On the physicochemical and catalytic properties of $H_5PV_2Mo_{10}O_{40}$ supported on silica

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Properties of $H_5PV_2Mo_{10}O_{40}$ (HPVMo) heteropolyacid supported on high area silica (375 $m^2\ g^{-1}$) were investigated. At low loadings interaction with surface OH groups leads to hydrolysis of Keggin anions into "triads" of edge-sharing octahedra strongly bound to the surface. Characteristic acidity is lost and methanol is oxidized to formaldehyde. At high loading unperturbed Keggin anions are present at the surface. Properties resemble those of unsupported acid. Thermally decomposed Keggin anions become reconstructed under exposure to water vapor. Dimethylether is mainly formed from methanol.

Keywords: heteropolyacid supported on silica; methanol oxidation; Keggin anion transformations at silica surface

1. Introduction

Heteropolyacids (HPA) with the Keggin structure (fig. 1) are known to be highly active heterogeneous catalysts, both in various acid type reactions and in oxidative processes [1]. Among them HPA of the general formula $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 0, 1, 2, 3$) were found to possess particularly good catalytic properties in selective oxidation of unsaturated aldehydes [1] and light paraffins [2,3]. However, the general drawback of HPA-catalysts is their relatively low thermal stability which may give rise to the Keggin unit (KU) decomposition under catalytic conditions. In the case of acids of the $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 0, 1, 2, 3$) series such degradation proceeds in the temperature range 650–700 K [4–7].

Therefore a number of studies have been carried out aiming at the improvement of HPA stability by supporting them on different carriers [8–24]. The majority of authors using silica as the support claim that deposition of HPA results in the destabilization of the KU, which decomposes into MoO_3 at temperature lower than the bulk acid [14–17]. Recently a series of papers appeared showing that silica sup-

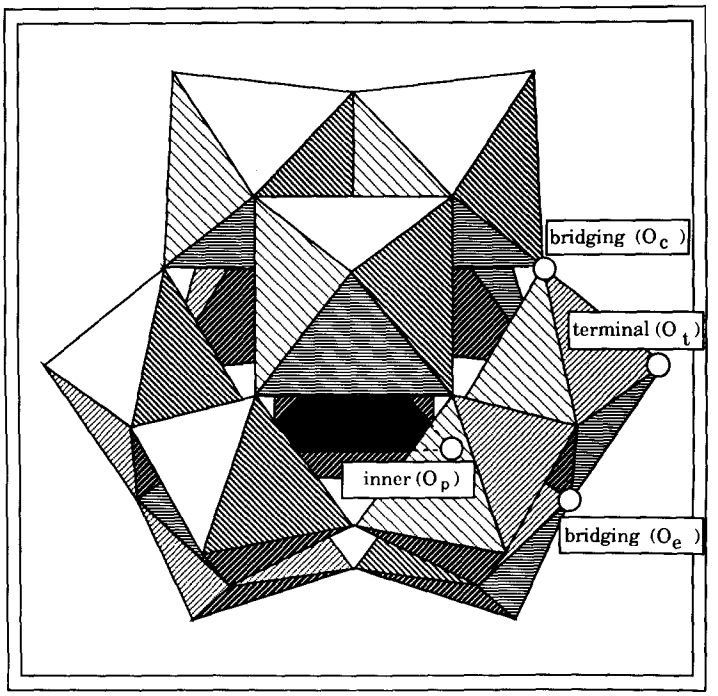

Fig. 1. Keggin unit structure.

ported HPA at low coverage is stabilized, because it undergoes dehydration resulting in the formation of a defected KU unit stable up to 823 K [18–24]. On the other hand it has been noticed that under certain circumstances products of the thermal decomposition of KU supported at the silica surface may be on exposure to water vapour reconverted to KU [4,10,23–29].

Much of the confusion may have arisen because such factors as surface coverage or water vapour pressure have not been sufficiently taken care of in studying the stabilizing effect of silica.

In spite of the extensive studies several questions remain yet not fully answered:

(a) which is the nature of species present at the silica surface at different surface coverages,

(b) which is their behaviour on thermal treatment and how is this behaviour influenced by the pressure of water vapour,

(c) how do these phenomena determine the catalytic properties?

It seemed therefore of interest to reinvestigate the modifications of the structure and properties of HPA induced by its dispersion at the silica surface and to unravel their influence on the behaviour in catalytic reaction. In view of the importance of vapour pressure particular care was paid to the maintenance of well defined experimental conditions, in which the presence of water was either completely eliminated or deliberately introduced.

SEM, TG-DTA and IR have been used to characterize the catalyst, and catalytic oxidation of methanol has been used as a probe reaction. It is known that this reaction is particularly sensitive to changes of surface structure which lead to variations in activities and selectivities [30–33]. $H_5PV_2Mo_{10}O_{40}$ (HPVMo) was selected as active phase because introduction of vanadium into $PMo_{12}O_{40}$ KU reduces the number of products in methanol oxidation practically to formaldehyde and dimethyl ether only, which makes conclusions from this probe reaction more straightforward.

2. Experimental

2.1. MATERIALS

HPVMo was prepared according to the method of Tsigdinos and Hallada [31] and purified by repeated crystallization from water. The composition determined by chemical analysis appears to be $H_{4.86}PV_{1.80}Mo_{10.14}O_{40}$ [6].

Silica (Rhone–Poulenc XOA 400, surface area 376 $m^2\ g^{-1}$) has been used as a support. Assuming that one KU occupies 144 $Å^2$, catalysts corresponding formally to 0.05, 0.1, 0.25, 0.5 and 1.0 monolayer coverage were prepared by impregnation of the support with the desired quantity of the acid solution, followed by evaporation to dryness at 350 K and calcination at 470 K for 2 h. They are hereafter referred to as 0.05 HPVMo/SiO_2, 0.1 HPVMo/SiO_2, 0.25 HPVMo/SiO_2 etc.

2.2. TECHNIQUES

Thermogravimetry. DTG/DTA experiments were carried out under ambient air with a derivatograph analyzer system F. Paulik & L. Erdey (made in Hungary). Experimental conditions were as follows: sample weight ca. 30 mg, heating rate 5 K per minute.

Scanning electron microscopy. Microstructural characterization of the surface topography of the catalyst particles was carried out with a Jeol 100 CX instrument equipped with an EDX analyzer allowing a rough chemical analysis of the elements present on the surface (area 20 × 20 μm). Powder-like material was deposited on adhesive tape fixed to a glass slide and then sprayed with gold to form a film of approximately 200 Å thickness.

Infrared spectroscopy. Infrared spectra were recorded on a FT-IR spectrometer Nicolet 800 at room temperature in KBr powder. The samples after drying and calcination were mixed in a dry-box with dried KBr without exposure to water vapour. In some experiments the samples were exposed to water vapour under controlled conditions and then mixed with KBr.

Catalytic measurements. The oxidation of methanol was used as a test reaction in a continuous-flow, fixed-bed microreactor at 533 K. The reactant feed was a

mixture of methanol, oxygen and helium in the ratio 7/16/77 mol%, which corresponds to CH_3OH partial pressure of 58.2 Torr. This mixture was obtained by passing the He/O_2 flow through a methanol saturator maintained at 11.3°C. Catalysts, previously calcined at different temperatures between 473 and 873 K, were held in a reactor (a pyrex tube, with an internal diameter of 3 mm) between two layers of quartz wool. The gas flow rate (34 ml/min) and catalyst weight (10–40 mg) were adjusted in order to secure relatively low methanol conversion which never exceeded 12%. On-line gas chromatographic analysis was used to determine the composition of the feed before or after the reactor. Catalytic measurements were performed after the steady state was reached usually about 0.5 h after the reagent mixture was admitted on to the catalyst. No carbon deposit was observed during catalytic experiments the carbon balance being always about 100%.

3. Results and discussion

3.1. SURFACE MORPHOLOGY

The SEM image of the unsupported HPVMo catalyst shows that it consists of agglomerates of irregular, cracked crystallites varying in size and habit. Pure SiO_2 support is composed of relatively well shaped, spherical particles with an average diameter of approximately 100–200 μm. Their surface is composed of very fine sub-particles of irregular shape arranged in a loose manner what accounts for a high specific surface area of ca. 376 $m^2\,g^{-1}$. The surface morphology of the supported samples is practically identical to that of the pure silica. No separate crystallites of the bulk phase of HPVMo were found either in the SEM image or by means of EDX spectra. However, EDX spectra show an increasing amount of vanadium atoms with the growing loading of SiO_2 with HPVMo. It may be thus concluded that our impregnation procedure resulted in a fairly uniform deposition of HPA on the surface of the silica support as found in refs. [23,34].

3.2. STRUCTURE OF SILICA SUPPORTED HPVMo

More information on the structure of the HPVMo supported on SiO_2 and its dependence on loading is provided by the FT-IR spectra, shown in figs. 2a and 2b for unsupported and silica supported HPVMo respectively. The IR spectrum of the unsupported HPA (fig. 2a) reveals bands characteristic of the $PMo_{12}O_{40}$ type KU i.e. bands at 1061, 960, 864, 790 and 590 cm^{-1} assigned to the stretching vibrations of P–O, Mo=O, Mo–O_c–Mo, Mo–O_e–Mo (see fig. 1) and the bending vibration of P–O respectively [36]. Spectra of vanadium substituted KU $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ in acids and their salts have been published by several authors [6,12,36,43]. The spectra reported in ref. [43] show the presence of shoulders at P–O and Mo=O bands but without assignment. However, such shoulders were not reported by

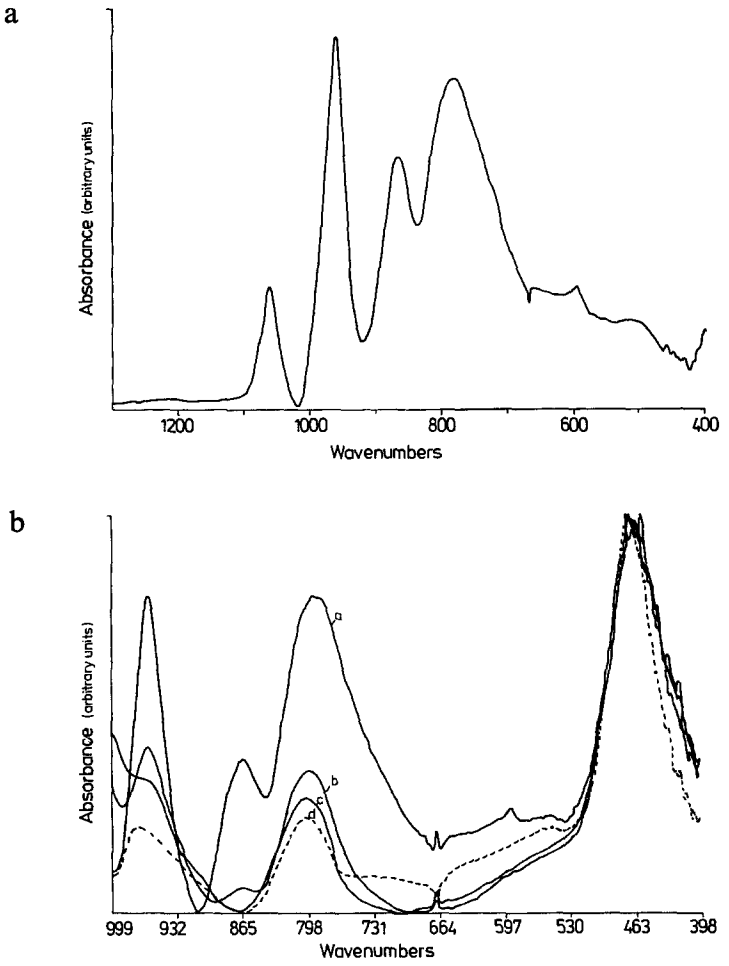

Fig. 2. (a) IR spectra of bulk HPVMo. (b) IR spectra of supported HPVMo: a) 1.0 HPVMo/SiO_2, b) 0.25 HPVMo/SiO_2, c) 0.1 HPVMo/SiO_2.

other authors, nor where they observed in our earlier studies, although direct experimental evidence indicated that vanadium is present in the KU [12]. IR spectra of $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ have been investigated in detail by Bielański et al. [6] who did not observe any shoulders but found that introduction of vanadium into the Keggin anion results only in a small shift of the position of the P–O band, this position being very sensitive to the degree of dehydration. It seems thus that the position of the P–O band cannot be taken as indicator of the presence or absence of substituted vanadium. Spectra of supported samples (fig. 2b) are shown without subtraction of SiO_2 absorption since this procedure can lead to the formation of artifact bands especially for the low loadings. Pure silica exhibits three main bands at 1100 cm^{-1} (broad and very strong), 800 cm^{-1} (medium) and 470 cm^{-1} (strong) which partly overlap with those of the KU.

It may be noted that at high loading (monolayer loading) the IR spectrum of the supported sample is identical to the superposition of the spectra of the unsupported HPVMo and that of silica indicating that the Keggin anions are unperturbed by the support. This is in line with the results obtained earlier by ^{31}P NMR and laser Raman spectroscopy [23] and shows that introduction of vanadium into the KU unit has no influence on the structure of its monolayer. It is linked to the surface probably by the electrostatic forces resulting from the protonation of the surface hydroxyl groups of silica by strongest acidic protons of the HPA as discussed in detail for the case of $H_4SiMo_{12}O_{40}$ [30]. As however at monolayer coverage of the surface by the HPVMo, each of which has the charge −5, the majority of protons remain unbound, the sample is expected to show acidity comparable with the free HPVMo.

A different picture emerges from the FT-IR spectrum of the sample containing 0.1 monolayer of HPVMo. Intensities of the band at 960 cm^{-1} due to the stretching vibration of the M=O group and the band at 790 cm^{-1} assigned to the Mo–O_c–Mo vibration decrease with HPVMo coverage (note that the band at 1061 cm^{-1} overlaps with that of silica). In contrast the band at 864 cm^{-1}, due to Mo–O_c–Mo vibration, disappeared completely. This is the vibration of bonds around the apex oxygens, which link together the groups of three edge-sharing MoO_6 octahedra (triads) in the KU, and the disappearance of this band may be taken as an indication of the cleavage of these bonds and the decomposition of the KU into triads.

At low coverage, when the surface is sparsely populated by the KU the system may be considered as composed of KU partially "immersed" in the bidimensional hydration layer at the silica surface. The point of zero charge of silica corresponds to pH = 2.5; the bidimensional layer provides thus a basic medium in comparison to the strongly acidic HPVMo. It is known from aqueous solution chemistry of HPA that the polyanions dissociate on raising the pH of the solution [37]. Thus, in the conditions prevailing at the silica surface hydrolysis of Mo–O_c–Mo bonds, corner-linking the triads of MoO_6 octahedra, takes place, resulting in the opening of the closed structure of the Keggin anion, which is transformed into its constituent triads more or less strongly connected together. This is in line with the earlier observations that the molecular structure of supported transition metal oxide monolayers follows the aqueous chemistry as a function of net pH at p.z.c. of the support and the oxide surface concentration [38].

The KU contains 12 bridging oxygen atoms O_c linking together the triads. Each triad is linked by six bridging oxygen atoms to the other three triads. Let us assume that in the process of deposition at the hydrated silica surface the KU becomes oriented so that the upper triad is parallel to the surface. It can be envisaged that the six Mo–O_c–Mo bridges between the remaining three triads become hydrolyzed and these triads are rotated by 135° around the Mo–O_c–Mo bridges linking them to the upper triad. Such transformation will result in the formation of a flat structure composed of four triads linked together through the six Mo–O_c–Mo bridges and linked to the surface of silica through the PO_4 tetrahedron, as well

as through some corner oxygen atoms of the triads replacing the missing oxygen atoms of surface SiO_4 tetrahedra (fig. 3). Indeed, the substitution of SiO_4 tetrahedra by PO_4 tetrahedra is well known in zeolite chemistry [39], and in compounds like silicocarnotite [40], where SiO_4 and PO_4 tetrahedra are linked together in the lattice. It can be expected that the Mo–O_c–Mo bridges remaining in such surface complex will have different vibrational characteristics than those in the Keggin unit and therefore the band at 864 cm^{-1} disappears completely although only one half of the bridges become hydrolyzed. The remaining bridges either become more rigid because of the interactions of the triads with the silica surface, or may dissociate if the triads move apart in the hydrated layer. It could be expected that in such circumstances the acidity of the supported HPVMo disappears and such system will show mainly redox properties. The catalytic experiments described later are indeed in line with such a conclusion.

Earlier spectroscopic studies showed [22] that the thermal stability of HPMo on silica surface at low loading is improved in comparison to bulk HPMo. This has been ascribed to the mechanism of dehydration which in case of heating of the isolated surface KU would result in the formation of detected Keggin units stable to 823 K and not in their decomposition, as observed at high loadings. In our model the stability is achieved through hydrolysis of KU at low loading into triads linked to the surface by multiple bonds and therefore strongly stabilized. The possibility of formation of triads in the case of silica supported HSiMo has been mentioned in ref. [34]. It cannot be excluded that on heating such triads undergo dehydration

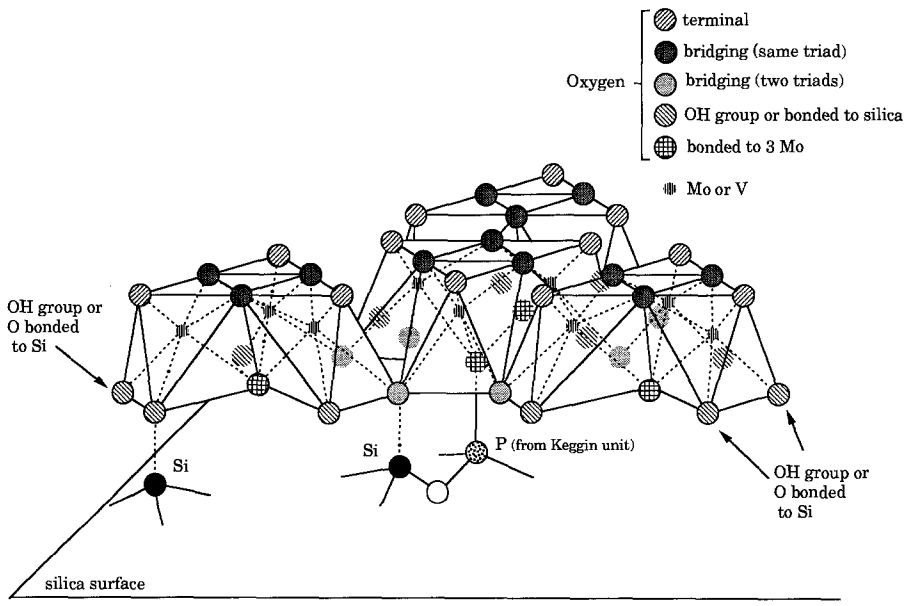

Fig. 3. Flat cluster of four triads of edge-linked MoO_6 octahedra formed at the silica surface by opening of Keggin anion through hydrolysis of half of Mo–O_c–Mo bridges between the triads.

with the formation of oxygen vacancies as postulated in ref. [24], although this is not reflected in the catalytic activity in the oxidation of methanol, as discussed later.

The FT-IR spectrum of the sample containing 0.25 monolayer in which the band at 864 cm^{-1} is already visible, albeit with a low relative intensity, may be taken as an indication that at such coverage some of the KU are already present at the surface in an unperturbed form and hence acid properties should partially build up.

3.3. THERMAL STABILITY

3.3.1. Thermogravimetric analysis

For the sake of comparison of the thermal behaviour of pure and supported HPVMo figs. 4a and 4b show the DTG/DTA results for bulk HPVMo and 0.5 HPVMo/SiO_2. This technique is particularly useful for determination of HPA thermal stability since, following the thermal loss of constitutional water, an exothermic peak appears due to the crystallization of the oxides resulting from the decomposition of the Keggin unit [4]. For unsupported HPVMo this peak appears at 677 K (fig. 4a). Dehydration of the sample, i.e. the release of molecular water indicated by the loss of weight and accompanied by a strong endothermic peak on the DTA line, is completed at about 470 K.

In contrast with the unsupported HPVMo in the case of the 0.5 HPVMo/SiO_2

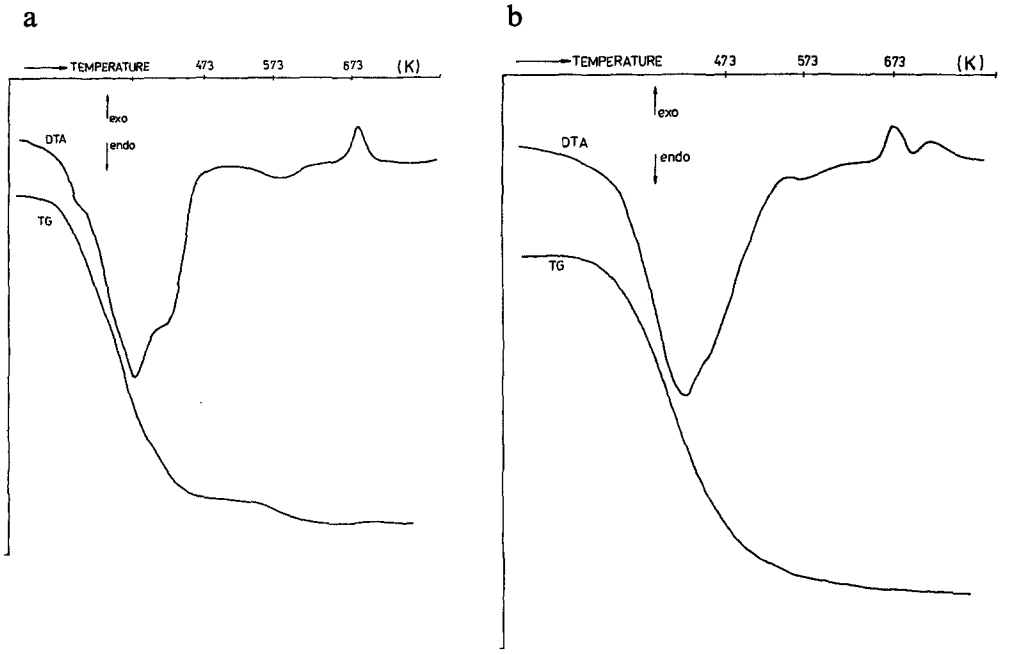

Fig. 4. DTG/DTA data for: (a) bulk HPVMo, (b) 0.5 HPVMo/SiO_2.

sample the presence of two exothermic peaks, a larger one at 674 K and a smaller one at 714 K, suggests that the thermal decomposition of the KU proceeds in two distinct steps. The first appears at practically the same temperature as for the unsupported HPVMo, while the second at a temperature about 40 K higher. It thus seems that some part of the supported HPVMo becomes thermally stabilized while the rest, probably forming multilayered clusters on silica surface, preserve the properties characteristic for the unsupported acid. The release of molecular water is completed at about 540 K, i.e. at a temperature about 70 K higher than in the case of unsupported acid, likely due to the strong hydrophilic properties of the silica support.

3.3.2. FT-IR study

The picture obtained from thermogravimetric analysis is confirmed by the studies of IR spectra of these samples in the course of heating. IR spectra of the same two samples, unsupported HPVMo and 0.5 HPVMo/SiO_2 after heating in air for two hours at increasing temperatures from 473 to 873 K are shown in figs. 5a and

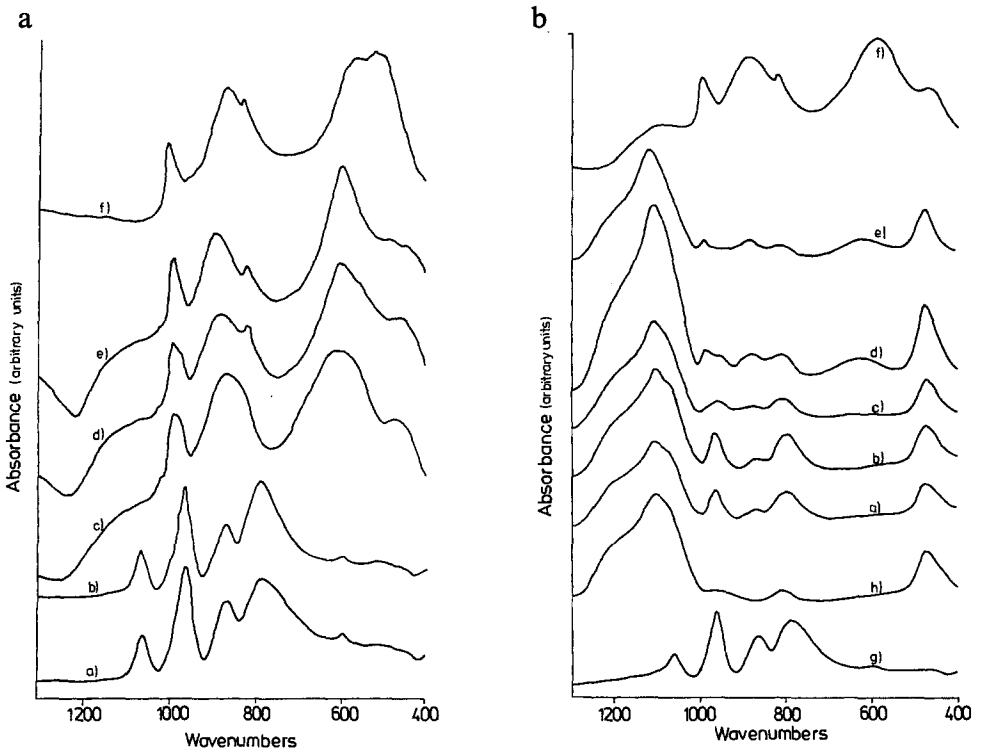

Fig. 5. (a) IR spectra of bulk HPVMo after thermal treatment at different temperatures: a) 473 K, b) 573 K, c) 673 K, d) 773 K, e) 873 K, f) pure MoO_3. (b) IR spectra of supported HPVMo after thermal treatment at different temperatures: a) 473 K, b) 573 K, c) 673 K, d) 773 K, e) 873 K, f) fully decomposed HPVMo, g) bulk HPVMo, h) pure SiO_2.

5b. Spectra of the unsupported samples heated at 473 and 573 K are practically identical and exhibit only the bands characteristic of the unperturbed Keggin unit (cf. fig. 2a). After treatment at 673 K bands typical for MoO_3, which is produced in the course of the total degradation of the KU, begin to appear. After calcination at 773 and 873 K only these bands remain in the spectra.

In the case of the 0.5 HPVMo/SiO_2 sample the three bands typical for Mo–O structural vibrations in the KU are not affected by treatment at 573 K and, by contrast with an unsupported HPVMo, they remain well preserved after calcination at 673 K. At this temperature the bands typical for MoO_3 begin only to appear. Some traces of bands corresponding to Keggin unit vibrations can still be recognized in spectra of samples pretreated at 773 K where MoO_3 patterns are already predominating. After calcination at 873 K only MoO_3 spectrum can be observed, as for unsupported HPVMo.

3.4. STRUCTURE MODIFICATIONS UPON VARIOUS TREATMENTS

It has been earlier found that thermally decomposed HPA supported on silica can be easily regenerated by water vapour exposure (see Introduction). As in the oxidation of methanol water is one of the reaction products, we have submitted the samples to the following treatments in air: (I) drying at 473 K (fresh samples: series F), (II) calcination for 2 h at 873 K (calcined samples: series C), and (III) calcination at 873 K followed by exposure to 18 Torr of water vapour at room temperature for 48 h (rehydrated samples: series W).

Fig. 6 shows the IR spectra of 0.5 HPVMo/SiO_2 samples of series F, C and W. Pretreatment at 873 K leads to the disappearance of the absorption bands characteristic of the KU and only MoO_3 bands are present: On rehydration the initial absorption spectrum typical of the KU reappears, whereas the MoO_3 spectrum disappears. For unsupported HPVMo, this phenomenon under the same conditions is not observed, indicating that it is the silica surface which provides an environment enabling the reconstruction of the fully decomposed KU after its decomposition products are exposed to water vapour.

3.5. CATALYTIC PROPERTIES

A question may be asked as to how these surface transformations influence the catalytic properties of the HPVMo system. In order to answer this question catalytic properties in methanol oxidation have been determined of samples of series F, C and W with different loadings. Results of these experiments are shown in fig. 7 and table 1. Samples of series F with high HPVMo coverage, which decompose on heating at 873 K, lose their catalytic activity, but regain it after reconstruction under the influence of water vapour.

In contrast to that, samples of low loading in which KU are transformed into triads of MoO_6 octahedra do not undergo any further transformations either on

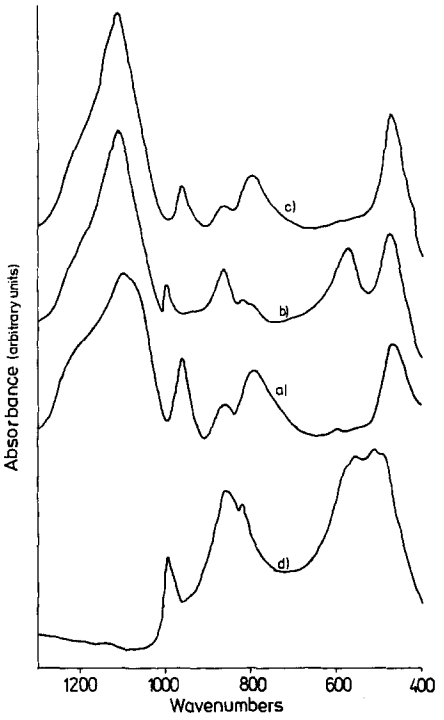

Fig. 6. IR spectra of 0.5 HPVMo/SiO_2 sample after: a) drying at 473 K (fresh sample), b) calcination at 873 K for 2 h, c) calcination at 873 K for 2 h followed by 48 h exposure to saturated water vapour at ambient temperature, d) MoO_3.

heating or on exposure to water vapour, their catalytic properties remain thus unchanged. This points to the high thermal stability of these species as postulated above. Only the disappearance of methyl formate to the benefit of methylal (table 1) may suggest the dehydroxylation of silica upon calcination or a slight modification in the nature of the active phase which cannot be detected by IR spectroscopy [32].

The well established mechanism of the transformation of methanol on oxide catalysts consists of the formation of a methoxy intermediate on acid sites on the catalyst (ref. [10] and references therein). This intermediate can either react with another methanol molecule to form dimethyl ether (acid–base pathway) or undergo a nucleophilic attack of surface oxide ion to form a precursor of formaldehyde (redox pathway). Thus, the ratio of selectivities dimethyl ether/formaldehyde is a measure of the acidic versus redox catalytic properties [10].

It could be expected that different structures of the surface layer at low and high coverages of HPVMo on silica will in a different way influence various elementary steps of the transformation of methanol and hence the selectivity of the reaction. Indeed dramatic changes of selectivity to the main reaction products are observed in the series of samples of different HPVMo loading as illustrated in fig. 8.

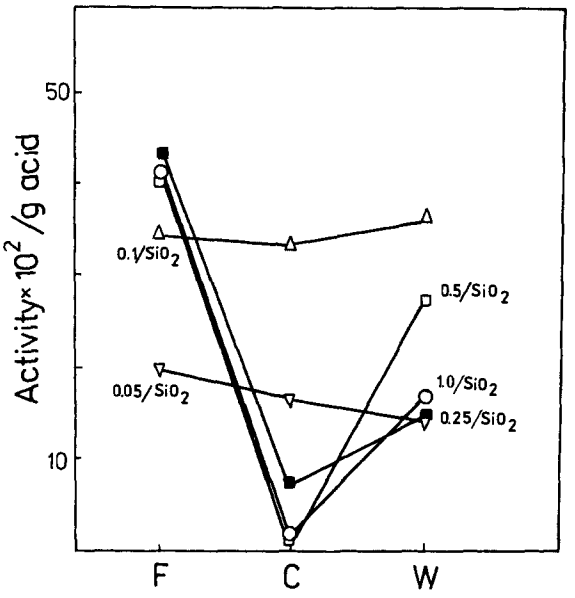

Fig. 7. Catalytic activity in CH_3OH oxidation of samples with different treatment: F, fresh sample (dried at 473 K for 2 h); C, calcined at 873 K for 2 h; W, calcined at 873 K for 2 h and exposed to saturated water vapour at ambient temperature for 48 h.

As it was already said, in low coverage samples of series F HPVMo seems to be present at the surface in form of triads strongly bound to the surface. One can expect that all protons of the HPVMo have been used to form bonds with the surface and such samples should show no acidity. Indeed, whereas high loading samples, which possess undecomposed KU behave as acidic catalysts giving mainly dimethyl ether, with the decrease of acid loading the selectivity to dimethyl ether at first slowly diminishes and then abruptly falls down, the reaction giving then only oxidized products, i.e. formaldehyde and methylformate. These results are in line with the data reported by Tatibouet [33] and Paukstis [27] for HSiMo supported on silica and seem to indicate that the observed effect is common to all HPA with the Keggin structure. Samples of series C, in which KU have been thermally decomposed, present mainly a redox behavior irrespective of the HPVMo loading, albeit an increasing tendency to form methylal at the expense of formaldehyde is observed on decreasing the HPVMo content. Negligible amounts of methyl formate are also formed.

The increased selectivity to dimethyl ether observed after reconstruction of KU by exposure of high loading samples of series W to water vapour, as compared to samples of series F of the same loading, suggests either a higher degree of HPVMo hydration [29,41,42] or partial formation of HSiMo known to be more acidic [1] and more selective to dimethyl ether [17,23] than HPVMo. A small shoulder on the broad

Table 1
Catalytic results in the methanol oxidation reaction for the series F, C and W

Catalyst		Activity [b]	Selectivities (%)			
coverage [a]	series		CH_3OCH_3	CH_2O	$(CH_3O)_2CH_3$	$HCOOCH_3$
1.0	F	411	50.0	43.2	4.2	1.6
1.0	C	9	11.4	87.0	0.2	0
1.0	W	168	68.8	27.6	3.0	0
0.5	F	409	40.1	53.5	3.4	1.8
0.5	C	5	7.0	76.5	0	0
0.5	W	272	70.2	26.9	4.5	0
0.25	F	430	32.6	55.5	7.2	3.6
0.25	C	66	17.5	65.1	14.1	0
0.25	W	155	31.3	54.3	11.3	0
0.1	F	350	15.1	59.0	12.1	11.4
0.1	C	341	17.4	57.0	24.7	0
0.1	W	369	22.0	56.2	20.3	0
0.05	F	193	2.2	63.7	0	31.7
0.05	C	161	1.9	62.4	30.1	3.8
0.05	W	142	0	93.8	0	0

[a] Coverages are expressed in theoretical monolayer.
[b] Activities are in mmol h^{-1} g^{-1}_{acid}.

peak of silica in the 1050–1070 cm^{-1} region (ν P–O vibration) indicates however that at least a part of the reconstructed KU contain phosphorus as the heteroatom.

4. Conclusions

Properties of silica supported HPVMo strongly depend on the degree of surface coverage in the range of 0.05–1.0 monolayer.

At low HPVMo loading interactions between silica OH groups and acidic protons of the HPVMo lead to hydrolysis of KU into the "triads" of edge-linked octahedra strongly bound to the surface. These catalysts do not undergo any structural changes either under thermal treatment sufficient to decompose unsupported heteropolyacid or under exposure to water vapour. Because protons have been used for protonation of the silica surface OH groups, the acidity characteristic for HPVMo practically disappears and thus oxidation of CH_3OH results only in the formation of oxidized products, i.e. formaldehyde and methyl formate.

In contrast, at high HPVMo loadings unperturbed KU are present at the silica surface. The properties of these samples are thus generally similar to those of the unsupported acid with only slight increase of the thermal stability. They are induc-

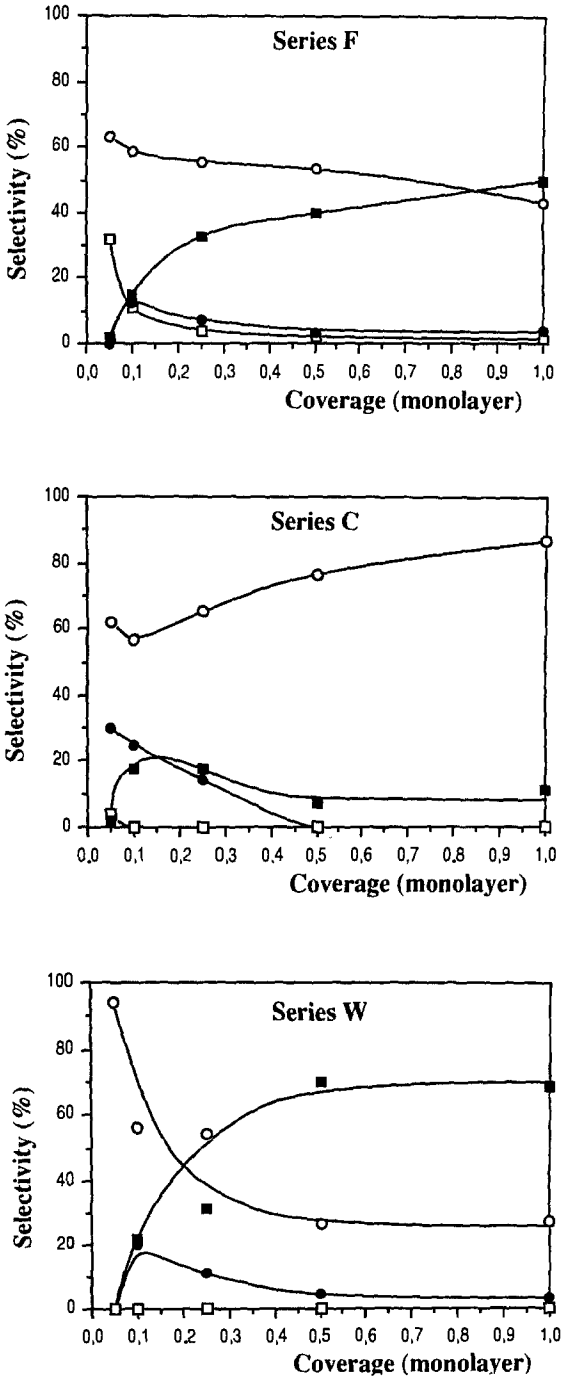

Fig. 8. Dependence of catalytic performance in CH_3OH oxidation on the degree of surface coverage. (■) $(CH_3)_2O$, (○) CH_2O, (□) $HCOOCH_3$, (●) $(CH_3O)_2CH_3$ methylal. Test conducted at 533 K.

ing the acidic pathway of methanol transformation leading to the formation of dimethyl ether. However, the presence of hydrophilic silica support allows a facile reconstruction of thermally fully decomposed Keggin anions under the exposure to water vapour.

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