Tungstophosphoric and molybdophosphoric acids supported on zirconia as esterification catalysts

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The preparation and characterization of supported acid catalysts, based on tungstophosphoric (TPA) or molybdophosphoric (MPA) acids using ZrO_2 as support, are presented. ZrO_2 was prepared from zirconium oxychloride aqueous solutions by adding ammonium hydroxide solution. Two different techniques were used to obtain the catalysts, equilibrium adsorption and incipient wetness impregnation. The catalyst characterization allowed us to determine the species present on the carrier surface and their acidic properties. The catalytic activity for esterification of acetic acid with isoamyl alcohol of the zirconia-supported TPA catalysts was greater than that corresponding to those based on MPA. Moreover, in the preparative conditions used, the incipient wetness impregnation led to heteropolyacids supported on ZrO_2 with better catalytic performance.

KEY WORDS: catalysts; impregnation; tungstophosphoric acid; molybdophosphoric acid; zirconia; esterification; isoamyl acetate

1. Introduction

Catalysis by heteropolyacids (HPA) and related compounds is a field of increasing importance. The HPA with Keggin-type structure [1] possess special characteristics that make them very useful in catalysis [2]. These HPA are stronger acids and they have a significantly higher catalytic activity in homogeneous and heterogeneous systems compared with conventional acid catalysts as sulphuric acid, silica–alumina or ion-exchange resins, among others.

The use of HPA as catalysts is important in the development of clean technologies, since it avoids the drawbacks of environmental pollution and corrosion of the conventional technologies. Other advantages that can be emphasized are the ability of recovering and reusing them in liquid phase reactions compared to the homogeneous catalysts and the possibility of their use in continuous processes.

There are many acid reactions in which this kind of catalysts can be used, as dehydration, cyclization, alkylation, condensation, esterification and etherification [3,4], among others. This fact involves a significant importance of the HPA for certain industries related to intermediary and fine chemical synthesis, as for instance those producing fragances, flavors, pharmaceuticals, foods.

A disadvantage of bulk HPA as catalysts lies in their relatively low stability and, also, their low surface area. To minimize these disadvantages, the HPA are usually supported on a carrier. Acidic or neutral solids such as active carbon, acidic ion-exchange resin, SiO_2 and ZrO_2 are suitable as supports [4–9]. Supporting heteropolyacids on solids with high surface area is also a useful method for improving catalytic performance. However, it is necessary to consider carefully the changes in the acid strength, the structure of the aggregates and the possibility of decomposition.

The study of ZrO_2 is of interest due to its properties, which allow their use as catalyst or support. The catalytic behavior of ZrO_2 in acidic reactions depends on the preparation method, the thermal treatments and, also, the addition of certain modifiers. So, the addition of oxoanions such as sulphate or phosphate, among others, to freshly precipitated zirconia has yielded solid materials with strong acidity and catalytic properties, greater than those of the single components [10–12].

There are several papers which deal with tungstates supported on ZrO_2, using isopolytungstates as precursors. Their characterization, especially the acidic properties and, less frequently, their use as catalysts in acid reactions were studied [13,14]. Nevertheless, at the present time, ZrO_2 has been seldom used as a HPA support [7].

The nature of the support and HPA loading may have an important effect on the activity and stability of the catalysts, particularly due to the characteristics of the interaction between the HPA and the support. In a previous paper [15] we have studied the preparation and characterization of acid catalysts based on tungstophosphoric acid using diverse ZrO_2 samples as support. These carriers were prepared by means of different gelation agents and temperatures of pre-treatments.

In the present work, another study about the HPA/ZrO_2 system is reported. The behavior of the tungstophosphoric acid (TPA) and molybdophosphoric acid (MPA) when supported on zirconia, from their water–ethanol solutions, is compared. These catalysts were prepared by the equilibrium

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adsorption and the incipient wetness impregnation methods. An analysis of the nature of the species present both in the impregnating solutions and in the solids, is carried out by different characterization techniques. The aim is to observe the influence, on such species, of the preparation method and of the interaction characteristics between TPA and MPA with the zirconia. Besides, the acidic properties of the catalysts were measured by a potentiometric titration method. Results of the esterification of acetic acid with isoamyl alcohol to obtain isoamyl acetate (banana oil) are presented and their correlation with the above-mentioned parameters is discussed.

2. Experimental

2.1. Support preparation

Zirconium hydroxide gel was prepared from 0.07 M zirconium oxychloride aqueous solution by adding dropwise an ammonium hydroxide solution (25% ammonia) up to pH = 9.5. The hydrogel was aged at room temperature (r.t.) for 144 h, then filtered and washed with deionized water and finally calcined for 24 h at 310 °C (named Z hereinafter). Textural properties were determined by nitrogen adsorption/desorption technique using a Micromeritics Acccusorb 2100E equipment.

2.2. Catalyst preparation

2.2.1. Incipient wetness impregnation

Support Z was impregnated by means of the incipient wetness method with ethanol–water (e-w) solutions (50% v/v) of TPA Fluka ($H_3PW_{12}O_{40}\cdot nH_2O$) or MPA Fluka ($H_3PMo_{12}O_{40}\cdot nH_2O$), with 120 g-W(Mo)/l concentration. Then, after the filling of the pores, the samples were dried at 70 °C for 24 h, and named as Z-TPA-W and Z-MPA-W catalysts, respectively.

2.2.2. Equilibrium adsorption impregnation

The support was also impregnated by an equilibrium adsorption method at 20 °C by contacting 1 g of Z with 4 ml of a 120 g-W(Mo)/l-TPA(MPA) solution in e-w, under constant stirring during 72 h. This time was long enough to attain equilibrium of the adsorption–desorption processes. The solids were separated from the solutions by centrifugation and then dried at 70 °C for 24 h, named as Z-TPA-E and Z-MPA-E catalysts, respectively.

2.3. Solution characterization

The UV-visible spectra of TPA(MPA) solutions were obtained through a Varian Super Scan 3 UV-visible double beam spectrophotometer with built-in recorder. The W(Mo) concentration in the solutions was determined by atomic absorption spectrophotometry, using an IL model 457 double beam single channel spectrophotometer.

2.4. Solid characterization

2.4.1. Textural properties

The specific surface area (S_{BET}), the pore volume and the mean pore diameter of the catalysts were determined by nitrogen adsorption/desorption technique using a Micromeritics Acccusorb 2100E equipment.

2.4.2. X-ray diffraction

XRD patterns of the solid samples were recorded. To obtain these graphs, a Philips PW-1732 device with built-in recorder was used. Conditions were as follows: Cu Kα radiation, Ni filter, 30 mA and 40 kV in the high voltage source, scanning angle from 5° to 55° and scanning rate of 1°/min.

2.4.3. Diffuse reflectance spectroscopy

The solid samples were studied by DRS, 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.

2.4.4. Fourier transform infrared spectroscopy

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

2.4.5. Nuclear magnetic resonance spectroscopy

The solids were analyzed by ^{31}P MAS-NMR spectroscopy. For this purpose, a Bruker MSL-300 equipment was employed, using 5 μs pulses, a repetition time of 3 s and working at a frequency of 121.496 MHz for ^{31}P at r.t., the resolution being 3.052 Hz per point. Phosphoric acid 85% was the external reference. A 5 mm diameter and 10 mm in height sample holder was used, the spin rate was 2.1 kHz. Several hundred pulse responses were collected.

2.4.6. Catalyst acidity

Catalyst acidity was determined by 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. The electrode potential variation was measured with an Instrumentalia S.R.L. digital pHmeter.

2.5. Catalytic activity

The test reaction was carried out in a conventional flow fixed-bed reactor, operating at atmospheric pressure, with a solid mass of 0.5 g. The gas employed as carrier was He. The acetic acid–isoamyl alcohol mixture (1 : 1 molar ratio) volumetric flow was 0.13 ml/min in a total flow of 50 ml/min. The temperature was set at 180 °C and both the reactants and reaction products were quantified by gas chromatography, using a thermal conductivity detector. The turnover number (TON) was calculated as the ratio between moles of ester formed at 4 h of reaction and moles of HPA in the catalysts.

3. Results and discussion

3.1. Characterization of solutions

In the preparation of supported HPA as acid catalysts, the identification of the species present in the impregnating solutions is particularly important. In aqueous solutions of TPA and MPA, the $[PW_{12}O_{40}]^{3-}$ and $[PMo_{12}O_{40}]^{3-}$ anions have a limited stability range; at pH 1.5–2, they are reversibly and quickly transformed into the lacunar species $[PW(Mo)_{11}O_{39}]^{7-}$ [2]. Thus, owing to the restricted stability in aqueous solutions and bearing in mind previous reports indicating that the addition of an organic solvent has a stabilizing effect on the Keggin type heteropolyanions in solution [16], TPA and MPA solutions in e-w 50% (v/v) were used.

The UV-visible spectra of HPA solutions in e-w before the contact with the support show a band at 265 nm for TPA and at 310 nm for MPA, in agreement with Nomiya *et al.* [17]. This band may be assigned to the oxygen–metal charge-transfer band of the tungstophosphate or molybdophosphate anions, respectively. The UV-visible spectra of the initial ATP solution and those obtained at different impregnation times of the Z support with the solution of 120 g-W/l are shown in figure 1. In all the spectra, the characteristic band of the $[PW_{12}O_{40}]^{3-}$ anion is present. The decrease of the band intensity with time is due to the decrease of the solution concentration while the anion is adsorbed on the support surface. Similar results were observed for MPA solutions before and after the contact with the support. So, the stabilizing effect of ethanol–water solution as solvent compared to water [18] for preparing the impregnation solutions is verified.

Reduction of HPA proceeds without substantial change of their structure. On reduction the MPA solutions are coloured mainly blue, producing the so-called heteropoly blues (HPB) [19]. Color variations with time were observed both in the initial and final MPA solutions; they are initially yellow and become greenish as a consequence of HPB formation. Reduction in TPA solutions was not observed.

3.2. Characterization of solids

The Z support has mainly a microporous structure, with pore diameters of less than 4 nm and specific surface area of 214 m^2/g. Each Keggin anion can be inscribed into a sphere of center X and radius approximate to 0.52 nm (radius = mean of the 12 X–O_d distances, where O_d is a terminal oxygen atom and X = P in our case) [20]. So, the penetration, and later adsorption, of the Keggin anions into the pores could be sterically affected, as it was observed in a previous paper [15].

The S_{BET} of Z-TPA-W and Z-MPA-W catalysts are lower than that of the support (table 1). On the other hand, the S_{BET} also decreases when Z support is impregnated using the equilibrium adsorption method, but in this case the decrease is greater. This may be explained taking into account the different preparation methods employed to obtain the cata-

Table 1
Total HPA concentration and specific surface area of support and catalysts.

Sample	C_T (mmol-TPA(MPA)/100 g-cat)	S_{BET} (m^2/g)
Z support	–	214
Z-TPA-E	5.24	186.1
Z-MPA-E	8.10	166
Z-TPA-W	2.23	210.8
Z-MPA-W	5.73	179.6

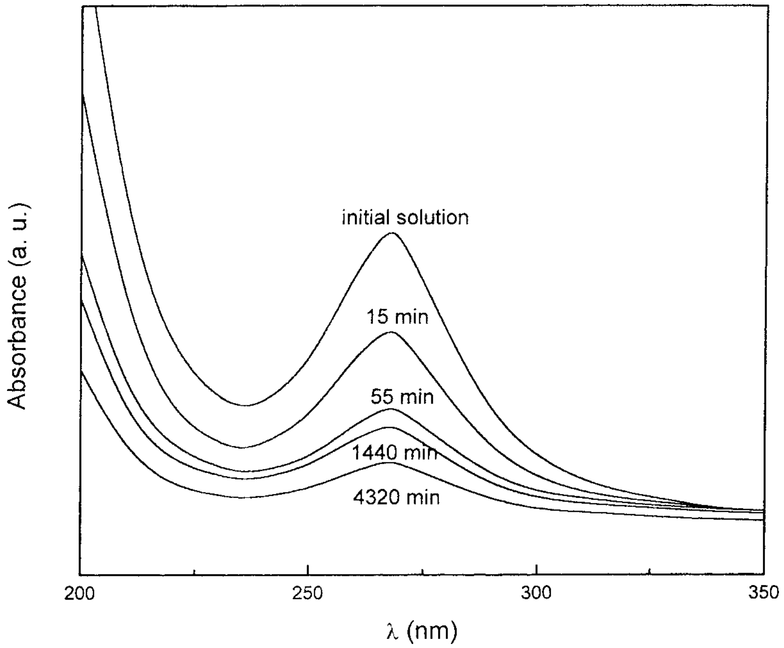

Figure 1. UV-visible spectra of the TPA ethanol–water solutions before and after the contact with zirconia up to 4320 min.

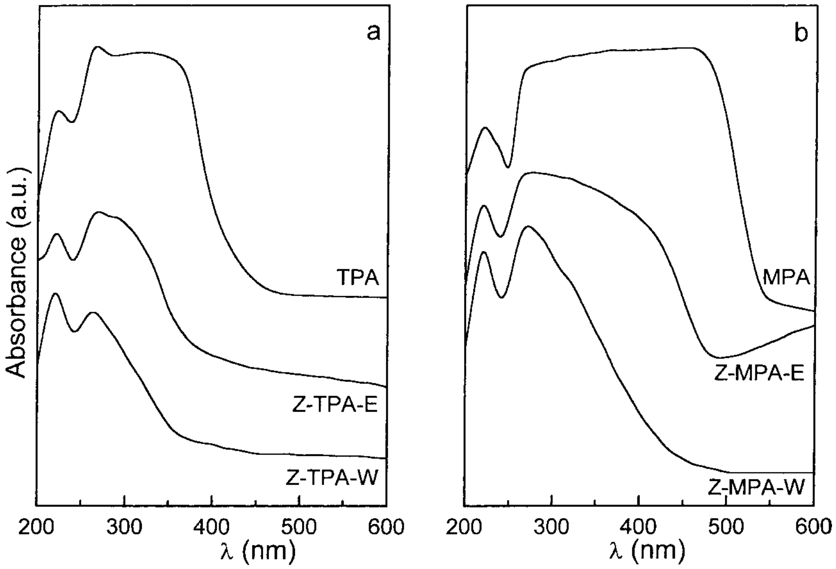

Figure 2. DRS spectra of bulk and supported TPA (a) and MPA (b).

lysts. In the incipient wetness method, the solution transport into the pores of the support is only performed by capillary action. On the other hand, in the equilibrium adsorption impregnation technique, the solute transport is the result of convective flow till the pores are filled up and then by diffusive mechanism, if there exists a solute–support interaction. This is the case for the HPA/Z system, so the greater impregnation time and impregnating solution volume involved in the equilibrium adsorption method led to an additional solute transport by diffusion. Then, the catalysts prepared by this latter technique contain a greater total solute concentration (C_T) compared to those prepared by the other method, when the same initial concentration of the impregnating solution is used. Thus the S_{BET} decrease, which may be attributed to the partial obstruction of the support pores, is more important than in the wetness impregnation. It may be pointed out that the S_{BET} changes caused by the impregnation are lower than that observed in the previous paper [15]. This is due to the lower concentration of the impregnating solutions, and the greater mean pore diameter and pore volume of the support used in the present work. These different textural characteristics were a consequence of the greater aging and washing times employed in the support preparation.

The XRD patterns of all the prepared samples are similar to that of the support. This may be a consequence of that the HPA impregnated on the support are highly dispersed like a non-crystalline form or crystallites low enough to give diffraction lines are present.

The adsorption of metallic oxoanions over oxide supports has been studied by several authors who have interpreted their results in terms of the oxide IEP (isoelectric point) [21–24]. Zirconia gel has an IEP between 6 and 7, typical of amphoterous transition oxides. Chlorine-free zirconia, prepared from n-butoxide, has an IEP of 7. The zirconia prepared from chloride precursors has always lower values of IEP, due to the presence of chloride ions retained in the gel matrix [25]; in our case the IEP is 6. This characteristic of the support surface leads to a particular interaction with the HPA, depending on the operative variables of the impregnation technique employed.

The charge transfer absorption spectra of most non-reduced polyanions obtained by DRS appear in the 200–500 nm region, and consist of bands which may be ascribed to oxygen-to-metal transfers. The Mo in octahedral coordination exhibits two absorption bands at 220 and 260 nm, whereas in the case of bulk MPA the latter band extends up to higher wavelength (530 nm) [5]. The bulk TPA spectrum presents a band at 212 nm and another broad band that extends from 250 to 450 nm [6].

The characterization of the catalysts obtained by incipient wetness impregnation (Z-TPA-W and Z-MPA-W) and equilibrium adsorption impregnation (Z-TPA-E and Z-MPA-E), carried out by DRS, showed that the spectra present a band approximately at 220 nm and another band which extends up to 400 and 490 nm for TPA- and MPA-based catalysts, respectively (figure 2). Therefore, in all cases, bands shorter than those corresponding to the bulk acids were observed. This may be a result of a possible partial degradation of the HPA when they interact with the support. However, the differences between the species present in the catalysts prepared by both methods could not be well established by this characterization technique, probably due to the fact that HPA concentrations in the samples are dissimilar (table 1).

Moreover, studies by means of FT-IR were performed. The spectrum of ZrO_2 presents a wide band with maximum between 400 and 700 cm^{-1} which extends up to 1150 cm^{-1}. For the bulk acid $H_3PW_{12}O_{40}$, the spectrum presents bands at 1081, 982, 888, 793, 595 and 524 cm^{-1} (figure 3(a)). On the other hand, the bands of the $[PW_{11}O_{39}]^{7-}$ anion are placed according to the literature at 1100, 1046, 958, 904, 812 and 742 cm^{-1} [26].

The spectra of the TPA-based catalysts are presented in figure 3(a). The Z-TPA-E solid presents bands at 1079, 981 and 888 cm^{-1}, which may be assigned to the bulk TPA,

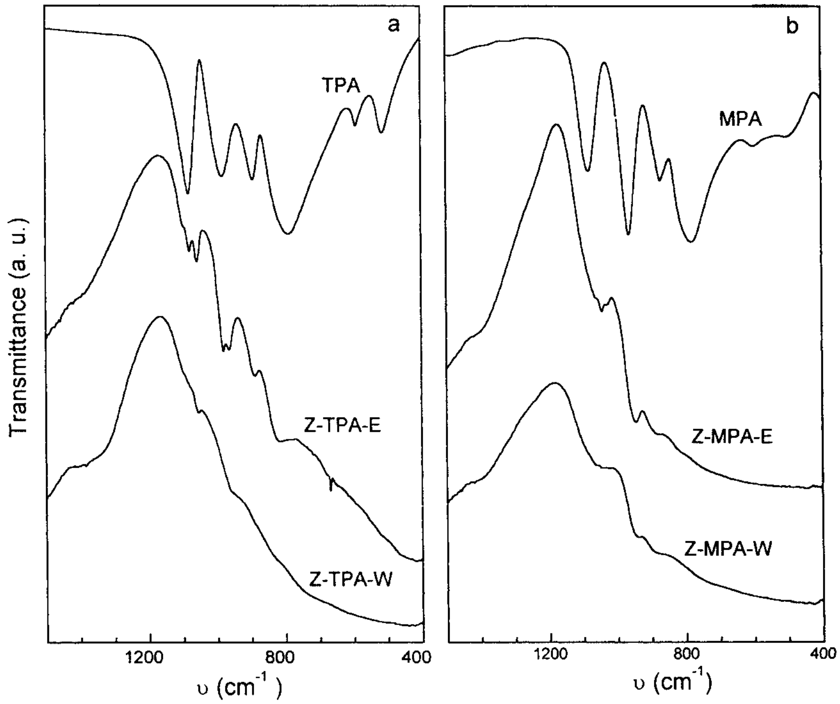

Figure 3. FT-IR spectra of bulk and supported TPA (a) and MPA (b).

and also bands at 1095, 1058, 964 and 816 cm^{-1} appear in the spectra, which may be assigned to the lacunar phase $[PW_{11}O_{39}]^{7-}$ or to dimeric species [27]. The partial transformation of the $[PW_{12}O_{40}]^{3-}$ anion into other species can take place as a result of the interaction with the support and/or the later drying process.

The main characteristic features of bulk $H_3PMo_{12}O_{40}$ are observed at 1064, 962, 869 and 787 cm^{-1} (figure 3(b)). The lacunar $[PMo_{11}O_{39}]^{7-}$ species present bands [2] at 1060, 1010, 930, 900, 860, 790 and 742 cm^{-1}.

For the Z-MPA-E catalyst, the spectrum presents a broad band with maxima at 1059, 1045 and 1021 cm^{-1} (figure 3(b)). Also, bands at 947 and 878 cm^{-1} are observed. The two maxima at 1059 and 1021 cm^{-1} could be assigned to the presence of degradated MPA Keggin species, which makes evident that, when the molybdophosphate anions interact with the zirconia at r.t., a degradation to the lacunar species begins.

The Z-TPA-W and Z-MPA-W FT-IR spectra show bands of low intensity, probably due to their low HPA concentration which favors that they are masked by the wide band of the support. As a consequence, the species present in these catalysts could not be well defined.

For a better definition of the species resulting through the interaction of both heteropolyacids with the support, wetness and in equilibrium impregnated, a study by ^{31}P MAS-NMR was performed. According to the literature [2], the bulk MPA chemical shift is found between −2.9 and −3.9 ppm and the bulk TPA chemical shift is observed between −15 and −15.6 ppm, depending on the hydration level. On the other hand, the chemical shift of the dimeric anion $[P_2W_{21}O_{71}]^{6-}$ was reported at −13.3 ppm [28], and that of the lacunar anions $[PW_{11}O_{39}]^{7-}$ at −10.4 ppm [28] and $[PMo_{11}O_{39}]^{7-}$ at −1.2 ppm [29].

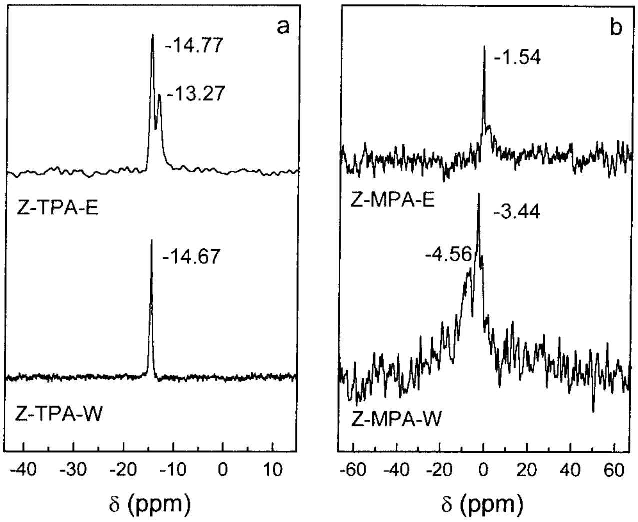

Figure 4. ^{31}P MAS-NMR of supported TPA (a) and MPA (b).

According to the recorded spectra, the r.t. dried Z-TPA-E catalyst shows (figure 4(a)) a partial transformation of the $[PW_{12}O_{40}]^{3-}$ anion (−14.8 ppm) into the dimeric $[P_2W_{21}O_{71}]^{6-}$ species (−13.3 ppm). When supporting MPA on Z using the equilibrium impregnation technique, *i.e.*, the Z-MPA-E catalyst, it can be seen (figure 4(b)) that the $[PMo_{12}O_{40}]^{3-}$ anion is completely transformed into the lacunar $[PMo_{11}O_{39}]^{7-}$ phase (−1.5 ppm) in the r.t. dried sample.

The impregnation of the HPA on zirconia by means of the incipient wetness impregnation technique led to the Z-TPA-W and Z-MPA-W catalysts that, dried at r.t., present

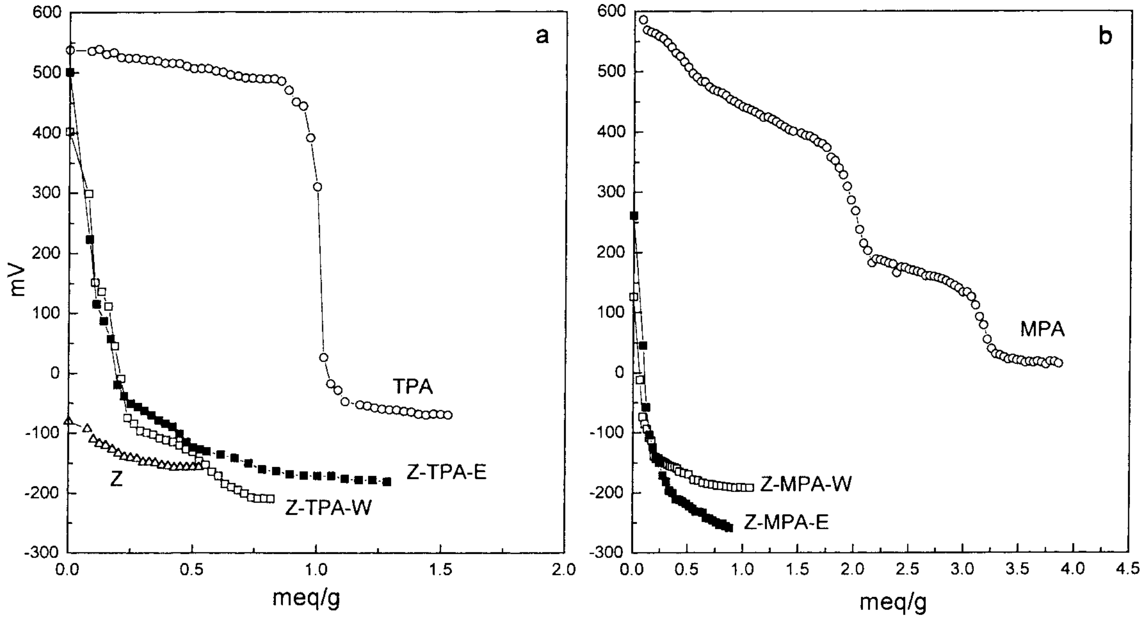

Figure 5. Potentiometric titration of bulk and supported TPA (a) and MPA (b).

spectra with the chemical shifts corresponding to the bulk acids in slight interaction or without interaction with the support (−14.7 ppm for TPA, −3.4 and −4.6 ppm for MPA) [5,6].

Then, the study of the catalysts by NMR allowed us to verify that the species present in the solid coincided with those in the impregnating solution in contact with the support only when the wetness impregnation method was used. During the equilibrium impregnation, the interaction between the $[PW(Mo)_{12}O_{40}]^{3-}$ anions and the surface hydroxyl groups of the support is greater than in the above-mentioned solids. This higher interaction degree leads to the transformation of the MPA Keggin anions into the lacunar species, and for TPA a partial degradation of the Keggin anions into dimeric species exists. The relative high value of the support IEP can favor the interaction. However, it is mainly a consequence of the excess of solution and the higher contact time between the HPA solutions and the Z support, used during the impregnation.

The acidity which presents the ZrO_2, which is a weakly acidic oxide, is modified by the subsequent impregnation, fundamentally due to the interaction of the HPA anions with the support surface groups. A potentiometric titration with n-butylamine was performed to estimate the acidity of the different systems prepared. The titration curves obtained for bulk MPA or TPA, zirconia and the different supported catalysts are shown in figure 5. As a criterion for interpreting the results obtained, it is suggested that the initial electrode potential (E) indicates the maximum acid strength of the acid sites and the value where the plateau is reached (meq/g-solid) indicates the total number of acid sites [30]. The acidic strength can be assigned according to the following scale: very strong site, $E > 100$ mV; strong site, $0 < E < 100$ mV; weak site, $-100 < E < 0$ mV and very weak site, $E < -100$ mV.

The catalysts obtained by impregnation of TPA on Z have a greater acidic strength than those based on MPA. In the case of Z-TPA-E, the initial potential value is 501 mV and for Z-TPA-W it is 402 mV, both slightly lower than that corresponding to the bulk acid (550 mV). The number of acid sites is very similar for both catalysts. For zirconia-supported MPA, the measured acid strength of Z-MPA-E is 261 mV and for Z-MPA-W 126 mV, rather lower than that corresponding to bulk MPA (573 mV), with a very low number of acid sites.

On the other hand, the HPA adsorbed concentration (C_a), determined by equilibrium adsorption, is lower for the Z-TPA system (3.78 mmol-TPA/100 g-cat) compared to that of the Z-MPA system (5.25 mmol-MPA/100 g-cat), indicating a lower TPA–support interaction than that corresponding to MPA–support. This lower TPA-Z interaction explains the different behavior of the TPA- and MPA-based catalysts because it implies a greater amount of free protons and so lead to the greater acidity observed. Besides, the acidity decrease of the HPA catalysts, compared to that of the corresponding bulk acid, is more marked for MPA. This may be attributed to the greater amount of protons engaged in the bond with the support.

Moreover, the differences in acidity between the catalysts prepared by both impregnation methods are not important. Notwithstanding, all the systems present a greater acidity than that corresponding to the support, −80 mV, which indicates that it is a weak acid oxide.

The use of the zirconia-supported HPA catalysts in the esterification of acetic acid and isoamyl alcohol showed high selectivity to the ester formation, though traces of 3-methyl-1-butene, 2-methyl-1-butene and isovaleric aldehyde were detected by means of GCMS.

The values of turnover number (TON) for the Z-supported catalysts are shown in table 2. It was observed that the

Table 2
Turnover number in the esterification of acetic acid with isoamyl alcohol.

	Catalyst					
	TPA	MPA	Z-TPA-W	Z-TPA-E	Z-MPA-W	Z-MPA-E
TON (mol-ester/mol-HPA)	6.48×10^2	2.49×10^2	1.40×10^4	7.93×10^3	6.51×10^3	3.97×10^3

catalytic activities of these supported HPA catalysts for the esterification are higher than that of bulk HPA. This could be explained taking into account that the catalytically active surface increases when the acid is dispersed on the support.

The TON values show that the catalysts based on TPA are more active than those prepared from MPA solution. These results are in agreement with the greater acidity observed for Z-supported TPA catalysts.

For this reaction, the catalysts prepared by the incipient wetness method, Z-TPA-W and Z-MPA-W, show higher TON values than the corresponding catalysts prepared by the equilibrium method, Z-TPA-E and Z-MPA-E. This behavior is mainly due to the lower species dispersion on the surface of the catalysts prepared by the equilibrium method. This is a consequence of the higher C_T in these catalysts compared with the corresponding to the catalysts obtained by the incipient wetness method, as above mentioned. Another possible reason is that the species present on these last catalysts are the Keggin anions while in the catalysts prepared by the equilibrium method a partial degradation of Keggin anions exists.

In short, in the operative conditions of preparation used in this work, the catalyst obtained by incipient wetness impregnation of zirconia with tungstophosphoric acid solution is the most active, of all the prepared catalysts, for the esterification reaction which leads to the isoamyl acetate. It is interesting to point out that this catalyst was also as active as a catalyst prepared in similar conditions but using a commercial silica as support [31].

4. Conclusions

The results showed that the zirconia-supported catalysts based on TPA are more active for the studied esterification reaction than those prepared from MPA solutions. Also, it was observed the importance in the catalyst performance of the preparation method and the operative variables involved. Particularly, it must be taken into account the impregnating solution concentration, solution volume, impregnation time, and the support textural characteristics, as pore diameter, pore volume and specific area. The incipient wetness impregnation led to HPA supported on ZrO_2 catalysts with high esterification activity and selectivity, thus obtaining an important product for flavor and fragance industries, with an ecofriendly technology. The isoamyl acetate can be used in different applications, as for instance flavor in mineral waters and syrups, perfume in diverse products, as shoe polish, and in the manufacture of materials like artificial silk and other textiles, among other uses.

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