# SURFACE STUDIES AND NATURE OF ACTIVE SITES OF SUPPORTED HETEROPOLYACIDS AS CATALYSTS IN METHANOL DEHYDRATION

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Different amounts of molybdo- and tungstophosphoric acids were supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to get information about their surface and catalytic properties. The surface study revealed that surface area, total pore volume and the mean pore radius decreased as the acid content increased. X-Ray diffraction analysis showed that there is no interaction between the acid and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Using a continuous flow system, methanol transformation was carried out under atmospheric pressure. Some experiments were made to determine the nature of active centers and reaction mechanism.

It was shown by amine titration that heteropolyacids in the solid state have a large number of acid sites<sup>1</sup>. Moffat et al.<sup>2</sup> concluded from chemisorption of ammonia that the acid strength increases with calcination temperature whereas that of the salt decreases in the order: H > Zn > Al > B > Mg > Ca > Na. Concerning the kind of heteropoly compounds supported on SiO<sub>2</sub>-200, the acidity was found to decrease<sup>3</sup> in the order:  $H_3PW_{12}O_{40}/SiO_2-200 > H_3PM_{012}O_{40}/SiO_2-200$ .

Misono and others<sup>4 - 8</sup> measured water content and surface area of 12-tungsto- and 12-molybdophosphoric acid after heat treatment in dry helium stream and after evacuation, respectively. They found that the dehydration of molybdophosphoric acid proceeds at temperature as low as 25 °C. Its surface area is about  $13 - 14 \text{ m}^2/\text{g}$  at 100 °C and decreases at the higher temperature. On the other hand, dehydration of tungstophosphoric acid proceeds at 100 °C, and the decrease in surface area with increasing temperature is smaller. Hayashi and Moffat<sup>9</sup> found that the surface area of the ammonium salt of tungstophosphoric acid is about 113 m<sup>2</sup>/g, significantly higher than that of the acid (3 - 6 m<sup>2</sup>/g). With the salt, its surface area increases slightly on heating to

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300 °C (163 m<sup>2</sup>/g). On further heating, the surface decreases monotonously to approximately 5 m<sup>2</sup>/g at 600 °C.

From X-ray structural analysis Bradly et al.<sup>10</sup> have deduced that the lattice constant of the tungstophosphoric acid,  $H_3PW_{12}O_{40}$ . 19  $H_2O$ , is 23.3 Å. The acid dehydrates to  $H_3PW_{12}O_{40}$ . 6  $H_2O$  with the lattice constant<sup>11</sup> 12.5 Å. They assumed that dehydration causes shrinking of the unit cell because adjacent heteropolyanions come much closer when water molecules between the anions are removed. From these results it was concluded that the water of crystallization is not zeolitic. Hayashi et al.<sup>12</sup> assumed that the active sites responsible for the conversion of methanol are Brønsted acid sites.

This work was oriented to get information about the nature of active centers for methanol transformation over heteropolyacids supported by  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

#### EXPERIMENTAL

Two series of supported 12-tungsto- and 12-molybdophosphoric acids on  $\alpha$ -alumina were used. Four samples from each series were prepared by impregnating 5.0 g of  $\alpha$ -alumina in an aqueous solution of the acid whose volume was just sufficient to produce 0.5, 1.0, 3.0 and 5.0 wt.%. The solvent, twice distilled water, was evaporated on a hot surface (70 °C) for 3 h and the sample was dried at 110 °C for 24 h. Molecular formula and acid content are shown in Table I.

The adsorption of nitrogen at -196 °C was determined by means of conventional volumetric apparatus<sup>13</sup>. X-Ray diffraction analysis was made for various catalysts on a Philips Diffractometer (PW-1390) under 40 kV and 30 mA with Ni filter and CuK $\alpha$  radiation.

Symbol	Chemical formula	Acid content/g Al <sub>2</sub> O <sub>3</sub>			
Symbol		mg	mmol	wt.%	
НРМо	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> . <i>x</i> H <sub>2</sub> O	500	0.2700	100.0	
0.5 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	0.5 H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> . <i>x</i> H <sub>2</sub> O/α-Al <sub>2</sub> O <sub>3</sub>	5	0.0027	0.5	
1.0 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	1.0 H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> . <i>x</i> H <sub>2</sub> O/α-Al <sub>2</sub> O <sub>3</sub>	10	0.0054	1.0	
3.0 HPMo/a-Al2O3	3.0 H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> . x H <sub>2</sub> O/α-Al <sub>2</sub> O <sub>3</sub>	30	0.0160	3.0	
5.0 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	5.0 H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> . <i>x</i> H <sub>2</sub> O/α-Al <sub>2</sub> O <sub>3</sub>	50	0.0270	5.0	
HPW	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> . <i>x</i> H <sub>2</sub> O	500	0.1800	100.0	
$0.5 \text{ HPW}/\alpha\text{-Al}_2O_3$	0.5 $H_3PW_{12}O_{40}$ . $x H_2O/\alpha$ -Al <sub>2</sub> O <sub>3</sub>	5	0.0017	0.5	
$1.0 \text{ HPW}/\alpha\text{-Al}_2O_3$	1.0 H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> . <i>x</i> H <sub>2</sub> O/α-Al <sub>2</sub> O <sub>3</sub>	10	0.0034	1.0	
$3.0 \text{ HPW}/\alpha\text{-Al}_2O_3$	$3.0 H_3 PW_{12}O_{40}$ . x $H_2O/\alpha$ -Al <sub>2</sub> O <sub>3</sub>	30	0.0100	3.0	
5.0 HPW/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	5.0 $H_3PW_{12}O_{40}$ . $x H_2O/\alpha$ -Al <sub>2</sub> O <sub>3</sub>	50	0.0180	5.0	

TABLE	I								
Chemical	formulae	and	acid	content	for	the	acid	samples	used

The catalytic activity of the samples was examined using methanol dehydration at 300 °C in a continuous flow system. The product was analyzed by GC on a Varian 3700 chromatograph connected to Varian 9176 recorder, using 4 m column packed with 10% squalane on Chromosorb.

## **RESULTS AND DISCUSSION**

# Surface Characterization of Supported Heteropolyacids

Adsorption–desorption isotherms of nitrogen at liquid nitrogen (–196 °C) were measured for supported and nonsupported catalysts pretreated at 350 °C. It was observed that some of the obtained isotherms showed characteristic behavior of the type III isotherms while the others were type II isotherms<sup>14</sup>. All the isotherms were found to be irreversible in all cases, exhibiting small hysteresis beyond  $P/P^0 = 0.5$ .

Specific surface area  $S_{\text{BET}}$ , BET-constant and the monolayer capacity  $V_{\text{m}}$  were determined for both types II and III as indicated in Table II in parentheses. Surface area derived from  $V_{1-t}$  plot  $(S_t)$ , mean pore radius calculated by  $V_{\text{P0.95}}/S_{\text{BET}}$ .  $10^4$  ( $\overline{r}$ ) and total pore volume at  $P/P^0 = 0.95 V_{\text{P0.95}}$  are summarized in Table II.

The  $S_{\text{BET}}$  values of all the samples are low (of the order 14 m<sup>2</sup>/g or less). These small values may be attributed to the fact that heteropolyanions of Keggin structure are packed units into which other molecules cannot penetrate. Furthermore, non-polar gaseous molecules are unable to enter the interstitial sites of HPA. These findings are in

Catalyst	BET <sub>const</sub>	$V_{\mathrm{m}}^{\ a,b}$	$S_{\rm BET}^{\ b,c}$	$S_t^{c}$	$V_{\mathrm{P0.95}}{}^{a}$	<i>r</i> , Å
α-Al <sub>2</sub> O <sub>3</sub>	10.0	3.4 (II)	14.8 (II)	14.2	0.031	21.3
$H_2O/\alpha$ - $Al_2O_3$	2.4	2.6 (III)	11.3 (III)	11.5	0.029	25.2
HPMo	34.0	0.8 (II)	3.6 (II)	4.2	0.010	28.8
0.5 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	13.0	2.6 (II)	11.3 (II)	11.5	1.019	17.3
1.0 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	3.5	2.5 (III)	10.9 (III)	10.5	0.020	20.3
3.0 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	1.6	2.0 (III)	8.7 (III)	8.8	0.020	31.4
5.0 HPMo/α-Al <sub>2</sub> O <sub>3</sub>	6.0	1.8 (II)	7.8 (II)	7.3	0.017	22.0
HPW	9.0	0.9 (II)	3.9 (II)	4.2	0.015	40.0
$0.5 \text{ HPW}/\alpha\text{-Al}_2O_3$	2.5	2.5 (III)	10.9 (III)	10.0	0.017	15.8
1.0 HPW/a-Al2O3	4.0	1.9 (III)	8.3 (III)	8.0	0.023	28.5
3.0 HPW/a-Al2O3	5.0	1.8 (III)	7.8 (III)	8.5	0.026	33.9
$5.0 \text{ HPW}/\alpha - \text{Al}_2\text{O}_3$	16.0	1.5 (II)	6.5 (II)	7.0	0.019	30.0

TABLE II Some surface characteristics of heteropolyacids supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> pretreated at 350 °C

<sup>*a*</sup> In cm<sup>3</sup>/g; <sup>*b*</sup> type of the isotherm in parentheses; <sup>*c*</sup> in m<sup>2</sup>/g.

agreement with those obtained for the BET surface area as calculated from the nitrogen adsorption.

## Effect of Acid Content on S<sub>BET</sub>, V<sub>P0.95</sub> and the Mean Pore Radius $\overline{r}$

The relation between the acid content and  $S_{\text{BET}}$  (Fig. 1) shows that the surface area of  $\alpha$ -alumina decreases gradually with increasing loading of HPA. These results may be explained by assuming that the impregnation with heteropolyacid results in blocking of the pores of  $\alpha$ -alumina, leading to a decrease of the accessibility of the pore system towards nitrogen molecules and resulting thus in an apparent decrease of the surface area.

In fact, 3.0 wt.% HPMo is enough to cover an area of 14.4 m<sup>2</sup>/g, based on that a Keggin unit covers<sup>15</sup> 144 Å<sup>2</sup>. It is also seen from Fig. 1 that the decrease in surface area is more remarkable in the case of HPW samples supported on  $\alpha$ -alumina. Indeed it is known<sup>15</sup> that the size of tungsten cation for the Keggin anion is greater than that of molybdenum, and this difference may be responsible for the observed decrease of surface area.

The data obtained for the effect of  $\alpha$ -alumina impregnation with HPA on the total pore volume and pore radius are given in Table II and shown in Figs 2 and 3. The results indicate a decrease in both  $V_{P0.95}$  and  $\overline{r}$  with the samples of 0.5 wt. % acid content. This may be due to the blocking of some micropores and might indicate an increased accessibility of the pore system towards nitrogen molecules. The observed increase in  $V_{P0.95}$  and  $\overline{r}$  up to 3.0 wt % acid content may be due to the strong acidity of HPA which attacks the alumina substrate and causes the widening of some mesopores. The increase in  $\overline{r}$  values reflects a limited ability of nitrogen molecules to measure the



narrower part of the total pore system (only mesopores). From Figs 2 and 3 it is seen that with 5.0 wt.% acid content, there is a small decrease in both  $V_{P0.95}$  and  $\overline{r}$ . This may be due to multilayer formation and deposition of the acid, which results in narrowing of the pores. The  $V_{P0.95}$  of the free acid samples is smaller than that of all the supported samples with high mean radius. This can be ascribed to the low surface area of these acids as a result of few micropores as well as to prevaling mesopores when compared to  $\alpha$ -alumina. The increase in *r* observed with HPW samples in comparison with HPMo samples may be due to the larger size of tungsten atom relative to molybdenum one in



FIG. 2 Dependence of total pore volume ( $V_P$ ) on acid content (HPA). For designation of points see Fig. 1



FIG. 3 Dependence of mean pore radius ( $\overline{r}$  in Å) on acid content (HPA). For designation of points see Fig. 1

the Keggin unit<sup>15</sup>. From the data given in Table II it follows that the pore parameters of  $\alpha$ -alumina impregnated in solution of both HPMo and HPW are changed due to the presence of water solvent and/or the acid.

One can thus conclude that (i) impregnation of  $\alpha$ -alumina in pure water and/or with HPMo and HPW acids results in a decrease of  $S_{\text{BET}}$  and pore volume, (ii) the  $\overline{r}$  value for the impregnated samples is strongly dependent on the mean radius ( $\overline{r}$ ) of the free acid. Thus, the mean pore radius of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with supported HPW is generally higher than that of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with supported HPMo.

## Pore Structure Analysis

In order to determine the porosity of investigated samples, the *t*-method developed by deBoer et al.<sup>16</sup> was applied. The  $V_{1-t}$  plots obtained for these samples are shown in Figs 4 – 6. The values of  $S_{\text{BET}}$  and  $S_t$  for all the samples are nearly the same. The result justifies the use of the methods by deBoer et al.<sup>16</sup> and by Mikhail et al.<sup>17</sup>. In general, the  $V_{1-t}$  plots of  $\alpha$ -alumina impregnated with molybdophosphoric acid (Fig. 5) do not show any characteristic deviation from the initial straight line. Only at very high relative pressure (in the capillary condensation region) there occurs upward deviation. This means that the total pore system of these catalysts consists of limited size meso-





pores. A somewhat different trend is observed with the HPW-impregnated catalysts (Fig. 6). An upward deviation appears around a *t*-value of 6 Å in all the cases. Such a behavior is characteristic of mesoporous solids exhibiting multilayer building inside the pores. However, the densely packed alumina surface with 0.5 wt.% HPW exhibits the small downward bending at the high *t*-value, indicating a limited number of the layers, i.e. limited pore dimensions.

Comparison of the texture parameters of the two series (shape of adsorption isotherms, *C*-values,  $S_{\text{BET}}$ ,  $\overline{r}$  and trend of the  $V_{1-t}$  plots) shows that the porous structure of both series is nearly the same. The HPW series is characterized by the relatively wider pores, the lower adsorbate-adsorbent interactions and the slightly lower surface areas.

## X-Ray Diffraction Analysis

The diffraction patterns of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, HPMo, HPW and their 0.5 and 5.0 wt.% supported samples when compared with A.S.T.M. cards<sup>18</sup> show that the heteropoly compounds can be assigned the structures H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> . 24 H<sub>2</sub>O and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> . 24 H<sub>2</sub>O. Also the structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is the same as given by A.S.T.M. cards<sup>18</sup>.





 $V_{\rm L}$  (in cm<sup>3</sup>/g) vs t (in Å) plots for supported HPMo samples. Acid content: **a** 0.5 wt.%, **b** 1 wt.%, **c** 3 wt.%, **d** 5 wt.%

The diffractograms of 0.5 and 5.0 wt.% HPA/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> differ only in line intensities, depending on the amount of the acid content. For the supported samples, the diffraction lines indicate that the supported acids are located on the surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as separate phases (new diffraction lines were not observed). However, the impregnation process resulted in a slight increase in the intensity of XRD patterns. This may be explained by that the doped acids might stimulate crystallization of  $\alpha$ -alumina. Thus, impregnation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with heteropolyacids is mainly associated with an increase in the amorphous character<sup>19</sup>. It is interesting to note that on supporting 0.5 wt.% HPA the well crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was formed in a greater extent than in the case of 5.0 wt.% acid.

From the results obtained by X-ray analysis it follows that there are no specific interactions between  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the free acids which would result from the supporting process.

## Nature of Active Centers and Reaction Pathway

*1*. In methanol transformation over this type of solid acid catalysts (100 - 300 °C) it was found that<sup>21</sup>:





- At lower reaction temperatures methanol undergoes dehydration to give dimethyl ether (Eq. (A)) and traces of methane by a parallel reaction.

$$2 \operatorname{CH}_{3} \operatorname{OH} \Longrightarrow \operatorname{CH}_{3} \operatorname{OCH}_{3} + \operatorname{H}_{2} \operatorname{O}$$
(A)

- At higher temperatures, methanol and dimethyl ether participate<sup>22</sup> in methane formation via a consecutive reaction (Eq. (B)),

$$2 \text{ CH}_3\text{OH} \iff \text{CH}_3\text{OCH}_3 \xrightarrow{-\text{H}_2\text{O}} \text{hydrocarbons.}$$
 (B)

By measuring the catalyst life time it was found that some catalysts require an "induction period" to form new active sites involved in the methanol conversion. After this period, the surface becomes saturated with the reactive species, which accounts for the constant rate of dimethyl ether formation. The proposed species are weakly adsorbed, as evident from the sharp decrease in the reaction rate when the alcohol-feed to the reactor had been stopped. The catalyst activity depends on the electronegativity of the central metal atom (Lewis acidity), which is evident from the increase in the reaction rate in the case of the more electronegative tungsten atom.

2. At 250 °C "pretreatment temperature", the rate of dimethyl ether formation over HPW increases on increasing the temperature from 250 - 500 °C, whereas the rate of methane formation starts to decrease at 300 - 500 °C (Fig. 7). On increasing the pre-treatment temperature, Brønsted acid sites are supposed to be converted to Lewis sites by loosing the structural water<sup>23</sup> (Eq. (*C*)).

Brønsted 
$$\stackrel{>300 \text{ °C}}{=}$$
 Lewis + H<sub>2</sub>O (C)

This result was explained by that Lewis acid sites play an important role in dimethyl ether formation, whereas Brønsted acid sites are required for methane formation.

3. Changes in pretreatment atmosphere (Fig. 8) were assumed to affect the number of acidic sites<sup>12</sup>. The effect of pretreatment environment on the catalyst activity was also studied. It was found that argon seems to be the most beneficial environment for the pretreatment which removes some of the more acidic Brønsted sites and leads to a beneficial shift in the acid site distribution (high dispersion of Brønsted sites). Further, hydrogen may increase the number of weakly bound acid sites which are attached to the

catalyst at the positions not normally occupied by hydrogen. Such sites are expected to be readily removed at 350 °C, and not easily replaced. Hence, the rate of methanol transformation to dimethyl ether and methane is greater in argon atmosphere than in hydrogen. It was also found that the pretreatment in the argon saturated with water vapour decreases the activity of HPMo to about 50% of its original value, as shown in Fig. 8. This may be due to H<sub>2</sub>O molecules which become strongly adsorbed on the most active catalyst sites because of their higher absorptivity. This results in a decrease of the affinity of HPMo for alcohol molecules. Similar results were obtained by Ohtsuka et al.<sup>24</sup> for the dehydration of *tert*-butyl alcohol over heteropoly compounds.

4. Effect of the water produced during methanol dehydration on the rate of both dimethyl ether and methane formation was evaluated in the following way: Acetic acid was feeded with methanol in the amount 1 mole % after about 3 h of the reaction (Fig. 9). It was observed that the rate of dimethyl ether formation increases whereas the rate of methane formation decreases sharply to about 8.5% of the value observed just





Effect of pretreatment temperature  $t_r$  (°C) on the rate r (mol/h kg) of dimethyl ether (1) and methane (2) formation at 250 °C over HPW





Effect of pretreatment environment on the rate r (mol/h kg) of dimethyl ether (a) and methane (b) formation at 300 °C.  $\Box$  Argon,  $\bigcirc$  hydrogen,  $\bullet$  water-argon atmosphere

before injection of acetic acid. This indicates that the release of  $H_2O$  of dehydration by  $CH_3COOH$  shifts the reaction towards dimethyl ether formation. With continuous removal of water from the reaction product, the rate of diffusion of methanol and of dimethyl ether into the pseudo-liquid phase<sup>25</sup> increases and, consequently, also the rate of methane formation increases according to Eqs (*A*) and (*D*) – (*F*).

$$CH_{3}OH \xrightarrow{CH_{3}COOH} CH_{3}OCH_{3} + H_{2}O + CH_{4}$$
(D)

$$CH_3COOH + H_2O \longrightarrow CH_3OH + HCOOH$$
 (E)

$$\text{HCOOH} \longrightarrow \text{CO} + \text{H}_2\text{O} \longrightarrow \text{CH}_4 \tag{F}$$



#### Fig. 9

Effect of injection of acetic acid (at point A) on the rate r (mol/h kg) of dimethyl ether ( $\bullet$ ) and methane ( $\bigcirc$ ) formation at steady state conditions over HPMo (300 °C, 10.6 kPa)



#### Fig. 10

Effect of injection of pyridine (at point P) on dimethyl ether ( $\bullet$ ) and methane (O) formation. For experimental conditions see Fig. 9

# Role of Brønsted Acid Sites in Reaction Mechanism

To investigate the role of "H<sup>(+)</sup>" in the catalytic process, pyridine was injected with methanol in 1 mole % (pyridine/alcohol) after 3 h from the beginning of the run at 300 °C (Fig. 10). It was found that the rate of methane formation decreased sharply to 8% of the value observed just before pyridine injection, whereas the rate of dimethyl ether formation increased to 18% within 15 min. Such a behavior may be due to the adsorption of pyridine on Brønsted acid sites to form the strongly adsorbed pyridinium ion<sup>26</sup>. This result indicates that methane formation proceeds on Brønsted acid sites. After that the rate of dimethyl ether formation decreases whereas the rate of methane formation increases. This may be explained by formation of new proton acid sites, H<sup>(+)</sup>, as a result of the high electronegativity of pyridine, which assists methane formation on the expense of the ether. The catalyst starts to be deactivated by increasing pyridine concentration on the surface.

On the basis of these results and previous studies<sup>27,28</sup> one can conclude that in methanol conversion the first step includes protonation of  $CH_3OH$  to form  $CH_3OH_2^{(+)}$  which reacts with another physisorbed methanol molecule to form dimethyl ether, regenerating proton. Methane could be formed from the ether which acts as a hydrogen transfer agent. The  $CH_3OCH_2^{(+)}$  species formed in this case may react further, i.e. it can isomerize or produce the lighter products,  $H_2$ , CO, CO<sub>2</sub> (Scheme 1).



Scheme 1

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