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Tungstophosphoric and tungstosilicic acids on carbon as acidic catalysts

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Abstract

Tungstophosphoric (TPA) and tungstosilicic acid (TSA) catalysts supported on carbon were studied. They were prepared by equilibrium and incipient wetness impregnation techniques. Solutions of TPA and TSA in 50% v/v ethanol–water were used to impregnate carbon at 20°C. The Fourier transform infrared and ^{31}P nuclear magnetic resonance spectroscopies of TPA and TSA supported catalysts dried at 70°C showed that the species present were the undegraded $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$ anion, respectively. X-ray diffraction of the impregnated solids showed the same diffraction patterns as the supports, possibly owing to a high dispersion of non-crystalline species. The scanning electron microscopy with energy dispersive X-ray analysis of the supported acids showed a uniform distribution of TPA and TSA in the carbon particles with low heteropolyacid content. In the samples with high content or prepared by incipient wetness method small grains of TPA and TSA were found. These grains showed to be nearly inactive for isopropanol dehydration. The specific conversion of the catalysts for this reaction increases regularly with the increase of the adsorbed heteropolyacid content.

Keywords: Tungstophosphoric acid; Tungstosilicic acid; Keggin phase; Equilibrium impregnation; Isopropanol dehydration; Carbon

1. Introduction

The use of heteropolyacids (HPA) as catalysts for fine organic synthesis processes is developing. Synthesis of antioxidants, medicinal preparations, vitamins and biologically active substances, for instance, have been reported and some are already applied in practice [1]. Then, these catalysts are very important for industries related with fine chemicals, as flavors, pharmaceutical and food industries, among others.

Heteropolyacids are more active catalysts for various reactions in solution than conventional inorganic and organic acids. They are used as industrial catalyst for several liquid-phase reactions [2–6], as alcohol dehydration [7], alkylation [8] or esterification [9] reactions. Among heteropolyacids, polytungstic acids are the most widely used catalysts owing to their high acid strengths, thermal stabilities, and low reducibilities.

Acid and oxidation reactions catalyzed by solid heteropoly compounds (gas–solid and liquid–solid systems) can proceed via three main ways of reaction named surface, bulk type I (pseudoliquid) and bulk type II catalysis [1–3].

In pseudoliquid catalysis, large amounts of the reactants were adsorbed between the polyanions in the

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ionic crystal by replacing water of crystallization or expanding the lattice, and reaction occurs there.

In bulk type II catalysis, although the principal reaction may proceed on the surface, the whole solid bulk takes part in the reaction owing to the rapid migration into the bulk of carriers such as protons and electrons.

In surface type catalysis, the reactions take place on the internal pore and external surfaces of solid catalysts. In general, the reaction rate is proportional to the catalyst surface area.

Supporting the heteropolyacids on solids with high surface areas is a useful method for improving catalytic performance in liquid–solid and gas–solid surface heterogeneous reactions. For instance, Hu et al. [10] have used catalysts based on heteropolyacids supported on silica and alumina, with good results, for the preparation of octyl phenol and nonyl phenol, through the alkylation reaction of phenol with 1-octene and nonene, respectively. These fine chemical products were widely used as surfactants.

The catalysts based on heteropolyacids have many advantages over liquid acid catalysts. They are non-corrosive and environmentally benign, presenting fewer disposal problems. Their repeated use is possible and their separation from liquid products is easier than the homogeneous catalysts.

The nature of the interaction between the HPA and the support fundamentally depends on the central and peripheral atoms which constitute the polyanion, the support, and the HPA loading on the support. It is necessary to pay attention to the changes in the acid strength, the structures of the aggregates, and the possibility of decomposition.

Schwegler et al. [11] have described the controlled adsorption and desorption of tungstophosphoric (TPA) and tungstosilicic acids (TSA) aqueous solutions, using characterized activated carbon supports. They found that in the catalysts prepared the amount of HPA loaded onto activated carbon is much higher than the amount remaining after extraction with organic solvents or water. The observed leaching should be taken into account when using these systems as catalysts in the liquid phase.

Activated carbon has been found to be able to entrap a certain amount of heteropoly acids. The HPA thus entrapped were hardly removed even by extraction with hot water or hot methanol [12]. Entrapped catalysts have proved to be convenient for liquid-phase and vapor-phase reactions.

In a previous paper [13], it was studied the equilibrium adsorption on activated carbon of TPA and TSA, both from solutions in ethanol–water 50% v/v. It was found that the adsorption strength was higher for the former acid than it was for the latter. In the catalysts obtained the species present were the anions $[P(Si)W_{12}O_{40}]^{3(4)-}$ with undegraded Keggin structure.

This paper aims to study the interaction between TPA or TSA and carbon, in catalysts prepared by equilibrium impregnation and leached with ethanol–water solvent, and also in the samples obtained by HPA addition to the original catalysts by means of incipient wetness method. The species present in all solids have been characterized by different physicochemical techniques. Also, the catalyst activity in the isopropanol dehydration reaction has been determined.

2. Experimental

2.1. Materials

The impregnating solutions were prepared from $H_3PW_{12}O_{40}\cdot nH_2O$ TPA (BDH) and $H_4SiW_{12}O_{40}\cdot n H_2O$ TSA (Mallinckrodt), respectively. A mixture of demineralized water and ethanol 96% (Soria), in volumetric ratio 1 : 1, was used as solvent.

The support used was commercial wood-based activated carbon (C) ground to a mean particle size of 1 mm, with a surface area of 960 m^2/g, a pore volume of 0.33 cm^3/g and average pore diameter below 2 nm. Before being utilized, this material was washed first in solution of NaOH 0.1 mol/dm^3, then in HCl 0.1 mol/dm^3 to eliminate the soluble acidic and alkaline impurities. Finally, it was chemically treated in solution of HNO_3 30% w/v heated by reflux for 2 h. The treatment with nitric acid makes the carbon more acidic [11] and shifted the isoelectric point from 6.9 to 2.7.

The K level was analyzed before and after the washing, the values were 0.026 and 0.006% K w/w. So, the procedure to clean up the wood based activated carbon had bring the K level down to near zero level.

The material, after the washing and chemical treatment, presented a surface area of 806 m^2/g, a pore volume of 0.26 cm^3/g and the average pore diameter below 2 nm.

2.2. Catalysts preparation

2.2.1. Equilibrium impregnation

The catalysts based on TPA or TSA supported on carbon were obtained using the equilibrium impregnation technique. The impregnation experiments were performed at 20°C contacting 1 g of support with 4 ml of solution under constant stirring for 72 h, which was a time longer than that required to reach equilibrium in the adsorption–desorption process. This was ensured in adsorption kinetic tests previously made with solutions of TPA and TSA in concentrations of 131 and 160 mg W/cm^3, respectively. Adsorbed tungsten concentration was calculated on the basis of the decrease of tungsten concentration in the solution, by means of a mass balance and assuming no variation in the solution volume.

The initial concentration of the solutions employed here covered a range of 6–146 mg W/cm^3 for both heteropolyacids. The adsorption tests were carried out at the pH reached by the solution when dissolving each acid in ethanol–water, which approximately varied from 2.5 to 1.1 as the concentration of either HPA increased. After the selected contact time, solid and solution were separated by centrifugation for their analysis. The samples obtained were named M1P to M6P and M1S to M6S.

The tungsten concentration in the solutions, both before and after contacting the carbon (C_i and C_e, respectively), was determined by atomic absorption spectrometry. The calibration curve method was used, with standards prepared in the laboratory. The equipment used was an IL Model 457 spectrophotometer, with single channel and double beam and monochromator of 330 mm focal distance. The light source was a hollow monocathode lamp. The analyses were carried out at a wavelength of 254.9 nm, bandwidth 0.3 nm, lamp current 15 mA, phototube amplification 800 V, burner height 4 mm and acetylene–nitrous oxide flame (11 : 14).

On the other hand, it was observed that the surface area and pore volume values of the catalysts were similar to those of the support.

2.2.2. Solute removal

Samples of carbon were impregnated with TPA or TSA solutions, following the previously described technique, thus obtaining samples named M7P and M7S. A fraction of M7P and M7S samples were contacted with pure ethanol–water at 20°C, for times ranging from 30 min to 72 h. For this leaching stage, the solid/solvent ratio was the same used during the impregnation. The catalysts contacted with the solvent for 72 h were named M7PR and M7SR, for the TPA and TSA based catalysts, respectively.

2.2.3. Solute addition

Another fraction of M7P and M7S samples dried at 70°C for 24 h, were impregnated again using the incipient wetness method. Samples M8P and M8S were obtained by impregnating 1 g of M7P and M7S samples with 0.8 cm^3 of 135 mg W/cm^3 TPA solution or 0.9 cm^3 of 141 mg W/cm^3 TSA solution, respectively.

On the other hand, samples M7P and M7S were twice impregnated by the incipient wetness method, with intermediate drying at 70°C, using the same volumes and concentrations of the solutions mentioned above, thus obtaining M9P and M9S samples.

2.3. Catalyst characterization

2.3.1. Fourier transform infrared spectroscopy

Spectra of representative solid samples prepared by equilibrium impregnation and dried at 70°C for 24 h were recorded. Also, the FT-IR spectra of the removed and added catalysts were obtained. For these analysis a Bruker IFS 66 FT-IR equipment, pellets in BrK and a measuring range of 400–1500 cm^{-1} were used.

2.3.2. Nuclear magnetic resonance spectroscopy

The same solid samples based on TPA and studied by FT-IR dried at 70°C, were analyzed by ^{31}P MAS-NMR. For this purpose, a Bruker MSL-300 equipment with a sample holder of 5 mm diameter and 10 mm in height was employed, using 5 μs pulses, a repetition time of 10 s and a frequency of 121.496 MHz for ^{31}P at room temperature, being the resolution of 3.052 Hz per point and the spin rate 2.1 kHz. The repetition time was 3 s, and several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference.

2.3.3. Thermogravimetric and differential thermal analysis

The TG-DTA measurements of representative samples dried at 70°C were carried out using a Shimadzu

DT 50 thermal analyzer. The thermogravimetry and differential thermal analysis experiments were performed under argon or nitrogen, respectively, using 25–50 mg samples and a heating rate of 10°C/min. Quartz cells were used as sample holders with α-Al_2O_3 as reference. The studied temperature range was 25–700°C.

2.3.4. Temperature programmed reduction

Samples dried at 70°C (100 mg) were screened (60–100 mesh) and were subjected to TPR using a mixture of H_2 (5%) in Ar flowing at 0.09 dm^3/min. The heating rate was kept at 10°C/min until reaching a temperature of 1000°C. The amount of H_2 consumed during reduction was determined using a thermal conductivity detector.

2.3.5. X-ray diffraction

XRD patterns were recorded on the same carbon samples impregnated with solutions of TPA or TSA that had been analyzed by FT-IR. The equipment used to this end was a Philips PW-1732 with built-in recorder, using Cu Kα radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 5 and 55° of 2θ at a scanning rate of 1°/min.

2.3.6. Scanning electron microscopy

The distribution of HPA molecules over the width of the granules of carbon was measured using a Philips Model 505 scanning electron microscope with energy dispersive X-ray analysis (EDAX) system. The secondary electron micrographs of selected solid samples were obtained.

2.3.7. Isopropanol dehydration

The isopropanol (Mallinckrot AR) dehydration measurements were carried out at atmospheric pressure, in a conventional flow fixed bed reactor, using 0.5 g of the catalysts dried at 70°C. The gas employed as carrier was helium and the isopropanol volumetric flow was 0.44 cm^3/min in a total flow of 50 cm^3/min. The LHSV used was 2.3 h^{-1}. The temperature was set at 180°C and the reaction products were quantified by gas chromatography, using a TC detector. The conversion was calculated as the ratio of isopropanol consumption to the initial quantity and the specific conversion as the ratio of the conversion and the amount of HPA present in the solid. It was proved that the reaction is not diffusionally-controlled, the Thiele modulus were calculated and the values found were below 1.41, which indicate that this reaction is not diffusionally controlled [14,15].

3. Results

3.1. Equilibrium impregnation

The support was washed with NaOH and with ClH to remove the acidic and basic soluble impurities, respectively, and in this way avoid the pollution of the products and reagents.

The oxidative treatment with nitric acid makes the carbon more acidic and shifts the isoelectric point of the carbon to lower values, decreasing the possibility of decomposition of the HPA as a consequence of the interaction with the support.

The amount of tungsten adsorbed on the support, C_a (mg W/g C), was calculated through a mass balance on the basis of the difference between the initial solute concentration in the solution, C_i (mg W/cm^3), and the equilibrium or final solute concentration in the solution, C_e (mg W/cm^3), and assuming negligible variation in the solution volume. The following expression was used:

$$C_a = (C_i - C_e)VM^{-1} \quad (1)$$

where V (cm^3) is the solution volume and M (g) is the support mass.

Total tungsten concentration in the catalysts, C_t (mg W/g C), was also calculated as

$$C_t = C_a + C_r \quad (2)$$

The occluded concentration, C_r (mg W/g C), was calculated taking into account the solution volume retained in the solid, V_r (cm^3), and C_e as

$$C_r = C_e V_r M^{-1} \quad (3)$$

The C_a, C_r and C_t values for both series of catalysts are presented in Table 1.

3.2. Solute removal

Fig. 1 shows the decrease of C_t as a function of the removal time for both M7P and M7S samples, the

Table 1
C_a, C_r and C_t values for catalysts prepared by equilibrium impregnation and solute addition

Sample	TPA-carbon			Sample	TSA-carbon		
	C_a (mg W/g C)	C_r (mg W/g C)	C_t (mg W/g C)		C_a (mg W/g C)	C_r (mg W/g C)	C_t (mg W/g C)
M1P	23	–	23	M1S	34	10	44
M2P	68	1	69	M2S	52	23	75
M3P	134	5	139	M3S	71	55	126
M4P	226	30	256	M4S	134	127	261
M5P	302	72	374	M5S	148	169	317
M6P	285	156	441	M6S	201	172	374
M7P	185	89	274	M7S	172	98	270
M8P	185	220	405	M8S	172	248	420
M9P	185	330	515	M9S	172	374	546

amount of HPA removed after 1 h was equal to the C_r value. The HPA removed after this time was more firmly attached to the support.

After 48 h, the removal of HPA from the catalysts was no longer observed in an important extent.

3.3. Solute addition

Table 1 shows the C_a, C_r and C_t values for samples obtained by incipient wetness impregnation of M7P and M7S catalysts, using TPA and TSA solutions, respectively. It could be considered that the added HPA are not firmly attached to the support. The amount of tungsten added by this impregnation can be assumed to be occluded in the pores, so it was summed up to the C_r values.

3.4. Catalyst characterization

3.4.1. Fourier transform infrared spectroscopy

In a previous paper [13], it was determined that the characteristic bands of the acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ appear in the FT-IR spectra of the TPA (M6P) and TSA (M6S) samples, respectively, dried at 70°C. Calcination at 365°C produces an increase in the intensity of the bands, due to HPA

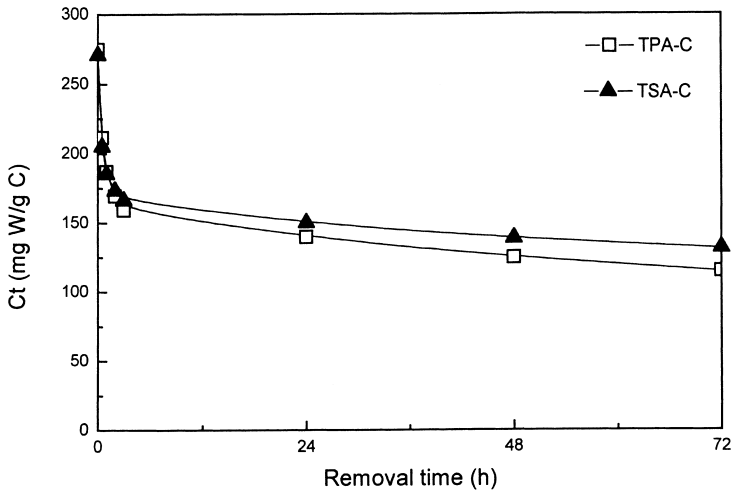


Fig. 1. Total tungsten concentration of M7P and M7S samples as a function of the removal time.

concentration increase as a consequence of carbon oxidation. The carbon degradation by oxidation was evident because the appearance of ashes and by a weight loss.

In the samples of TPA and TSA on carbon with lower tungsten content (M3P and M3S) dried at 70°C, it was observed [13] that the spectra were similar to that of the carbon used as support, owing to the fact that the low supported amount of HPA do not allow the characteristic bands of the acid to be detected. The spectra of both samples calcined at 365°C showed the characteristic bands of heteropolyacids, due to the samples at this temperature loss carbon as above-mentioned.

The results obtained confirm that the primary Keggin structure remains unaltered after the interaction with carbon, during the equilibrium impregnation of TPA or TSA from their solutions in ethanol–water, as much at low concentrations as at high amounts of the acids on the support.

FT-IR spectra of M7P, M8P and M9P TPA-samples and the corresponding TSA samples, dried at 70°C, are similar to that of M6P and M6S samples, respectively. Also, the behavior showed by these samples calcined at 365°C was similar to that previously described for the M6P and M6S samples.

3.4.2. Nuclear magnetic resonance spectroscopy

^{31}P MAS-NMR spectrum of TPA supported on carbon (sample M6P) dried at 70°C showed only one broad band with maximum at −17.1 ppm, which may be attributed to the $[PW_{12}O_{40}]^{3-}$ species. The upfield shift observed in this spectrum with respect to that of bulk TPA (maximum at −15.3 ppm) might be due to the interaction of TPA with the support, as established by Kozhevnikov et al. [16].

The spectra corresponding to the M8P and M9P samples also presented a broad band at −17.1 ppm and they were similar to that of M6P sample.

3.4.3. Thermogravimetric and differential thermal analysis

The DTA of bulk TPA shows two endothermic peaks at 65 and 189°C associated with the loss of water, and an exothermic peak at 590°C. The second endothermic peak is associated with the dehydration of $H_3PW_{12}O_{40}{\cdot}6H_2O$ phase and the exothermic one is assigned to the Keggin's anion decomposition. The TG diagram shows that the decomposition takes place without appreciable weight loss.

Rocchiccioli-Deltcheff [17] has reported that at temperatures exceeding 450°C constitutional water molecules are lost. According to Mioc et al. [18], during these processes, Keggin's anions are not disturbed too much and they are transformed at about 600°C in a new monophosphate bronze type compound PW_8O_{26}.

The DTA and TG diagram of bulk TSA are similar to the diagram of TPA acid. The endothermic peaks associated with the loss of water appear at 68 and 188°C, and the exothermic peak assigned to the Keggin's anion decomposition at 534°C.

DTA of the M7P and M7S samples showed endothermic features below 100°C similar to the DTA characteristics of the support. No other signals were observed. Apparently, the transformation of supported TPA and TSA does not involve an important thermal change as a consequence of the HPA dispersion on the support.

The same features are shown by DTA diagram of M9P and M9S catalysts prepared by incipient wetness impregnation of M7P and M7S samples, respectively.

The TG diagram of these samples show a rapid decrease of the weight below 100°C (less than 4%) and a continuous weight loss from 250 to 650°C (almost 20%). The same features were observed for the support.

On the other hand, mechanical mixtures of TPA and TSA with M7P and M7S (M9PM and M9SM samples, respectively) were also prepared, with equal concentrations as those in the M9P and M9S samples obtained by the incipient wetness method, and their DTA and TG diagrams were recorded. In M9PM sample, it was observed the endothermic peak associated with the dehydration of $H_3PW_{12}O_{40}{\cdot}6H_2O$ phase at 168°C and the exothermic peak assigned to the Keggin's anion transformation at 593°C.

The M9SM sample shows the same behavior. The endothermic peak associated with appearance of the anhydrous phase $H_4SW_{12}O_{40}$ is seen at 169°C, and the exothermic peak assigned to the Keggin's anion decomposition at 526°C.

These results allow us to suggest that the grains of TPA or TSA on the support surface of samples M9P and M9S are more dispersed than in the mechanical mixture samples.

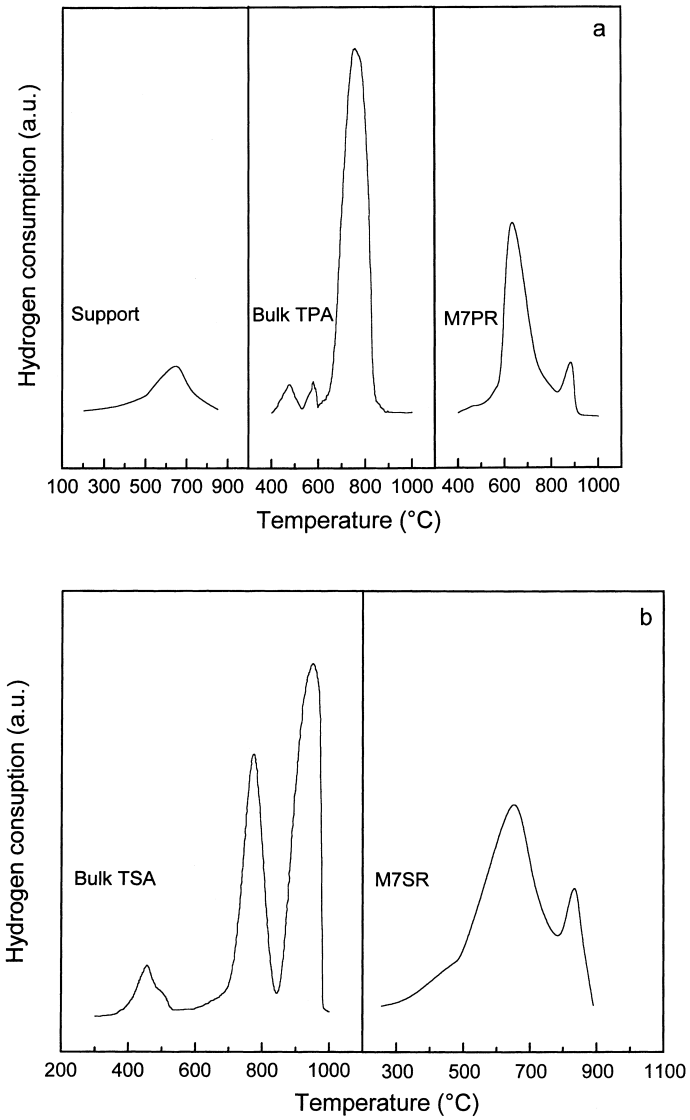


Fig. 2. TPR profiles of (a) support, bulk TPA and M7PR catalyst and (b) bulk TSA and M7SR catalyst.

3.4.4. Temperature programmed reduction

The TPR pattern of the support is shown in Fig. 2a. A broad band with a maximum at 644°C is observed. The TPR pattern of bulk TPA (Fig. 2a) presents two weak peaks at 452 and 574°C, and also a strong peak at 749°C. The weak peaks are assigned to the deprotonation of the acid with concurrent non-reductive loss of lattice oxygen [19]. The strong peak appears at a temperature higher than TPA decomposition temperature. It is probably due to extensive reduction of the constituent oxides of the decomposed acid.

The TPR pattern of bulk TSA (Fig. 2b) shows a weak peak at 440°C with a shoulder at 500°C, and two intense peaks at 764 and 926°C. As in the case of TPA, the weak peak could be assigned to the deprotonation of the acid. In this case, two peaks appear at a temperature higher than decomposition temperature of TSA. This fact indicates that the reduction beha-

vior of decomposed TSA is unlike that of the TPA acid. This is probably due to the decomposition in oxides, which reduce at different temperatures.

The TPR pattern of M7PR removed catalyst (Fig. 2a) presents a strong peak at 614°C overlapping the band of the support, and a weak peak at 892°C. The strong peak is assigned to the reduction of species adsorbed on the support. As a result of their high dispersion, these species interacting with the support, which are decomposition products of the TPA adsorbed at room temperature, are more easily reducible than the species of the decomposed bulk TPA. On the other hand, the peak at 892°C is assigned to the reduction of species with different interaction

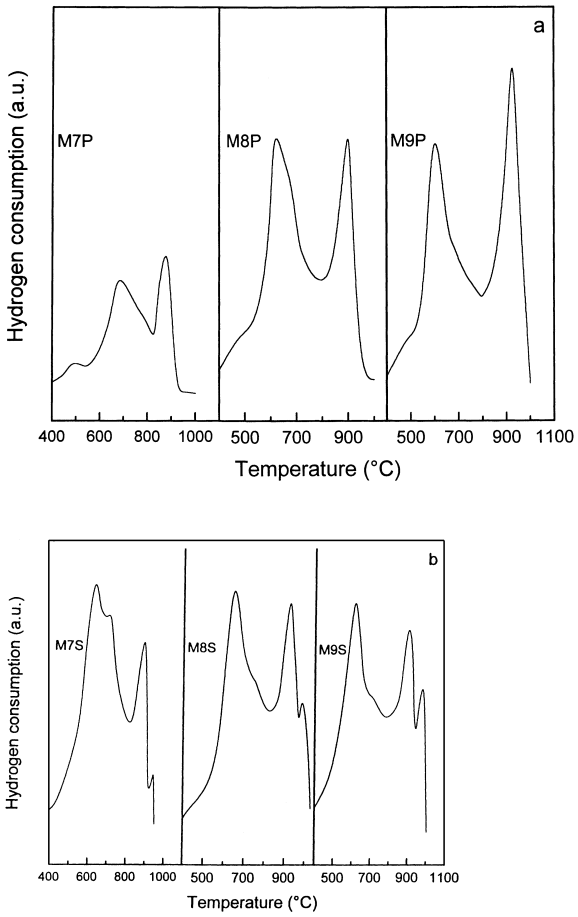
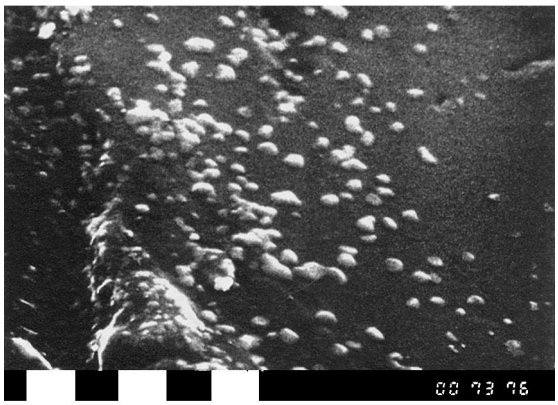
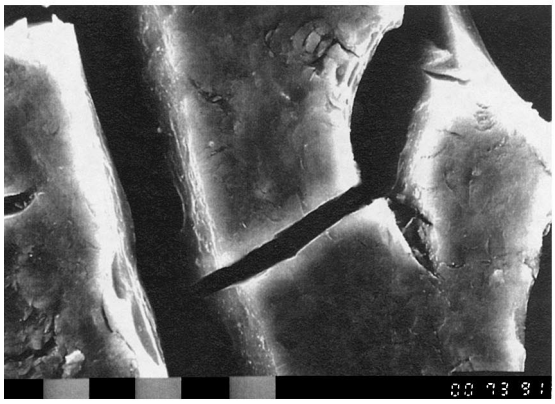


Fig. 3. TPR profiles of (a) M7P catalyst and samples with TPA added by incipient wetness impregnation and (b) M7S catalyst and samples with TSA added by incipient wetness impregnation.


(a)


(b)

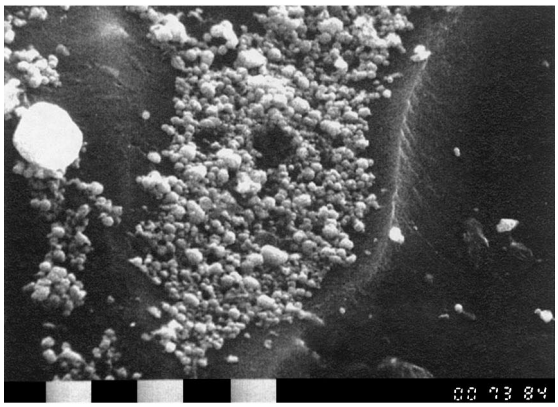

(c)

Fig. 4. Secondary electron micrograph of M7P (a), M7PR (b) and M8P (c) samples (bar size = 1 μm).

and dispersion on the support surface than the above mentioned one.

The comparison with the TPR pattern of M7P sample (Fig. 3a) shows that in the latter the intensity of the peak at 882°C increases related to the peak at lower temperature. The appearance of a shoulder at 520°C, also present in M8P and M9P samples, assigned to the deprotonation of the acid, and the noticeable increase of the peak at 882°C are the result of the increase in the amount of less dispersed species interacting with the support.

The TPR profiles of samples with TPA added by incipient wetness impregnation (M8P and M9P) are shown in Fig. 3a. For M8P sample, the TPR pattern show a increase in the intensity of both peaks. However, in the case of M9P sample, the intensity of the peak at high temperature increases and the maximum shifts toward higher reduction temperatures compared with the M7P sample. This behavior is related to the HPA grain growth when the C_r values increase, so their specific surface decreases and, as a result, the reduction becomes more difficult.

On the other hand, the TPR pattern of M7SR sample (Fig. 2b) presents a strong peak at 659°C overlapping the band of the support, and a peak at 867°C. As in the case of M7PR sample, the peaks are assigned to the reduction of species which have different interaction with the support and dispersion on its surface.

The TPR pattern of M7S sample (Fig. 3b) shows a peak at 583°C and other at 892°C. The appearance of a shoulder at 679°C and a small peak at 943°C was observed, probably as the result of the increase in the amount of species less dispersed and interacting with the support. The comparison of this pattern with the corresponding samples with TSA added by incipient wetness impregnation (M8S and M9S), shown in Fig. 3b, lets us to observe a greater intensity of the peak at higher temperature when the amount of species less firmly attached to the support increases.

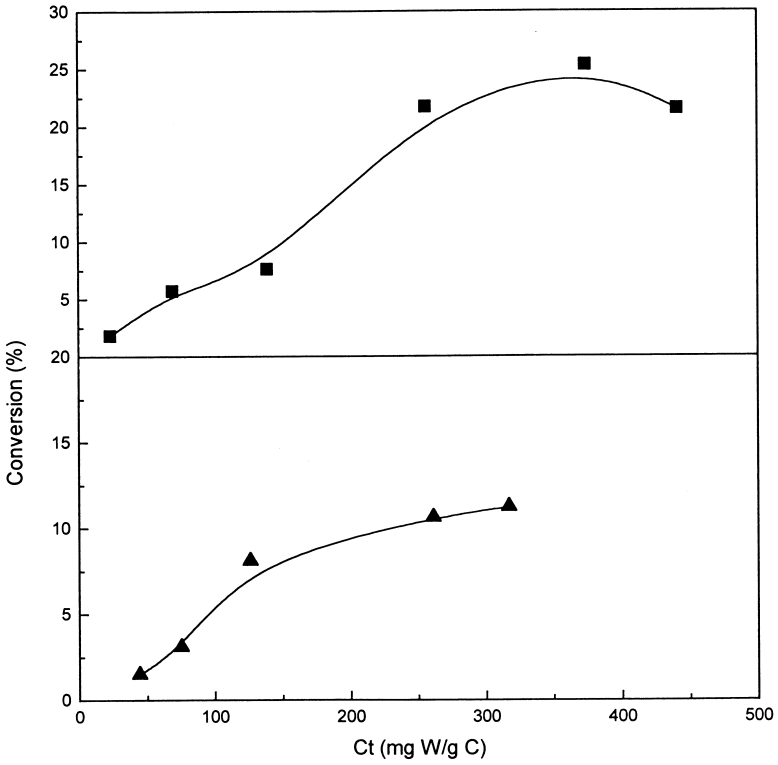


Fig. 5. Isopropanol conversion as a function of the total HPA content: TPA (■) and TSA (▲) supported catalysts.

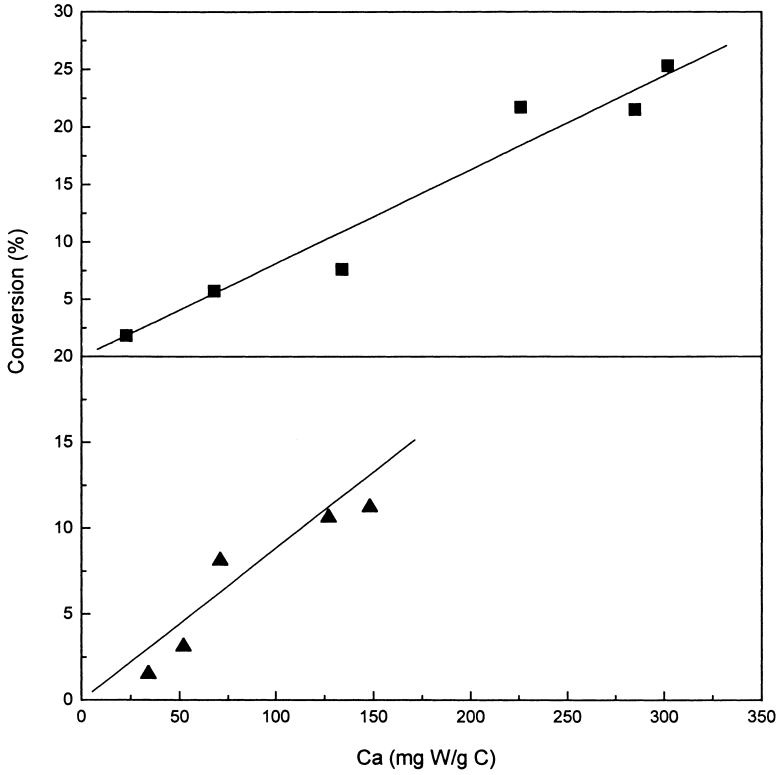


Fig. 6. Isopropanol conversion as a function of the adsorbed HPA content: TPA (■) and TSA (▲) supported catalysts.

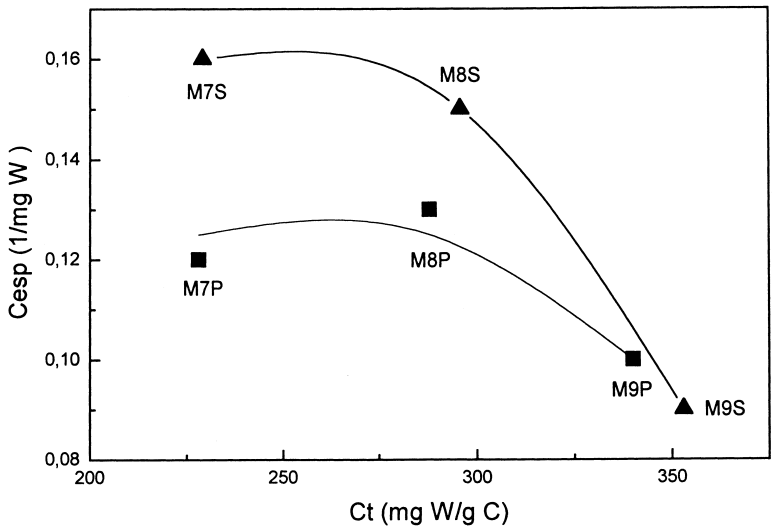


Fig. 7. Isopropanol specific conversion of samples obtained by incipient wetness impregnation of M7P and M7S catalysts.

3.4.5. X-ray diffraction and SEM-EDAX

The characteristics of XRD patterns of impregnated catalysts dried at 70°C are similar to that of the support, so neither the diffraction lines of HPA nor those of other crystalline phases were detected. From these results it can be inferred that the species present onto the support surface are highly dispersed as a non-crystalline form, because of the interaction with the support.

For the samples with low C_r values, the results obtained by EDAX show a uniform distribution of both HPA in the external surface of carbon particles. No uniform distribution is obtained in the samples with high C_r values, impregnated with TPA or TSA solutions. The secondary electron micrographs of M7P (Fig. 4a) and M7S samples show small grains of HPA on the external surface of support. These grains are not present in the removed M7PR (Fig. 4b) and M7SR catalysts.

On the other hand, the amount and size of HPA grains increase in M8P (Fig. 4c) and M8S samples as a result of the solute added by incipient wetness impregnation.

3.4.6. Isopropanol dehydration

In the working conditions used, it was found that isopropanol does not react on the bare support and it dehydrates to propene on the TPA and TSA supported catalysts, though traces of acetone and diisopropylether were detected by means of GCMS.

Fig. 5 presents the change of the conversion in the dehydration of isopropanol as a function of the total HPA content (C_t). For increasing C_t values, both TSA and TPA supported samples show a rapid increase of the isopropanol conversion until reaching an almost constant value when C_t values are close to 200 and 250 mg W/g C, respectively. However, it can be seen (Fig. 6) that the isopropanol conversion increases regularly with the increase of the adsorbed HPA content (C_a).

The specific conversion (C_{esp}) of samples obtained by incipient wetness impregnation of M7P and M7S catalysts, show a trend to decrease with the increase of C_t (Fig. 7) fundamentally for samples with C_t greater than 290 mg W/g C. Those samples have the same C_a value. So, we can suggest that the HPA that was added by incipient wetness impregnation is nearly inactive for isopropanol dehydration at 180°C.

4. Discussion

The acid activity of catalysts based on tungstophosphoric and tungstosilicic acids supported on carbon depends on the preparation technique and the different operative variables, since they both determine the nature of the HPA species present on the surface, their concentration, their dispersion and their interaction with the support.

During the impregnation of carbon with the heteropolyacids, from their ethanol–water solutions, the main species in the solutions are the ions $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$, according to the results found both by UV–VIS and ^{31}P NMR spectroscopies [13], which disappear from the solution as they are adsorbed on the carbon. The strong interaction between the HPA and carbon is assumed to be of the electrostatic type due to transfer of protons to the carbon. In this regard, the adsorption behavior of TPA and TSA seems to be related to the basicity of the HPA anion. An important factor, which determine the large acid strength of the heteropolyacids having the Keggin structure, is that in heteropolyanions the negative charge is spread over large anions, then the electrostatic interaction between proton and anion is small. An additional factor is possibly the dynamic delocalizability of the charge. The change in the electronic charge caused by deprotonation may be spread over the entire polyanion unit.

The acid strength increases when central Si atom is replaced by P, that is to say when the valence of central atom increases. This order is reasonable, since the sizes of the polyanion are nearly the same; thus the interaction between the proton and polyanion would decreases as the negative charge of polyanion decreases.

The pK values of TPA in ethanol are $pK_1 = 1.6, pK_2 = 3.0, pK_3 = 4.1$ and the values corresponding to TSA are $pK_1 = 2.0, pK_2 = 3.96, pK_3 = 6.3$ [3]. Then, TSA is less strongly adsorbed because it is the weaker acid.

Protons transferred from HPA to the activated carbon may be localized on different functional groups [20]. At low pH values, groups such as hydroxyl, diol or ether can be protonated, together with other less basic groups. So, TPA (the stronger acid) could transfer protons to less basic groups and, as a result, a higher C_a value is observed.

On the other hand, we have proved by FT-IR and ^{31}P NMR-MAS spectroscopies that the acids $H_3PW_{12}O_{40}$

and $H_4SiW_{12}O_{40}$ retain their Keggin-type structure when supported from ethanol–water solutions on carbon.

Izumi et al. [12] have found that the amount of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ firmly entrapped on activated carbon can be determined by extraction.

The amount of HPA dissolved out from samples obtained by equilibrium adsorption, after a short period of leaching with ethanol–water, is equal to C_r. On the basis of this result it is possible to assume that the HPA occluded concentration (C_r) is weakly attached to the support.

After 48 h of removal, the supported acids are not appreciably dissolved, so they can be used as catalysts in both liquid phase and vapor phase reactions with no HPA leakage.

The presence of dispersed HPA interacting with the carbon, in the sample obtained by equilibrium adsorption and subsequently washed with ethanol–water, was also observed by TPR. On the other hand, this technique allows to corroborate that in the catalysts obtained by addition of HPA to the samples obtained by equilibrium adsorption there are also TPA and TSA with different dispersion. This HPA fraction is occluded in the pores and scarcely interacting with the support.

The isopropanol dehydration has been used by several authors [21,22] as a test reaction for comparing the acidity of different catalysts and it proceeds quickly on acidic sites [22]. Isopropanol decomposition can form either propene and water (dehydration) or acetone and hydrogen (dehydrogenation). At high temperatures (300–600°C), rupture of the C–C bonds can occur to give alkanes, CO and CO_2 [23]. In the operative conditions used in the present work, the dehydration reaction takes place.

In a previous work [24], it was determined that bulk TPA presents higher isopropanol specific conversion than bulk TSA and also that the specific conversion increases when both HPA are supported on carbon.

These results are in accordance with a report by Izumi et al. [7] who established that, the catalytic activities of the heteropolyacids usually agree with the acid strength in solution. On the other hand, these author found that above 150°C, the reactions catalyzed by supported HPA take place mainly on the surface or in the outer layers of the HPA crystals, which retain little amount of water, so they form a too rigid structure that isopropanol molecules cannot penetrate.

The isopropanol dehydration takes place on the protons associated to the HPA anions. The protons engaged with the surface groups of support, lose their ability to take part in the dehydration reaction.

Bulk TPA and TSA have a low surface area (2 and 3.6 m^2/g, respectively), but when adsorbed on the support they become dispersed (samples with low C_r values), as concluded by TPR, XRD and SEM-EDAX studies, so allowing the catalytically active surface to be increased. Taking into account the mean pore diameter and the surface area of the carbon and that by FT-IR it can be seen that TPA and TSA are not degraded, they may be adsorbed as separated entities.

These facts would have to permit a better access of the isopropanol molecules towards the protons associated to the anions, so the conversion increase in parallel with the increase in the HPA adsorbed concentration C_a.

On the other hand, the HPA occluded fraction (C_r) is present as small grains on the support surface. These grains grow when the retained solute concentration increases. The HPA occluded is nearly inactive for isopropanol dehydration at 180°C, because isopropanol molecules cannot penetrate into the grains. As a result, the specific conversion decreases with the increase of the C_t in the samples with high C_r values.

5. Conclusion

The equilibrium impregnation of activated carbon with ethanol–water solutions of TPA or TSA allows to obtain, in the preparative conditions reported in this work, catalysts in which the primary Keggin structure is preserved and the adsorbed species are well dispersed on the support surface. The dispersion thus obtained leads to an increase of the total amount of catalytically active protons. The use of such catalysts in the reaction of isopropanol dehydration permits a better accessibility of isopropanol molecules to the active sites, so obtaining greater specific conversions than that of the bulk acids.

The addition of HPA by means of incipient wetness impregnation to the catalysts contributes to the appearance of a HPA fraction weakly attached to the support surface as small particles. This quantity exhibits

scarce activity as a result of the isopropanol molecule hindrance to diffuse into the particles.

It has been observed that the isopropanol dehydration is mainly catalyzed by the species adsorbed on the support surface.

The HPA present as particles are fastly removed through washing of the catalysts with ethanol–water solvent due to the low interaction with the support. The solids thus obtained, which present strongly adsorbed species on the support, can be used as catalysts in liquid phase reactions without an appreciable loss of active phase, so being attractive for many processes in replacement of conventional liquid catalysts.

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