomerization can thus occur by subsequent interactions between additional dimethyl ether molecules and the surface species or as a result of interaction between the surface species and those which have desorbed.

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