HETEROPOLY ACIDS SUPPORTED ON α-Al_2O_3 AS SOLID ACID CATALYSTS FOR METHANOL TRANSFORMATION

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Transformation of methanol into dimethyl ether and methane was carried out over two heteropoly acids supported on α-Al_2O_3 under atmospheric pressure and at 300 °C. The samples were characterized physicochemically (S_{BET}, X-ray diffraction and acidity). The effect of reaction time, temperature, methanol partial pressure and of the content of the supported acid were studied. The results showed that α-Al_2O_3 increased the catalyst life. The selectivity towards dimethyl ether and methane formation depended on the type of the acid and its content. The results indicate that dimethyl ether is formed by surface reaction whereas methane formation proceeds in the bulk of the catalyst.

Heteropoly acids when loaded on a suitable support work as an active solid acid catalyst better than typical solid acid catalysts such as silica–alumina supported phosphoric acid. The use of heteropoly compounds requires to load them on an appropriate support since their surface areas are small[1]. In the heteropoly acid/ion exchanger system, protons originating from the ion exchanger can interact with the supported heteropoly anions and exhibit the higher activity than those of the resin which does not bear these anions[2]. Serwicka et al.[3] proposed that interaction with the support leads not only to the strengthening of the heteropoly acid structure but also to its pronounced acid-base properties.

The aim of the present study was to examine the effect of an inert carrier such as α-Al_2O_3 on the catalytic activity of heteropoly acids for methanol transformation.

EXPERIMENTAL

Two series (five samples each) of 12-tungsto-(HPW) and molybdophosphoric acid (HPMo) (obtained from BDH) supported on α-Al_2O_3 were used. Each sample was prepared by impregnating 5 g of α-Al_2O_3 with an aqueous solution of the acid whose volume was just sufficient to produce 0.5, 1.0,

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3.0 and 5.0 wt.%. The solvent, twice distilled H_2O, was evaporated at 70 °C and then dried at 100 °C. The α-Al_2O_3 was obtained by heating γ-Al_2O_3 at 1 200 °C in air for 24 h (Table I).

The nature of the solid phases was investigated by means of X-ray analysis. X-Ray diffraction patterns were obtained with a Philips PW-1390 instrument at 40 kV and 30 mA with Ni filter and CuKα radiation. The adsorption isotherms of nitrogen at −195 °C were determined by means of a conventional volumetric apparatus. S_{BET} (total pore volume) and total pore radius $(\bar{r})$ values are given in Table II. To characterize the acidity of heteropoly acids, the hydrolysis of ethyl acetate was carried out. The ester (30 ml) was mixed well with an aqueous solution of a given heteropoly acid (100 ml, $5 \,.\, 10^{-3}$ molar) at 60 °C for 3 h. The reaction products was titrated with $5 \,.\, 10^{-2}$ molar solution of NaOH.

In a continuous flow system, methanol was transformed to dimethyl ether (DME) and CH_4 at 300 °C. All measurements were carried out using the catalyst (0.5 g) pretreated at 350 °C for 3 h in a flow of pure and dry argon (40 ml min^{-1}). Using a glass evaporator, the argon was saturated with methanol and then introduced to the reactor inlet. The saturator was kept at a constant temperature to give the desired partial pressure of methanol (to give conversion less than 15%). The reaction mixture was analyzed chromatographically, using Varian 3700 gas chromatograph connected to Varian 9176 recorder. The column (4 m long) was packed with 10% Squalane on Chromosorb.

TABLE I
Chemical formulae and acid content of the samples used

Abbreviation	Formulae	Acid content[a]		
		mg	mmol	wt.%
HPMo	$H_3PMo_{12}O_{40} \,.\, x\, H_2O$ (free)	500	274	100
0.5 HPMo/α-Al_2O_3	0.5 $H_3PMo_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	5	2.7	0.5
1 HPMo/α-Al_2O_3	1.0 $H_3PMo_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	10	5.4	1.0
3 HPMo/α-Al_2O_3	3.0 $H_3PMo_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	30	16.4	3.0
5 HPMo/α-Al_2O_3	5.0 $H_3PMo_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	50	27.3	5.0
HPW	$H_3PW_{12}O_{40} \,.\, x\, H_2O$ (free)	500	177	100
0.5 HPW/α-Al_2O_3	0.5 $H_3PW_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	5	1.7	0.5
1 HPW/α-Al_2O_3	1.0 $H_3PW_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	10	3.5	1.0
3 HPW/α-Al_2O_3	3.0 $H_3PW_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	30	10.6	3.0
5 HPW/α-Al_2O_3	5.0 $H_3PW_{12}O_{40} \,.\, x\, H_2O/\alpha$-$Al_2O_3$	50	17.7	5.0

[a] Per g α-Al_2O_3, except free HPMo and HPW (molecular weights of HPMo and HPW calculated without $x\, H_2O$).

RESULTS AND DISCUSSION

Influence of Reaction Time on Catalyst Activity

First of all, it should be mentioned that X-ray diffraction analysis showed that there is no specific interaction between α-Al_2O_3 and the doped acids. Hydrolysis of ethyl acetate at 60 °C has proved that HPMo is less acidic than HPW.

Initial catalyst activity (defined as the rate of DME formation in mol h^{-1} g^{-1}) as a function of the acid content is represented graphically in Fig. 1. It is evident that the

TABLE II
Some surface characteristics of heteropoly acids supported on α-Al_2O_3 pretreated at 350 °C

Catalyst	$V_{P(0.95)}$[a]	S_{BET}[b]	$\bar{r}$[c]
α-Al_2O_3	0.031	14.8	21.3
H_2O/α-Al_2O_3	0.028	11.3	25.2
HPMo	0.010	3.6	28.8
0.5 HPMo/α-Al_2O_3	0.019	11.3	13.7
1 HPMo/α-Al_2O_3	0.020	10.9	20.3
3 HPMo/α-Al_2O_3	0.022	8.7	31.4
5 HPMo/α-Al_2O_3	0.017	7.8	22.0
HPW	0.015	3.9	40.0
0.5 HPW/α-Al_2O_3	0.017	10.9	15.8
1 HPW/α-Al_2O_3	0.023	8.3	28.5
3 HPW/α-Al_2O_3	0.026	7.8	33.9
5 HPW/α-Al_2O_3	0.019	6.5	30.0

[a] $V_{P(0.95)}$ Total pore volume; [b] S_{BET} the specific surface area (m^2g^{-1}); [c] $\bar{r}$ mean pore radius (Å), defined as $V_{P(0.95)} \cdot 10^4/S_{BET}$.

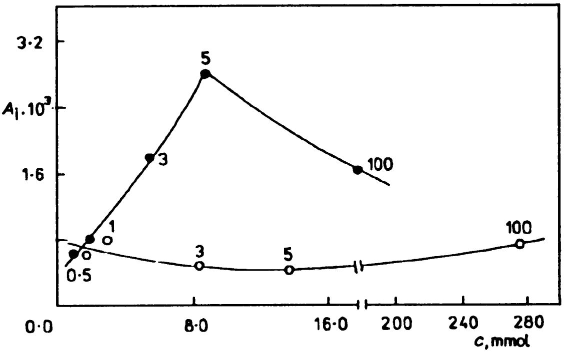


FIG. 1
Initial catalyst activity as a function of the acid content c for DME formation at 300 °C over supported HPW (●) and HPMo (○). Numbers at points denote the content of the acid in wt.%

samples studied differ in their initial activity. This difference depends on the kind of the acid used. For HPMo samples their initial activities are very similar to that of the free acid. All of them are less active than HPW samples especially when compared to the samples with the high acid content. This behavior can be due to the high electronegativity of tungsten central atom which enhances the catalyst acidity, as evidenced from the hydrolysis of ethyl acetate at 60 °C. The increase in the initial activity of HPW samples in spite of the decrease of their S_{BET} (Table II) can be also explained by adopting the "pseudo-liquid phase" concept[4]. This concept proposes that methanol and water molecules are absorbed in the catalyst bulk, increasing thus the reaction zone and consequently also the reaction rate.

To investigate the effect of reaction time on the catalyst activity (in terms of the reaction rate in mol h^{-1} g^{-1}), the reaction was carried out at 300 °C for about 4 h under a constant methanol partial pressure (13.3 kPa) (Figs 2 and 3). It was found that the activity of the free HPMo for DME formation increases greatly through the first 10 min. After 60 min, the activity decreases to 10% of its initial value and then it remains constant. This activity decrease can be due to coke formation on the most acidic centers.

The observed increase in the activity of the free acid and of the two supported samples (0.5 and 3.0 wt.%) at the beginning of the run can be explained by the existence of an induction period. Through this period, new and more active sites are formed and participate in the reaction pathway[5]. It was found that the supported samples are more stable than the free acids, which is evidenced by the values of residual activity A_r (Table III).

The poorer stability of the activity of HPMo in comparison with HPW may be also due to the larger $\bar{r}$ value (40 Å) of HPW relative to HPMo (28.8 Å), as the blocking of

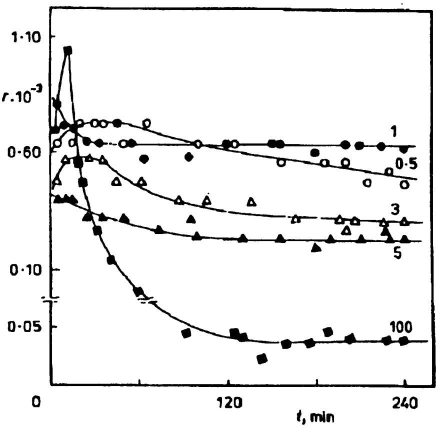


FIG. 2

Influence of the reaction time on stream t toward the rate of DME formation r (mol h^{-1} g^{-1}) at 300 °C and 13.3 kPa over supported HPMo. Numbers at curves denote the content of the acid in the catalyst

catalyst pores by carbon deposite is more pronounced with the catalysts having the narrower pores.

Effect of Reaction Temperature on Selectivity Towards DME and Methane Formation

In the temperature range of 100 – 350 °C, methanol is transformed into DME and methane over HPMo and HPW. The reaction was carried out under a constant methanol partial pressure of 12 kPa. In the temperature range of 100 – 200 °C, the selectivity to DME formation is low on most samples (Fig. 4). Over HPW, the rate of DME formation increases gradually till a maximum is reached at about 175 °C. The high selectivity for the ether formation may be due to the generation of a great number of weaker acidic sites which exist at the lower reaction temperatures. The adsorption–desorption of am-

TABLE III
Values of initial (A_i), final (A_f) and residual ($A_r = A_f/A_i$) activity for methanol transformation over supported HPMo and HPW at 300 °C and 13.3 kPa

HPMo(HPW)/α-Al_2O_3 wt.%	HPMo			HPW		
	A_i	A_f	A_r	A_i	A_i	fA_r
100[a]	0.68	0.04	0.06	1.60	1.30	0.81
0.5	0.64	0.48	0.75	0.64	0.56	1.00
1.0	0.80	0.64	0.80	0.80	0.74	0.93
3.0	0.48	0.32	0.67	1.80	1.60	0.89
5.0	0.40	0.24	0.60	2.80	1.80	0.64

[a] The free acid.

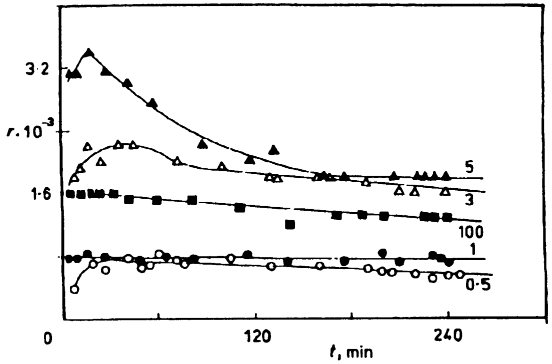
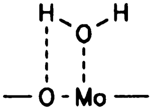


FIG. 3
Influence of the reaction time on stream t toward the rate of DME formation r (mol h^{-1} g^{-1}) at 300 °C and 13.3 kPa over supported HPW. For designation see Fig. 2

monia over heteropoly molybdates showed that the weak acidity predominates at lower temperatures[6]. At the higher reaction temperatures (200 – 350 °C), the rate of DME formation increases gradually depending on the nature of the catalyst used. Over HPW, DME may be dissociated to another species like CO, H_2, H_2O, CH_3 which can participate in methane formation. Concerning methane formation, its rate increases gradually from 200 – 300 °C (Fig. 5). This result indicates that methane may be formed on the stronger acidic sites generated in this temperature region. It was assumed that the water of dehydration can be adsorbed as depicted by structure A, changing Lewis acidic and basic sites to Brønsted acidic sites which are necessary for methane formation[7].



A

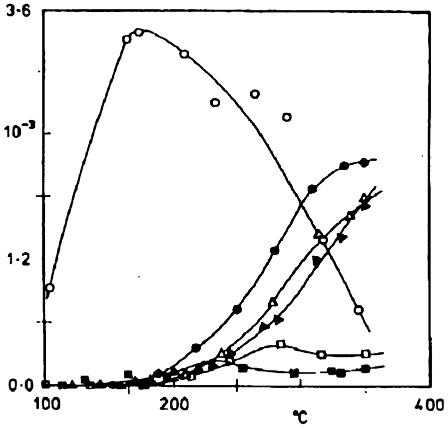


FIG. 4

Effect of reaction temperature on the rate of DME formation r (mol h^{-1} g^{-1}) at constant partial pressure of methanol 12 kPa over free (O) and supported (Δ 0.5 wt.%, ● 5.0 wt.%) HPW and free (■) and supported (▲ 0.5 wt.%, ❒ 5.0 wt.%) HPMo

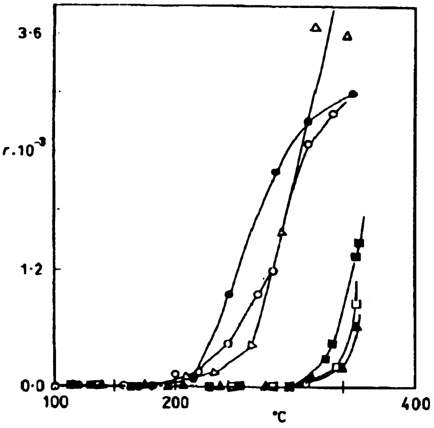


FIG. 5

Effect of reaction temperature on the rate of methane formation r (mol h^{-1} g^{-1}) at constant partial pressure of methanol 12 kPa over free (Δ) and supported (▲ 0.5 wt.%, ❒ 5.0 wt.%) HPW and free (■) and supported (O 0.5 wt.%, ● 5.0 wt.%) HPMo

Effect of Methanol Partial Pressure on the Rate of DME and Methane Formation

The rate of DME and methane formation as a function of methanol partial pressure was studied with the free HPMo at 220 and 320 °C, respectively (Fig. 6). At low partial pressures, the reaction rate is proportional to the partial pressure of methanol. This may be explained by the continuous absorption and/or adsorption of methanol molecules both in the bulk and on the catalyst surface. The rate increases with the methanol pressure till the constant rate is reached. This "saturation" pressure depends on the reaction temperature and on the nature of the catalyst. Above the saturation value, the more alcohol molecules will be left unreacted.

The formation of DME was explained by assuming that in methanol conversion the first step includes protonation of CH_3OH to form $CH_3OH_2^+$ intermediate. This process includes C–O bond cleavage leading to methylation of the Keggin unit via rapid electrophilic attack at the oxygen atom of physisorbed CH_3OH by the surface CH_3 group, yielding DME and regenerating the proton. This means that DME was formed from two molecules, one of which was strongly adsorbed and the other one become from the gas phase. Plotting $1/\sqrt{r}$ against $1/p$ gives the straight line. The adsorption coefficient K_A, the rate constant k and energy of activation ΔE are listed in Table IV. On the other side, it was found that methane formation obeys the first order kinetics. The values of K_A, k and ΔE are presented in Table V. The higher activation energies obtained for methane formation (29.4 and 222.6 kJ mol^{-1}) in comparison with DME formation (21.0 and 29.4 kJ mol^{-1}) over HPW and HPMo, respectively, may be explained by the consecutive mechanism responsible for methane formation on the expense of the ether. However, the large difference existing between $\Delta E(CH_4)$ over HPMo (222.6 kJ mol^{-1}) and $\Delta E(CH_4)$ over HPW (29.4 kJ mol^{-1}) may be due to the stronger Brønsted acidity of HPW which is required for methane formation.

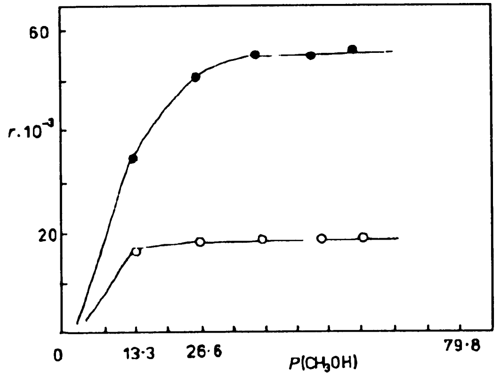


FIG. 6
Effect of methanol partial pressure $P(CH_3OH)$ kPa on the rate r (mol h^{-1} g^{-1}) of formation of: ○ dimethyl ether (220 °C) and ● methane (320 °C) on HPMo

Effect of Acid Content

Under the reaction conditions used α-Al_2O_3 seems to be catalytically inactive. Consequently the catalytic activity is only affected by the amount of the supported acid and by the surface area of the support.

TABLE IV
Rate constant k (mol h^{-1} g^{-1}), adsorption coefficient K_A (kPa^{-1}) and apparent activation energy ΔE (kJ mol^{-1}) for dimethyl ether formation

Catalyst	Rection temperature		$k \,.\, 10^{-3}$	$K_A \,.\, 10^{-4}$	ΔE
	°C	K			
HPMo	180	435	20.16	3.5	29.4
	200	473	29.76	8.3	
	220	493	37.88	7.1	
0.5 HPMo/α-Al_2O_3	180	453	1.67	1.3	25.2
	200	473	8.93	2.2	
	220	493	12.2	5.3	
	240	513	14.7	3.3	
5 HPMo/α-Al_2O_3	180	453	11.43	1.9	29.4
	200	473	16.33	3.0	
	220	493	28.57	2.46	
HPW	120	393	96.39	23	21.0
	140	413	121.21	37	
	160	433	142.96	35	
	180	453	216.23	15.2	
0.5 HPW/α-Al_2O_3	300	573	21.7	1.6	71.4
	320	593	29.4	2.7	
	340	613	55.5	4.9	
	360	633	62.5	13	
5 HPW/α-Al_2O_3	260	533	86.2	2	29.4
	280	553	111.1	33	
	300	573	135.1	28	
	320	593	151.5	33	

TABLE V
Rate constants k (mol h^{-1} g^{-1}), adsorption coefficient K_A (kPa^{-1}) and apparent activation energy ΔE (kJ mol^{-1}) for methane formation

Catalyst	Rection temperature		k . 10^{-3}	K_A . 10^{-4}	ΔE
	°C	K			
HPMo	280	553	0.74	1.33	222.6
	300	573	10.8	0.4	
	320	593	25.0	0.7	
	340	613	200.0	28.0	
0.5 HPMo/α-Al_2O_3	220	493	0.9	0.9	100.8
	240	513	1.2	2.26	
	260	533	2.6	1.0	
	280	553	13.3	3.3	
5 HPMo/α-Al_2O_3	220	493	1.4	2.5	151.1
	240	513	4.35	0.7	
	260	533	33.3	3.0	
	280	553	66.6	13.3	
HPW	300	573	80.0	0.97	29.4
	320	593	105.2	7.6	
	340	613	111.1	20.9	
0.5 HPW/α-Al_2O_3	300	573	0.9	7.0	130.2
	320	593	2.78	1.2	
	340	613	4.76	2.0	
	360	633	14.3	2.4	
5 HPW/α-Al_2O_3	300	573	15.6	1.2	143.8
	320	593	50.0	2.2	
	340	613	125.0	4.1	
	360	633	250.0	8.3	

Role of DME Formation

The specific rate of DME formation (in mol h^{-1} m^{-2}) and the specific surface area (in $m^2 g^{-1}$) as a function of the acid content (in mmol) are presented in Fig. 7. Over HPMo samples the rate of the ether formation decreases gradually with the decreasing surface area and with the increasing acid content. This behavior may be explained by assuming that DME is formed on the external catalyst surface. It is also assumed by Izumi et al.[8] that the number of effective surface protons decreases due to the growth of crystallites size with the increasing acid content.

With HPW samples, however, the situation is different. At low acid contents, the rate of DME formation depends on the amount of the acid. This result may be explained by assuming that the dispersion of the acid on the support is high, which gives more space for the surface reactions to proceed. By increasing the acid content, the surface protons begin to accumulate and the reaction rate decreases. The previous studies supposed that at higher acid contents, the crystallites of the acid undergo aggregation, and the reaction seems to be catalyzed mainly by the surface protons of heteropoly acid crystallites[8].

Role of Methane Formation

It was observed (Fig. 8) that the rate of methane formation increases with the increasing acid content and decreasing surface area. This may be explained by the assumption that methane formation depends on the amount of the bulk acid. At the higher acid concentrations, the rate of methane formation over HPW samples increases sharply. This means that methane formation depends on the acidity in the bulk acid and/or in the bulk near the surface.

On the basis of the present and other similar studies[6,9] one can conclude that

– DME formation is a surface reaction,

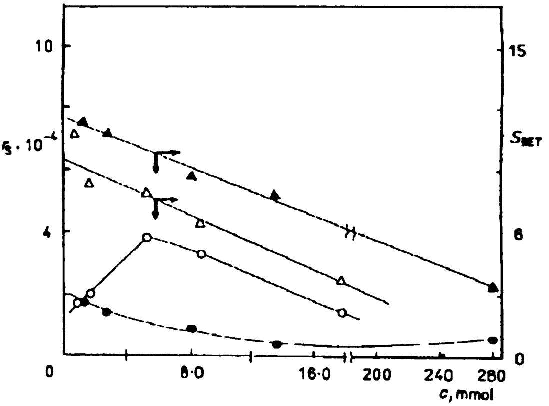


FIG. 7

Effect of acid content c on the specific reaction rate r_s (mol h^{-1} m^{-2}) and specific surface area S_{BET} (m^2/g) in DME formation at 350 °C over HPW (empty marks) and HPMo (full marks)

- methane formation is a bulk reaction which requires H^+ from H_2O of dehydration and/or from the catalyst itself, and
- the use of an inert α-Al_2O_3 as the support for heteropoly acids improves their acidity and stability for some acid catalyzed reactions.

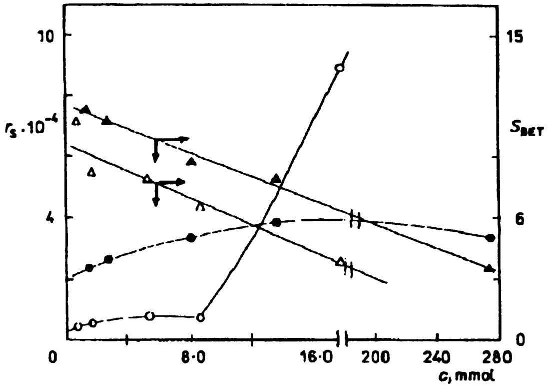


FIG. 8
Effect of acid content c on the specific reaction rate r_s (mol h^{-1} m^{-2}) and specific surface area S_{BET} (m^2/g) in methane formation at 350 °C over HPW and HPMo (for designation see Fig. 7)

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