

The Existence and Stability of the Silica-Supported 12-Molybdophosphoric Acid Keggin Unit as Shown by Raman, XPS, and ^{31}P NMR Spectroscopic Studies

S. KASZTELAN,^{*,1,2} E. PAYEN,^{*,†} AND J. B. MOFFAT^{‡,1}

^{*}Laboratoire de Catalyse Hétérogène et Homogène and [†]Laboratoire de Spectroscopie Infra-Rouge et Raman, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France; and

[‡]Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Silica-supported 12-molybdophosphoric acid catalysts developed for partial oxidation of methane have been characterized by laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy, and ^{31}P NMR spectroscopy after preparation, calcination, and use in catalytic tests performed at high-temperature (570°C) and atmospheric pressure. It is shown that the 12-molybdophosphoric acid (HPMo) Keggin unit (KU) can be deposited uniformly on the silica surface in a highly dispersed form up to a coverage of 0.04 KU nm⁻². Aggregates are then formed for loading up to about 0.12 KU nm⁻². At higher loading these aggregates are likely to grow to give particles of 12-molybdophosphoric acid. Both LRS and ^{31}P NMR spectroscopic results demonstrate that the highly dispersed HPMo is stable up to calcination or reaction temperatures of about 580–600°C. On the contrary, the particles of HPMo present on the highly loaded catalysts disappear after catalytic testing to give MoO₃ as shown by LRS. The increase in stability of the supported HPMo KU compared with that of bulk HPMo is proposed to be the result of the interaction of the KU with some surface site of the silica, giving the highly dispersed and dehydrated HPMo species thought to be responsible for the catalytic activity for methane partial oxidation. © 1990 Academic Press, Inc.

INTRODUCTION

Heteropoly compounds are of great interest in the field of heterogeneous catalysis owing to both their acid properties on the one hand and their oxydoreductive properties on the other (1, 2). These compounds have been studied mainly as bulk catalysts where large specific surface area is often not required. When high-surface-area catalysts are necessary, it is of interest to deposit the heteropoly compound on a high-surface-area support.

Several supports such as silica, kieselguhr (3–5), or carbon (6) have been considered. In the case of alumina, it has been shown

that heteropoly acids were decomposed during the preparation (7), a process recently investigated in the case of 12-molybdophosphoric acid on alumina by liquid ^{95}Mo NMR studies (8). Few data have been reported on the characterization of supported HPMo. It has been shown that at low loading no particles of HPMo could be detected on silica, suggesting a high dispersion of that compound (5).

Recently, we have investigated the properties of such silica-supported catalysts for the partial oxidation of methane by N₂O at atmospheric pressure and at high temperature from 550 to 650°C (9, 10). It has been found that a thermally sensitive species was responsible for the methane conversion activity and that this species disappeared at calcination temperatures higher than 580°C. In addition, extraction of the supported spe-

¹ To whom correspondence should be addressed.

² Present address: Institut Français du Pétrole, B.P.311, 92506 Rueil Malmaison Cedex, France.

cies, both after calcination at a different temperature and after catalytic testing using acetonitrile as a solvent and IR as the analytical technique, demonstrated that the HPMo was still present after such drastic treatment, whereas it is known that bulk HPMo is decomposed at temperatures lower than 370°C (10).

From this evidence, it was proposed that the thermally sensitive species was the HPMo Keggin unit (KU) itself and that this species was responsible for the catalytic activity. Indeed, Raman and infrared spectroscopy of acetonitrile solutions obtained after a MoO₃/silica catalyst active for methane oxidation was washed show that 12-molybdosilicic acid (HSiMo), the analogue of HPMo, was present and could be responsible for the catalytic properties of this catalyst (11).

We report in this work further evidence for the existence and high stability of a HPMo species on the surface of silica before and after catalytic testing for methane oxidation.

EXPERIMENTAL

Preparation of Catalysts

A set of silica-supported 12-molybdophosphoric acid catalysts has been prepared by impregnation of a high-specific-area silica (Davison-Grace Grade 400, 740 m² g⁻¹) with an aqueous solution (20 ml of solution per 10 g of support; solution pH 2-3) of purified 12-molybdophosphoric acid (BDH Analar grade) followed by drying of the solid and solution at 110°C overnight and calcination usually at 350°C, 2 h (9). These samples will be labeled with the weight percent of HPMo followed by the symbol HPMo. The sample containing 23 wt% HPMo (23-HPMo) has also been calcined at different temperatures and for various periods of time. The series of samples with various loadings has been previously tested in methane oxidation reactions performed at atmospheric pressure and 570°C (9, 10). Hereafter, the samples obtained before and after use in a catalytic test will be labeled as BT

and AT, respectively. The loadings of the samples after calcination and after catalytic testing are reported in Table 1. All samples have been stored in air before characterization.

XPS Measurements

The samples were analyzed in a Leybold LHS10 spectrometer equipped with an Al anode (300 W, 1486.6 eV). The samples were first dried (110°C, 2 h) and then ground in a mortar, and the powder was pressed on an indium foil mounted on the sample probe before introduction into the spectrometer. Binding energies (BE) of the various elements have been referenced to the Si_{2p} level at 103.4 eV and the O_{1s} level at 533 eV. This gives C_{1s} peak at 284.8-284.9 eV. A comparison of XPS binding energies did not show any differences between the samples. The values for the binding energies for the main peak recorded are constant over the series of samples with the Mo_{3d} doublet at 233.3-236.3 eV and P_{2p} at 134.8 eV. The Mo_{3d}/Si_{2p} XPS intensity ratios have been determined by integration of the Mo_{3d} and Si_{2p} peaks. The variations of this ratio for the samples with different HPMo loadings have been compared to a calculated curve obtained by assuming a uniform distribution of Mo and Si in the catalyst, leading to the relationship according to Kerkhoff and Mouljin (12),

$$(I_{\text{Mo}}/I_{\text{Si}})_{\text{xps}} = (\sigma_{\text{Mo}}/\sigma_{\text{Si}}) \times (E_{\text{Mo}}/E_{\text{Si}})^{1.77} \times (\text{Mo/Si})_{\text{at}}$$

with the cross section σ obtained from Scofield (13) and $E^{1.77}$ obtained from the linear dependence of the spectrometer's transmission factor on the kinetic energy E and $E^{0.77}$ the dependence of the photoelectron escape depth of the element x with the kinetic energy according to Penn (14). The variation in the (Mo_{3d}/Si_{2p}) ratio with the KU surface density D in KU nm⁻² is given by

$$(I_{\text{Mo}}/I_{\text{Si}})_{\text{xps}} = (\sigma_{\text{Mo}}/\sigma_{\text{Si}}) \times (E_{\text{Mo}}/E_{\text{Si}})^{1.77} \times (12M_s \times S/A)D$$

where A is Avogadro's number, M_s is the

TABLE 1

Loading of the Silica-Supported 12-Molybdophosphoric Acid Samples before and after Catalytic Testing for Methane Oxidation

Calcined			After testing		
wt% HPMo	$\mu\text{mol KU g}_s^{-1}$	KU nm^{-2}	wt% HPMo	$\mu\text{mol KU g}_s^{-1}$	KU nm^{-2}
1.16	5.2	0.004	1.22	5.4	0.004
3.08	14.0	0.011	2.52	11.5	0.009
6.49	30.7	0.025	4.44	20.9	0.017
8.32	40.2	0.033	6.6	31.2	0.025
9.80	48.1	0.039	9.06	44.2	0.036
11.1	55.3	0.045	9.92	47.9	0.039
16.0	84.3	0.068	12.8	67.4	0.05
17.2	92.1	0.075	14.4	73.7	0.06
21.2	119.	0.097	15.2	82.3	0.067
23.0	132.	0.108	18.5	101.	0.082
25.3	150.	0.122	18.6	101.	0.082
30.9	198.	0.161	25.3	147.	0.12
39.0	283.	0.230	31.5	203.	0.165

SiO_2 molecular weight, and S is the support surface area.

Laser Raman Measurements

The Raman spectra have been recorded on a Raman microprobe Mole from Jobin-Yvon. The exciting light source was an Ar^+ laser emitting the 488 nm line with the power at the sample kept as low as possible, i.e., at about 1 mW. An investigation of the effect of the laser beam has shown that spectral changes appeared at high power of the laser beam (15).

NMR Measurements

^{31}P solid-state NMR spectra were recorded on a CXP 100 Bruker spectrometer operating at 40.481 MHz. Usually, 10,000 scans were collected except for samples with very low loading where 100,000 scans were recorded. A solution of 85% H_3PO_4 has been taken as the reference.

RESULTS

In Fig. 1 are reported the Raman spectra of catalysts containing various amounts of HPMo calcined at 350°C for 2 h. For com-

parison the Raman spectra of bulk HPMo are also reported (spectrum 1a). It is similar to previously published spectra of 12-molybdophosphoric acid (16–18). In this spectrum the main Raman bands can be found at 998, 970, 610, and 247 cm^{-1} . They can be respectively assigned to ν s $\text{Mo}-\text{O}_t$, ν s $\text{Mo}-\text{O}_i$, ν s $\text{Mo}-\text{O}_c$, and ν s $\text{Mo}-\text{O}_a$, with the subscript t standing for the terminal bond, c for the oxygen bridging two molybdenum, and a for the oxygen linking the Mo and the central hetero atom (19).

In Fig. 1, all of these Raman bands are observed for the supported HPMo samples whatever the loadings higher than 3 wt% HPMo. In addition, no evidence for the presence of molybdenum trioxide and molybdate or isopolymolybdate (see Table 2 for characteristic Raman bands) can be found. For the very low HPMo loading of 3 wt%, a Raman spectrum can be found with a broad band at 980–990 cm^{-1} .

It should be noted that the bulk HPMo is very easily decomposed even under low power of the laser beam (15). The decomposition leads to the formation of molybdenum trioxide detected by its strong Raman band

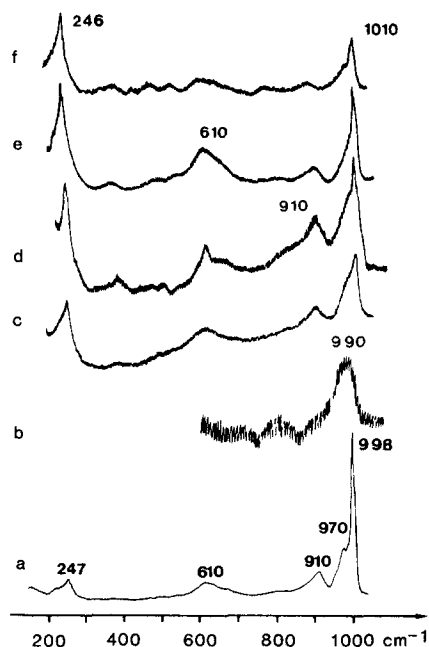


FIG. 1. Laser Raman spectra of the variously loaded silica-supported 12-molybdophosphoric acid catalysts calcined at 350°C. (a) Bulk HPMo, (b) 3 wt%, (c) 11.1 wt%, (d) 25.3 wt%, (e) 31 wt%, (f) 39 wt%.

at 820 and 998 cm^{-1} and an unidentified species with a band at 850 cm^{-1} . In the case of the supported species the effect of the power of the laser beam has also been investigated (15). Although changes occurred in the 850–1050 cm^{-1} wavenumber range, no degradation products were identified and the changes were found to be reversible on exposure to a wet atmosphere. Similarly, the

calcination under dry oxygen has also been investigated and spectral modification without generation of degradation products and reversibility of the modification upon exposure to air have been observed. Quite similar effects are found in the case of alumina-supported oxomolybdate species (20–23) and have been assigned to dehydration of the supported species with no degradation.

The spectra reported in Fig. 1 demonstrate that the HPMo KU is still present on the silica support after preparation, calcination, and transfer in the wet atmosphere for a wide range of loadings. The different spectra observed at very low loading may correspond to a partially degraded molybdophosphoric species as will be discussed later.

Further indications of the existence of the supported KU are obtained from a comparison of the Raman spectra of the 23-HPMo sample calcined at different temperatures and for various periods of time. In Fig. 2 the 23-HPMo sample calcined at 350°C for 16 h shows the characteristic bands of the HPMo with the main band at 1010 cm^{-1} . After calcination at 450°C for 16 h, small bands at 820 and 990 cm^{-1} appear, showing the presence of MoO_3 in the sample. Slightly larger MoO_3 bands appear after calcination at 550°C whereas at higher temperatures, MoO_3 bands predominate. In view of the very high diffusion cross section of MoO_3 compared to that of the supported oxomolybdenum species, as demonstrated by Wachs *et al.*

TABLE 2

Position of the Main Raman Band of Several Supported Molybdenum-Containing Species

Compound	Support	Main Raman band (cm^{-1})	Ref.
$\text{H}_3\text{PMO}_{12}\text{O}_{40}$	SiO_2	1010, 970, 610, 247	This work
$\text{H}_4\text{SiMo}_{12}\text{O}_{40}$	SiO_2	984, 967, 904, 625, 250	11
MoO_3	Al_2O_3	995, 820, 662, 380, 371, 341	23
Molybdate	Al_2O_3	945, 853, 320	23
Heptamolybdate	Al_2O_3	965, 860, 360	23

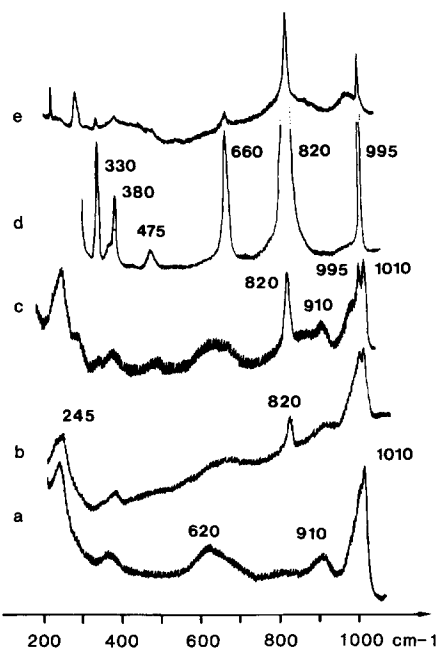


FIG. 2. Laser Raman spectra of the 23 wt% 12-molybdophosphoric acid supported on silica catalyst calcined at different temperatures and durations. (a) 350°C, 26 h; (b) 450°C, 16 h; (c) 550°C 3 h; (d) 550°C, 90 h; (e) 700°C, 3 h.

(24), the small band present at 450 and 550°C should not be interpreted as reflecting the presence of large amounts of MoO_3 resulting from a degradation of a large amount of the HPMo KU but rather to a very small quantity of MoO_3 corresponding to a small amount of the KU completely decomposed.

In Fig. 3 the Raman spectra of the 11.1-HPMo, 21.2-HPMo, and 23-HPMo samples after catalytic test at 570°C for several hours (9, 10) are compared. Interestingly, the characteristic Raman bands of the 12-molybdophosphoric acid species are still present and dominant for the 11.1-HPMo and 21.2-HPMo samples. However, on the spectra of the 23-HPMo sample the presence of strong MoO_3 Raman bands, as well as the 850- cm^{-1} band which may correspond to HPMo decomposition products, indicates the decomposition of a large amount of the HPMo KU. Nevertheless,

bands at 1010 cm^{-1} seen in spectra c, d, and e suggest that some HPMo still resists complete decomposition. Thus, it appears that at low loading the HPMo KU can be recovered after treatment under rather extreme conditions.

Further evidence of the presence of the supported KU on the calcined catalysts can be obtained from ^{31}P NMR spectra of the samples at different loadings, calcination temperatures, and times. All the recorded spectra showed one more or less broad peak. The NMR peak positions and full widths at half maximum (FWHM) are reported in Table 3. These results are consistent with the ^{31}P NMR spectra of heteropolymolybdate (1). The samples with loadings equal to and lower than 31-HPMo all give a ^{31}P NMR peak characteristic of the HPMo. The calcination at 600°C for 16 h can be seen as the limit of existence of the HPMo (Table 3).

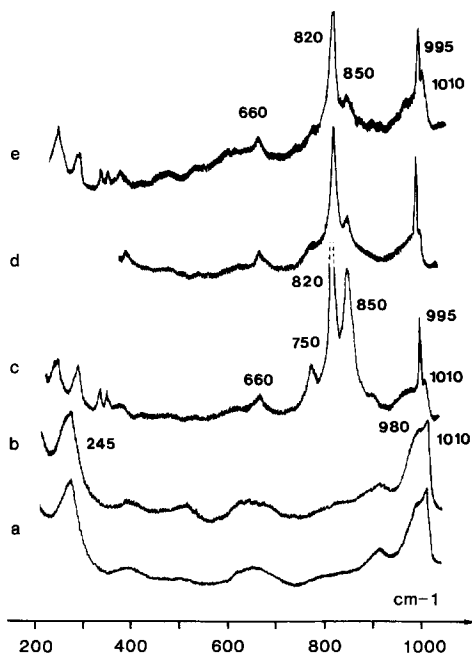


FIG. 3. Laser Raman spectra of silica-supported 12-molybdophosphoric acid catalysts with increasing loading after test for methane oxidation by N_2O at 570°C for 3 h. (a) 11.1 wt%, (b) 21.2 wt%, (c) 23 wt%, (d) 25 wt%, (e) 31 wt%.

TABLE 3

^{31}P NMR Peak Parameters of Silica-Supported 12-Molybdophosphoric Acid Catalyst: (a) 23-HPMo Calcined at Various Temperatures and for Various Lengths of Time; and (b) with Different Loadings and Calcined at 350°C, 2 h.

Treatment	NMR ^{31}P peak position (ppm)	FWHM (Hz)
Bulk HPMo	-8	1.5
200°C, 2 h	-8	1.0
350°C, 16 h	-8	1.2
450°C, 16 h	-8	1.1
550°C, 16 h	-8	1.2
AT (570°C, 4 h)	-8	1.1
600°C, 16 h	-5	1.8
730°C, 16 h	-5	9.4

(b)

Loading (wt%)	NMR ^{31}P peak position (ppm)	FWHM (Hz)
Bulk HPMo	-8	1.5
1.2	-8	1.5
8.3	-8	1.2
16.	-8	1.0
31	-8	1.1
39	-8	4.1

After a test at 570°C for 4 h the position and FWHM of the ^{31}P NMR line are unchanged from those observed for HPMo at lower temperatures, thus demonstrating that the structure of the heteropoly anion is recovered after the test for methane oxidation.

The dispersion of the supported species on the silica surface is also relevant to the present work. The variation in the $\text{Mo}_{3d}/\text{Si}_{2p}$ XPS intensity ratio versus the KU loading (Fig. 4) is similar to that obtained for different supported oxide species such as, for example, the system $\text{MoO}_3/\text{Al}_2\text{O}_3$. Three different sections can be identified in this curve. The first (linear) part up to a loading of 0.04 KU nm^{-2} , i.e., about 10 wt% HPMo, indicates the presence of a first type of dispersion. The slope of that line is close to the position of the calculated curve for a monolayer dispersion. It is likely that single

or small aggregates of KU are dispersed over the surface in this range of loading. Then a change of slope occurs that can be interpreted as corresponding to the appearance of larger aggregates up to a plateau reached at 0.10 KU nm^{-2} or ca. 23 wt% HPMo, at which loading large aggregates are formed.

The curve representing the variation in the XPS intensity ratio with the KU loading obtained for the samples tested for methane oxidation has a similar shape with three parts showing that no drastic changes in the dispersion have occurred. This curve is shifted in position toward lower loading and, in particular, the first part of the curve is now close to the theoretical line for a monolayer coverage. This shift is consistent with the small loss of Mo during the test (see Table 1). It can be conjectured that the molybdenum lost is that which is less strongly fixed.

DISCUSSION

The silica-supported 12-molybdophosphoric acid catalysts have been previously studied for their catalytic properties for methane partial oxidation using N_2O (9, 10, 25). The characterization of these catalysts by XPS, LRS, and ^{31}P NMR has been under-

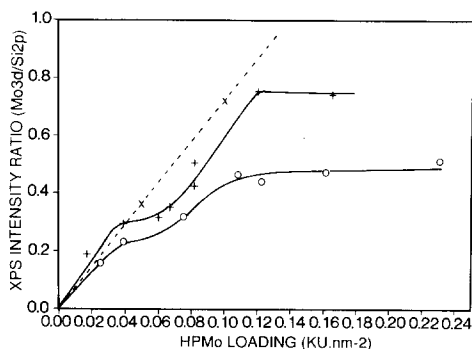
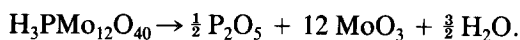
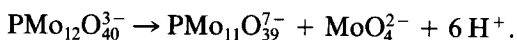


FIG. 4. Evolution of the XPS $\text{Mo}_{3d}/\text{Si}_{2p}$ intensity ratio versus the 12-molybdophosphoric acid loading for the series of catalysts calcined at 350°C (O), 2 h, and after catalytic testing at 570°C, 3 h (+), as calculated for a monolayer dispersion (---).

taken in order to provide information on the supported species and to determine their subdivision on the surface of the silica support. Evidently, in view of the very high temperature used for the methane oxidation reaction, i.e., 570°C, the comparison of the results obtained on the catalysts before and after testing was of particular interest. In particular, it has been shown previously that the activity for methane conversion was dependent on the temperature of calcination of the catalysts with a constant activity up to 550°C followed by a sharp decrease to no detectable activity for a calcination temperature of 730°C. Thus, it was concluded that the active phase was thermally degraded at calcination temperatures higher than 550°C (10). Bulk heteropoly compounds are known to be irreversibly degraded for temperatures in general higher than 350°C (1, 2) according to the reaction



The Raman spectra of the silica-supported samples with low loading are notably different from that of bulk HPMo. This may result from partial degradation in solution due to the very small concentration. The chemistry of the heteropoly anion in aqueous solution is well documented (1) and the stability of the species in solutions of concentration as low as 0.1 M has been demonstrated (16). However, the effect of the increase in the pH of the 0.1 M HPMo solution was found to lead to the removal of one Mo from the KU according to the reaction



This degraded anion may be the precursor for the isopolyanion formed at pH 4.8 (18). Such removal of one Mo from the KU may result in a decrease in wavenumber of the ν s Mo–O_t band, as observed. However, other species and especially isopolymolybdate may also be obtained. At higher concentration in solution, partial degradation of the KU is unlikely under the acid condition used

and as a result the HPMo species is predominant on the support after a mild calcination at 350°C, as shown by Raman spectroscopy.

The XPS results indicate a dispersion of very small aggregates of a small number of KU before the appearance of larger particles. At very low loading it is even possible that each KU is isolated from every other KU on the surface, with the appropriate number of cations. It seems unlikely that these HPMo species are obtained by recombination of degradation products on exposure to moist air (26, 27), a phenomenon occurring also for bulk HPMo (28). In addition, it is unlikely that 12-molybdosilic acid KU (HSiMo), the analogue of HPMo species, is present on the support surface, as this would imply a degradation of the HPMo, exchange of P by Si, and recombination into the HSiMo KU.

Upon calcination the irreversible degradation of the KU evidently occurs at 550°C since MoO₃ is detected in large amounts. Such a high temperature indicates a strong enhancement of the stability of the supported KU anions compared to that of the bulk compound. Similarly, after catalytic tests at high temperatures the KU is still detected for samples with loading less than 0.10 KU nm⁻². In view of the very small surface densities of the KU in the first part of the curve (Fig. 4) it is likely that highly exposed KU still exist after the test.

If we take into consideration the results of the extraction of the soluble HPMo by acetonitrile both after calcination under different conditions and after catalytic testing (10), it is clear that we have a wide body of evidence showing that thermal stability of the HPMo KU is increased by supporting it on silica. However, it appears that the HPMo KU well dispersed on the surface, i.e., at low loading, are more stable than the large aggregates. This again suggests that it is the interaction of the KU with some sites of the silica surface that stabilize the KU, although silica is not known as a support which interacts very strongly with supported species.

It should also be noted that the KU is electrically negatively charged and is subjected in the bulk to strong electric fields. In contrast, when the anion is isolated, the absence of the surrounding highly charged species may permit sufficient structural relaxation to increase the stability.

These conclusions emphasize the importance of the heteropoly oxometalate anion in methane partial oxidation compared to that of oxomolybdenum species. The very different behavior of the silica-supported HPMo and Mo species upon doping by cesium (25) also suggests that the species of catalytic importance are not oxomolybdenum species. In addition, the amount of Cs needed to poison the HPMo/silica catalysts corresponds closely to 3 Cs⁺ per KU, i.e., to an exchange of the proton by the Cs⁺, again suggesting the presence of the heteropoly anion on the support.

In conclusion, the results obtained in this work clearly suggest that HPMo KU species can be obtained well dispersed on the silica surface at low loading and these supported species have a thermal stability improved in comparison to bulk HPMo. The silica-supported HPMo catalysts appear, therefore, to be an interesting model system for the investigation of catalytic properties under conditions for which bulk HPMo would normally be decomposed.

Note added in proof. The samples studied in this work have been stored in air prior to characterization and are therefore in hydrated form. Under the conditions employed in the partial oxidation of methane it is expected that the active species would be in a dehydrated state. In a recent publication E. M. Serwicka and C. P. Grey (*Colloids Surf.* **45**, 69 (1990)) have pointed out that exposure of calcined samples to moist air would lead to reconstruction of the KU from the decomposed product. However, the nature of the latter was not specified. We have also found that the signature of the acid (hydrated) form of the KU is recovered after exposure of the sample calcined at temperatures lower than 550°C to moist air, that is, provided that well-defined molybdenum

oxide is not formed during the heat treatment. We consider the sample calcined at a temperature lower than 550°C to be a lacunary (dehydrated) form of the KU and not a decomposition product. However, the possibility of the fragmentation of the KU into some unknown entity during calcination cannot be ruled out. In this case this entity would be the thermally stable species we assumed responsible for the catalytic activity. In either case the explanation of the high stability of the active species, whether a decomposition product different from common molybdenum oxides or the dehydrated KU, is an intriguing question.

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