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Catalytic Behavior of Unsupported and Heteropolysalt-Supported $H_{3+n}PV_nMo_{12-n}O_{40}$ Heteropolyacids in the Test Reaction of CH_3OH Oxidation

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Methanol oxidation has been used here to study the acid and redox properties of heteropolyacids of the $H_{3+n}PV_nMo_{12-n}O_{40}$ (n = 0, 1, 2, 3) series, both unsupported and supported on the potassium salt $K_3PMo_{12}O_{40}$. Increased vanadium content was found to improve selectivity to formaldehyde by favoring oxidative dehydrogenation at the expense of dehydration. This result is consistent with a reaction mechanism based on HOMO–LUMO interaction. Supported acids generally shown higher activity than the corresponding unsupported catalysts. For unsupported acids, activity was found to be governed mainly by absorption rates and stability of the secondary structure, whereas for supported acids whose structure was stabilized by the support, the influence of vanadium content was found to be a function of the overall proton concentration.

INTRODUCTION

Heteropolycompounds have long been used as catalysts, but only recently have their catalytic properties been investigated in detail (*1*). Heteropolyacids with Keggin structure (Fig. 1) are the best known and are particularly attractive for mechanistic studies since they present a well characterized microsurface. The versatility of their composition allows one to control easily the acidic and redox properties. Furthermore, it has been demonstrated recently that it is possible to improve their stability and further modify their properties by deposition on more thermally stable heteropolysalts, such as $K_3PMo_{12}O_{40}$ (*2–5*) or SiO_2 (*5*).

Catalytic test reactions can be used in conjunction with physico-chemical methods to determine catalyst properties. In the present work, we investigate the catalytic behavior of the $H_{3+n}PV_nMo_{12-n}O_{40}$ (n = 0, 1, 2, 3) series of heteropolyacids, unsupported and supported on $K_3PMo_{12}O_{40}$, for the test reaction of methanol oxidation.

From solution studies, it is known that acidic and redox properties of these compounds depend on the degree of vanadium substitution (*6*). One may expect the same trend for solid catalysts. Oxidation of methanol is particularly suitable to get some insight into the acid and redox functions of the catalysts, since they determine the spectrum of the reaction products (*7*). It was demonstrated recently by Sorensen and Weber (*8*) that gradual substitution of tungsten by vanadium in the $H_3PW_{12}O_{40}$ heteropolyacid results in an increasing production of formaldehyde (product of oxidative dehydrogenation) at the expense of dimethylether (product of dehydration). At higher temperatures, strongly acidic heteropolycompounds convert methanol into hydrocarbons via a dimethylether intermediate (*9–11*). In consequence, modifications of acid and redox properties through either

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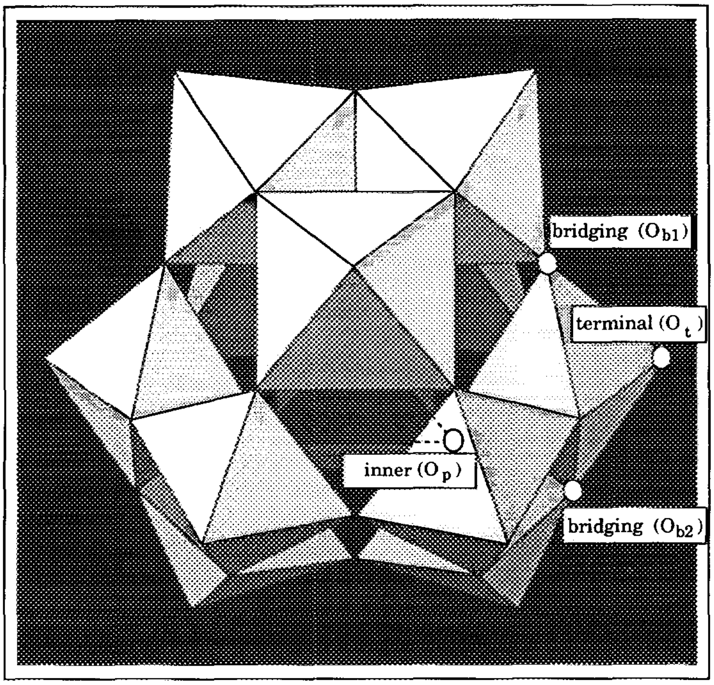

FIG. 1. Structure of the Keggin unit.

upon substitution by vanadium or upon addition on a support should change the product selectivity in the oxidation of methanol.

EXPERIMENTAL

Materials

The $H_{3+n}PV_nMo_{12-n}O_{40}$ (n = 1, 2, 3) heteropolyacids were prepared according to the method of Tsigdinos and Hallada (*12*). $H_3PMo_{12}O_{40}.xH_2O$ was obtained from Fluka Chemie AG. The water content of crystalline acid hydrates was found to correspond to the formulae $H_3PMo_{12}O_{40}$, 28 H_2O; $H_4PVMo_{11}O_{40}$, 32 H_2O; $H_5PV_2Mo_{10}O_{40}$, 31 H_2O; and $H_6PV_3Mo_9O_{40}$, 30 H_2O, as determined from thermogravimetric analysis. These samples will be referred to as H_3, H_4, H_5, and H_6. The $K_3PMo_{12}O_{40}$ support, abbreviated K_3, was prepared by the method described by Tsigdinos (*13*) from the stoichiometric quantities of $H_3PMo_{12}O_{40}$ and K_2CO_3. Catalysts corresponding in theory to a coverage of one monolayer by the acid component were prepared by impregnation of the support with the necessary quantity of aqueous solution of the respective acid, assuming that one Keggin anion occupies 144 Å^2 (*14*). These samples are referred to as H_3/K_3, H_4/K_3, H_5/K_3, and H_6/K_3. All catalysts, unsupported and supported, were subjected to thermal treatment in air at 300°C for 3 h. The BET surface area of calcined samples was measured to be 1–2 m^2/g for the unsupported acids, 2–4 m^2/g for the supported acids, and 70 m^2/g for the support.

Techniques

Catalytic testing. The catalytic reaction was carried out in a flow microreactor in the range 200–290°C with a mixture of methanol, oxygen, and helium in the ratio 7/16/77 (mol%). The reactor, a Pyrex tube with an internal diameter of 3 mm, contained about 10 mg of the catalyst held between two layers of quartz wool. On-line gas chromatographic analysis was used to determine the composition of the feed and the reaction products. The gas flow rate (34 ml/min) was adjusted in order to secure relatively low methanol conversion, which never exceeded 20%.

In a blank experiment with no catalyst in the reactor, it was checked that no methanol conversion occurred in the whole temperature range investigated (200–290°C). Catalytic measurements were performed after steady state was reached, usually within 0.5 h after the beginning of the experiment or the change of reaction temperature. During the catalytic experiments, no carbon deposit was observed; the carbon mass balance was always about 100%. To check the reproducibility of results, catalytic experiments were carried out at least three times in selected experimental conditions. It was found that dispersion of the results was within ±8%. In separate pulse adsorption experiments, consecutive small amounts of CH_3OH (0.5 μl) were injected on the catalyst (0.5 g) placed in the microreactor and kept in a stream of helium at 260°C. The amount of CH_3OH adsorbed before steady state was reached was calculated from gas chromatographic analysis.

Scanning electron microscopy. Microstructural characterization of surface morphology of the catalyst particles was carried out with a JEOL 100 CX instrument equipped with an ASID 4D high-resolution scanning accessory operating at 100 kV.

Infrared spectroscopy. Infrared spectra were recorded on an FT-IR spectrometer Digilab FTS-14V at room temperature in KBr powder.

X-ray diffraction. Powder X-ray diffraction data were obtained with a DRON 2 diffractometer using Cu*Kα* radiation.

RESULTS

Catalyst Characterization

Detailed physico-chemical characterization of both unsupported and supported acids is presented elsewhere (*15*). The use of XRD, electron microscopy, laser Raman spectroscopy, EPR, thermal analysis, and TPD of pyridine provided clearly that supporting the catalysts results in thermal stabilization of the acids and in modification of their acid–base and redox properties.

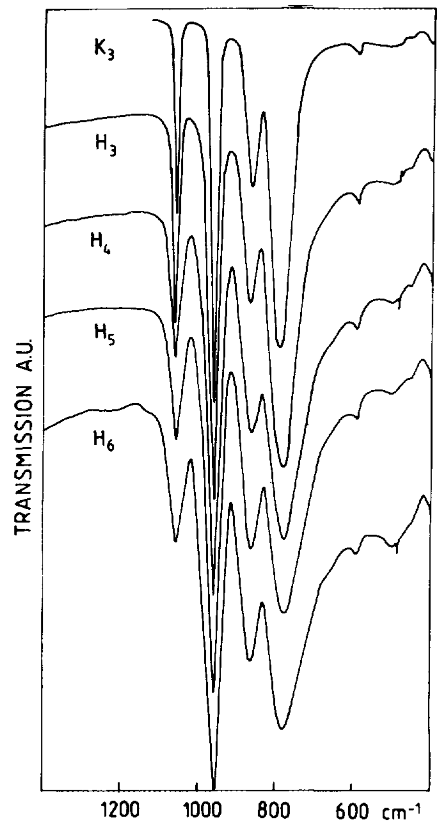

FIG. 2. IR spectra of calcined (300°C) acids (H_3, H_4, H_5, H_6) and of calcined potassium salt (K_3).

In view of the relatively weak thermal stability of the heteropolyacids investigated here, it was important to check whether after calcination the bulk of the catalysts was still made of undecomposed Keggin units. Figure 2 gives the IR spectra of calcined acid samples and neutral potassium salt used as a support. In the range of 700–1100 cm^{-1}, the samples display a number of well developed peaks characteristic of the Keggin structure. On the basis of data given by Rocchiccioli-Deltcheff *et al.* (*16*), the sharp peak at 1065 cm^{-1} corresponds to the vibration of P–O bond, that at 960 cm^{-1}

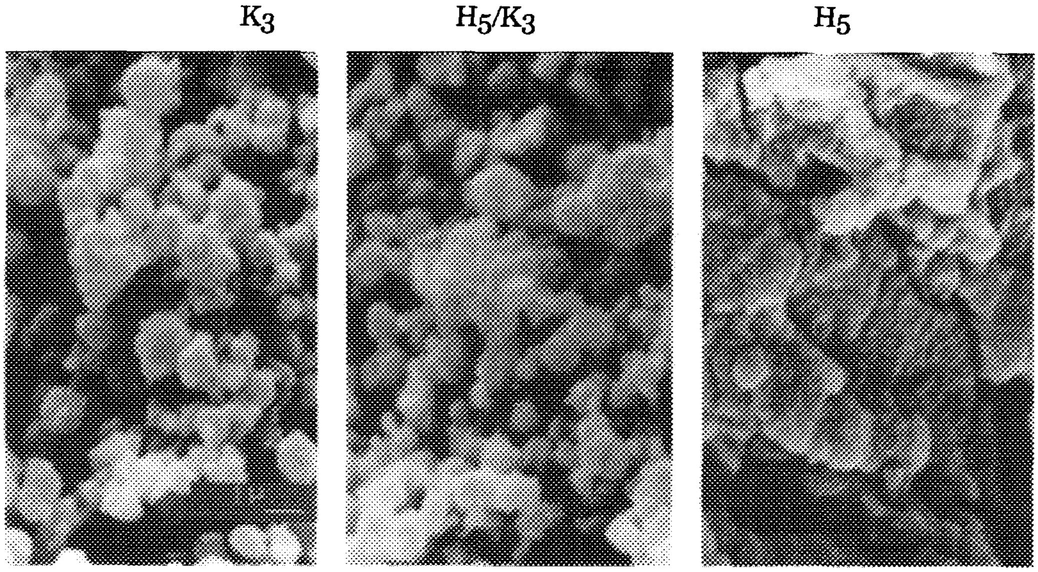

FIG. 3. SEM photographs (6000 ×) of calcined (300°C) samples (a) K_3, (b) H_5/K_3, and (c) H_5.

to the vibration of Mo=O_t while the two peaks at 790 and 860 cm^{-1} can be assigned to the vibrations Mo–O_{b2}–Mo and Mo–O_{b1}–Mo, respectively (as indicated on Fig. 1). The spectra show that substitution of Mo by V atoms in the heteropolyanion structure does not influence the IR spectra to any significant extent, except for a broadening of the IR bands. A very slight shift towards lower frequencies can also be observed for the Mo–O_b–Mo bands when the vanadium content is increased. We have not observed any band which can be assigned to a possible decomposition product of the Keggin unit (e.g., MoO_3).

Figures 3a–3c show the SEM micrograph of the calcined K_3, H_5/K_3, and H_5 catalysts at the same magnification. Other unsupported and supported acids have identical micrographs. There is an obvious difference in crystal habit between the K_3 support and the unsupported acid phase. The potassium salt is composed of small, well formed, round or hexagonal crystallites, of ca. 1 mm in diameter, whereas the H_5 acid sample consists of agglomerates or irregular crystallites varying in shape and dimension. The surface morphology of the supported acid H_5/K_3 closely resembles that of the K_3 support. In particular, no separate irregular crystallites typical of the unsupported acid phase can be found, although the amount of the acid deposit represents about 25% of the catalyst weight.

Figures 4a–4d give the X-ray diffraction patterns of the unsupported H_5 acid of various formal hydration degrees (a–c), and of the K_3 support (d). Similar patterns are obtained for other members of the series. They show that the hydrates are not a single-phase material. The X-ray data also show that the structure is very labile and changes easily with the amount of hydration water. Strong dehydration makes the samples amorphous. Structure lability is an important feature of these compounds. When used as solid catalysts, they may easily absorb polar molecules such as H_2O, alcohols, and amines, and catalytic reactions may thus proceed not only at the surface, but also in the bulk (*1*). X-ray data show additionally that the tendency of the acid hydrates to lose their crystallinity upon thermal treatment at 100°C increases with the number of vana-

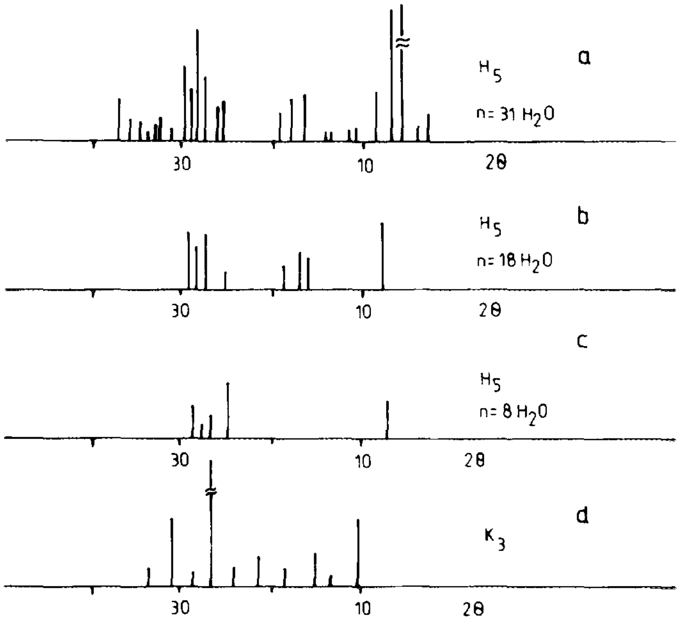

FIG. 4. Powder X-ray diffraction patterns of (a–c) H_5 acid of various hydration degree, and (d) K_3 support.

dium atoms. This observation agrees well with earlier results of Jerschkewitz *et al.* (*17*), who found that, upon increasing substitution with vanadium, the members of the $H_{3+n}PV_nMo_{12-n}O_{40}$ series show an increased tendency to lose both crystallization and constitutional water. The support, on the other hand, gives the typical powder pattern of the $K_3PMo_{12}O_{40}$ cubic structure, which is known to be very rigid, with no bulk absorptive ability.

Catalytic Test

In our conditions, the main products of methanol partial oxidation are dimethylether CH_3OCH_3, formaldehyde CH_2O, and at lower reaction temperatures, methylal $(CH_3O)_2CH_2$. In some cases, significant amounts of CO and methyl formate $HCOOCH_3$ are formed. In all experiments, only traces of CO_2 can be detected in the gas phase products.

Figures 5a and 5b illustrate the variation of selectivity as a function of reaction temperature for the unsupported H_3 and H_5 catalysts. The variation observed for H_5 is representative of all other vanadium containing acids. H_3 differs from the vanadium containing acid samples since it leads to a broader spectrum of products as significantly higher yields of CO and $HCOOCH_3$ are found. On all samples, the selectivity to dimethyl ether is high and appears to be only weakly dependent on the temperature. On the contrary, the selectivity toward products of oxidative dehydrogenation, formaldehyde and methylal is a strong function of reaction temperature. The yield of CH_2O increases with temperature, whereas that of $(CH_3O)_2CH_2$ rapidly falls. On the vanadium containing samples, a distinctly smaller amount of CO is formed, while methyl formate is hardly detectable.

Figures 5c–5e shows the dependence of selectivity on reaction temperature for the support K_3 alone and two supported acids, H_3/K_3 and H_5/K_3. Here again all the supported acids which contain vanadium show a similar dependence. It may be seen that after deposition on the K_3 support, the acid

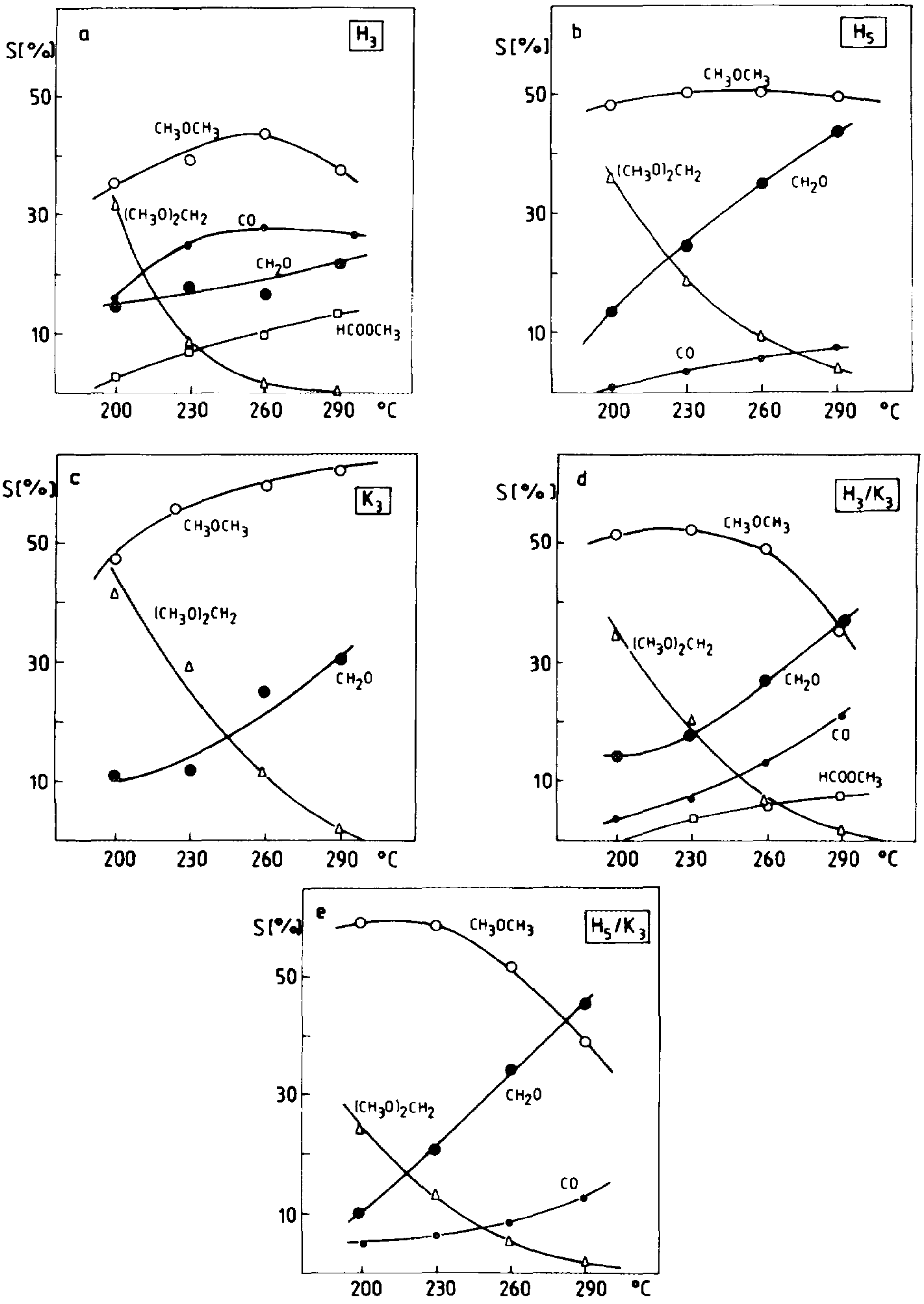

FIG. 5. The temperature dependence of selectivity for samples (a) H_3, (b) H_5, (c) K_3, (d) H_3/K_3, and (e) H_5/K_3.

TABLE 1

Selectivities and Conversion for Methanol Oxidation

Catalyst	T(°C)	Conv. (%)	Selectivity (%)				
			$(CH_3)_2O$	CH_2O	$(CH_3O)_2CH_2$	$HCOOCH_3$	CO
H_3	200	2	36	13	31	3	16
	230	7	39	19	9	7	25
	260	9	45	16	1	10	28
	290	17	37	23	0	13	27
H_4	200	4	53	7	35	0	4
	230	9	60	20	12	0	8
	260	16	56	29	3	1	11
	290	12	48	38	1	3	10
H_5	200	2	48	13	36	0	2
	230	5	47	29	20	0	4
	260	17	50	36	9	0^a	6
	290	11	49	43	3	0^a	5
H_6	200	2	45	11	39	0	4
	230	4	50	20	25	0	6
	260	7	47	37	11	0^a	5
	290	12	45	46	4	0^a	5
K_3	200	2	51	8	40	1	0
	230	2	57	8	33	2	0
	260	5	60	26	12	1	0
	290	11	64	31	3	1	1
H_3/K_3	200	2	47	13	35	1	4
	230	4	52	17	21	4	8
	260	7	49	26	7	6	12
	290	9	38	35	2	4	21
H_4/K_3	200	3	56	12	29	0	3
	230	4	49	25	21	0	5
	260	7	53	30	8	2	6
	290	10	44	43	4	2	7
H_5/K_3	200	5	60	9	25	0	4
	230	7	59	21	13	0	7
	260	11	51	35	5	1	8
	290	15	39	47	2	1	11
H_6/K_3	200	5	61	7	26	0	6
	230	8	55	22	11	0^a	11
	260	14	45	39	4	0^a	12
	290	20	34	50	1	0^a	13

[a] Traces.

without vanadium produces significant amounts of CO and methyl formate. Only traces are produced by vanadium containing catalysts and none by the support alone.

Selectivities and activities of the catalysts are compared in Table 1 and Fig. 6, respectively. Experimental conversions in Table 1 have been adjusted by varying the quantity of catalyst in the reactor to obtain low methanol conversion and for a given temperature, to be as close as possible at methanol isoconversion. Activities in Fig. 6 are expressed per gram of acid component. It may be seen that substitution with vanadium causes opposite effects for unsupported and supported heteropolyacids. While introduction of vanadium lowers the catalytic activity of unsupported acids, the supported sam-

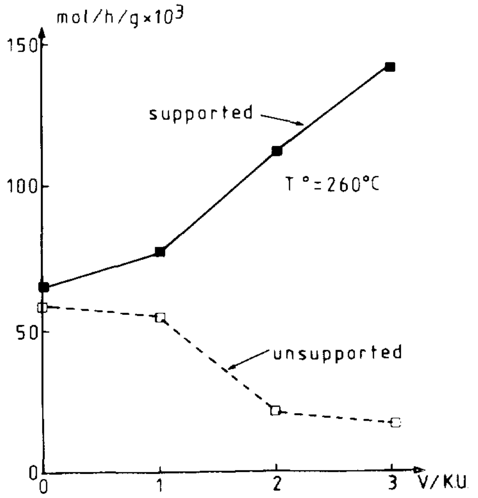

FIG. 6. Catalytic activity in CH_3OH oxidation at 260°C for unsupported acids (□) and supported acids (■).

ples become more active as the number of vanadium atoms increases. The overall activity of supported samples is generally higher than that of the acids. For K_3, whose BET surface area is comparable to those of the supported samples, the activity is orders of magnitude lower than for the catalysts containing the acid phase.

DISCUSSION

Methanol conversion may proceed along different reaction pathways and yield different slates of products. The main products obtained under our experimental conditions are dimethylether, formaldehyde, and methylal, in agreement with previous findings (*8*, *18*). We have also observed small amounts of methyl formate and carbon oxides. If these latter products were formed by the same route as formaldehyde, as mentioned by Liu *et al.* on MoO_3/TiO_2 catalysts (*19*), formic acid could be expected to be the intermediate species between formaldehyde and methyl formate or carbon oxides. The addition of small amounts (0.2% ≈ 1.5 Torr) of formic acid to the reaction feed at 260°C does not change the rates of dimethyl ether, formaldehyde, and methylal formation, but leads to the total conversion of formic acid into equal amounts of methyl formate and carbon monoxide, suggesting that, under the reaction conditions, if formic acid was the intermediate species between formaldehyde and methyl formate or CO, the selectivities to methyl formate and CO should be approximately equal.

The experimental data (Table 1) show that CO selectivity is always much higher than methyl formate selectivity. This observation and the absence of formic acid poisoning of the formation of the main reaction products (dimethyl ether, formaldehyde, and methylal) are not consistent with the expected mechanism of methyl formate and carbon monoxide formation by further oxidation of formaldehyde and strongly suggest that methyl formate and carbon oxides are formed by a direct route, which is different from the one considered for the formation of dimethyl ether, formaldehyde, and methylal. Consequently, we should then only consider these three products in order to investigate the influence of vanadium substitution.

When discussing the oxidation route, it should be kept in mind that the formaldehyde surface intermediate may either desorb as formaldehyde or react with additional methanol molecules to give methylal. This latter reaction prevails at low temperature. The main oxidation products (formaldehyde and methylal) need only the presence of one labile oxygen per site, whereas the formation of the minor oxidation products ($HCOOCH_3$, CO_x) which requires more than one oxygen atom must occur on different sites as previously suggested. Thus, the rate of the oxidative dehydrogenating route (DHG) should be estimated from the sum of the formaldehyde rate and the third of the methylal rate, since the methylal formation can be described as the condensation of two methanol molecules of adsorbed formaldehyde followed by water elimination. The DHG selectivity calculated as the ratio of the DHG rate to the total rate corresponds to the sum of the formaldehyde selectivity

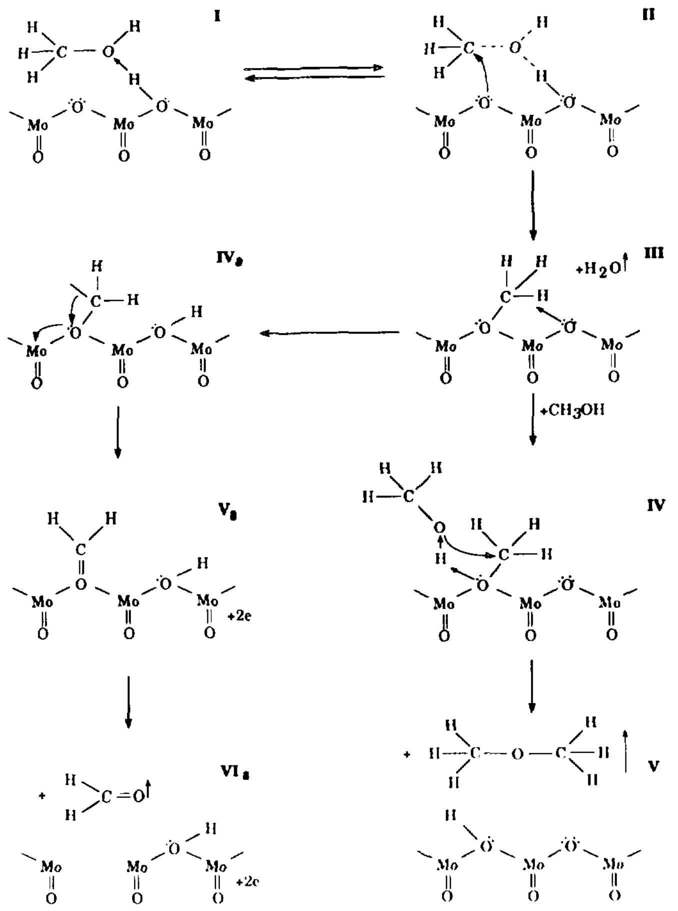

FIG. 7. Mechanism of CH_3OH interaction with the Keggin unit as catalyst.

and the third of the methylal selectivity, since the rates are expressed relative to the methanol consumption.

The mechanism leading to the formation of the two major products (dimethylether and formaldehyde) may be represented by the scheme given in Fig. 7. The first three steps (I–III) are common to both reaction pathways acid and redox. The first step consists in an electrophilic attack of the acidic proton associated with the Keggin unit on the methanolic oxygen to form a protonated methanol species (configurations I and II). Recently Highfield and Moffat presented IR spectral evidence for the formation of such an intermediate on the $H_3PW_{12}O_{40}$ heteropolyacid (*20*). Subsequent nucleophilic attack of a lone pair of a neighboring Keggin bridging oxygen on the positively charged carbon atom results in C–O bond cleavage and gives a methoxy group attached in a bridging position to the Keggin unit (configuration III). Reactions from I to V proceed on the catalyst acid centers and lead to the formation of dimethylether (DME), the product of methanol dehydration. Since in the investigated reaction DME is the predominant product (Table 1), we conclude that the reaction proceeds mainly along this reaction pathway. It is worthwhile to men-

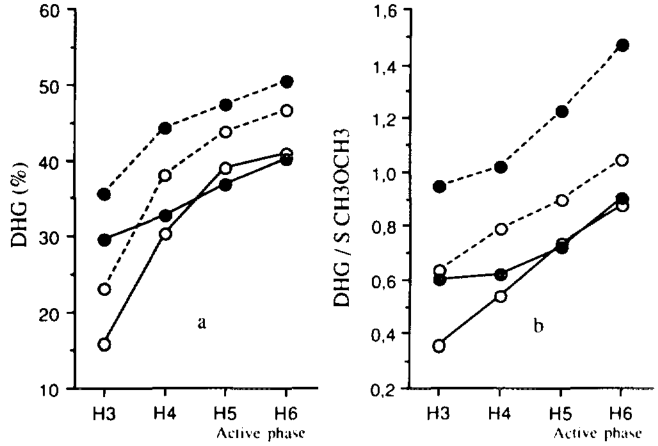

FIG. 8. Influence of vanadium content on selectivities (a) *S* DHG (CH_2O + 1/3$(CH_3O)_2CH_3$) and (b) *S* DHG/*S*$(CH_3)_2O$ at 260°C (—) and at 290°C (----) for unsupported acids (○) and supported acids (●).

tion here that DME could also be formed from the reaction of two neighboring methoxy groups, which would indeed remove one of the bridging oxygens of the Keggin unit. This process may contribute to the formation of dimethyl ether at high temperature.

Due to the presence of redox centers, a parallel reaction proceeds and formaldehyde, the product of oxidative dehydrogenation of CH_3OH is also formed (route through configurations IVa–VIa). The adsorbed form of formaldehyde (configuration Va) can then react with two methanol molecules to form the methylal (low temperature) or directly desorbs in the gas phase (high temperature), leading in both cases to the formation of an oxygen vacancy (configuration VIa).

The influence of vanadium content on the DHG route is shown in Figs. 8a and 8b. The DHG selectivity is clearly enhanced by vanadium substitution (Fig. 8a). The DHG to dimethyl ether selectivities ratio (Fig. 8b), which increases also with vanadium content, indicates that the redox route (configuration IVa) is more favored than acid route (configuration IV) by vanadium substitution.

The desorption of formaldehyde leaves behind an oxygen-deficient, partially reduced catalyst, which subsequently reoxidizes by reaction with gaseous oxygen. According to Farneth *et al.* (*24*), H abstraction from an adsorbed methoxy group is expected to be a relatively slow reaction on heteropolyacid catalysts. Therefore, the balance between dehydration and redox routes will be determined by the ratio between the H-abstraction rate and the rate of methanol reaction on methoxy groups (CH_3OCH_3 formation). Any facilitation of this step should result in the increase of the rate ratio $r_{CH_2O}/r_{CH_3OCH_3}$ and CH_2O selectivity. As seen from Fig. 8a and Table 1, selectivity to DHG (CH_2O + 1/3$(CH_3O)_2CH_2$) increases with the number of vanadium atoms in the Keggin unit, both for unsupported and supported acids. From the O^{17} NMR data reported by Maximovskaya *et al.* (*25*), it is known that the electron density of the bridging oxygen of the Mo–O–Mo bond type systematically increases with the number of vanadium atoms. We may therefore interpret the enhanced selectivity to formaldehyde as the result of the increased driving force for a nucleophilic attack on the C–H bond of the methoxy group (configuration III), pushing the conversion of the methoxy intermediate along the oxidative pathway.

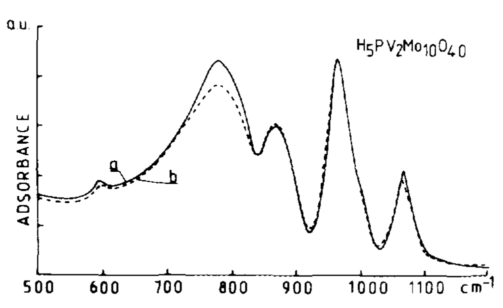

FIG. 9. IR spectra of H_5: (a) fresh sample and (b) sample after reduction by CH_3OH in absence of air at 260°C.

Simultaneously, higher proton affinity of such bridging oxygens and higher oxidation potential of vanadium, in comparison with molybdenum, facilitate proton abstraction and electron transfer to the Keggin anion and consequently promote formaldehyde desorption. Thus, the observed selectivity dependency on reaction temperature of the main oxidation products is consistent with the proposed reaction mechanism.

According to our scheme in Fig. 7, the bridging oxygen is abstracted from the Keggin anion during formaldehyde desorption. This mechanism is supported by the results of our IR experiments, which are presented in Fig. 9. It shows the spectra in the region of the Keggin unit structural vibrations obtained for the fresh H_5 catalyst (a), and for the same sample after weak reduction by pulses of CH_3OH at 290°C in the absence of gaseous oxygen (b). As it is seen, such weak reduction influences only the intensity of the 860-cm^{-1} band which correspond to the Mo–O_{bl}–Mo bridging corner oxygen vibration (*16*). Simultaneously, the intensity of the Mo–O_t band at 960 cm^{-1} remains unaffected, indicating that no double-bond oxygen Mo=O_t is removed from the Keggin unit during CH_3OH oxidation. A slight change in the intensity of the P–O band at 1065 cm^{-1} may arise from a partial loss of phosphorus tetrahedral symmetry (*26*).

As we can expect for methanol oxidation on $H_3PW_{12}O_{40}$ heteropolyacid (20), C–O bond cleavage with formation of a methoxy group attached to the surface to be the rate-determining step. It implies that catalytic activity depends on the concentration of acid centers capable to protonate CH_3OH and form surface CH_3–O groups. This conclusion is in line with the low values of activation energy observed in our experiments (Table 2).

Then, assuming that the same rate-determining step is present in the case of our catalysts, we can explain the observed trends in catalytic activity. We should turn our attention to the fact that, as seen from X-ray data (Fig. 4), the secondary structure of the investigated acids is very labile. It is known that heteropolyacids of this type behave in a reaction with polar reactants as pseudo-liquid phases (*1*) and that the rate of the catalytic reaction depends on solubility of the reactant in the bulk of the acid.

Although the solubility of CH_3OH within the $H_{3+n}PV_nMo_{12-n}O_{40}$ series may be different for each particular member of the series, various experimental data indicate that the ability of the $H_{3+n}PV_nMo_{12-n}O_{40}$ heteropolyacids to absorb polar compounds decreases with increasing vanadium substitution. Jerschkewitz *et al.* (*17*) studied the hydration/rehydration ability of this series. They found that upon increasing substitution with vanadium, the members of acid series show an increased tendency to lose both the water of crystallization and the constitutional water. Pyridine absorption data (*21*) also prove that the ability of the acids to retain pyridine at elevated temperature decreases for higher vanadium content. Ad-

TABLE 2

Total Activity for Methanol Oxidation

T (°C)	H_3	H_4	H_5	H_6	H_3/K_3	H_4/K_3	H_5/K_3	H_6/K_3
200	5.0	11.1	5.4	5.0	26.4	28.8	53.2	47.2
230	20.2	26.2	13.4	12.1	44.0	44.8	79.2	84.4
260	58.4	45.3	20.8	18.0	65.5	77.6	113.3	144.0
290	90.1	75.3	29.8	32.2	92.4	118.0	172.0	200.0
E_a[a]	13.7	12.4	10.4	11.3	8.9	8.5	7.4	9.3

Note. Activities are expressed in mmol/h/g of acid phase.
[a] Expressed in kcal/mol.

ditionally, we checked in separate pulse experiments (see experimental) the ability of these acids to absorb CH_3OH at 260°C. The amount of CH_3OH retained by unsupported acids progressively decreases from 1.0 to 0.8 to 0.4 and to 0.3 (arbitrary units) with the increasing number of vanadium atoms along the series H_3, H_4, H_5, and H_6, respectively. Therefore, we believe that the decrease in catalytic activity upon substitution with vanadium in the acids (Fig. 6) reflects primarily a decrease in absorption capabilities. The situation is different for the supported acid layers (Fig. 6), as it appears from our recent physicochemical studies (*15*) that the properties of thin acid layers supported on the surface of isostructural salt $K_3PMo_{12}O_{40}$ are modified to a great extent. Raman spectroscopy (*22*) shows that the secondary structure remains similar throughout the series, but becomes more rigid, due to a better epitaxial match with the support. Thus, no significant differences in the absorption ability should be expected. The results of our pulse experiments on the supported acids layers, performed in the same way as in the case of acids, clearly support this assumption, since only traces of retained alcohol were observed.

Consequently, as it is the methoxy group formation which is the rate-limiting step, the catalytic activity will depend only on the concentration of Brønsted acid sites in the supported acid layer. From the stoichiometric formula, it follows that the concentration of protons increases with the number of vanadium atoms. The acidity measurements (*21*) show that most of the protons present in the samples are weak acid centers, which are rather firmly bound to the Keggin anions. These relatively weak acid sites are capable to ensure methanol protonation, as shown by methanol TPD data (*23*).

Therefore, the increasing catalytic activity of the supported series reflects the increasing number of Brønsted acid sites as the value of n in the $H_{3+n}PV_nMo_{12-n}O_{40}$ series increases. The generally higher activity of the supported acids indicates that the secondary structure of the stabilized acid coats provides more capacious reaction field than the labile lattices of unsupported acids.

CONCLUSIONS

Increasing vanadium content in catalysis of the $H_{3+n}PV_nMo_{12-n}O_{40}$ series enhances oxidative dehydrogenation of methanol to formaldehyde, at the expense of dimethylether, the dehydration product. The use of a heteropolysalt as a support increases the activity of the acids due to the stabilizing influence of the acid secondary structure. Substitution of molybdenum by vanadium causes a decrease in activity by a decreased ability of the catalyst to adsorb methanol, due to loss of secondary-structure organization. In the case of supported samples, with stabilized acid coats, the activity is a function of the overall proton concentration.

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