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Structural Features and Thermal Stability of Titania-Supported 12-Molybdophosphoric Heteropoly Compounds

S. Damyanova

Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

J. L. G. Fierro*

Instituto de Catalisis y Petroleoquimica, CSIC, Campus UAM, Cantoblanco,
28049 Madrid, Spain

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The structure and thermal decomposition of unsupported and titania-supported 12-phosphoromolybdic acid (HPMo) and its Co and Ni salts have been studied by different techniques including X-ray diffraction, thermogravimetric analysis, FT-infrared, Raman, and X-ray spectroscopic techniques. The transformation of heteropoly anion of bulk HPMo begins at a temperature lower than for its TiO_2-supported counterpart with the formation of a mixture of α- and β-MoO_3. In the thermal transformation of TiO_2-supported HPMo, two steps have been identified. The intermediate species formed between the hydrated form of the heteropoly compound and the crystallized molybdenum oxides display the same nuclearity and composition as that of the Keggin precursor. The stability of the HPA supported on titania increases due to the anion-support interaction and this is even enhanced in the Co- and Ni-exchanged homologues.

1. Introduction

Keggin-type heteropoly acids, mainly 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), and their salts have attracted much interest since they possess strong acidity.[1] These bulk compounds catalyze many reactions much more effectively than the conventional protonic acids, such as sulfuric and nitric acids, and even more than BF_3 etherate. It has been proposed that such a high catalyst efficiency of these heteropoly acids is essentially due to those specific properties of the heteropoly anion which can be characterized by very weak basicity and great softness, in addition to the large molecular size of the heteropoly anion. When supported on a suitable carrier, they also work as active solid acid catalysts to be comparable with, or to exceed, supported phosphoric acid, silica−alumina, and acidic zeolites. Indeed, there have been reported a number of gas-phase reactions over supported HPX (X = Mo, W) catalysts such as olefin hydration,[2] alcohol dehydration,[3] oxidation of hydrocarbons,[4] methanol conversion to hydrocarbons,[5] decomposition of carboxylic acids,[6] isomerization of 1-butene,[7] and others.[8−11] Homogeneous catalysis by polyoxometalates is also a rapidly growing area, as a consequence of the unusual versatility of these catalysts and their compatibility with environmentally and economically attractive conditions.[12]

Heteropoly compounds in the solid state are composed of heteropoly anion, cation, and water and/or organic molecules. This three-dimensional arrangement is called the secondary structure, whereas the heteropoly anion is the primary structure.[1] The primary structure is rather stable, but the secondary structure depends markedly on the interactions with metal ions, protons, and water or neutral molecules. It has been demonstrated that both salt formation and removal of crystallization water molecules is accompanied by important changes in the X-ray diffraction patterns, reflecting the secondary structure varies to a large extent, whereas the framework vibrations characteristic of the primary structure remain unchanged. Therefore, it becomes imperative for understanding the catalysis of heteropoly compounds to distinguish between the primary and secondary structure.

The thermal instability of the bulk form of heteropoly acid and its strong tendency to be hydrolyzed is well-known.[1,8] The thermal stability depends on the constituent elements, structure, and interaction between the heteropoly compound and the carrier substrate.

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Table 1. Chemical Analysis of Bulk Compounds

sample	Mo (wt %)	Ni(Co) (wt %)	P (wt %)
HPMo	12.3		0.33
NiPMo	12.7	0.99	0.34
CoPMo	12.5	0.97	0.35

Therefore, from the catalytic point of view it appears of great interest to find a suitable support to stabilize the heteropoly anion structure and the heteropoly anion itself to be maintained under the reaction conditions. It has been reported that silica and activated carbon are good supports on which to fix HPMo, and thus the anchored HPMo acts as a solid acid catalyst even in water or in organic solvents without significant leaching during operation.[6] In our previous work[13] we found TiO_2-supported HPMo catalysts to be very active and selective systems for the conversion of methanol into dimethyl ether.

The present work is a continuation of our preliminary study[11] whether the deposition of 12-molybdophosphoric acid and its Co(Ni) salts on titania can lead to a stabilization of the heteropoly anion. In this paper we present a detailed characterization, before and after calcination at different temperatures, of bulk and titania-supported HPMo and its Co(Ni) salts in order to investigate the thermal transformation of these compounds. The samples were characterized using thermal analysis (TGA-DTA), X-ray diffraction (XRD), infrared (IR), Raman, and X-ray photoelectron spectroscopic (XPS) techniques.

2. Experimental Section

2.1. Sample Preparation. Commercially available (Aldrich, reagent grade) 12-molybdophosphoric acid, abbreviated as HPMo, was used as a starting material. Metal salts were prepared from aqueous solutions of the parent HPMo, to which the stoichiometric amounts of Ni and Co nitrates (Merck, reagent grade) were added, as described by Tsigdinos.[14] The chemical analysis of the elements of bulk compounds (Mo, Co-(Ni), and P) is presented in Table 1. The titania-supported HPMo (denoted HPMo/T) and its Co and Ni salts (denoted as CoPMo/T and NiPMo/T, respectively) were prepared by conventional wetness impregnation of TiO_2 powder with aqueous solutions of purified HPMo and its corresponding salts, respectively. The TiO_2 support was prepared by hydrolysis of $TiCl_4$ followed by dehydration of $Ti(OH)_4$ xerogel at 373 K and then calcination at 773 K. The BET area of the powder sample was 70 m^2/g and phase proportion resulted in 85% anatase and 15% rutile.

2.2. Characterization. The elemental analysis (Mo, Co-(Ni), P) were determined using a Perkin-Elmer 3030 atomic absorption spectrophotometer, following acid digestion of the samples. Powder X-ray diffraction patterns of the samples were recorded on a Seifert 3000P diffractometer with a nickel-filtered Cu Kα ($\lambda = 0.154$ 18 nm) radiation scanning 2θ angles ranging from 5 to 75°. Thermogravimetric analysis was performed with a Perkin-Elmer TGA 7 instrument which allowed both TGA and TDA curves to be recorded simultaneously. The experiments were conducted at a heating rate of 10 K/min, under He flow (60 mL/min), from room temperature up to 873 K. Framework vibration spectra in the range 1200−600 cm^{-1} were recorded on a FTIR Nicolet 5 ZDX spectrophotometer working at a resolution of 4 cm^{-1} and averaged over 100 scans. Self-supporting wafers were prepared by pelleting the samples 1:100 diluted in KBr. Raman spectra were obtained with Bruker FT-Raman spectrophotometer. The samples were irradiated with the 1064 nm exciting line, working with a power no higher than 10 nW to avoid sample volatilization. The samples were placed in a stationary sample holder and kept in an ambient environment. To obtain good signal-to-noise ratios at reasonable acquisition times, all spectra were averaged over 1000 scans. Photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and Mg Kα ($h\nu = 1253.6$ eV, 1 eV $= 1.6302 \times 10^{-19}$ J) 120 W X-ray source. The powder samples were pressed into small Inox cylinders and then mounted on a heater placed in a pretreatment chamber. Prior to being moved into the analysis chamber the samples were evacuated in the pretreatment chamber of the instrument at a temperature ranging from 343 to 723 K for 2 h. The residual pressure in the ion-pumped analysis chamber was maintained below 5×10^{-9} Torr during data acquisition. The intensities of Mo3d$_{5/2}$, Co2p, Ni2p, P2p, and Ti2p$_{3/2}$ peaks were estimated by calculating the integral of each peak after smoothing and subtraction of the "S-shaped" background and fitting the experimental curve to a combination of Gaussian and Lorentzian lines of variable proportion. The binding energies (BE) were referenced to the C 1s peak at 284.9 eV, this reference giving BE values with an accuracy of ±0.1 eV.

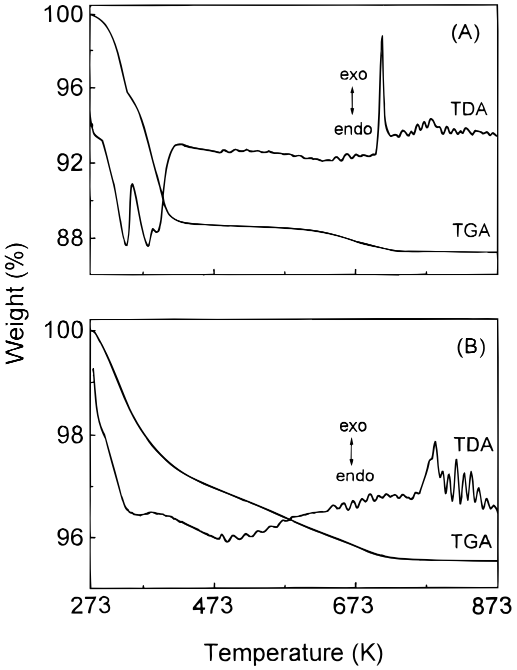

Figure 1. DTG and DTA curves for bulk HPMo (A) and titania-supported HPMo (B).

3. Results

3.1. Thermogravimetric Analysis. TGA and TDA curves for bulk and titania-supported HPMo are displayed in Figures 1A,B, respectively. The TDA curve for the HPMo sample in Figure 1A shows three endothermic peaks between 343 and 403 K, which are accompanied by a considerable weight loss (TGA curve) corresponding to the elimination of crystallization water (nH_2O) in accordance with the findings of Hayashi and Moffat.[15] Neither weight changes nor thermal effects are observed in the temperature range 423−623 K, suggesting the formation of anhydrous heteropoly an-

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ions (HPA).[16] In the temperature window of 623−723 K there is a new weight loss, although less marked, associated to removal of constitutional water ($\cong 1.5H_2O$ for $H_3Pmo_{12}O_{40}\cdot nH_2O$).[17] This broad weight loss is due to the removal of the last molecules of the constitutional water and the consecutive and slow solid-state reaction which yields the molybdenum oxide, as confirmed by the exothermic peak at 708 K. Hodnett and Moffat[18] suggested that this loss of water involves a deprotonation of the catalyst with concurrent loss of lattice oxygen, but the primary Keggin unit is retained. The weak and broad exothermic peak at 773 K can be assigned to the crystallization of the oxides resulting from the total decomposition of the Keggin units. The TG curves are consistent with previously published results.[19−21]

For titania-supported HPMo two endothermic peaks are observed (Figure 1B) The first peak at 363 K would be assigned to the water desorbed from the titania support and to removal of some part of the crystallization water of the supported HPMo phase, while the second peak at 493 K could be related to the loss of another fraction of this water. This assignment is in agreement with the results obtained from the Mg salt of HPMo supported on silica.[22] The continuous weight change up to about 708 K without any plateau indicates the absence of a steady state as already found for unsupported HPMo. Since around 708 K there is no well-defined exothermic peak, it is probable that HPA was partly destroyed due to loss of some constitutional water, similarly to bulk HPMo. Another fraction of the HPA is not yet destroyed and is preserved up to a higher temperature. The strongest exothermic peak at 793 K could be associated with the breakdown of the Keggin anion and crystallization of the molybdenum oxides, as expected from data in the literature

3.2. XRD Measurements. The XRD patterns of bulk samples heated at different temperatures are displayed in Figure 2A. No peaks are observed for HPMo up to 573 K. The presence of several lines of monoclinic β-MoO_3 and some lines of orthorhombic α-MoO_3[23,24] is clearly seen in the X-ray diffractogram of the bulk HPMo at 623 K (Figure 2a). The peak intensity of the α-MoO_3 phase increases with temperature and those of β-MoO_3 decrease. Upon treatment at 773 K, only the lines characteristic of the α-MoO_3 phase are present (Figure 2A). Only broad and weak diffraction patterns are observed for CoPMo and NiPMo samples at 623 K. Upon treatment at 773 K, the XRD patterns show an α-MoO_3 phase. The XRD patterns of titania-supported NiPMo and CoPMo heated at 773 K (Figure 2B) almost coincide and differ from that of the parent HPMo/T sample by some shift of reflections and a redistribution of their intensities. Mixture of α- and β-MoO_3 phases is observed in the diffractograms of the samples.

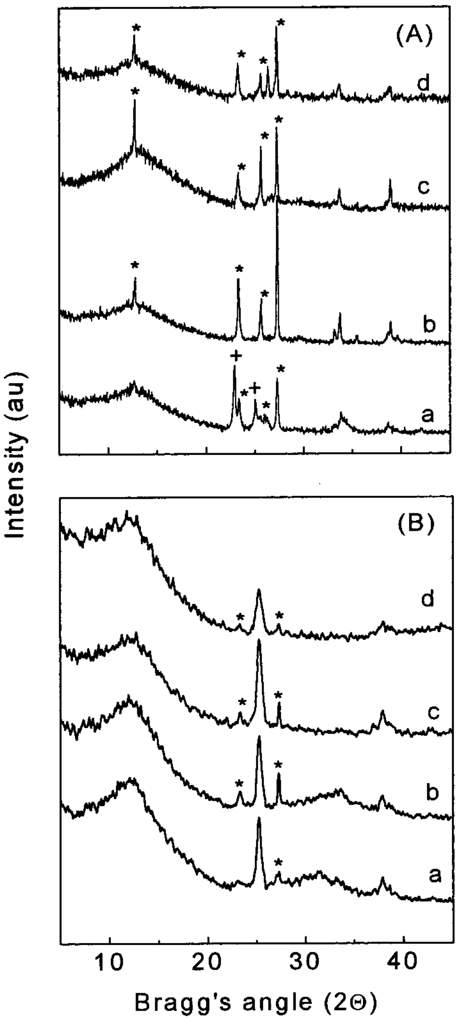

Figure 2. XRD patterns of unsupported (A) and titania-supported samples (B) calcined at different temperatures: (a) 623 K for HPMo and HPMo/T, respectively, (b) 773 K for HPMo and HPMo/T, respectively; (c) 773 K for NiPMo and NiPMo/T, respectively, and (d) 773 K for CoPMo and CoPMo/T, respectively. The symbols (*) and (+) correspond to α-MoO_3 and β-MoO_3 phase, respectively.

3.3. Raman Spectra. *3.3.1. Unsupported Samples.* Raman spectra of bulk and titania-supported HPMo samples pretreated at different temperatures are shown in Figures 3A−C and 4A−C, respectively. The Raman spectra of dried bulk HPMo (Figure 3A) is similar to previously reported spectra of 12-molybdophosphoric acid.[16,8] In this spectrum, the main bands character-

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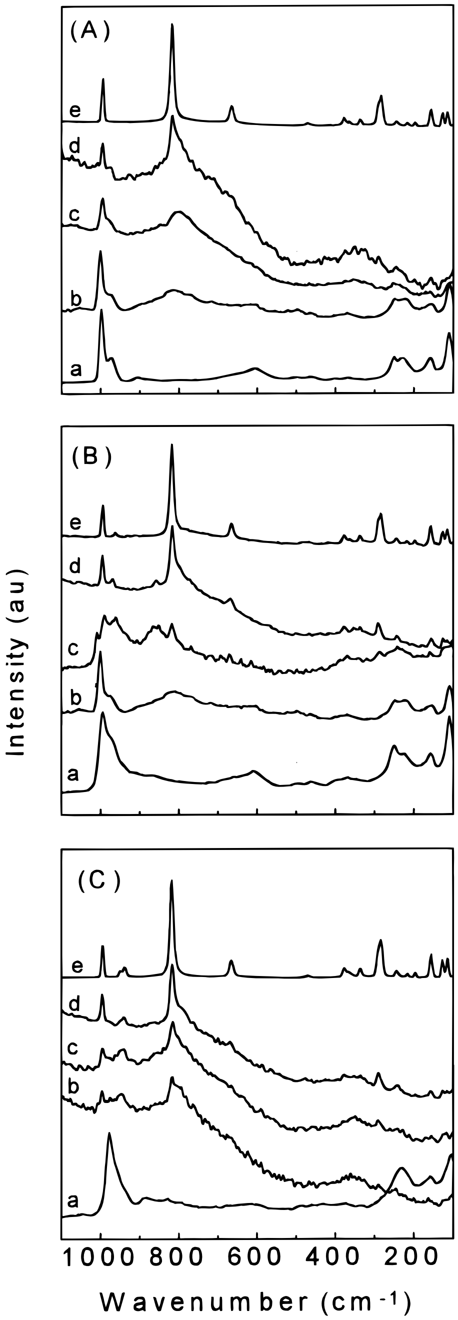

Figure 3. Raman spectra of unsupported HPMo (A), NiPMo (B), and CoPMo (C) calcined at different temperatures: (a) 343, (b) 523, (c) 623, (d) 773, and (e) 873 K.

istic of heteropoly anion with Keggin structure ($PMo_{12}O_{40}^{3-}$) are observed at 1000, 977, 906–873, 610, and 251 cm^{-1}, which can be respectively assigned to stretching modes $\nu_s(Mo-O_t)$, $\nu_{as}(Mo-O_t)$, $\nu_s(Mo-O_b-Mo)$, $\nu_s(Mo-O_c-Mo)$, and $\nu_s(Mo-O_a)$.[16] All of these bands remain unchanged for bulk NiPMo, suggesting that the Keggin unit structure is retained after nickel incorporation (Figure 3B). However, the initial Raman spectrum of HPMo changes when cobalt is added: (i) the principal band at 1000 cm^{-1} is broader and shifts to 993 cm^{-1}; (ii) the band at 251 cm^{-1} with an important bridge stretching character undergoes a significant decrease to 231 cm^{-1} (Figure 3C). The same effect has been found by Kasztelan et al.[25] for Cs substituted HPMo samples. The observed downshift of the $Mo-O_t$ stretching mode would be a consequence of the perturbation of the Keggin anion by cobalt because of formation of the substituted heteropoly anion. This leads to weakening of the $Mo-O_t$ bond, and consequently the longer $Mo-O_t$ bond induces a lower wavenumber. Rocchiccioli-Deltcheff et al.[16] detected the loss of anion–anion interaction when large counterions such as *tert*-butylammonium are employed. On the other hand, a partial degradation of the Keggin unit can occur during preparation of the salt, resulting in a mixture of HPMo, substituted HPMo, and isopolymolybdates. The latter is revealed by broadening of the main Raman band.

On increasing the temperature further, some changes occurred in the spectra of bulk samples, especially in the range 950–750 cm^{-1}. This region is related to the stretching vibrations of the bridges between trimolybdic groups of the Keggin structure, sensitive to the dehydration process induced by the thermal treatment.[16] The band at ca. 250 cm^{-1}, which is related to the $\nu_s(Mo-O_a)$ vibration, decreases after thermal treatment, suggesting a decrease of anion–anion interaction. A splitting of the $Mo-O_d$ band at 1006 and 988 cm^{-1} at 623 K is observed for NiPMo, indicative of a loss of anion symmetry.[26] Although changes occurred in the spectra, no degradation products of bulk (well defined) MoO_3 were identified. Especially for CoPMo, relatively small bands at 993 and 818 cm^{-1} were observable at 623 K, showing formation of some MoO_3 as a result of degradation of a small portion of HPA. Raman bands at 993, 820, and 666 cm^{-1} assigned to MoO_3[27] are present in the spectra of all the samples after treatment at 773 K. At a higher temperature (873 K), the MoO_3 bands dominate the spectra.

3.3.2. Supported Samples. The detection of Raman bands in titania-supported samples (Figure 4A–C) is limited by the condition that the phases must be long-range ordered. The observation of water evolution revealed by the weight change (Figure 1B) complements the structural information without crystallinity. Most probably, a loss of crystallinity occurred after the heteropoly compound was supported. This could be indicative of a better local dispersion of the molybdenum species on the surface as a result of some disorder of the oxidized phase coming from HPA distortion. In all the spectra of supported samples, no evidence for the presence of molybdenum trioxide can be found up to 623 K. After treatment at 623 K the titania-supported NiPMo and CoPMo samples displayed bands at 636, 517, 394, and 150 cm^{-1}, which can be assigned to vibrational modes for anatase.[28] For the HPMo/T sample these bands were observed at a higher temperature (773 K). This means that some agglomeration of the particles occurs on titania surface. Larger MoO_3 bands appear at 773 K, at a higher temperature than that for unsupported samples.

3.4. Infrared Spectra.

Additional information on the structure of the samples and its dependence on thermal treatments is provided by FTIR. The FTIR spectra for unsupported and supported heteropoly compounds are displayed in Figures 5A–C and 6A–C, respectively. These are analyzed below.

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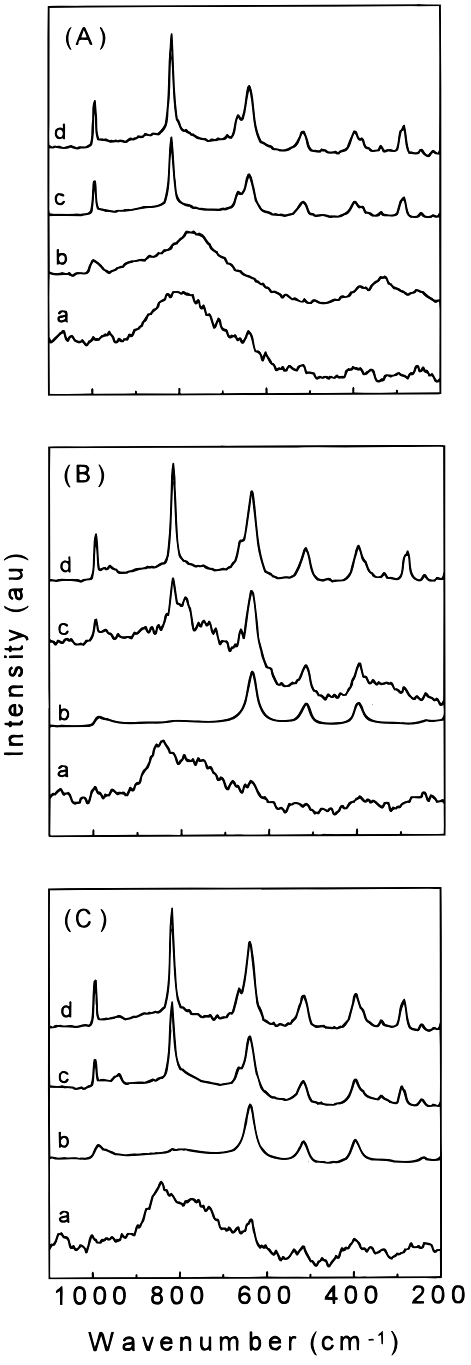

Figure 4. Raman spectra of titania-supported samples HPMo/T (A), NiPMo/T (B), and CoPMo/T (C) at different calcination temperatures: (a) 343, (b) 623, (c) 773, and (d) 873 K.

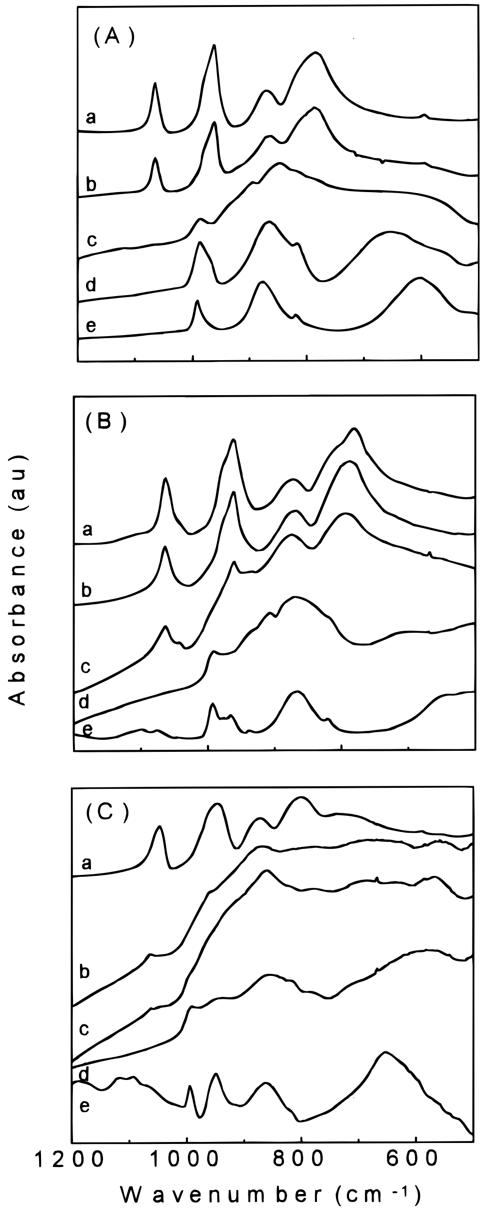

Figure 5. Infrared spectra of unsupported samples: (A) HPMo calcined at (a) 343, (b) 573, (c) 623, (d) 673, and (e) 773 K. (B) NiPMo calcined at (a) 343, (b) 523, (c) 573, (d) 673, and (e) 873 K. (C) CoPMo calcined at (a) 343, (b) 523, (c) 573, (d) 673, and (e) 873 K.

3.4.1. Unsupported Samples. The IR spectra of bulk HPMo (Figure 5A) show bands at 1065, 963, 873, 787 and 595 cm^{-1} assigned to stretching vibrations ν_{as}(P−O$_d$), ν_{as}(Mo−O$_t$), ν_{as}(Mo−O$_b$−Mo) and ν_{as}(Mo−O$_c$−Mo), respectively, characterizing the Keggin unit.[29] The substitution of H^+ by Co^{2+} ions results in some shifting and broadening of the bands for the CoPMo sample (from 1063 to 1051 cm^{-1} and from 962 to 950 cm^{-1}; Figure 6C). For Al^{3+}, NH^{4+}, and Na^+ salts of $H_3PW_{12}O_{40}$, characterized by photoacoustic spectroscopy,[30] such a decrease in the frequencies has already been interpreted as weakening of anion−anion interactions and increasing the anion−cation interactions. The spectrum of NiPMo remains unchanged compared to that of HPMo, but with only limited broadening of the 962 cm^{-1} band. The spectra of HPMo and NiPMo heated at 523 K are practically identical and exhibit only the bands characteristic of the Keggin unit (Figure 5A,B). Upon further treatment both samples show a drop in band intensity. At 573 K, HPMo preserves KU bands. A splitting of the band at 1064 and 1041 cm^{-1} and a small shift of the Mo−O$_t$ bond stretching vibrations to a higher wavenumber is observed for NiPMo, as a result of the hydration state of the sample. The former band is attributed to the triply degenerated asymmetric stretching vibration of the central PO_4 tetrahedron, and the appearance of a splitting of this band implies a lowering of the symmetry from T_d to C_{2v}.[29] Shifting of the Mo−O$_t$ bond is due to a loss of hydrogen bonding between terminal oxygen and water molecules leading to an increased anion−cation interac-

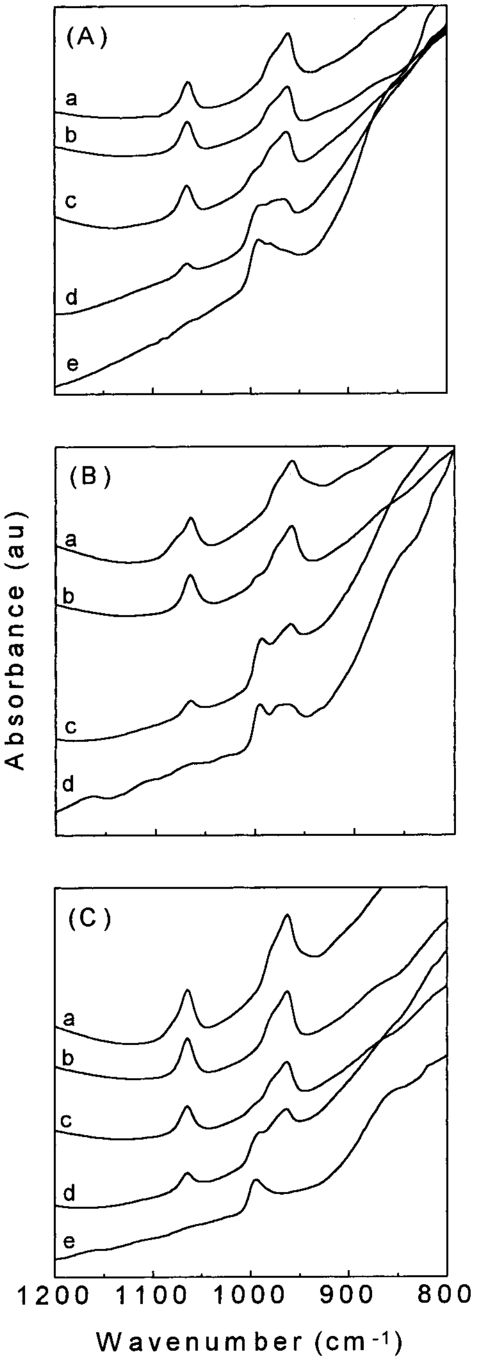

Figure 6. Infrared spectra of titania-supported samples: (A) HPMo/T calcined at (a) 343, (b) 523, (c) 623, (d) 673, and (e) 873 K. (B) NiPMo/T calcined at (a) 343, (b) 523, (c) 673, and (d) 873 K. (C) CoPMo/T calcined at (a) 343, (b) 523, (c) 623, (d) 673, and (e) 873 K.

tion.[16,26] The latter is in agreement with the previous observation for pyridinium molybdophosphates and has been attributed to symmetry loss of the HPA.[31] This was supported by the results from the Raman spectra. A broadening of the IR spectra with some presence of the 1065 cm^{-1} band at 623 K is observed for HPMo, indicative of a strong disorder of the HPA structure and transformation to molybdenum oxides, which agree with the results from DTG and XRD. Further heating to 673 and 773 K results in the observation of MoO_3 bands at 991, 880, and 816 cm^{-1} as a consequence of the total loss of the Keggin structure. The same is observed for NiPMo, but at 873 K bands of phosphates at 1096, 1076, 965, and 939 cm^{-1} appear[32,33] (Figure 5B).

Table 2. Binding Energies (eV) of Core Electrons and Surface Atomic Ratios of Titania-Supported Samples

sample (treatm)	Mo $3d_{5/2}$	Ni $2p_{3/2}$ (Co $2p_{3/2}$)	P2p	Mo/Ti	Ni/Ti (Co/Ti)	P/Ti
HPMo/T (343 K)	232.2		132.9	0.408		0.054
HPMo/T (523 K)	232.1		133.0	0.317		0.050
HPMo/T (623 K)	232.2		133.4	0.433		0.064
HPMo/T (723 K)	232.2		133.7	0.413		0.066
NiPMo/T (343 K)	232.2	854.5	132.7	0.509	0.081	0.048
NiPMo/T (523 K)	232.2	854.6	132.8	0.474	0.077	0.046
NiPMo/T (623 K)	232.0	855.4	132.9	0.619	0.128	0.060
NiPMo/T (723 K)	231.9	855.2	132.9	0.586	0.109	0.065
CoPMo/T (343 K)	232.1	781.5	132.8	0.417	0.070	0.044
CoPMo/T (523 K)	232.2	781.3	132.8	0.375	0.067	0.045
CoPMo/T (623 K)	232.1	781.4	132.9	0.533	0.112	0.056
CoPMo/T (723 K)	232.0	781.2	133.1	0.491	0.096	0.055

For CoPMo, it is difficult to define clear IR peaks within the 523–623 K range (Figure 5C), probably due to an amorphization of the heteropolyanion phase. The increase of the background absorption is a result of the loss of water and/or protons.[25] However, the Keggin structure is still present up to 623 K, as judging from the preservation of the Mo–O_t stretching vibration. Increasing the temperature, bands of MoO_3 and phosphates are observed, similar to HPMo and NiPMo.

3.4.2. Supported Samples. The IR spectra of titania-supported samples are displayed in Figure 6A–C. It can be emphasized at this point that no subtraction of TiO_2 absorption was considered to avoid artifacts introduced in the net spectra and more specifically in the lower wavenumber region. Titania bands below 900 cm^{-1} overlap with those of the heteropoly anion, and therefore this region is not discussed. The bands characteristic of HPA with some shifts of the stretching modes $\nu_{as}(P-O_d)$ and $\nu_{as}(Mo-O_t)$ to lower wavenumbers relative to those of unsupported HPA are revealed in the spectra of all the samples. A broadening on the higher wavenumber side of these bands has occurred after impregnation, especially for CoPMo/T and NiPMo/T samples. The latter can be associated with the loss of the symmetry of the heteropoly anion structure and increase of cation–anion and/or anion–support interaction after supporting on a titania surface. These bands are preserved up to 723 K, which contrasts with the unsupported counterparts. This behavior is consistent with TDG experiments. The band of MoO_3 appears only as a shoulder at 623 K and becomes well developed at higher temperatures. As already observed for unsupported samples, only MoO_3 with a few bands of phosphates can be discerned at 873 K.

3.5. X-ray Photoelectron Spectra. Photoelectron spectroscopy has been used to reveal not only the chemical state of the elements but also their abundance. The binding energies (BE) of various core-levels (P 2p, Mo $3d_{5/2}$, and Co $2p_{3/2}$ or Ni $2p_{3/2}$) are summarized in Table 2. XPS spectra of the HPMo/T sample, treated at different temperatures, are shown in Figure 7. The BE for Ti $2p_{3/2}$ level at 458.5 eV remains unchanged after different temperature treatments, confirming that

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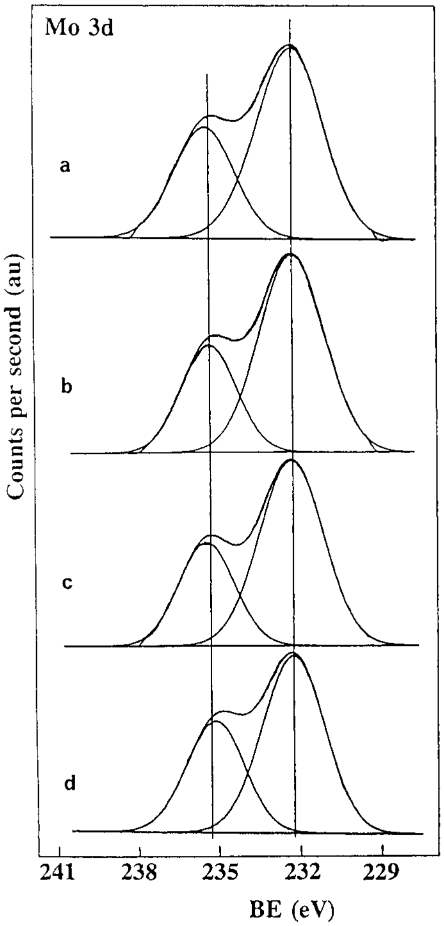

Figure 7. XPS spectra of titania-supported HPMo treated at (a) 343, (b) 523, (c) 623, and (d) 723 K.

the oxidation state of titanium is constant Ti^{4+}. The BE of Ni $2p_{3/2}$ for NiPMo/T samples characterize octahedrally coordinated Ni^{2+} ions.[9] The BE of Co $2p_{3/2}$ is slightly higher than that expected for Co^{2+} ions in Co_2O_3.[34] This means that Co^{2+} ions are, probably, in close interaction with Mo and/or Ti atoms. The Co $2p_{3/2}$ BE of 781.2 eV is consistent with the presence of some surface $CoTiO_3$[34] at a higher temperature (723 K). As illustrated in Figure 7, the BE of the Mo $3d_{5/2}$ core level is invariant for all samples and coincides with the value expected for fully oxidized molybdenum, Mo^{6+}.[25] However, the color of the samples changes to blue under vacuum treatment, suggesting that some photoreduction of molybdenum oxide occurs under sample exposure to the X-ray source within the analysis chamber of the spectrometer, as already observed in a previous work.[35] This phenomenon has been confirmed by recording the vibrational spectrum of the chemisorbed NO molecule on the outgassed oxidic samples,[36] showing that coordinatively unsaturated Mo sites are easily formed by evacuation. The BE of P 2p for the HPMo/T sample increases from 132.9 to 133.7 eV with increasing temperature (Table 2), suggesting that the chemical environment of phosphate changes on raising the pretreatment temperature. The shift to higher BE of the P 2p core level is indirect proof of the destruction of the Keggin unit and the subsequent interaction of the phosphate anion at the TiO_2 surface. As stated above, the IR spectra revealed formation of phosphates structures at high temperatures which is consistent with the change in the BE of the P 2p core level in phosphates.

Surface (XPS) atomic ratios have been calculated from peak intensities and atomic sensitivity factors.[37] The variations in the XPS Mo/Ti atomic ratios, taken as an indication of the molybdenum distribution on titania, with temperature are reported in Table 2. The large XPS Mo/Ti ratios for all samples indicate that Mo is primarily well dispersed on the TiO_2 surface. This XPS ratio is larger for NiPMo/T and CoPMo/T samples than for HPMo/T, probably due to perturbation of the heteropoly anion by counterions. A slight decrease of XPS Mo/Ti is observed upon treatment at 523 K, suggesting some aggregation of the anchored anions as induced by the water expelled from the Keggin units upon drying. However, this ratio increases slightly with increasing temperature up to 523 K probably as a consequence of the breaking of large oxoanions (secondary structure) into smaller structures that remain well dispersed on the TiO_2 surface. Finally, higher temperatures may lead to some aggregation of dispersed MoO_3 units into tridimensional crystals. The increased temperature causes an increase of the XPS P/Ti atomic ratios, possibly due to coverage of the surface by P atoms. Probably, amorphous Ti phosphates[33] are formed as intermediate species after treatment at higher temperatures (above 623 K).

4. Discussion

4.1. Structural Features. *4.1.1 Unsupported Samples.* The FTIR and Raman spectra of bulk CoPMo differ markedly from those of HPMo and NiPMo. The impregnation step of the cobalt salt has not been investigated in detail, and it is difficult to provide definitive information on the mechanism of the exchange of Co^{2+} by H^+. The change in the spectra is, on one hand, an indication of some degree of structural disorder, probably due to the presence of salt and acid coming from the nonstoichiometry between anion and cation. On the other hand, this would result from some partial degradation of the HPA occurring during impregnation with a solution of the initial salt leading to an increase in pH. It is well-known[1,38–41] that the increase in pH leads to partial decomposition of the heteropoly anion:

$$Mo_{12}O_{40}{}^{3-} \rightarrow PMo_{11}O_{39}{}^{7-} + MoO_4{}^{2-} + 6H^+$$

This degraded anion can be a precursor for the formation of isopolymolybdates or complexes with the cation.[1,8] Such removal of molybdenum from HPA results in a decrease of the $\nu(Mo-O_t)$ stretching mode. These phenomena may take place with the heteropoly com-

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pounds either in supported form or in solution. The absence of any Raman or IR signal for isopolymolybdates does not mean that these compounds did not occur. Therefore, we can assume that the HPA substituted with Co^{2+} ions is strongly perturbed compared to the free heteropoly anion, leading to a substantial change in the $Mo-O_t$ stretching modes. McGarvey et al.[42,43] have proposed that the alkaline earth salts of 12-molybdophosphoric and 12-tungstophosphoric acids are mixtures of the parent acid and divalent cation salt.

4.1.2. Titania-Supported Samples. The decrease in intensity and broadening of the characteristic IR bands of supported HPA is an indication of the degree of anion distortion. This would be a consequence of a direct interaction between HPA and the support surface which can weaken the interaction between bonds in the heteropoly anion. The broadening of the background absorption in the Raman spectra also supports this. However, there are no obvious differences among the samples.

According to the classification of the carriers concerning the isoelectric point, TiO_2 is more basic than SiO_2.[44] This fact could be responsible for a strong interaction of HPMo with the titania surface. It should be noted that HPA is electrically negatively charged. During impregnation the HPA could be linked to the surface by the strongest acidic protons of the HPA similarly to findings in ref 45. The surface would become positively charged by formation of $Ti-OH_2^+$ groups, which are able to strongly attract the HPA through electrostatic interaction. Cobalt and nickel as a electropositive counterion can also modify the electrostatic interaction between HPA and the support. It could be assumed that during the initial impregnation, at a slightly higher pH, Co ions exchange with the protons of surface hydroxyl groups, creating an even distribution of surface Ti−O−Co bonds. Also, some hydrolysis of $Mo-O_b-Mo$ bonds after anchorage cannot be excluded. This leads to partial distortion of the Keggin anion, resulting in opening of the Keggin structure into so-called "triads" by breaking the bridging $Mo-O_b-Mo$ bonds. The latter has been proposed by Tatibouet[22] for $H_5PV_2Mo_{10}O_{40}$ and $HMgPMo_{12}O_{40}$ supported on silica. These authors concluded that the interaction with surface OH groups leads to hydrolysis of the Keggin anions into "triads" of edge-linked MoO_6 octahedra strongly bound to the surface. The absence of strong endothermic peaks in TDA curves at a lower temperature (below 373 K) means that some dehydration of the HPA has occurred during the impregnation step, coming from this interaction. However, the presence of broad band in the Raman spectra in the wavenumber range of 950−800 cm^{-1} related to $\nu(Mo-O_b-Mo)$ stretching modes means that these bonds are well preserved and still present on the surface of CoPMo/T and NiPMo/T samples after drying and on the HPMo/T sample up to 623 K. As a consequence of these phenomena, a loss in the crystallinity of the supported HPC and a significant disorder of the heteropoly anion symmetry caused by the support would be expected. The supported HPC undergoes morphological transformation into an amorphous form in which the Keggin anions are still present, but the long-range order created by the hydration water is lost. It is known[46] that the structural parameters of HPA catalyst are largely determined by the hydration water network between the anions.

4.2. Thermal Stability of Heteropoly Anion Structure. The thermal behavior of bulk HPMo can be summarized as follows: crystallization water is eliminated between 358 and 393 K; the anhydrous form is stable within the range 393−603 K and the loss of constitutional water takes place between 623 and 708 K. The heteropoly anion decomposes with formation of a mixture of phosphorus and molybdenum oxides within the temperature range 703−723 K, assigned to the strong exothermic peak on the TDA curve (Figure 1A). β-MoO_3 dominates in this temperature range and begins to transform into α-MoO_3 after treatment at 773 K, which corresponds with the beginning of the second exothermal of the TDA curve.

In the case of CoPMo and NiPMo samples, α-MoO_3 appears at 773 K without β-MoO_3 formation at a lower temperature. This means that the Keggin anion decomposition occurs at a higher temperature when Co and Ni are present. It is evident that transformation of the HPA to the corresponding oxides is modified by the presence of these cations and the stability of the intermediate species between the hydrated form of the HPA and the increase in crystallized molybdenum oxide in the presence of the metal counterions. Earlier work has shown[47] that the salts of the heteropoly acids prepared with monovalent cations have a higher thermal stability than those of the parent acids.

A different picture emerges after supporting HPMo on the titania surface. The thermal decomposition of the supported HPA proceeds in two steps supported by slow elimination of the water up to about 708 K and the exothermic peak at 793 K in the TDA curve (Figure 1B). The first temperature is practically the same as for bulk HPMo. It should be proposed that some part of the supported HPMo behaves as unsupported and at a lower temperature is still decomposed. The remaining HPA becomes more rigid due to the interactions of the protons with the titania surface. The preservation of the IR bands at 1065 and 960 cm^{-1} at 673 K, characteristic of $P-O_d$ and $Mo{=}O_t$ bonds (Figure 6) clearly indicate that heteropoly anions are not totally destroyed. Above 773 K the transformation of HPA to molybdenum oxides and P_2O_5 or phosphates is complete. The transformation of supported HPA in the temperature range 708−793 K occurred without any detectable water evolution, indicating that some protons from the Keggin structure remain in the decomposition products as has been observed by Ilkenhans et al.[48] The latter could be a result of grafting of the Mo species onto the titania surface by the formation of Mo−O−Ti bonds. This is supported by increasing the XPS Mo/Ti ratio after treatment at 623 K.

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In the literature there are different opinions about the stability of 12-molybdophosphoric acid on different supports.[27,49−52] Rocchioli-Deltcheff et al.[27] have shown that silica support induces destabilization of HPMo. The transformation of HPA into β-MoO_3 begins at 523 K, a temperature lower than for the unsupported one. Cheng and Luthra[51] have concluded that the decomposition of HPMo on alumina is a result of the strong interaction between the support and HPA, which leads to formation of aluminum salt. Contrary to these findings Moffat[52] found that HPMo is strongly stabilized by the silica support up to 853−873 K.

The existence and stability of the anhydrous phases are not well defined in the case of supported HPMo. Perhaps, the loss of constitutional water takes place in a significantly larger temperature range compared to unsupported HPMo, and this process occurs slowly. After treatment at a higher temperature, the interaction between HPA and the support becomes stronger so that the dehydration process via extraction of terminal oxygen atoms by the protons is very slow. It should be noted that some unsaturated $Mo^{\delta+}$ ions could be obtained as a result of both the heating process and the strong anion−support interaction. This is consistent with the reduction mechanism proposed for 12-molybdophosphates;[53] when the temperature is raised, water is formed from oxygen atoms of the anion and protons producing coordinatively unsaturated Mo atoms, i.e., the loss of water involved a deprotonation of the catalyst with concurrent loss of lattice oxygen. According to the observations of Pope et al.,[54] the original structure of PMo_{12} was retained by electrochemical reduction by 1 electron/anion. The observed Mo^{5+} signal became broader with increasing temperature due to rapid hopping of the electron among 12 equivalent Mo atoms in a Keggin anion.[54] In agreement with Eguchi et al.[55] the losses of the IR band intensities also arise from the structural perturbations occurring in the partial reduction of the anion. Structural collapse via reduction−dehydration is also in agreement with the NH_3 temperature-programmed desorption results reported in ref 56, which showed loss of both NH_3 and H_2O to occur concomitantly with structural collapse.

Finally, it can be concluded that the stability of the HPA supported on titania increases due to the anion−support interaction. The transformation of the heteropoly anion begins to appear after its support, but this process is very slow during heating and is completed at a temperature higher than in the unsupported anion. The results show that the Keggin unit precursor is a very thermally sensitive species. The intermediate species formed between the hydrated form of the heteropoly compound and the crystallized molybdenum oxides have the same nuclearity and composition as those of the Keggin precursor. These species are stable on the titania surface at temperatures much higher than those found for the bulk form. The introduction of Co and Ni increase the stability of these species.

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