

## The Interaction of Cesium Ions with Silica-Supported 12-Molybdophosphoric Acid

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Received October 25, 1989; revised September 11, 1990

The characterization by X-ray photoelectron spectroscopy (XPS), laser Raman spectroscopy (LRS), <sup>31</sup>P NMR spectroscopy, and ion scattering spectroscopy (ISS) of cesium-doped silica-supported 12-molybdophosphoric acid (HPMo) is reported. The addition of cesium to a silica-supported 12-molybdophosphoric acid catalyst has been shown in previous work to poison the catalytic properties for partial oxidation of methane of the original HPMo catalyst. In this work it is shown that the HPMo anions, Keggin Units (KU) are not decomposed upon addition of Cs up to 3 Cs per KU although modification of the surface dispersion of the HPMo seems to occur. Evidence of a direct interaction between the KU and the cesium ions has been obtained from Raman, XPS, and ISS spectroscopies, resulting from an ion exchange between the proton of the acid and the Cs ions. XPS studies show that the Cs ions are well dispersed up to a loading corresponding to the exchange of the three H<sup>+</sup> by 3 Cs<sup>+</sup>. In addition an electronic perturbation of Cs and Mo is detected by XPS as well as a shift of the main Raman band corresponding to a weakening of the Mo-O, bond in accordance with the electronic effect of Cs deduced from the catalytic results. © 1991 Academic Press, Inc.

### INTRODUCTION

Silica-supported 12-molybdophosphoric acid (HPMo) catalysts have been found in this laboratory to be an alternative to supported molybdenum catalysts for methane oxidation by N<sub>2</sub>O (1, 2). Heteropolyacids are known for their exchange properties (3, 4) and therefore further work was directed toward the application of this property to prepare doped catalysts in order to investigate possible promoters of the methane oxidation reaction (5, 6). The effect of a monovalent cation, cesium, was first examined (5) followed by a variety of mono-, di-, and trivalent cations (6).

The catalytic properties of salts of hetero-

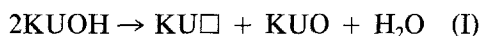
polyoxometalates in the bulk form have been extensively studied for oxidation reactions (7, 8), acid-catalyzed reactions (9, 10), and redox process (8, 11). In general, the addition of monovalent cations has a profound effect on the catalytic properties. For example, the partially saturated cesium salt of 12-molybdophosphoric acid was shown to possess an increased activity for the partial oxidation of butane (12, 13). The oxidative dehydrogenation on the bulk salt of HPMo has been found to decrease with the increasing electronegativity of the cation. This has been interpreted as a weakening of the Mo-O, bond as the cation become less electronegative (14).

Similar conclusions have been reached in previous work from this laboratory in the case of methane partial oxidation over supported doped HPMo catalysts (5, 6). Three effects of the dopant were identified from

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the catalytic results. The first one is the poisoning effect resulting from the exchange of all the protons of the KU. The proton was therefore considered important in the catalytic process. However, its role has been proposed to be as the initiator of a catalytic cycle of methane oxidation through the generation of oxygen vacancies ( $\square$ ) followed by the removal of water according to the reaction (5, 15)



rather than as the initiator of an acidic-catalyzed process. Evidently the substitution of the proton by the cation eliminates this reaction and this was referred to as a blocking effect.

Since, depending on the cation, either an enhanced or decreased activity was found when two of the three protons were exchanged, the second effect was taken to be electronic in nature. In the case of cesium the effect was positive and was attributed to the weakening of the Mo–O<sub>i</sub> bond by the strongly electropositive cation. The third effect was related to the activity of the cation itself in the oxidation reaction and involved primarily transition metal cations (5).

In order to provide further information on the aforementioned effects, additional characterization studies would be of value. In the case of supported heteropolyacid and salts no extensive characterization work has been reported. In previous work (16) characterization of the silica-supported 12-molybdophosphoric acid by XPS, Raman, and <sup>31</sup>P NMR spectroscopies has been undertaken in order to find evidence that the HPMo Keggin Unit was stable under the test conditions as suggested by the catalytic results (2). The results have confirmed that the Keggin Unit itself could be the thermally sensitive species which, however, remained stable on the silica surface at temperatures much higher than those found with the bulk form (2). The addition of Cs can therefore be said to occur on a supported KU catalytic system.

In the present work the effect of Cs on the

existence of the KU on the silica support and of the interaction between the KU and Cs are examined with XPS, LRS, ISS, and <sup>31</sup>P NMR spectroscopy.

## EXPERIMENTAL

### Catalyst Preparation

The preparation of the 16 wt% 12-molybdophosphoric acid on silica (Davison-Grace Grade 400, 740 m<sup>2</sup> g<sup>-1</sup>) has previously been described (16). After calcination at 350°C, 2h, the samples were impregnated with cesium carbonate solution to produce a series of samples symbolized by *x*-CsPMo with *x* the number of Cs added per 12-molybdophosphoric acid Keggin Unit. The different values of *x* were: *x* = 0.63, 1.45, 2.15, 2.85, 3.6, 4.3, 5.6, 6.9, and 8.3. The samples were then calcined at 350°C during 2 h and stored in air.

### XPS Measurements

As previously described (16), the samples were analyzed in a Leybold LHS10 spectrometer equipped with an Al anode (300 W, 1486.6eV) after drying at 110°C. Binding energies (BE) of the various elements have been referenced to the Si<sub>2p</sub> level at 103.4 eV corresponding to the O<sub>1s</sub> level at 533 eV and giving a C<sub>1s</sub> peak at 284.8–284.9 eV and P<sub>2p</sub> at 134.8 eV. The BE of other elements is discussed in the text.

The determination of the Mo<sub>3d</sub>/Si<sub>2p</sub>, Cs<sub>3d5/2</sub>/Si<sub>2p</sub> XPS intensity ratios has been performed by integrating the Mo<sub>3d</sub>, Cs<sub>3d5/2</sub>, and Si<sub>2p</sub> peaks. The variations of the Cs<sub>3d5/2</sub>/Si<sub>2p</sub> ratio of the samples containing various amounts of Cs have been compared with a calculated curve obtained by assuming a uniform distribution of Cs and Si in the catalyst leading to the relationship (17)

$$(I_{\text{Cs}}/I_{\text{Si}})_{\text{XPS}} = (\sigma_{\text{Cs}3d5/2}/\sigma_{\text{Si}2p})x(E_{\text{Cs}3d5/2}/E_{\text{Si}2p})^{1.77}x(\text{Cs/Si})_{\text{at}}$$

with the cross section  $\sigma$  obtained from Scofield (18) and  $E^{1.77}$  obtained from the linear dependence of the spectrometer's transmis-

sion 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 (19). The variation of the  $(\text{Cs}_{3d5/2}/\text{Si}_{2p})$  with the Cs surface density  $D_{\text{Cs}}$  in  $\text{at. nm}^{-2}$  is also usefully obtained. This is given by

$$\begin{aligned} (I_{\text{Cs}}/I_{\text{Si}})_{\text{xps}} \\ = (\sigma_{\text{Cs}_{3d5/2}}/\sigma_{\text{Si}_{2p}})x(E_{\text{Cs}_{3d5/2}}/E_{\text{Si}_{2p}})^{1.77} \\ \times (M_s x S/A) D_{\text{Cs}} \end{aligned}$$

with  $A$  the Avogadro's number,  $M_s$  the  $\text{SiO}_2$  molecular weight, and  $S$  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  $\text{Ar}^+$  laser emitting the 488-nm line with a low power at the sample (about 10 mW) to reduce the effect of the heating power of the laser beam which has been shown to lead to slight spectral modifications (20).

### NMR Measurements

$^{31}\text{P}$  solid-state NMR spectra were recorded on a CXP 100 Bruker spectrometer (40.481 MHz) with collection of 10,000 scans except for samples with very high Cs loading where 100,000 scans were recorded. A solution of 85%  $\text{H}_3\text{PO}_4$  has been taken as the reference.

### Ion Scattering Measurements

The ion scattering experiments have been performed with a Leybold LHS10 spectrometer. Experimental conditions have been reported in detail elsewhere (21) except that in the present work the analyses were performed with a  $^{20}\text{Ne}^+$  ion beam in order to distinguish cesium from molybdenum. A surface area of 4  $\text{mm}^2$  was rastered and the broad band of secondary ions was attenuated by using a flooding electron beam.

## RESULTS

The Raman spectra of the calcined CsPMo samples containing various amounts

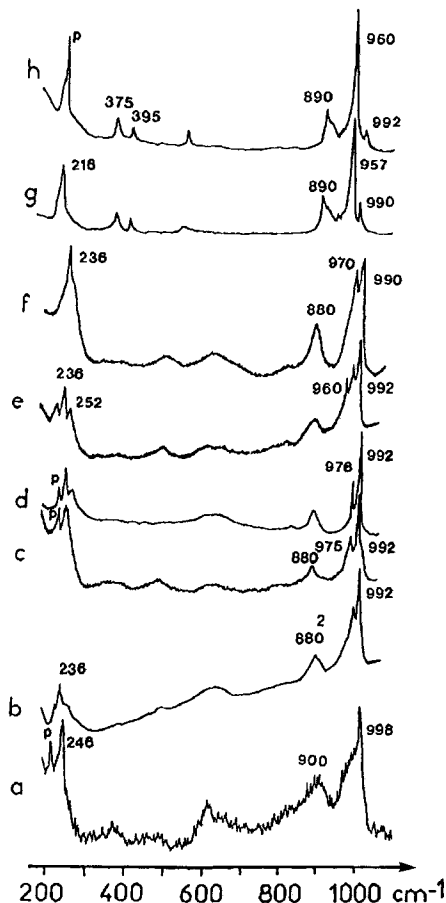


FIG. 1. Laser Raman spectra of cesium doped silica-supported 12-molybdophosphoric acid (16 wt%) catalysts calcined at 350°C, 2 h. (a) 16 wt% HPMo, (b) 0.63-CsPMo, (c) 1.45-CsPMo, (d) 2.85-CsPMo, (e) 4.3-CsPMo, (f) 5.6-CsPMo, (g) 6.9-CsPMo, (h) 8.3-CsPMo. Plasma lines of the laser are indicated by P.

of Cs are reported in Fig. 1. Clearly the initial Raman spectra 1a of the supported HPMo catalyst changes when cesium is added. Several features can be noted. None of the spectra in Fig. 1 show characteristic bands of  $\text{MoO}_3$  (strong bands at 995 and 820  $\text{cm}^{-1}$ ) and molybdate  $\text{MoO}_4$  species (main band at 890  $\text{cm}^{-1}$  and a characteristic band at 320  $\text{cm}^{-1}$ ).

At low Cs loading, up to 5.6-CsPMo sample (spectra 1b, 1c, 1d, 1e, and 1f) small shifts of the Raman bands relative to the

HPMo sample are observed. The  $998\text{ cm}^{-1}$  band shifts to  $992$ , and the  $910\text{ cm}^{-1}$  band to  $880\text{ cm}^{-1}$ . The other band remains unchanged showing that the KU structure is retained after addition of Cs. The shifts can be related to the effect of the substitution of the proton by cesium to produce the substituted cesium salt with one to three cesium ion per KU. Such a substitution would alter the hydrogen bonded interaction and therefore the Mo–O<sub>i</sub> bond stretching vibration. A weakening of the Mo–O<sub>i</sub> bond and consequently a longer Mo–O<sub>i</sub> bond induces a lower wavenumber. It can also be argued that the loss of anion–anion interaction as detected when large counterions such as tert-butyl ammonium are employed (22) is responsible for the shifts. However the small ionic radii of the cesium ion compared to the organic anion make such effects relatively unlikely. The samples analyzed by LRS must be considered hydrated after a long period of time in the atmosphere. For the supported acid or partially substituted cesium salts, thermal treatment of the sample can influence the position of the main band of the Raman spectra as shown elsewhere (20). In Fig. 1 the doublet found at loading up to the 4.3 CsPMo sample is more or less defined. This is likely a result of the state of hydration of the sample which is influenced by the power of the laser beam or a calcination prior to the recording of the Raman spectra (20). In the case of the cesium salt it has been shown that these treatments do not change the position of the band but sharpen it. We assume therefore that the observed downshift of the Mo–O<sub>i</sub> stretching mode is primarily the consequence of the perturbation of the KU by the cesium ion because of the formation of substituted KU.

A net change of the Raman spectra occurs for the 6.9–CsPMo and 8.3–CsPMo samples (spectra 1g and 1h). A well-defined spectra is obtained with sharp bands at  $960$ ,  $890$ ,  $395$ ,  $375$ , and  $216\text{ cm}^{-1}$ . Bands at  $992\text{ cm}^{-1}$  indicate that some substituted HPMo are still present. The identification of the spe-

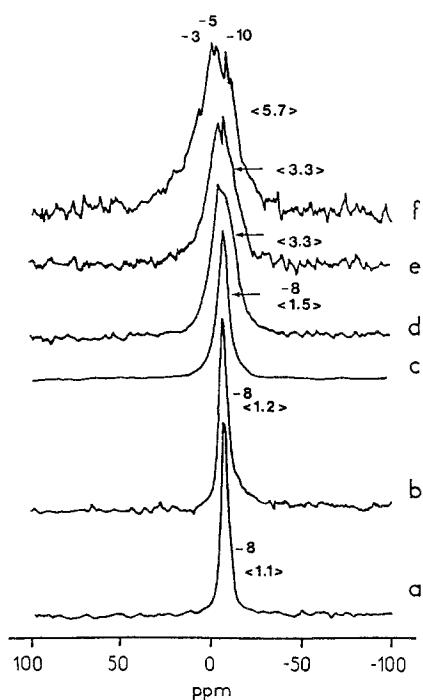


FIG. 2.  $^{31}\text{P}$  NMR spectra of the cesium-doped silica-supported 12-molybdophosphoric acid catalysts calcined at  $350^\circ\text{C}$ , 2 h. The widths of the peaks are shown in brackets. (a) 0.63–CsPMo, (b) 1.45–CsPMo, (c) 2.15–CsPMo, (d) 2.85–CsPMo, (e) 4.3–CsPMo, (f) 8.3–CsPMo.

cies giving these well-defined spectra is made by analogy with reported spectra of cesium isopolymolybdate (23). Indeed the Raman band at  $960$  and  $216\text{ cm}^{-1}$  can be correlated to the M–O stretching mode and Mo–O–Mo bending mode of an isopolymolybdate species (23, 24).

In Fig. 2 are reported the  $^{31}\text{P}$  NMR spectra of the calcined samples. Up to the 2.15–CsPMo sample, the  $^{31}\text{P}$  chemical shift is characteristic of the supported HPMo (16). Then for loading from 2.85 to 4.3 Cs per KU, a splitting of the peak is observed and at 8.3 Cs a broadening of the  $^{31}\text{P}$  NMR band is evident. It must be noted that as the amount of cesium increases, the number of scans required to obtain a satisfactory signal-to-noise ratio increases significantly, particularly in the case of the 8.3–CsPMo

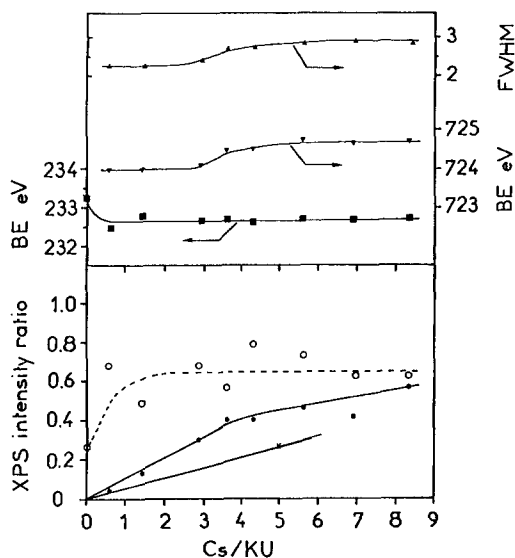


FIG. 3. Evolution of XPS data versus cesium loading of the 12-molybdophosphoric acid catalysts. (a)  $\text{Mo}_{3d5/2}$  binding energies ( $\blacksquare$ ), (b)  $\text{Cs}_{3d5/2}$  binding energies ( $\blacktriangledown$ ), (c)  $\text{Cs}_{3d5/2}$  FWHM ( $\blacktriangle$ ), (d)  $\text{Mo}_{3d}/\text{Si}_{2p}$  intensity ratio ( $\circ$ ), and (e)  $\text{Cs}_{3d5/2}/\text{Si}_{2p}$  intensity ratio ( $\bullet$ ).

sample. Although perturbation by Cs can be invoked to explain this broadening it is more likely due to a partial degradation of the KU with formation of adsorbed phosphate ion, far less sensitive than the P in the KU. The doublet of the 2.85-CsPMo can be interpreted as the appearance of a mixture of HPMo, substituted HPMo, and phosphate. Therefore the Raman spectra 1g and 1h should probably be assigned to cesium isopolymolybdate generated through the degradation of the KU.

The variations of the  $\text{Mo}_{3d}/\text{Si}_{2p}$  and  $\text{Cs}_{3d5/2}/\text{Si}_{2p}$  intensity ratios versus the amount of Cs added are reported in Fig. 3 and can be compared to the curve calculated according to the model devised by Kerkhof and Mouljin for homogeneous distribution of supported species (17). Two interesting observations may be noted. First, it appears that the Cs is well dispersed up to a loading of 3.85 Cs per HPMo KU as a straight line is obtained and this line is quite close to the theoretical line for a uniform distribution. For higher amounts of Cs a decreased slope

shows that all the Cs are not detected by XPS and therefore belong to aggregates. Second, the  $\text{Mo}_{3d}/\text{Si}_{2p}$  intensity ratio is quite constant but higher than the initial HPMo sample by 50%. Similarly that for  $\text{O}_{1s}/\text{Si}_{2p}$  remains constant. Thus the addition of Cs has slightly perturbed the dispersion of the HPMo. It is worth recalling here that in the previous work (16) it was found that the HPMo sample used in this investigation was not perfectly dispersed and was rather described as small aggregates of HPMo which may therefore be broken down into smaller particles or even isolated KU.

The variations of the  $\text{Mo}_{3d}$  and  $\text{Cs}_{3d5/2}$  XPS binding energy (BE) versus the amount of Cs are also reported in Fig. 3. The BE of the  $\text{Cs}_{3d5/2}$  level increases with the Cs loading from 724.0 ( $\pm 0.1$ ) eV to 724.7 ( $\pm 0.1$ ) eV, the latter value found for 5 wt% Cs on silica. The transition takes place between the 2.85-CsPMo and 4.3-CsPMo samples. This change of BE energy is probably not the result of charging effects as the BE of other elements remain constant. In addition it can be seen in Fig. 3 that the full width at half maximum (FWHM) of the  $\text{Cs}_{3d5/2}$  level follows the same variations with an increase beginning for loading larger than 2.85 and reaching a plateau for 5.6 Cs. These two facts strongly suggest that two different cesium species coexist for loadings higher than 2.85 Cs per KU.

The first binding energy (724.7 eV) can be assigned to cesium isopolymolybdate species consistent with LRS results. The second species (724.0 eV) evidently exists over the entire range of Cs loading and may be assigned to the cesium ion interacting with the KU. The shift to lower BE of the  $\text{Cs}_{3d5/2}$  level shows that the  $\text{Cs}^+$  ions become less positive. This can be due either to a different crystallographic environment of the Cs ion or to a charge transfer from the KU to the Cs. In addition, electronic perturbation of the Mo is evident from Fig. 3 in which a decrease of 0.6 eV of the  $\text{Mo}_{3d}$  BE is observed on introduction of 0.6 Cs per KU to the HPMo sample. The BE remained

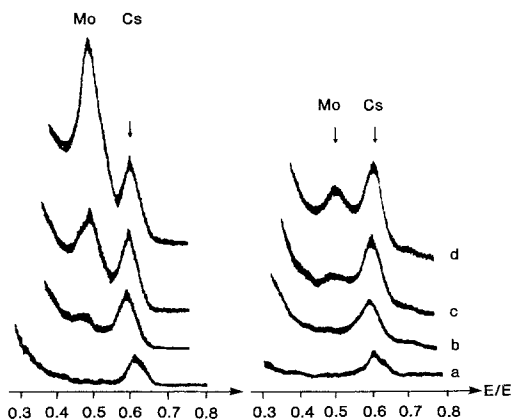


FIG. 4.  $^{20}\text{Ne}^+$  Ion Scattering spectra of the 0.63-CsPMo and 5.6-CsPMo samples taken at different  $^{20}\text{Ne}^+$  ion beam energies. All the spectra have been recorded at the same detector sensitivity. Ion energies: (a) 500, (b) 1000, (c) 1500, (d) 2000 eV.

constant for larger amounts of Cs. Such a change in BE corresponds to molybdenum becoming more negative (i.e., less positive) and can be interpreted as a charge transfer from the strongly electropositive cesium ion toward the molybdenum, through an oxygen ion. However this explanation is in contradiction with the fact that the Cs ion is also more negative in the presence of HPMo. So far no clear interpretation of these facts can be given. However it can be concluded that the substituted KU is strongly perturbed relative to the free KU.

In order to confirm that cesium and molybdenum are in close interaction, the surface composition has been probed with ion scattering spectroscopy to obtain information on the atomic composition of the top layer of the compound. To separate the signals of Cs and Mo, the  $^{20}\text{Ne}^+$  ion has been used. The ISS spectra of the 0.63-CsPMo and 5.6-CsPMo samples recorded successively at 500, 1000, 1500, and 2000 eV ion energies are reported in Fig. 4. All these spectra were reported at the same detector sensitivity so that the intensities can be compared (all other conditions were identical).

Different ion energies were employed in order to optimize the response. At low en-

ergy the element may not be seen because the neutralization of the ion is too strong, an effect dependent on the nature of the target atom (25–27). This may be observed in Fig. 4 for molybdenum which is not detected at 500 eV whatever the Cs loading because of a strong neutralization of the ions impinging on Mo, whereas Cs is still detected. This effect changes with the incident ion energies as can be seen in Fig. 4. The most significant spectra in this case are therefore those obtained at 2000 eV at which both elements can be detected quite clearly.

The comparison in Fig. 4 of the relative intensity of the Mo at 2000 eV shows that the peak associated with this element is strongly diminished when Cs is added. This effect corresponds to the so-called shielding effect (27) of the large Cs ion which protects the neighboring Mo ion from being struck by an incident  $^{20}\text{Ne}^+$  ion. This observation demonstrates the proximity of the two elements and therefore the direct interaction between the KU and the Cs ion.

#### DISCUSSION

These results facilitate a rather complete description of the catalytic system under study. The addition of Cs to the HPMo KU results first in the exchange of protons producing a partially substituted HPMo KU. This is shown by both Raman and  $^{31}\text{P}$  NMR which demonstrates that the KU is still present. No other Cs species are present according to XPS data. Thus, no degradation of the KU is evident within this range of cesium content during the preparation of the sample. However, Raman, XPS, and ISS data demonstrate that a direct interaction of the Cs with the KU has occurred.

The impregnation step of the cesium salt has not been investigated in detail and, therefore, it is difficult to provide definitive information on the mechanism and extent of the exchange of the protons by the cesium ions. It can be argued that the Cs ion replaces the  $\text{H}^+$  ion either on the KU in interaction with the support or with the KU in solution after dissolution and redistribution

of the substituted KU during drying and calcination. Such redeposition may be a cause of the better dispersion of the species observed by XPS. However, it is generally believed that precipitation does not produce a good dispersion of a species on a support and this explanation may be ruled out. On the other hand, the redispersion effect can be related to a phenomenon observed in bulk heteropoly acids in which the addition of cations heavier than the proton have resulted in substantial increases in surface area (28). It has been shown that certain heteropoly salts prepared with monovalent cations have relatively large surface areas and intrinsic microporous structures which appear to result from both translational and rotational reorientation of the secondary structure of the parent acid (29).

At loadings higher than 2.85 Cs per KU, the KU apparently reaches a saturation point with respect to the Cs cations. This is also evident in the extinction of the catalytic activity for methane oxidation (5). Since it has been claimed (30) that in the case of the potassium salt only the trisubstituted salt is formed, the formation of a heteropoly salt in which only one or two protons (per KU) have been substituted by Cs may be questioned. Previous work (6) on the catalytic properties of HPMo/SiO<sub>2</sub> catalysts doped with a variety of mono-, di-, and trivalent cation has suggested a rather different view although so far not substantiated by characterization studies. These results suggested that a gradual exchange of the proton occurs with an increasing difficulty in total exchange by the heavier cation. For example in the case of Li<sup>+</sup> it was considered that the total exchange was not attainable with the experimental procedure adopted since a substantial amount of catalytic activity was still found after deposition of a large amount of Li. Since, in the case of Cs, the complete poisoning of the activity was attained gradually it may be concluded that the substitution of the proton by Cs was gradual and reached completion at 3 Cs per KU.

At higher Cs loading, the formation of a

cesium isopolymolybdate species is observed probably mixed with some totally substituted KU. This conclusion is supported by XPS data which clearly show the appearance of an additional Cs species. This implies that some degradation of the HPMo has possibly occurred during the impregnation by a solution of cesium carbonate, leading to an increase of the pH of the solution to a value sufficiently high to encourage decomposition of the anion.

The present work provides further evidence that the poisoning of the activity of the HPMo catalyst for methane partial oxidation with N<sub>2</sub>O is the result of the substitution of the proton leading to a blocking of the dehydration reaction (I) as proposed earlier (5, 15).

In addition to this blocking effect an electronic effect is clearly shown in the present work. Both the decrease of the Raman Mo–O<sub>t</sub> bond stretching wavenumber and the observations from XPS provide evidence for the existence of an electronic effect. Interestingly, the effect involves the intact KU and manifests itself on sites that are generated by the remaining protons, as shown by the catalytic results.

#### CONCLUSIONS

The addition of Cs to a silica-supported 12-molybdophosphoric catalyst is shown, particularly, by Raman and <sup>31</sup>P NMR spectroscopies, to leave the structure of the heteropoly anion intact. However, Raman, <sup>31</sup>P NMR, and ISS show that a direct interaction of the Cs ions with the KU occurs as would be expected from an ion exchange between the H<sup>+</sup> and the Cs<sup>+</sup> ions. The exchange may take place either with the heteropoly oxometalate in supported form or in solution.

XPS studies reveal that the Cs ions are well dispersed up to a loading of 3.85 Cs per KU, i.e., corresponding to the exchange of all the protons with possible formation of aggregates of cesium isopolymolybdate at higher loading. In addition the XPS data show that the addition of Cs leads to a more

favorable dispersion of the KU. As a consequence of the interaction between the KU and the Cs, an electronic influence is exerted by the strongly electropositive Cs ion on the KU as shown by the variation of the Mo<sub>3d</sub> XPS binding energy, Raman band shifts, and a shift of the <sup>31</sup>P NMR peak.

#### ACKNOWLEDGMENTS

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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