

Conversion of methanol over metal salts of 12-molybdophosphoric acid

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The effect of ionic size of the counter cation and its electronegativity on the conversion of methanol to dimethyl ether and methane over sodium, calcium, magnesium and zinc salts of dodecamolybdophosphoric acid has been studied. The reaction has been carried out in a flow system. It has been found that the zinc salt which has the highest electronegativity and the smallest cation radius is the most active catalyst. The higher activity observed at lower calcination temperatures may be explained by the concept of pseudo liquid phase. The results indicate that methane is formed by a consecutive reaction. The effect of pyridine on both products has also been studied. It is found that the formation of ether is more inhibited by pyridine than methane. Ether formation follows a second order equation of Langmuir-Hinshelwood type, whereas methane formation follows a first order equation.

The dehydration of methanol to dimethyl ether is a well known reaction catalysed by solid acidic oxides^{1,2}, while its conversion into hydrocarbons on heteropoly compounds has been reported only during the last decade³⁻⁸. Ono *et al.*^{9,10} found that copper(II) and silver(I) salts of dodecatungstophosphoric acid and dodecatungstosilicic acid are active catalysts for the conversion of methanol into dimethyl ether and hydrocarbons. It was found^{3,8,11} that dimethyl ether is a precursor for hydrocarbons and that the weakly acidic sites may be sufficient to catalyze the formation of the ether. The active sites are assumed³ to be Brönsted acid sites. The catalytic activity of tungstophosphoric acid and its salts is proportional to acid strength^{8,12,13}.

The acidity of the salts of heteropoly acids¹⁴⁻¹⁷ is due to: (i) the dissociation of the water coordinated to metal cation (M^{n+}), (ii) proton generation from H_2 or H by the reduction of metal cations like Ag^+ and Cu^{2+} , and (iii) protons are formed by the partial hydrolysis of anions in the preparation process. The acidic properties of molybdophosphoric acid and tungstophosphoric acid, i.e., the amount of acidity, its type (Brönsted or Lewis) and its strength were studied by many authors¹⁸⁻²¹. From IR spectra of adsorbed pyridine it was found^{18,21} that pyridine is present in the form of the pyridinium ion. Number of surface acidic protons on heteropoly acids is comparable with the number of Brönsted acid sites on silica-alumina²² and heteropoly acids are stronger in acidity¹⁸ than $Al_2O_3-SiO_2$. The changes in the calcination conditions may alter both the number and strength of the acidic sites³. The acidity of salts of dodecamolybdophosphoric acid is strongly af-

ected by the electronegativity of the cation as well as its amount^{23,24}. Salts of cations with lower electronegativity are less acidic whereas the most electronegative cation has the maximum activity.

The aim of this work is to study the activity of the catalyst with time, the effect of calcination temperature, to compare the catalytic activity of Na, Ca, Mg and Zn salts of 12-molybdophosphoric acid towards the conversion of methanol, the effect of pyridine on ether and methane formation and to throw some light on the reaction mechanism.

Materials and Methods

The procedure, apparatus and catalyst preparation have been given elsewhere^{10,25}. The particle size of the catalysts used is 0.2-0.3 mm except with the calcium salt (≤ 0.1 mm) which was difficult to obtain in the required particle size. Each catalyst specimen was activated by heating at 400°C in a stream of pure and dry H_2 for 4 hrs before measurements, then the temperature was lowered to the desired reaction temperature. A series of ether and methane standards in argon were prepared to determine the amount of the ether and methane produced. The effect of pyridine (5% and 19% v/v in the alcohol feed) on the formation of both ether and methane at constant temperature and constant argon flow was studied. The reaction products were analysed chromatographically using 3700 Varian Gas Chromatograph with flame ionisation detector. The column used was packed with 10% squalane supported on chromosorb. All the chemicals used in this study were pure grade as indicated by chromatographic analysis.

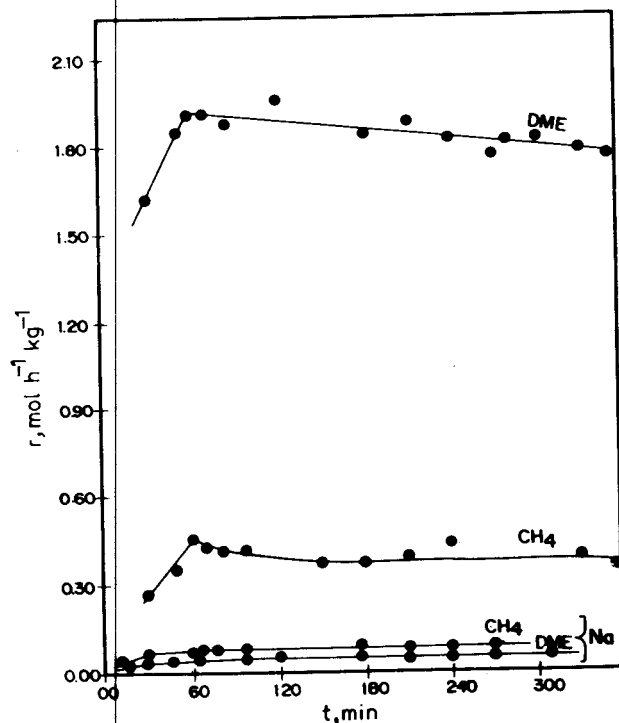


Fig. 1—Check of the activity of sodium and magnesium salts of molybdophosphoric acid towards the formation of dimethyl ether and methane at different time intervals. [$P_{\text{CH}_3\text{OH}} = 102$ torr, temp. = 300°C .]

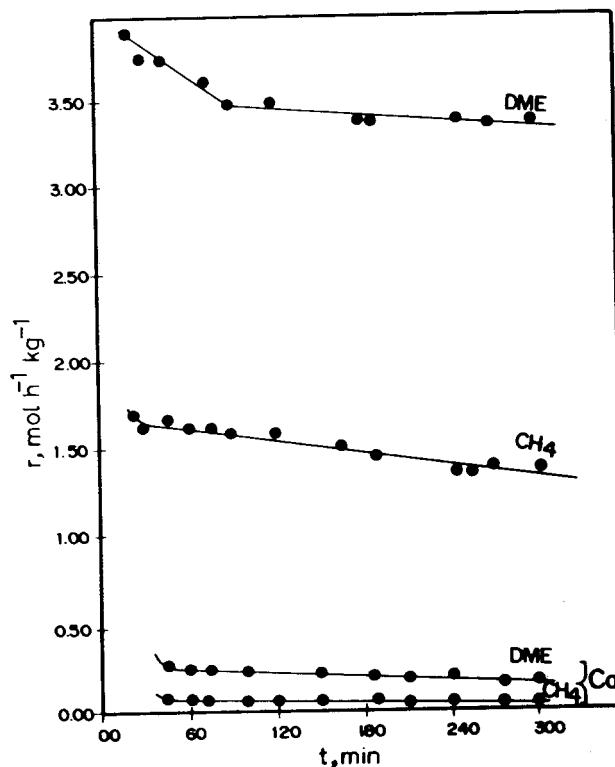


Fig. 2—Check of the activity of calcium and zinc salts of molybdophosphoric acid towards the formation of dimethyl ether and methane at different time intervals. [$P_{\text{CH}_3\text{OH}} = 102$ torr; temp. = 300°C .]

Results

Catalyst activity with time

The activities of all the catalysts used towards the conversion of methanol were determined in terms of the rate formation of both the products. The activity was checked at different time intervals under fixed experimental conditions. It was observed with Na salt catalyst (Fig. 1) that the activity towards ether and methane formation increases with time from the beginning of the run and reaches a constant value after 90 min for ether and 75 min for methane, then it remains constant for about $3\frac{1}{2}$ hrs. The activity of Mg salt catalyst towards ether formation reaches after 6 hrs to 91% of the steady state value obtained after one hr from start of the run. The activity towards methane formation reaches the steady state after one hr and then remains nearly constant for 5 hrs. It was observed that the activity of Ca and Zn salts towards ether formation decreases to 62% and 87% of the original activity whereas methane formation decreases to 51% and 80% of its original value respectively (Fig. 2).

Effect of calcination temperature on the catalyst selectivity towards dimethyl ether and methane formation

Formation of ether and methane was studied over

Zn salt pretreated at 250, 300 and 400°C in H_2 atmosphere for 4 hrs. The reaction temperature was in the range 110 – 392°C and the partial pressure of methanol was kept fixed at 102 torr. The results (Fig. 3) show that ether formation proceeds at a very low rate up to 110°C , then increases sharply until a maximum is reached at 250°C for both samples pretreated at 250° and 300°C , whereas a shift in the temperature of the maximum to 360°C was observed with the sample pretreated at 400°C . It was also observed that higher calcination temperature inhibits greatly ether formation and has little effect on methane formation.

Effect of partial pressure of methanol on the rate of dimethyl ether and methane at different temperatures

The rates of ether and methane formation were measured at 280, 300 and 320°C at partial pressure of methanol ranging from 30–485 torr over calcium, magnesium and zinc salts of molybdophosphate. With sodium salt the reaction was investigated in the temperature range 300, 320 and 340°C . The results obtained are given in Table 1. It was observed that the rate of ether and methane formation is propor-

Table 1—Effect of partial pressure of methanol on dimethyl ether and methane formation at different temperatures over four catalysts pretreated at 400°C

$P_{\text{CH}_3\text{OH}}$ torr	r.mol.h ⁻¹ .kg ⁻¹					
	280°		300°		320°	
	DME	CH ₄	DME	CH ₄	DME	CH ₄
	<i>Ca Salt</i>					
31	0.063	0.013	0.165	0.062	0.266	0.153
58	0.109	0.021	0.208	0.079	0.319	0.183
102	0.179	0.030	0.285	0.087	0.390	0.204
211	0.183	0.040	0.333	0.111	0.552	0.241
397	0.185	0.041	0.353	0.109	0.585	0.273
485	0.211	0.043	0.357	0.120	0.574	0.281
	<i>Mg Salt</i>					
31	0.581	0.122	0.984	0.303	1.407	0.624
58	0.994	0.172	1.476	0.396	2.169	0.761
102	1.265	0.190	1.800	0.452	2.742	0.899
211	1.386	0.211	2.109	0.481	2.922	0.843
397	1.530	0.234	2.169	0.468	3.134	0.874
485	1.540	0.250	2.290	0.499	3.194	0.888
	<i>Zn Salt</i>					
31	1.864	0.765	2.043	1.054	2.990	2.025
58	2.043	0.807	2.534	1.354	3.826	2.413
102	2.382	0.938	3.635	1.627	4.377	2.630
211	2.927	0.934	4.571	1.703	6.261	3.030
397	3.142	0.963	4.769	1.762	6.660	2.957
485	3.259	0.957	4.893	1.772	6.969	3.023
	<i>Na Salt</i>					
	300°		320°		340°	
	DME	CH ₄	DME	CH ₄	DME	CH ₄
31	0.0006	0.0047	0.004	0.0058	0.006	0.009
58	0.0020	0.0058	0.009	0.0080	0.015	0.013
102	0.0030	0.0074	0.011	0.0110	0.024	0.018
211	0.0080	0.0086	0.021	0.0120	0.035	0.019
397	0.0110	0.0083	0.025	0.0130	0.046	0.022
485	0.0130	0.0080	0.028	0.0135	0.045	0.021

tional to partial pressure of methanol until a saturation value is reached. The saturation partial pressure was increased as the reaction temperature increased.

Effect of temperature on catalyst selectivity towards ether and methane formation

The catalytic reaction was investigated at different temperatures varying between 100–400°C at constant partial pressure of methanol (102 torr) over four catalysts. It was observed that the rate of ether formation increased with reaction tempera-

ture until a maximum value at about 360°C after which it decreased. However, methane was formed at a very slow rate in the beginning then increased gradually and sharply as the reaction temperature increased up to about 386°C. With Na salt the ether formation begins at higher temperature than the other catalysts (above 260°C) and increased gradually with temperature up to 300°C, then increases sharply until 398°C (Fig. 4). It was observed that at higher reaction temperatures the rate of methane formation increased as the rate of ether decreased (Fig. 5). This may be explained by the decomposi-

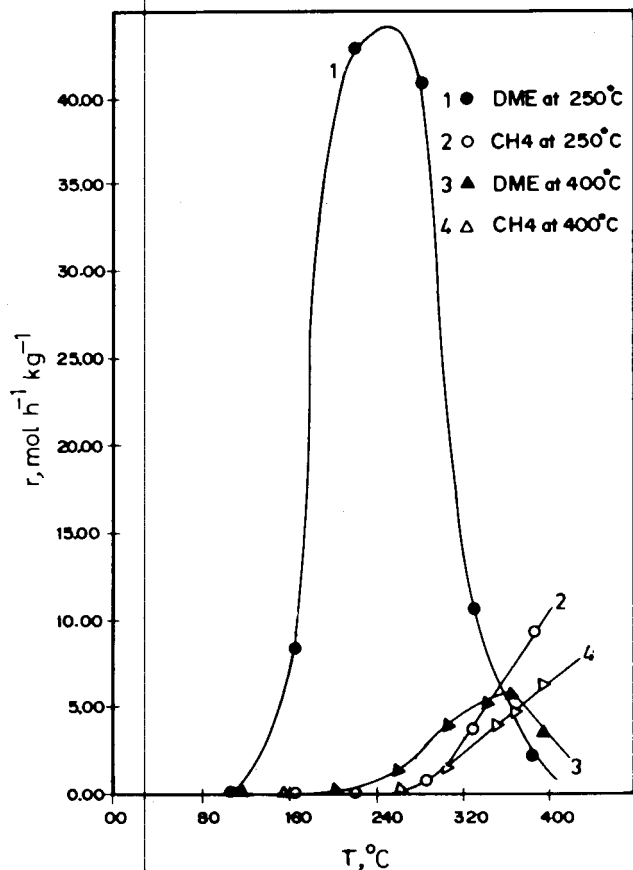


Fig. 3—Effect of temperature on the rate of formation of dimethyl ether and methane over zinc molybdophosphate pretreated at 250° and 400°C. [$P_{\text{CH}_3\text{OH}} = 102$ torr]

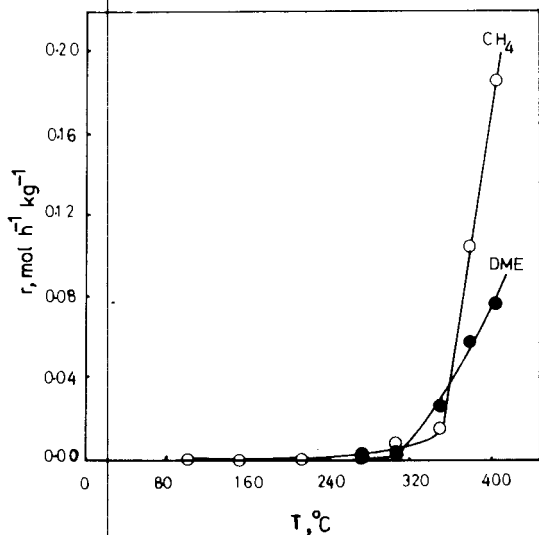


Fig. 4—Effect of temperature on the rate of formation of dimethyl ether and methane over sodium molybdophosphate pretreated at 400°C. [$P_{\text{CH}_3\text{OH}} = 102$ torr]

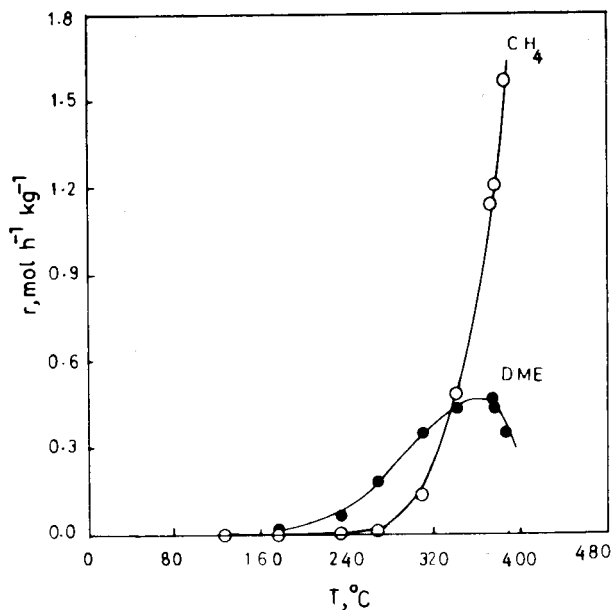


Fig. 5—Effect of temperature on the rate of formation of dimethyl ether and methane over calcium molybdophosphate pretreated at 400°C. [$P_{\text{CH}_3\text{OH}} = 102$ torr]

tion of ether to methane in a consecutive manner. The result is in agreement with the conclusion of several authors^{3,8,11}.

Formation of dimethyl ether and methane from preadsorbed methanol

The rate of ether and methane formation from preadsorbed methanol as a function of time was measured at 320°C over Ca, Mg and Zn salts under constant argon flow 0.195 mol/h. The results indicate that both ether and methane disappear from the reaction mixture after a few minutes from stopping the alcohol feed to the reactor (Fig. 6). The Na salt was not investigated because of its very low activity under non-steady state conditions.

Effect of pyridine on the formation of dimethyl ether and methane

The poisoning effect of pyridine on Zn salt catalyst towards ether and methane formation was investigated. The catalyst was previously pretreated at 400°C in H_2 for 4 hrs and the study was carried out at 349°C. The flow rate of argon was kept constant at 0.195 mol/h. The concentrations of pyridine in alcohol feed were 5% and 19% (v/v). The results show that 5% pyridine inhibits the catalyst activity towards ether and methane formation by about 5% and 2% of the original value, whereas 19% pyridine decreases the rate by about 19% and 10% respectively.

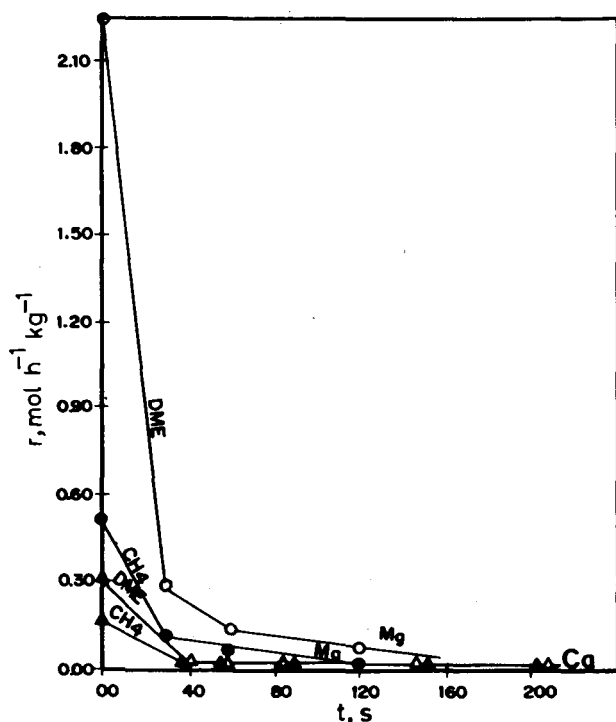


Fig. 6—Rate of formation of dimethyl ether and methane at 320°C from preadsorbed methanol over calcium and magnesium molybdophosphate pretreated at 400°C

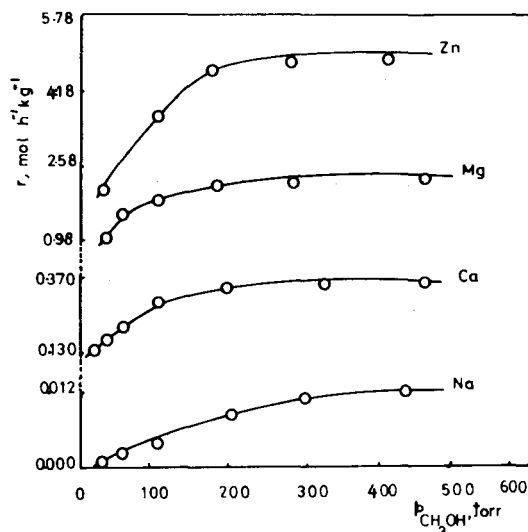


Fig. 7—Effect of partial pressure of methanol on the rate of formation of dimethyl ether at 300°C

Effect of counter cation on dimethyl ether and methane formation

The comparison between the activity of the four salts in terms of the reaction rate towards ether and methane formation at constant temperature 300°C and partial pressure of methanol 300 torr is given in Figs 7 and 8. It is observed from Fig. 7 that the ratio

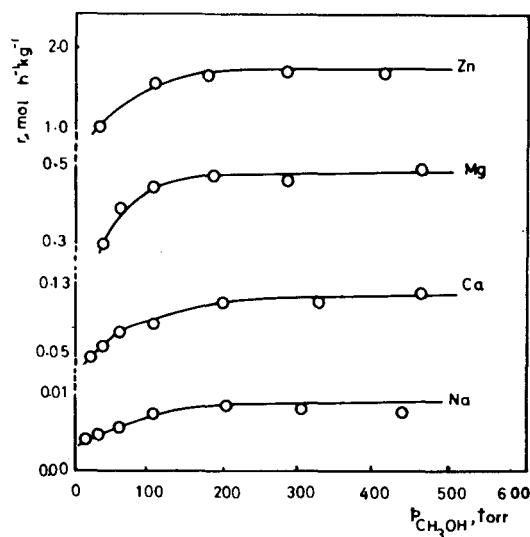


Fig. 8—Effect of partial pressure of methanol on the rate of formation of methane at 300°C

between the activities for ether formation over Na, Ca, Mg and Zn salts is 1:35:220:478 respectively. For methane formation (Fig. 8) the activity is 1:14:57:207 over the four catalysts respectively.

Test for the validity of Langmuir-Hinshelwood mechanism

The kinetics of ether and methane formation was tested by the validity of Langmuir-Hinshelwood Eqs (1) and (2).

$$r = \frac{kK_A P}{1 + K_A P} \quad \dots (1)$$

$$r = k \left[\frac{K_A P}{1 + K_A P} \right]^2 \quad \dots (2)$$

Plots of $1/r$ against $1/P$ (for model 1) and $1/\sqrt{r}$ versus $1/P$ (for model 2) are linear. From these plots the values of the adsorption coefficient, K_A , and the rate constant, k , for ether and methane formation were calculated. By comparing the theoretical values of ether and methane formation with those obtained experimentally, a suitable model was concluded. It was found that ether over Zn salt at 320°C approaches the second order equation Fig. 9. The activation energy over Na, Ca, Mg and Zn salts were found to be 13.4, 10.0, 10.6 and 11.5 kcal/mol respectively. It is observed from Fig. 10 that the experimental values for methane formation are in a good agreement with model (1). The activation energies were 19.4, 29.3, 20.7 and 20.5 kcal/mol respectively. It was observed that the higher activation energy for ether formation over Na salt agrees with its

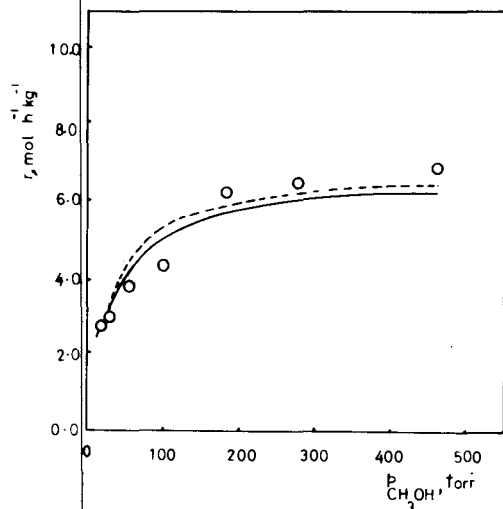


Fig. 9—The variation of rate of dimethyl ether formation over zinc molybdophosphate at 320°C with the high partial pressures of methanol. [○, Experimental values; —, values calculated from model (1); --, values calculated from model (2)]

low activity whereas the other values are comparable and reflect their activity. For methane formation the activation energy are nearly the same except the Ca salt because its particle size was efficient (≤ 0.1 mm).

Discussion

The observed increase in the catalyst activity with time (Fig. 1) may be explained by adopting the induction period concept, i.e., the reaction requires some time to generate new active centers through catalytic process. The decrease in the activity of Ca and Zn salt towards ether and methane formation (Fig. 2) may be explained by the irreversible consumption of the active centers and/or the partial blocking of Brönsted centers by carbon deposits²⁶ which is evident from the dark colour of the catalyst observed at the end of the run.

Decrease in the rate of ether formation with the increase in calcination temperature may be explained by adopting the conclusion of Matsuda *et al.*²⁷ They concluded that at lower calcination temperature where the catalyst surface has more Lewis acidity, higher activity towards ether formation is observed, whereas at higher calcination temperature the amount of Lewis acid centers decreases and consequently the rate of ether formation decreases greatly. This may explain the important role of Lewis acidity in ether formation. Besides, as methane formation decreases slightly by increasing the calcination temperature from 250 to 400°C. The higher activity observed at lower calcination temperatures may also be explained by adopting the concept of

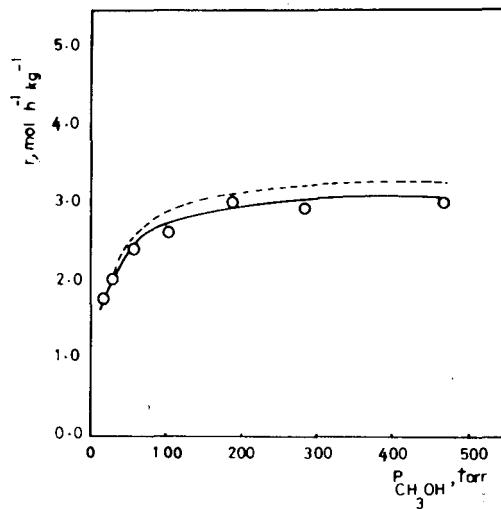


Fig. 10—The variation of the rate of methane formation over zinc molybdophosphate at 320°C with the high partial pressures of methanol. [○, Experimental values; —, values calculated from model (1); --, values calculated from model (2)]

pseudo liquid phase^{16,20,28,29}. This concept assumes that at lower calcination temperature the water produced during the dehydration reaction is adsorbed in the bulk thus increasing the reaction zone. This probably increases the proton acidity which increases the catalyst activity towards the conversion of methanol.

The relation between the reaction temperature and the rates of ether and methane formation (Fig. 5) may be explained by assuming that ether is a precursor for methane^{8,11}. This conclusion is evident from the sharp increase in methane formation after injecting dimethyl ether into the feed under steady state conditions. The increase in methane formation may be also due to the direct formation of methane from methanol and the degradation of higher hydrocarbons³.

The disappearance of both products from the reaction mixture after one minute from stopping the alcohol feed to the reactor may be explained by: (1) the existence of a weakly adsorbed methanol species required for the formation of ether and methane, (2) the rapid conversion of the preadsorbed species to products, (3) in absence of alcohol feed to the reactor, no water is produced which is necessary for promoting the conversion of the adsorbed species.

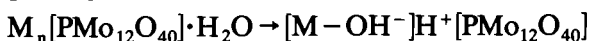
The inhibition of ether and methane by pyridine may be explained by assuming that the acid centers participating in the formation of both products are poisoned. It is observed that ether formation is more inhibited than methane in the presence of 5% and 19% pyridine in the feed of methanol. This result may be explained by assuming that the active cen-

Table 2—Effect of cation radius, and electronegativity on the rate of formation of dimethyl ether and methane at 102 torr methanol and 300°C

Cation	Electro- negativity	Ionic radius (Å)	r_{DME} , mol.h ⁻¹ .kg ⁻¹	r_{CH_4} , mol.h ⁻¹ .kg ⁻¹
Na	1.01	—	0.004	0.007
Ca	1.04	1.06	0.285	0.09
Mg	1.23	0.78	1.800	0.45
Zn	1.66	0.69	3.640	1.64

ters involved in ether formation are strongly affected by pyridine rather than the those involved in methane formation. However, it may also be assumed¹³ that methane is mainly formed in the bulk which is not accessible to the bulky molecules of pyridine. Pyridine adsorbed on heteropoly compounds exists as pyridinium ion (as evident from IR spectra) as a result of interaction with Brönsted acid centers^{18,19,30}. These Brönsted acid centers are proposed to participate in methane formation by a carbenium ion mechanism^{3,8,31,32}. It is assumed by Hayashi and others^{3,8,12,13,33} that the activity towards hydrocarbon formation is influenced by the concentration and strength of Brönsted acid sites.

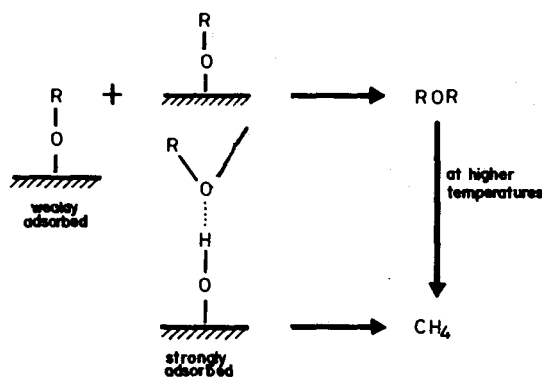
The results given in Table 2 indicate that the activity of the catalyst is affected by the ionic size of the counter cation and its electronegativity. It is observed that as the ionic radius increases the activity towards both ether and methane formation decreases. Zinc salt, the most active catalyst among the three catalysts studied, has the smallest cation radius. The Na salt was not considered in this comparison since it is a monovalent cation. It is shown from the data given in Table 2 that Zn cation being the most electronegative has the maximum activity towards ether and methane formation. This result is in a good agreement with the following equation²⁷.



The higher the electronegativity of the element the stronger is its tendency to attract the OH⁻ anion thus producing a strongly acidic site by increasing the protonic nature of H⁺.

From the results obtained in this study the proposed mechanism for the conversion of methanol may be given as in Scheme 1:

According to Scheme 1, ether molecule may be formed from the participation of two adjacent surface alkoxide groups whereas methane formation requires a surface alkoxide and a carbenium ion. Ether formation follows a second order equation of Langmuir-Hinshelwood type whereas methane formation obeys a first order equation of the same type.



Scheme 1

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