Catalysts based on supported 12-molybdophosphoric acid

Patricia G. Vázquez, Mirta N. Blanco and Carmen V. Cáceres *

Centro de Investigación y Desarrollo en Procesos Catalíticos (CINDECA), UNLP-CONICET, 47 No. 257, 1900 La Plata, Argentina
E-mail: hds@nahuel.biol.unpl.edu.ar

Received 7 December 1998; accepted 14 May 1999

Catalysts preparation by equilibrium adsorption of 12-molybdophosphoric acid in water–ethanol solutions onto silica, titania, carbon and alumina is studied. The solute/support interaction follows the decreasing order: alumina, carbon, silica and titania. It is observed that the molybdophosphoric acid keeps its Keggin-type structure after being supported at room temperature on all supports. This species is stable up to 500 °C on silica, 400 °C on titania or carbon and 250 °C for alumina. The acidity of the supported heteropoly acid decreases in the following order: silica $>$ titania $>$ carbon $>$ alumina.

Keywords: molybdophosphoric acid, titania, silica, alumina, carbon, equilibrium adsorption impregnation

1. Introduction

The increasing use of catalyst-based production methods in the emerging industries has been favored by the continuous innovation observed over the last decade for the different catalytic processes [1].

Catalysis based on heteropoly acids (HPA) and related compounds is a growing and important field in which new and promising developments are being carried out both at research and technological levels [2]. Among the emerging industries, those involved in the synthesis of fine chemicals are at the leading edge in this class of catalytic processes [3].

The HPA with Keggin-type structure [4] possess special characteristics that make them very useful in catalysis; for instance, their highly acidic nature is very interesting in industrial reactions [5]. HPA-catalyzed oxidations of organic substances in liquid phase can be carried out both in homogeneous phase and in a two-phase system (aqueous/organic) using H_2O_2 as the oxidant. HPA containing molybdenum or tungsten catalyze various oxidations, examples of which are the epoxidation of olefins, oxidation of alcohols or phenols in homogeneous phase or two-phase systems [2].

Catalytic reactions are assumed to take place in the whole heteropoly compound volume in bulk-type reactions; for this reason the catalyst is referred to as showing pseudo-liquid behaviour. By contrast, as in surface-type reactions the activity correlates with the surface area, it becomes sensitive to preparation method and catalyst pretreatment. For this type of reactions, the HPA exhibiting low surface area can be deposited onto a solid acting as a support. In this regard, the support can either play only a mechanical role or modify the catalytic properties of the precursor deposited on the surface by favoring growth of certain structures or by inducing different types of interaction [6].

A disadvantage of HPA as catalysts lies in their low stability, and various factors can cause it. In molybdophosphoric acid (MPA), problems appear with thermal decomposition, acidity changes and loss of the active phase, the last being due to formation of a volatile molybdic acid [7]. To minimize the disadvantage, the HPA were supported on different carriers [8] and, also, impregnating solutions in different solvents were employed [9].

The problem of HPA thermal stability was studied by several authors, but contradictory results has been published. For instance, Öhlmann et al. [10,11] have found that HPA thermal stability decreases when supported on silica whereas Rao et al. [12] inferred that, in this system, Keggin structure is stable up to 200 °C and Moffat et al. [13–15] have concluded that silica-supported MPA keeps stable up to 570 °C.

Therefore, for a better understanding of these catalysts, in the present work we studied the behaviour of MPA when impregnated by an equilibrium adsorption technique from its water–ethanol solutions on four different supports: silica, alumina, titania and carbon. Firstly the interaction characteristics of MPA and the support by means of adsorption isotherms is shown, and then a detailed analysis of the nature of the species present both in the impregnating solutions and in the solids is carried out. Besides, results of a test reaction are presented to determine the acidic characteristics of the catalysts obtained here. These results were, in addition, compared with those provided by a potentiometric titration method.

2. Experimental

2.1. Adsorption studies

To obtain each experimental point of the molybdenum adsorption isotherms at 20 °C, 1 g of support and 4 ml of

---

* To whom correspondence should be addressed.

MPA ($H_3PMo_{12}O_{40}\cdot xH_2O$, Merck p.a.) solution of known concentration were shaken, for a given time. The solvent employed was a 1 : 1 (in volume) mixture of water and ethanol (Soria 96%). The supports used were SiO_2 Grace (surface area (S_{BET}): 311 m^2/g, average pore diameter (apd): 4 nm), TiO_2 (anatase) Riedel–de Häen (S_{BET}: 9.8 m^2/g), Al_2O_3 spheralite (S_{BET}: 282 m^2/g, apd: 4.2 nm) and activated carbon (S_{BET}: 806 m^2/g, apd: 2 nm).

Each adsorption isotherm was obtained using known MPA contents in the solution; the initial concentration range being 5–120 mg Mo/ml. To determine the optimum contact time required to achieve equilibrium between support and impregnating solution, adsorption kinetic measurements were previously performed, but for only one initial MPA concentration (120 mg Mo/ml); the contact time was varied from 5 min to 72 h. The solid was separated from the solution by centrifugation and dried at room temperature (r.t.) for 24 h. Then it was calcined during 6 h in the range of 100–400 °C, and for the sample on silica between 100 and 600 °C.

2.2. Quantitative molybdenum analysis

Mo concentration in the solutions was measured by atomic absorption spectrometry with an IL 457 model double-beam spectrophotometer (Instrumentation Laboratory Inc.). The analysis was carried out under the following conditions: wavelength 313 nm; band width 0.5 nm; lamp current 7 mA; phototube amplification 700 V; burner height 7 mm and acetylene/air flame in 7 : 14 ratio.

2.3. UV-visible spectroscopy

Spectra of MPA solutions, in the range 200–600 nm, were obtained with a Varian Super Scan 3 double-beam UV-visible spectrophotometer with built-in recorder, using quartz cells of 0.5 mm optical path.

2.4. Nuclear magnetic resonance spectroscopy

The MPA solutions were analyzed by ^{31}P NMR. A Bruker MSL-300 equipment linked to a SOLIDCYC.DC pulse program was utilized, using 5 μs pulses, a repetition time of 10 s and a frecuency of 121.496 MHz for ^{31}P at 24 °C, the resolution being 3.052 Hz per point. Phosphoric acid 85% was employed as external reference. The same equipment and similar conditions were used to obtain ^{31}P MAS-NMR spectra of solids. A sample holder of 5 mm diameter and 10 mm in height was used, the spin rate being 2.1 kHz. The repetition time was 3 s and several hundred pulse responses were collected.

2.5. Fourier transform infrared spectroscopy

A Bruker IFS 66 equipment, pellets in BrK and a measuring range of 400–1500 cm^{-1} were used to obtain the FT-IR spectra of the solid samples.

2.6. Diffuse reflectance spectroscopy

The solid samples were studied in the range 200–600 nm, using a UV-visible Varian Super Scan 3 equipment, fitted with a diffuse reflectance chamber with inner surface of $BaSO_4$. Samples were compacted in a teflon sample holder to obtain a sample thickness of 2 mm.

2.7. X-ray diffraction

The XRD patterns were obtained by using a Philips PW-1714 diffractometer with built-in recorder. The conditions used were: Cu Kα radiation (1.5417 Å), nickel filter, 30 mA and 40 kV in the high voltage source, scanning angle (2θ) from 5 to 60° and scanning rate of 1° per minute.

2.8. Catalysts acidity: isopropanol dehydration

The isopropanol (Mallinckrot AR) dehydration measurements were accomplished in a conventional flow fixed-bed reactor, operating at atmospheric pressure and 180 °C, with a solid mass of 0.5 g. The isopropanol volumetric flow was of 0.44 ml/min in a total flow in He of 50 ml/min. The conversion was calculated as the ratio of the isopropanol consumption to the initial quantity, determined by GC, after a time of 4 h under reaction.

Potentiometric titration. A small quantity of 0.1 N n-butylamine in acetonitrile was added to a known mass of solid, and agitated for 3 h. Later, the suspension was titrated with the same base at 0.05 ml/min [16]. The electrode potential variation was measured with an Instrumentalia S.R.L. digital pH meter.

3. Results

3.1. Adsorption kinetics

The adsorption of Mo and P integrating the same structure was carried out using a heteropoly acid, which presents a primary structure of Keggin type, with general formula $[XM_{12}O_{40}]^{(8-n)-}$, where M are poly or addenda atoms, X is the central or heteroatom and n is the X valency [4]. It is formed by a central tetrahedron XO_4 surrounded by twelve octahedra MO_6, that comprise four groups of three edge-shared octahedra, the M_3O_{13} triad [17]. The secondary structure is considered to be that formed by the spatial arrangement of polyanions, cations and other components.

From the adsorption kinetics study performed with MPA solutions in water–ethanol, with initial concentration of 120 mg Mo/ml, it was found that the adsorbed concentration, C_a (g Mo/100 g support) remains constant after contact times varying from 2 to 24 h, according to the support considered. To ensure that the equilibrium had been reached, a time of contact between the solution and support of 72 h was used.

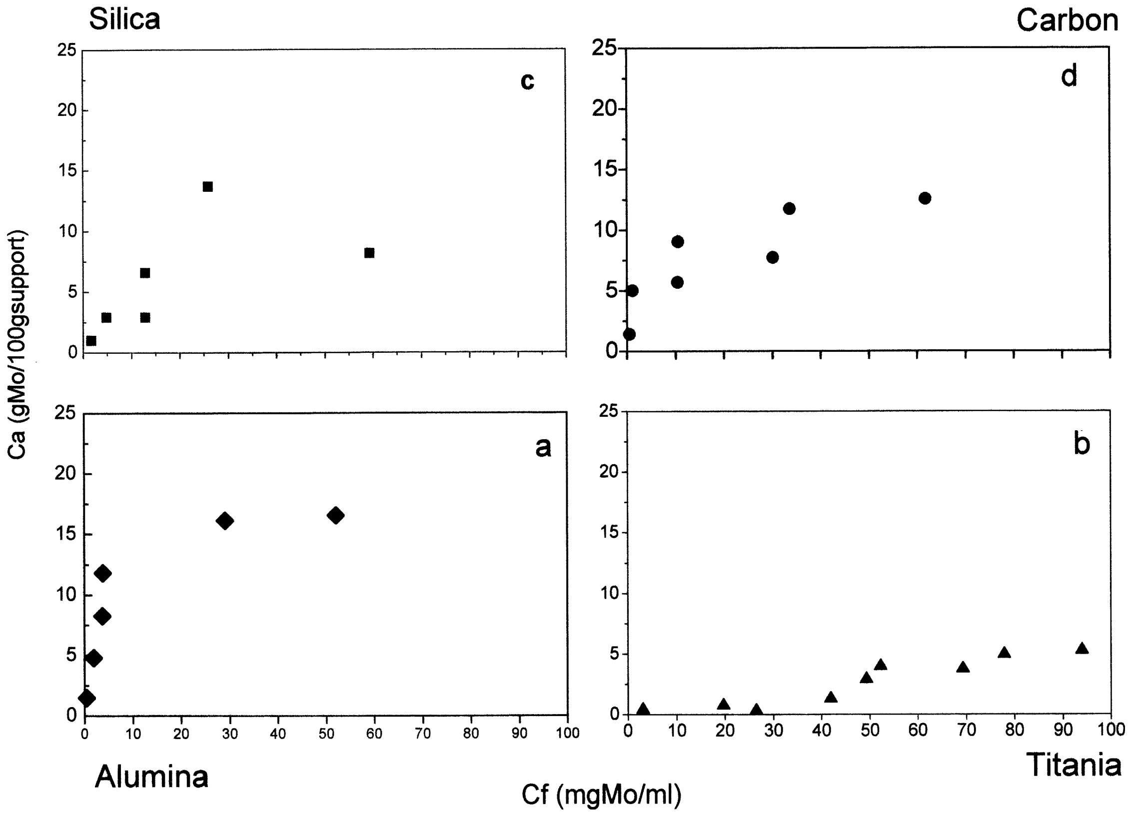

Figure 1. Mo adsorption isotherms on alumina (a), titania (b), silica (c) and carbon (d) from MPA solutions in ethanol–water at 20 °C.

3.2. Adsorption isotherms on different supports

3.2.1. Alumina

Figure 1(a) shows the adsorption isotherm of $H_3PMo_{12}O_{40}$ on alumina, expressed as C_a as a function of the final equilibrium concentration in solution (C_f). As the concentration of the solution increases, a raise in the adsorbed amount of Mo on the support is observed until a plateau (constant C_a) is reached. The isotherm presents only one plateau; this could imply that only one main species is adsorbed over the studied concentration range.

The initial solution pH did not show any important variation, as the concentration increases. It is worth to point out that the pH values of these original solutions (near 1) indicate that the MPA is more acidic than the corresponding oxoacids of its constitutional elements, and also than that of the ordinary mineral acids [18]. The strong acidity is due to the fact that the negative charge is delocalized in the atoms that make up the heteropoly anion, so that a low surface charge density in the outer part of such structure is created. This is particularly caused by the double bond between molybdenum and the terminal oxygen O_d, which polarizes the negative charge from O_d to Mo [5]. Also, by extended Hückel method, it was probed that the activity of heteropoly compounds in acid-catalyzed processes is inversely related to net atomic charges on the outer oxygen atoms [19]. When solution and support are contacted, the surface OH of Al_2O_3 becomes protonated; this fact can lead to an increase of solution pH. If so, MPA depolymerization releasing protons can be produced, according to the following reaction:

$$PMo_{12}O_{40}^{3-} + 3H_2O \rightarrow PMo_{11}O_{39}^{7-} + MoO_4^{2-} + 6H^+ \quad (1)$$

The solution pH measurements after the solution–support contact led to verify an appreciable change in pH only at very low concentration (5 mg Mo/ml). So, it is possible to assume that the $PMo_{12}O_{40}^{3-}$ species does not depolymerize when solutions in water–ethanol are used, since organic solvents stabilize such species. In this case, the anion–anion repulsion force should be more intense than that corresponding to aqueous or acidified with HCl solutions, therefore, the anion–support interaction should be greater [20].

3.2.2. Titania

In the MPA adsorption on titania, slight variations in pH were observed for the final solutions in relation to the initial one (pH = 1). pH values of the final solutions were between 0.8 and 1. The unimportant variations of pH allow the assumption that the depolymerization of the $PMo_{12}O_{40}^{3-}$ anion to $PMo_{11}O_{39}^{7-}$ (reaction (1)), would not be significant.

On the other hand, it is known that the hydroxyl groups of a titania surface in contact with solution tend to be either positively or negatively charged below or above the isoelectric point (IEP) of titania (anatase = 6.2) [21], according to the equilibrium $Ti\text{–}OH_2^+ \rightleftharpoons Ti\text{–}OH \rightleftharpoons Ti\text{–}O^-$. Above the IEP of titania, the hydroxyl groups tend to be negatively charged, so that it is relatively hard for the anions to be adsorbed on the titania surface, due to electrostatic repulsion. Below the IEP, the adsorbed amount of the anions should be favored, as in our working conditions, due to the low pH values of the initial as well as the final solutions.

Figure 1(b) shows that the adsorption isotherm of $H_3PMo_{12}O_{40}$ on titania has a sigmoidal shape; it presents very low initial values of C_a and later, for MPA concentrations above 50 mg Mo/ml in the final solutions, it tends to reach a plateau of C_a values. The isotherm shape indicates a low anion–support interaction. The initial slope shows that adsorption becomes easier as concentration in solution increases. Hence, at low concentration, it is possible that the solute molecules meet competition with molecules of the solvent, for the surface support sites [22]. At high concentration, the presence of one plateau indicates the adsorption of only one main molybdenum species, possibly the molybdophosphate anion.

3.2.3. Silica

Figure 1(c) shows the adsorption isotherm of $H_3PMo_{12}O_{40}$ on silica. It is observed that C_a increases almost linearly up to a relatively high C_f value (25 mg Mo/ml). The isotherm shape characterized by a little pronounced slope indicates a weak interaction of the acid and the support. This would be due to certain covalent character of the silanol groups that prevail onto the support surface. The lower possibility of surface ionization makes MPA interaction poor, so deposits of Mo compounds on the surface are formed. The impregnation induces amorphization of these deposits [23]. The MPA adsorbed amount is high, indicating the absence of competence between solute and surface support groups, and that MPA deposits would form patches on the silica surface. The behaviour allows the assumption that the support is almost inert from the interaction point of view and it is in agreement with the IEP of pure silica that is close to 2 [24]; as a consequence, interaction of Mo compounds with the silica surface by electrostatic interaction is hindered.

The pH changes in the solutions after the contact with silica were not very important, so initial solution (120 mg Mo/ml) presented $pH = 1$ and, after the contact, $pH = 1.7$.

3.2.4. Carbon

It is generally agreed that the interaction of ions with surface groups is more complex in the case of carbon than for other carriers [25] and that the nature of the interaction between the active metal species and the surface functional groups of carbon is not well understood [26]. The interaction is influenced by the physical and chemical properties of the carbon. The latter depend upon factors such as the nature of the precursor, the carbonization conditions, surface functionality and the presence of impurities [27].

Figure 1(d) shows the adsorption isotherm of $H_3PMo_{12}O_{40}$ on activated carbon. Regarding pore structure, activated carbon usually displays a complex network of pores with various shapes although it is generally characterized by a high microporosity. The carbon used in this work presents a high surface area but the average pore diameter is of the same order as the MPA ion size. Then it can be considered that only some micropores of the surface are available for adsorption. This correlates with the fact that C_a values are comparable with those obtained on alumina, though this support presents a lower surface area with higher average pore diameter. According to the isotherm slope, the interaction of most of the deposited phase is considerably strong, though less than with alumina, in agreement with Vissers et al. [28].

The solution pH did not experience important changes during the carbon impregnation.

3.3. Solution characterization

3.3.1. UV-visible

The UV-visible spectra as a function of the contact time with TiO_2 (from 5 min to 72 h) of a solution initially containing 120 mg Mo/ml are shown as an example in figure 2. An absorption maximum at 310 nm, belonging to the O–M charge-transfer band of the molybdophosphate anion [20], was observed in the time range studied. This fact indicates the presence of only one species, the undegraded Keggin phase. All spectra corresponding to impregnating solutions in contact with alumina, silica and carbon also show the characteristic band of the $PMo_{12}O_{40}^{3-}$ species.

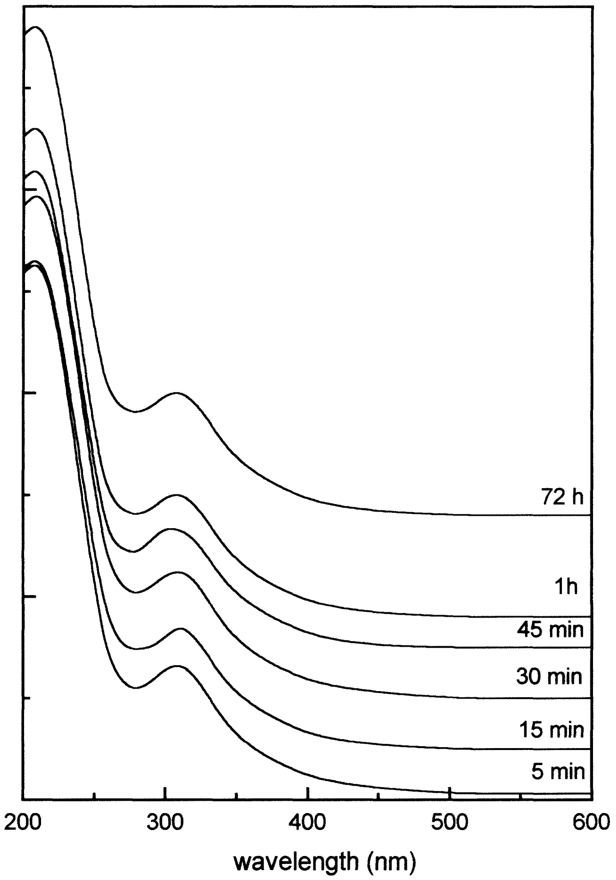

Figure 2. UV-visible spectra of initial 120 mg Mo/ml impregnating solution after the adsorption on titania at different times.

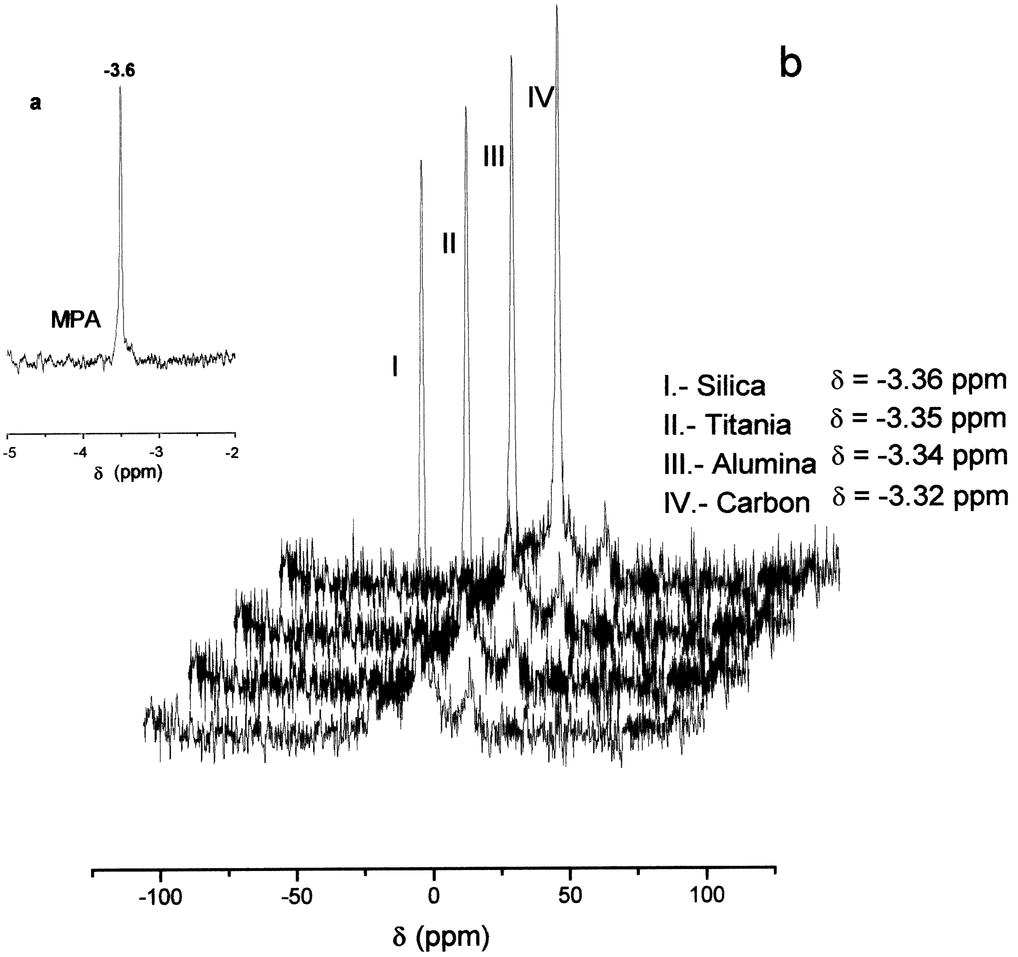

Figure 3. ^{31}P NMR spectra of MPA impregnating solutions (initial 120 mg Mo/ml) before (a) and after (b) the adsorption on silica, titania, alumina and carbon.

Table 1
Chemical shifts and assigned species of bulk and supported MPA.

Bulk MPA	MPA/A	MPA/T	MPA/S	MPA/C
−3.41	−3.25 $[PMo_{12}O_{40}]^{3-}$	−3.51 $[PMo_{12}O_{40}]^{3-}$	−3.55 $[PMo_{12}O_{40}]^{3-}$	−7.49 $[PMo_{12}O_{40}]^{3-}$
−3.83	−10.76		−4.19 $[H_2PMo_{12}O_{40}]^{-}$	

Reduction of HPA proceeds without substantial change of their structure. On reduction the HPA solutions are coloured mainly blue, producing the so-called heteropoly blues (HPB) [29]. Color variations with time were observed both in the original and final solutions; they are initially yellow and become greenish as a consequence of HPB formation.

3.3.2. NMR

The ^{31}P chemical shift (δ) provides important information concerning the species present in solution and in solid. So, the chemical shift for ^{31}P in aqueous solution at −3.9 ppm is assigned to $H_3PMo_{12}O_{40}$ and it is correlated with the P–O$_a$ bond strength (ν(P–O$_a$)) [6].

The ^{31}P NMR spectra of MPA solutions in water–ethanol with initial concentrations of 120 mg Mo/ml, both before and after the adsorption on silica, titania, alumina and carbon are shown in figure 3. The chemical shift observed in the spectrum of the initial solution is seen at −3.6 ppm and those of final solutions occur at −3.36, −3.35, −3.34 and −3.32 ppm for silica, titania, alumina and activated carbon, respectively. The ^{31}P chemical shift observed for the heteropoly anion in water–ethanol indicates that the central atom is protected by the four groups of three edge-shared MoO_6 octahedra (M_3O_{13} triad), so $PMo_{12}O_{40}^{3-}$ is neither depolymerized nor degraded as a consequence of the contact with the supports.

3.4. Solid characterization

3.4.1. NMR

Table 1 shows ^{31}P MAS-NMR chemical shifts (δ) in ppm for bulk MPA, and MPA-impregnated alumina (MPA/A, 30.0 g Mo/100 g Al_2O_3), titania (MPA/T, 17.5 g Mo/100 g

TiO_2), silica (MPA/S, 36.7 g Mo/100 g SiO_2) and activated carbon (MPA/C, 27.4 g Mo/100 g C) samples; these were obtained by equilibrium adsorption of a 120 mg Mo/ml solution during 72 h and dried at room temperature.

According to several authors, the bulk acid chemical shift is found between -2.9 and -4.8 ppm [6]. The spectrum obtained exhibits two lines, one at -3.41 and the other at -3.83 ppm, which can be assigned to the acid in different hydration levels [6].

The MPA on γ-Al_2O_3 spectrum presents lines at -3.25 and -10.76 ppm. The first chemical shift corresponds to the Keggin unit and the second one cannot be strictly assigned. A similar shift was observed by Rao et al. [12]; it may be due to MPA interacting with the support surface or partially reduced MPA [17] interacting with the support or other unidentified species. It must be pointed out that the line assigned to the lacunar anion, at -1.2 ppm, is not observed.

The spectrum of the MPA/T sample presents only one line with maximum at -3.51 ppm. This suggests that the structure of the supported molybdophosphate anion keeps intact.

For the MPA on silica sample two lines were observed: -4.19 and -3.55 ppm. Due to the characteristics of the signal, it may be proposed that the shift at -3.55 ppm is due to MPA without interaction on the silica surface and the shift at -4.19 ppm can be assigned to MPA weakly interacting with surface groups of the support [6], as the peak is notably enlarged related to the line at -3.55 ppm. On the other hand, this is in accordance with the proposal of Kasztelan et al. [15] and Mastikhin et al. [30], who concluded that three types of supported HPA are present on the silica surface: isolated or highly dispersed surface HPA at low concentrations, then aggregates or clusters are formed and, at high loadings, crystals or particles of HPA are present.

The spectrum of MPA supported on carbon shows one broad band with maximum at -7.49 ppm, which may be attributed to the $PMo_{12}O_{40}^{3-}$ species. The shift observed in this spectrum is greater than for titania and silica, but lower than for alumina. It must be pointed out that the signal broadening could indicate that the present species interacts with the support, in agreement with results in section 3.2.4 about the interaction in the system MPA/C.

3.4.2. FTIR

The oxygen atoms in MPA structure fall into four classes of symmetric-equivalent oxygens [6]: X–O_a–M_3, M–O_b–M, connecting two M_3O_{13} units by corner sharing; M–O_c–M, connecting two M_3O_{13} units by edge sharing and terminal O_d–M. The main characteristic features of bulk $H_3PMo_{12}O_{40}$ are observed at: 1064 cm^{-1} (P–O_a); 962 cm^{-1} (Mo=O_d); 869 cm^{-1} (Mo–O_b–Mo); 787 cm^{-1} (Mo–O_c–Mo); 378 and 342 cm^{-1} (bending vibrations) [31].

Samples dried at room temperature. The FT-IR spectra of MPA/T (figure 4(a)) indicate that titania presents a broad band with maxima in the 400–900 cm^{-1} zone which masks the MPA bands placed at 869 cm^{-1} and lower frequencies. Two characteristic bands of the anion (1064 and 962 cm^{-1}) are observed in the remaining zone of the spectrum, suggesting that the Keggin phase does not experience modifications in r.t. dried MPA/T sample.

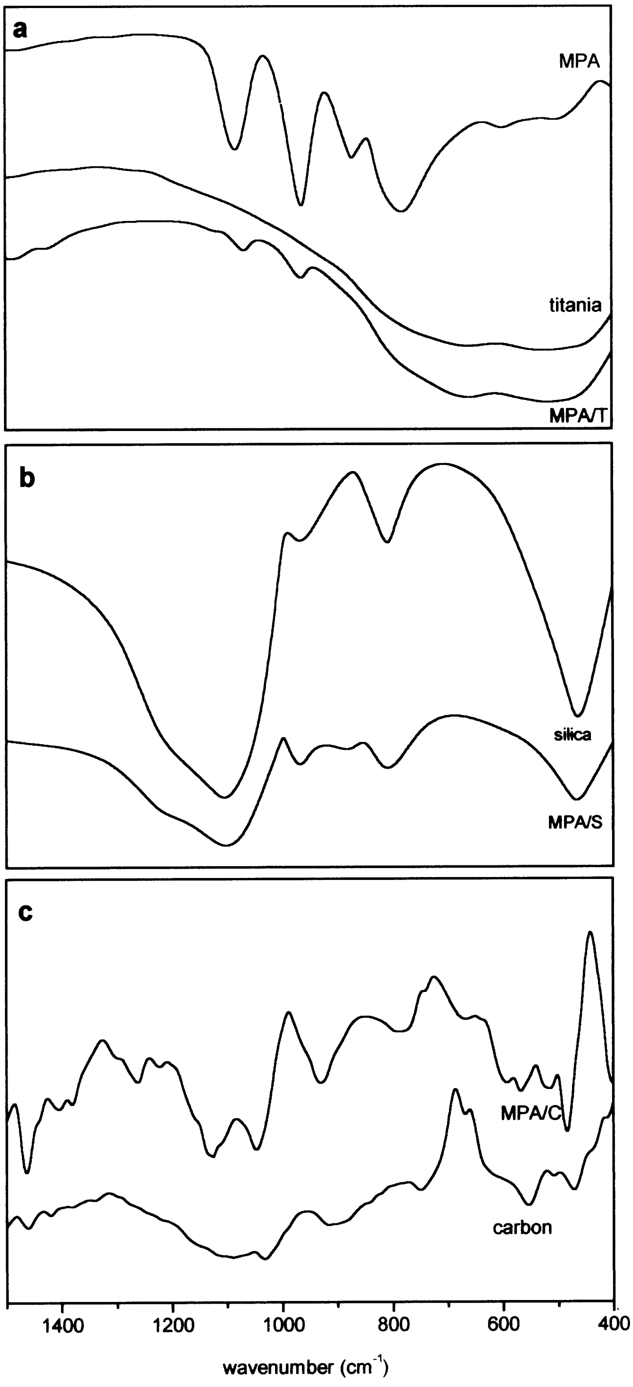

Figure 4. FT-IR spectra of bulk MPA, titania, silica, carbon and r.t. dried samples – MPA/T (a), MPA/S (b) and MPA/C (c).

As reported in literature [23], silica exhibits three main bands at 1100, 800 and 470 cm^{-1} (figure 4(b)). The MPA band placed in the 1100 cm^{-1} region of the MPA/S spectrum is masked by that of silica. Anyway, information can still be obtained from the less affected regions which show

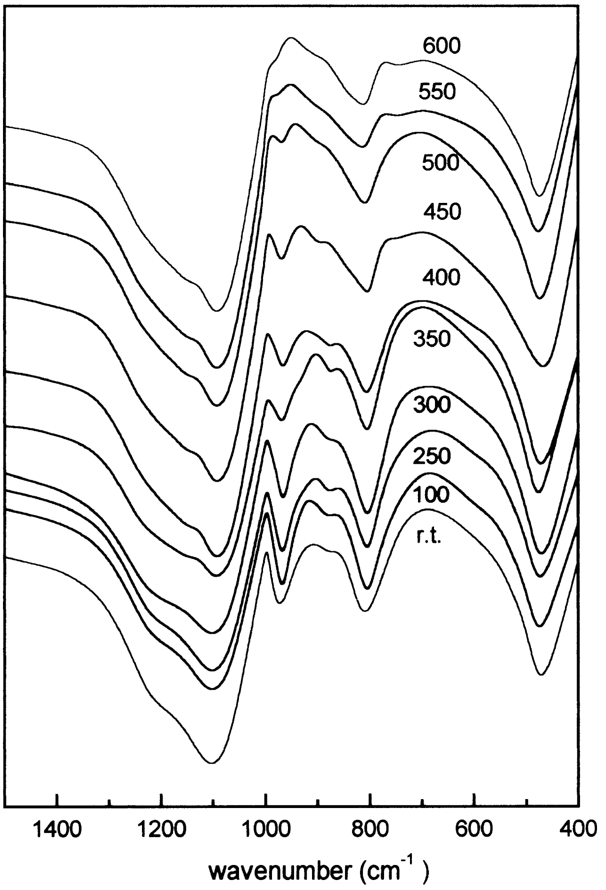

Figure 5. FT-IR spectra of MPA/S dried at r.t. and calcined at different temperatures.

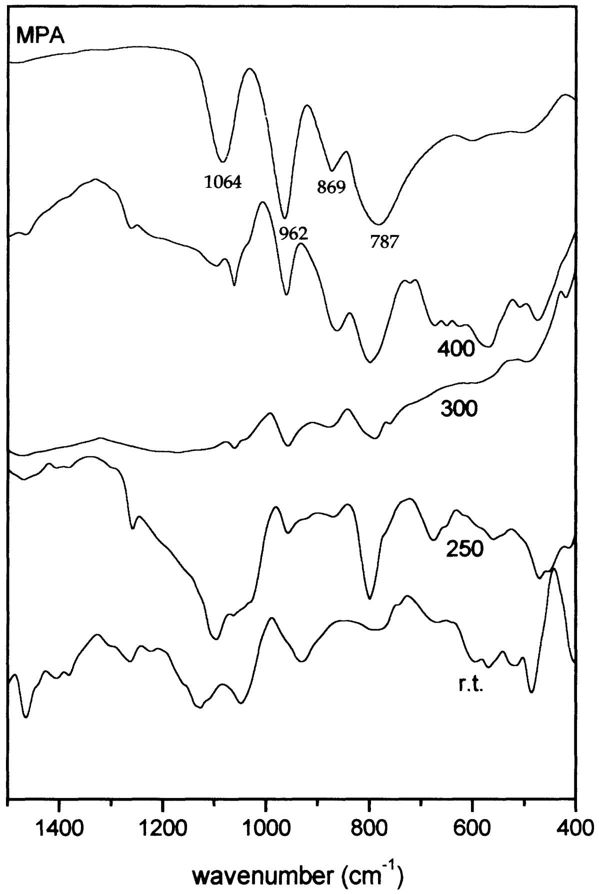

Figure 6. FT-IR spectra of MPA/C dried at r.t. and calcined at different temperatures.

an intensity increase of the band placed at 962 cm^{-1} plus a small, non-overlapped band at 869 cm^{-1} that confirm the presence of the undegraded anion.

For carbon, figure 4(c) allows us to observe that the spectrum of the sample dried at room temperature is alike that of the support. Difficulties are faced with this sample when attempting to find a well-defined spectrum [32].

Calcined samples. For bulk MPA, the typical features of the Keggin structure are observed in the FT-IR spectra at temperatures below 300 °C; only small shifts of the frequencies are seen. A strong modification can be noticed at 450 °C [33].

For the MPA/T sample calcined below 350 °C, no modifications are observed in the 1064 and 962 cm^{-1} bands, in agreement with reports by Damyanova and Fierro [34], who have observed that the 1000–900 cm^{-1} region of the spectra does not show any evidence of degradation to MoO_3 at 350 °C. The intensity of such bands decreases beyond 350 °C, becoming hardly perceptible at 400 °C because it is masked by the widening of the support band [33] or, else, it vanishes owing to the start of Keggin unit degradation.

When submitting the MPA/S sample to thermal treatment, no significant changes in the FT-IR spectra are observed for calcination temperatures below 350 °C (figure 5). However, the intensity of the bands at 869 and 962 cm^{-1} decreases and these bands disappear above 500 °C. This behaviour indicates that the Keggin phase begins its decomposition at 350 °C and the spectra obtained above 500 °C show that it becomes completely degraded to MoO_3, since a band is observed at 755 cm^{-1}, which is assigned to this compound.

For the MPA/C sample, significant changes are observed in the FT-IR spectra at 400 °C. The characteristic bands of MPA are well defined (figure 6) due to carbon degradation leading to an MPA concentration increase and to a decrease of support bands. The support degradation was evident by the appearance of ashes and weight loss.

3.4.3. DRS

The charge transfer absorption spectra of most non-reduced polyanions appear in the 200–500 nm region, and consist of bands which may be ascribed to oxygen-to-metal transfers. The tetrahedral Mo exhibits two absorption bands at 220 and 260 nm, whereas Mo in octahedral coordination presents, in addition to those bands, another band at higher wavelength.

The DRS spectrum corresponding to bulk MPA at room temperature is shown in figure 7(b). The spectra of MPA with thermal treatment up to 440 °C show that up to 350 °C the Keggin phase remains unaltered.

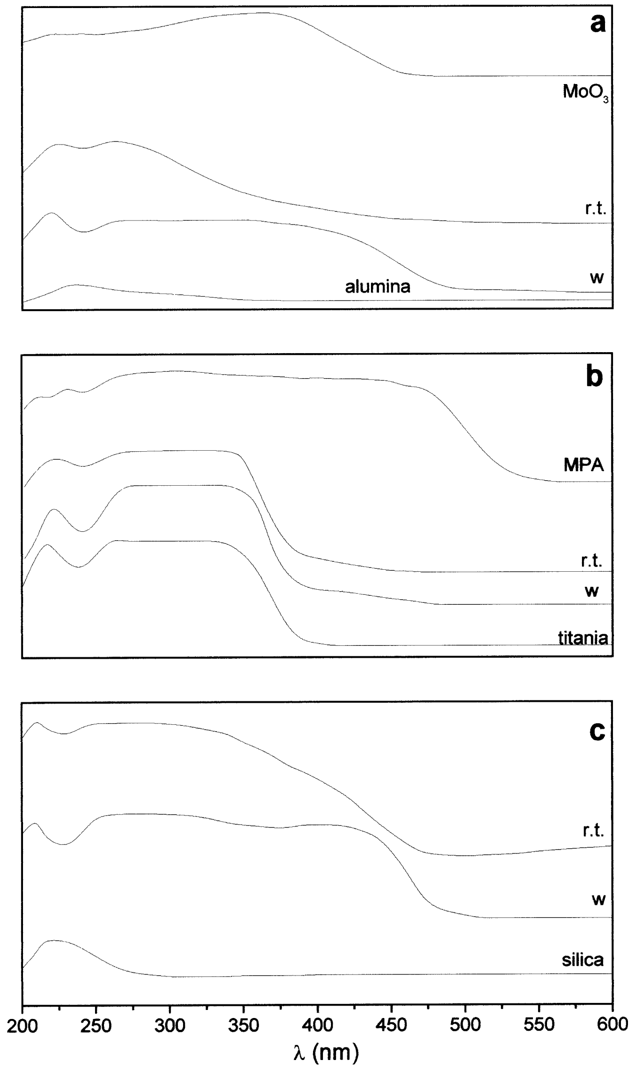

Figure 7. Diffuse reflectance spectra of bulk MPA, molybdenum oxide, titania, silica, alumina and wet and r.t. dried samples of MPA/A (a), MPA/T (b) and MPA/S (c).

Figure 7(a) shows wet and r.t. dried MPA/A sample spectra which present one band sufficiently extended that could be assigned to undegraded $H_3PMo_{12}O_{40}$. Wet and r.t. dried MPA/T sample spectra (figure 7(b)) present one band at 220 nm and another that extends up to 480 nm. Although this absorption band is partially overlapped with that of the support, which appears in the same region up to 400 nm, it can nevertheless be observed that the band extends beyond wavelengths of 400 nm, suggesting the presence of the undegraded $H_3PMo_{12}O_{40}$ species. For the wet and r.t. dried MPA/S samples, the MPA band has similar behaviour to that presented by the MPA/T system, also suggesting the presence of undegraded $H_3PMo_{12}O_{40}$ species (figure 7(c)).

It can be seen by DRS that MPA degradation in the MPA/A sample begins at 250 °C and becomes evident at 400 °C, where the spectrum characteristics are alike those of MoO_3. For the calcined MPA/T sample at 250 and 400 °C, the bands are sufficiently extended, so indicating the presence of an intact Keggin structure up to 400 °C. The spectra of the MPA/S sample calcined up to 500 °C exhibit an extended band, so it can also be assumed that the Keggin phase remains mostly undegraded. However, the changes observed in the FT-IR spectra show a partial transformation of $PMo_{12}O_{40}^{3-}$ species from 350 °C and a totally degraded Keggin structure for temperatures higher than 500 °C.

Table 2
Isopropanol conversion.

Catalyst	Isopropanol conversion (%)	Concentration (g Mo/100 g)	Specific conversion (1/mmol Mo)
Bulk MPA	7.0	63.0	2.12
MPA/A	3.8	29.55	2.47
MPA/T	3.0	17.49	3.29
MPA/S	26.9	31.83	16.12
MPA/C	4.5	30.16	2.98

3.4.4. XRD

The XRD patterns of the r.t. dried supported samples show no crystalline structure. This may be due to a high dispersion of solute on the support surface or that MPA not interacting with the support is present in amorphous form.

3.4.5. Acidity

Isopropanol dehydration. It was found that isopropanol decomposes to propene by dehydration; only traces of acetone and diisopropyl ether were detected by means of GCMS. The conversion obtained for this reaction, catalyzed by supported MPA samples dried at room temperature, are presented in table 2 together with the value obtained for bulk MPA.

The isopropanol dehydration reaction has been used to determine the acidity of various catalysts [35]. The MPA/S sample presented the highest conversion, much above that obtained when using the bulk acid. This result could be attributed to the presence of the undegraded anion in weak interaction with the support and to a sufficiently high dispersion, as it was demonstrated by the adsorption isotherm and the characterizations carried out. In MPA/T, the specific conversion is 50% higher than in the bulk acid, and it is slightly above that of MPA on carbon and Al_2O_3. In the last system, the species is partially degraded at the reaction temperature but, in spite of that, the conversion keeps comparable to that of the bulk acid because of dispersion onto the support.

Potentiometric titration. The titration curve obtained for bulk MPA, silica and MPA/S samples are shown in figure 8. As a criterion for interpreting the results obtained, it is suggested that the initial electrode potential (E) indicates the maximum acid strength of the surface sites and the range where the plateau is reached (meq/g solid) indicates the total number of acid sites [16]. The acidic strength of surface sites can be assigned according to the following scale [36]: very strong site (vs), $E > 100$ mV; strong site (s), $0 < E < 100$ mV; weak site (w), $-100 < E < 0$ mV; and very weak site (vw), $E < -100$ mV.

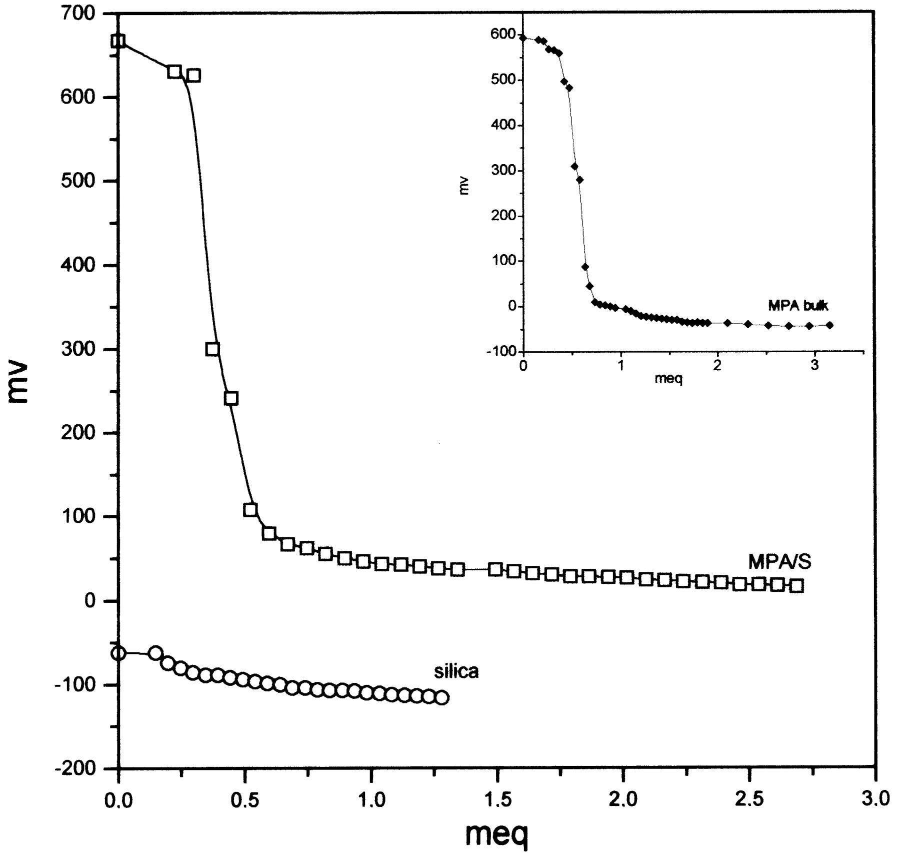

Figure 8. Potentiometric titration curve of bulk MPA, silica and MPA/S.

Table 3
Potentiometric titration results.

Sample	Maximum acid strength (mV)	Total number of acid sites (meq/g support)
Bulk MPA	593 vs	1.0
MPA/A	53 w	1.0
MPA/T	554 vs	1.2
MPA/S	667 vs	1.5
MPA/C	300 vs	1.0

The MPA/S sample presents a higher number of acidic sites and greater maximum acid strength (table 3) compared to bulk MPA, whereas the MPA/T sample behaves similarly to it. Acidity in MPA/C is even lower while MPA/A hardly presents an acidic character, but these samples present the same number as bulk MPA. This technique complements the characterization tests mentioned previously and confirms the isopropanol dehydration results, since the acidity ordering obtained by both techniques is similar. Although bulk MPA possesses the highest acid strength, this characteristic is not reflected by isopropanol dehydration results owing to the very low specific surface area.

4. Discussion

The catalytic activity of supported HPA depends on the nature of the support, species present on the solid, interaction between them and on the thermal stability; hence the importance of studying the adsorption isotherms to investigate the type of interaction presented by the MPA and each support. Also, it is important to follow posible MPA changes when using its solutions to impregnate different supports and during thermal treatments.

The species present in the impregnating solutions were characterized before and after contacting the supports. Although all ^{31}P NMR tests revealed the undegraded MPA anion as the main species, the little chemical shift variations found may be explained in terms of electron density changes around the P atom [37]. The little chemical shifts variations do not indicate the presence of any other species different from the $PMo_{12}O_{40}^{3-}$ anion, as confirmed by the UV spectra recorded for the final solutions (figure 2). It must be emphasized that water–ethanol solvent play a stabilizing role for the Keggin structure, since the $PMo_{11}O_{39}^{7-}$ species may be present in the final solutions of pH close to 2 if it is considered that the $PMo_{12}O_{40}^{3-}$ species exists in acidic aqueous solutions of pH below 1.5 [38].

Concerning the characterization of the species present on the catalysts, it should be pointed out that their FT-IR spectra confirmed the presence of the main components of the solid but not the minor species, which were not detected partly because of the strong overlap of absorption bands [38] and partly owing to the presence of the supports. There is a good correlation between FT-IR frequencies and the corresponding NMR chemical shifts. So, the occurrence of a hole, as in $PMo_{11}O_{39}^{7-}$, weakens the P–O_a bond, as shown by the change of the mean P–O_a frequencies, and induces a decrease of the δ value [37]. Therefore, by means of these techniques and by taking DRS results into account, the nature of the species adsorbed onto the solid at room temperature as well as those present after drying and calcination can be distinguished with considerable certainty.

NMR results for r.t. dried MPA/A samples provide two chemical shifts, the signal at $\delta = -10.76$ ppm would indicate a strong MPA adsorption with the Al_2O_3 hydroxyl groups, while that appearing at -3.25 ppm is ascribed to the non-interacting or weakly interacting MPA species. The band observed in the DRS spectrum obtained for the r.t. dried MPA/A sample is sufficiently extended, thus confirming the presence of $PMo_{12}O_{40}^{3-}$ species.

NMR, FT-IR and DRS results for the r.t. dried MPA/T sample indicate $PMo_{12}O_{40}^{3-}$ as the existing species. If the NMR chemical shifts of MPA/A, $\delta = -3.25$ and -10.76 ppm, are compared with that presented by the MPA/T system ($\delta = -3.51$ ppm), indicative of Keggin-structured species in weak interaction, it can be inferred that the interaction is much weaker in TiO_2. A similar conclusion was achieved on the basis of isotherm results, particularly the initial slopes. The anions react with the hydroxyl groups of the titania similarly to those of alumina, and the role played by the coordinatively unsaturated Ti^{4+} in titania is the same as that of surface Al^{3+} sites in alumina [39]. But, in titania and alumina there are some differences: the Ti^{4+} are coordinated only tetrahedrally and the hydroxyl groups are uniformly distributed on the titania surface providing a homogeneous surface for heteropoly anion adsorption unlike in alumina, where Al^{3+} ions are coordinated octahedrally and tetrahedrally, and hydroxyl groups are ordered in parallel rows [40]. This dissimilar adsorption site distribution may influence the nature of the final adsorbed species. The low amount of solute adsorbed on titania may be a consequence of the homogeneous site distribution, which decreases the accessibility of the solute to the adsorption sites.

A more complex situation is found in carbon-supported catalysts owing to the variety of oxygen functional groups present on the carbon surface. Thus, the chemical shift placed at $\delta = -7.49$ ppm of NMR spectra, whose band width results very similar to that at $\delta = -10.76$ ppm in the alumina sample, may be representative of a species in strong interaction with the support surface, though to a lesser extent compared to alumina, as can be concluded from the corresponding adsorption isotherms. The characteristics of the interaction established between the heteropoly anion and the support may be caused by MPA dispersion onto this support since active carbon surface atoms seem to influence dispersion [41]. In addition, physical properties of carbon material such as metal interaction and adsorption capacity are significant contributions to the properties of the molybdenum supported on carbon [42]. Schwegler et al. [43] assume that the interaction between HPA and carbon comes from electrostatic attraction, caused by proton transfer to the carbon. The type of bonding that causes the strong HPA adsorption is not easy to identify as chemical or physical.

Two very close NMR chemical shifts are obtained for silica that agree with those assigned by Rocchiccioli-Deltcheff et al. [23] for high loadings, i.e., (i) mere deposits of MPA microcrystals, similar to unsupported MPA (-3.55 ppm) and (ii) MPA anions interacting with the hydroxyl groups at the silica surface via formation of Si–OH_2^+ groups (-4.19 ppm). The important signal placed at -3.55 ppm would agree with the above-mentioned MPA segregation onto silica surface. The other signal would reveal the silica as a support showing a weak interaction with such heteropoly acid, as shown by the adsorption isotherm. FT-IR and DRS results indicate that the existing species in both wet and r.t. dried MPA/S sample is the $PMo_{12}O_{40}^{3-}$ anion.

For all the systems studied, no crystalline structures were observed in the DRX patterns recorded for r.t. dried samples. This would suggest a high solute dispersion onto the support surface or the presence of non-interacting MPA in a non-crystalline form.

Although various authors have studied MPA thermal stability, including some works by our group [20,33], the FT-IR and DRS characterization conducted in this work added new information, indicating deep changes from 350 °C. Protons are released at higher temperatures together with oxygen atoms from the poly anion (1.5 H_2O, usually called constitution water [31]). Destruction of the Keggin structure begins above 430 °C as evidenced by DTA [20].

Concerning the thermal stability of titania-supported MPA samples, the techniques used to characterize the catalysts revealed that the species is stable up to 400 °C.

As far as the thermal treatment of the MPA/S system is concerned, it can be pointed out that although some studies have been conducted by other authors, their results are not in complete agreement. Kasztelan et al. [15] have analyzed results of soluble MPA extraction by acetonitrile in calcined samples and stated that HPA thermal stability increases when supported on silica. Rocchiccioli-Deltcheff et al. [23] have reported that the fact of supporting MPA on silica induces a decrease in the thermal stability; transformations begin at 250 °C and a total degradation is achieved at 350 °C. In turn, the results obtained in the present work by FT-IR and DRS show that the $PMo_{12}O_{40}^{3-}$ species stays undegraded up to 350 °C, temperature above which decomposition starts; the species becomes completely degraded above 500 °C.

The thermal stability of the MPA/C system is similar to that of titania-supported MPA. However, as observed by DRS, heteropoly acid stability is much lower when using alumina support where the $PMo_{12}O_{40}^{3-}$ species begins to be degraded above 250 °C.

Catalysts acidity verified through the test reaction and potentiometric titration means that these catalysts can be used in various acidic reactions. The acidic character of the different systems is represented in decreasing order as follows: MPA/S $>$ MPA/T $>$ MPA/C $>$ MPA/A.

Acidity and interaction degree between heteropoly acid and the support are related but the interaction order is generally the opposite, i.e., the acidity decreases as the interaction gets stronger. However, the rule does not hold when comparing MPA/S and MPA/T systems. According to the adsorption isotherms, MPA interaction is stronger on silica than on titania, implying higher acidity in MPA/T, when, in fact, the opposite was observed. This particular behaviour may be due to the fact that the specific surface area, and so the acidity is lower in titania.

Thus, on the basis of the studies conducted here, it is concluded that the molybdophosphoric acid keeps its Keggin-type structure when supported at room temperature on silica, titania, carbon and alumina. On the other hand, the supported structure does not experience changes if temperatures are maintained below 350 °C, except for alumina. In this regard, the supported species stays mainly undegraded up to 250 °C for alumina, 400 °C for titania or carbon, and 500 °C for silica. Therefore, there is a wide range of conditions in which supported MPA can be used as a catalyst. These properties are of great importance in the synthesis of intermediates used to obtain fine chemical products.

Acknowledgement

The authors thank to Dr. L. Pizzio, Lic. A. Concellón, P. Villabrille, L. Osiglio and G. Valle for their experimental contribution.

References

[1] I.E. Maxwell, Cattech 1 (1997) 5.
[2] Y. Ono, in: *Perspectives in Catalysis,* eds. J.M. Thomas and K.I. Zamaraev (Blackwell, Oxford, 1992).
[3] I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311.
[4] J.F. Keggin, Proc. Roy. Soc. London A 144 (1934) 75.
[5] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269.
[6] T. Okuhara, N. Mizuno and M. Misono, in: *Advances in Catalysis*, Vol. 41, eds. D.D. Eley, W.O. Haag and B. Gates (Academic Press, New York, 1996).
[7] O. Watzenberger, Th. Haeberle, D.T. Lynch and G. Emig, in: *Studies in Surface Science and Catalysis,* Vol. 55, eds. G. Centi and F. Trifirò (Elsevier, Amsterdam, 1990).
[8] M.J. Bartoli, L. Monceaux, E. Bordes, G. Hecquet and P. Courtine, in: *Studies in Surface Science and Catalysis*, Vol. 72, eds. P. Ruiz and P. Delmon (Elsevier, Amsterdam, 1992).
[9] M. Fournier, R. Thouvenot and C. Rocchiccioli-Deltcheff, J. Chem. Soc. Faraday Trans. 87 (1991) 349.
[10] H.G. Jerschkewitz, E. Alsdorf, H. Fichter, W. Hanke, K. Jancke and G. Öhlmann, Z. Anorg. Allg. Chem. 526 (1985) 73.
[11] R. Fricke and G. Öhlmann, J. Chem. Soc. Faraday Trans. I 82 (1986) 263.
[12] K.M. Rao, R. Gobetto, A. Iannibello and A. Zecchina, J. Catal. 119 (1989) 512.
[13] J.B. Moffat and S. Kasztelan, J. Catal. 109 (1988) 206.
[14] S. Kasztelan, E. Payen and J.B. Moffat, J. Catal. 112 (1988) 320.
[15] S. Kasztelan, E. Payen and J.B. Moffat, J. Catal. 125 (1990) 45.
[16] R. Cid and G. Pecchi, Appl. Catal. 14 (1985) 15.
[17] M. Pope, *Heteropoly and Isopoly Oxometallates* (Springer, Berlin, 1983).
[18] I.V. Kozhevnikov and K.I. Matveev, Appl. Catal. 5 (1983) 135.
[19] J.B. Moffat, J. Mol. Catal. 26 (1984) 385.
[20] M. Castillo, P. Vázquez, C. Cáceres and M. Blanco, J. Chem. Soc. Faraday Trans. 92 (1996) 2997.
[21] D.S. Kim, Y. Kurusu, I.E. Wachs, F.D. Hardcastle and K. Segawa, J. Catal. 120 (1989) 325.
[22] C.H. Giles, T.H. MacEwan, S.N. Nakhawa and D. Smith, J. Chem. Soc. (1960) 3973.
[23] C. Rocchiccioli-Deltcheff, A. Aouissi, S. Launay and M. Fournier, J. Mol. Catal. A 114 (1996) 331.
[24] L. Wang and W. Hall, J. Catal. 77 (1982) 232.
[25] P. Ehrburger, Adv. Colloid Interface Sci. 21 (1984) 275.
[26] G.M.K. Abotsi and A.W. Scaroni, Carbon 28 (1990) 79.
[27] V.H.J. de Beer, F.J. Derbyshire, C.K. Groot, R. Prins, A.W. Scaroni and J.M. Solar, Fuel 63 (1984) 1095.
[28] J.P.R. Vissers, B. Scheffer, V.H.J. de Beer, J.A. Moulijn and R. Prins, J. Catal. 105 (1987) 277.
[29] E. Papaconstantinou, Chem. Soc. Rev. 18 (1989) 1.
[30] V. Mastikhin, S. Kulikov, A. Nosov, Y. Kozhevnikov, Y. Mudrakovsky and M. Timofeeva, J. Mol. Catal. 60 (1990) 65.
[31] C. Rocchiccioli-Deltcheff, A. Aouissi, M. Bettahar, S. Launay and M. Fournier, J. Catal. 164 (1996) 16.
[32] P. Vázquez, L. Pizzio, M. Blanco, C. Cáceres, H. Thomas, S. Bendezú, R. Arriagada, R. García and R. Cid, in: *Actas XVI Simposio Iberoamericano de Catálisis,* Vol. 1 (1998) p. 79.
[33] A. Concellón, P. Vázquez, M. Blanco and C. Cáceres, J. Colloid Interface Sci. 204 (1998) 256.
[34] S. Damyanova and J.L.G. Fierro, Appl. Catal. A 144 (1996) 59.
[35] J. Sonh and H. Jang, J. Mol. Catal. 64 (1983) 402.
[36] G. Pecchi, Tesis, Universidad de Concepción, Chile (1980).
[37] R. Massart, R. Contant, J.M. Fruchart, J.P. Ciabrini and M. Fournier, Inorg. Chem. 16 (1977) 2916.
[38] G.B. McGarvey and J.B. Moffat, J. Mol. Catal. 69 (1991) 137.
[39] J.A.R. van Veen, H. de Wit, C.A. Emeis and P.A.J.M. Hendriks, J. Catal. 107 (1987) 579.
[40] M. Breysse, J.L. Portefoix and M. Vrinat, Catal. Today 10 (1991) 489.
[41] J.P.R. Vissers, S.M.A. Bouwens, V.H.J. De Beer and R. Prins, Carbon 25 (1987) 485.
[42] R.S. Drago, V. Young, N. Kob, D.J. Singh and G.C. Grunewald, Micropor. Mater. 10 (1997) 51.
[43] M.A. Schwegler, P. Vinke, M. van der Eijk and H. van Bekkum, Appl. Catal. A 80 (1992) 41.