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Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions

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Abstract

Catalysts based on Keggin-type heteropolyacids supported on silica were prepared for their use in dehydration of alcohols in liquid phase. Species present in the catalysts were characterized by diverse physicochemical techniques, disclosing that both molybdophosphoric and tungstophosphoric acids are found with their primary Keggin structure intact. Their catalytic behavior was studied in the dehydration of alcohol of interest for the production of intermediary compounds for fine chemical industries. Specifically, the dehydration of 1,2-diphenylethanol, 1-(3,4-dimethoxyphenyl)-2-phenylethanol and cholesterol was studied. It was obtained a process for the direct dehydration of cholesterol. It was found that the catalysts are very active and selective, also allowing an easy separation from the reaction medium. The same catalysts were used several times without appreciable loss of catalytic activity and after the reaction they showed physicochemical properties similar to those of the original catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Supported heteropolyacids; Silica; Alcohol dehydration; Keggin phase

1. Introduction

Alcohol dehydration reactions generally occur by heating the alcohol with a strongly acidic compound such as H₂SO₄, KHSO₄ or H₄PO₃, although other Brønsted acids and some Lewis acids have been used as catalysts [1]. The necessary conditions are usually drastic for primary alcohol (concentrated H₂SO₄, 170–180°C), milder for secondary and even more so for tertiary alcohol (H₂SO₄ 20%, 80–90°C).

It is important to develop new catalysts to replace the acids commonly used in these reactions. Among

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the advantages afforded by the use of Keggin-type heteropolyacids (HPAs) may be mentioned: greater catalytic activity as they are stronger acids, milder experimental conditions and a lower proportion of side reactions [2]. Another advantage is that no toxic wastes would be produced, thus helping to incorporate clean technologies for environmental care.

It has been observed that neutral HPA salts are entirely inactive in acid-catalyzed homogeneous reactions, so that HPA protons play a leading role in the promotion of the reaction. They are particularly effective in reactions occurring *via* intermediary protonated cations, such as carbonium cations, oxonium ions and oxocarocations. Besides, the presence of heteropolyanions as conjugated bases speeds up the reactions very efficiently, unlike the case of conventional proton acids in which the counteranion is not involved in the activation of the reactants [3].

The above-mentioned reactions may be carried out in aqueous or organic medium. In the latter case, the differences in catalytic efficiency between HPAs and conventional acids are attributable to certain qualitative dissimilarities in acidic properties. For instance, it has been observed that HPA acidity is greater than that of *p*-toluenesulfonic acid at the same concentration [4]. It is suggested that this effect is due to the lower susceptibility of HPAs to solvation by polar organic molecules compared with other conventional acids of smaller molecular size.

Baba and Ono [5] have studied 1,4-butanediol dehydration, both in aqueous solutions and in dioxane, using an HPA as catalyst. They found that the reaction is 70 times faster in the latter solvent, attributing this behavior to the inhibitory effect exerted by water.

The dehydration of alcohols of low molecular weight using HPAs as catalysts has been widely studied [6,7]. Thus, Misono and coworkers [8–10] reported the results obtained in the dehydration of ethanol. On the other hand, Baba et al. [11] presented experimental data related to the dehydration of 1-butanol. In most cases, it was observed that the activity is much greater than that of conventional solid acids as silica-alumina.

To carry out heterogeneous reactions in liquid phase, it is common that HPAs are supported on a carrier, in order to ensure high dispersion since bulk HPAs have low specific surface. The catalytic activity of supported HPAs depends on several variables,

such as carrier type, HPA concentration and pretreatment conditions. Therefore, it is necessary to perform basic studies that allow determining the effect of the different variables to obtain appropriate conditions for the preparation of supported catalysts, which are particularly useful in non-polar liquid medium reactions, where HPAs are insoluble. Furthermore, in the case of supported HPAs, catalyst recovery and reutilization is easier and the production of effluents harmful to the environment could be avoided.

Izumi and Urabe [12] used HPAs supported on activated carbon in the intermolecular dehydration of butanol and *t*-butyl alcohol in liquid phase. They proposed that carbon is an excellent carrier to entrap HPAs, so that there is no loss of active component during the reaction.

A measure of acid strength of supported HPAs may be obtained by evaluating catalytic activity in the dehydration of isopropanol in vapor phase. Vázquez et al. [13] have studied the behavior of diverse catalysts based on HPAs supported on silica, titania or alumina. They found that these catalysts present specific conversion higher than that of bulk acids. In addition, the acidity of the catalysts is related to the interaction between the solute and the support, to the species present on the carrier surface and to the support characteristics that influence the dispersion of the active component.

According to previous studies [14,15], silica proved to be a support with useful properties to obtain catalysts for acid reactions. Accordingly, this work was performed to determine the results of the preparation and characterization, by diverse physicochemical techniques, of catalysts based on HPAs supported on this carrier for dehydration reactions. In particular, the catalytic behavior of molybdophosphoric (MPA) and tungstophosphoric (TPA) acids supported on silica (S), after washing with the solvent used as reaction medium, is studied in the dehydration of 1,2-diphenylethanol, 1-(3,4-dimethoxyphenyl)-2-phenylethanol and cholesterol.

2. Experimental

2.1. Materials

Impregnating solutions were prepared from $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (Merck) or $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$

(Fluka). The solvent was a mixture of demineralized water and 96% ethanol (Soria), in a 1:1 volumetric ratio. Solution concentration employed was 120 g Mo(W)/l. The support was SiO₂ (Grace) with a specific surface area of 311 m²/g and a mean pore diameter of 3.4 nm.

2.2. Catalyst preparation

Catalysts based on MPA or TPA supported on silica were prepared using the equilibrium impregnation technique. Experiments were performed at 20°C; 1 g of support was placed in contact with 4 ml of solution under constant stirring. Contact time was 72 h, long enough to attain equilibrium of adsorption–desorption processes. Solution and solid were then separated by centrifugation and catalysts dried at room temperature for 24 h and calcined at 200°C for 3 h.

Solids thus obtained were washed with the solvent in which the reaction was carried out (chloroform or toluene) for three periods of 24 h, in a system with continuous stirring. Lastly, catalysts were thermally treated in the same conditions as before washing, and hereinafter will be termed catalysts MPA/S and TPA/S.

2.3. Quantitative analysis in solution

The concentration of molybdenum or tungsten both in impregnating solutions, before and after being in contact with the support, and in washing solutions, was determined by atomic absorption spectrophotometry. The calibration curve method was used, with standards prepared in the laboratory. The equipment used was an IL model 457 double beam single channel spectrophotometer, fitted with a 330 mm focal distance monochromator and a hollow monochromator lamp as light source. The analysis was carried out in the following conditions for W(Mo): wavelength, 254.9(313) nm; band width, 0.3(0.5) nm; lamp current, 15(7) mA; phototube amplification, 800(700) V; burner height, 4(7) mm and acetylene-nitrous oxide flame ratio, 11:14(7:14).

2.4. Catalyst characterization

2.4.1. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of SiO₂ and MPA/S and TPA/S catalysts were recorded. Spectra of bulk acids were also obtained. A Bruker IFS 66 FT-IR equipment was used, with pellets in KBr and a measuring range of 400–1500 cm⁻¹.

2.4.2. Diffuse reflectance spectroscopy (DRS)

DRS spectra of the samples mentioned in the previous item were recorded between 200–600 nm. An UV–VIS Varian Super Scan 3 spectrophotometer was used, to which a diffuse reflectance chamber was attached. The chamber presents an integrating sphere 73 mm in diameter and an internal surface of barium sulfate.

2.4.3. X-ray diffraction (XRD)

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 K α radiation; Ni filter; 30 mA and 40 kV in the high voltage source; scanning angle (2θ) from 5 to 55° and scanning rate, 1° min⁻¹.

2.4.4. Acidity measurements

Catalyst acidity was measured by means of potentiometric titration. A small quantity of 0.05N *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. Dehydration reactions

Reactions were carried out in a glass batch reactor at atmospheric pressure. Alcohol chosen to be dehydrated were dissolved in chloroform or toluene and the catalyst (0.1 meq cat/meq alcohol, otherwise stated) was added to the solution. The resulting mixture was heated to reflux and the reaction was followed by thin layer chromatography. On completion, the catalyst was separated by filtration and the solvent was removed in vacuum. Reaction products were suitably purified and identified by physical and

spectroscopic data. Catalysts separated from the reactions were washed with chloroform or toluene and dried at room temperature, prior to reutilization. Conversion was calculated as moles of alcohol transformed by every 100 mol of initial reagent and the yield for each product as number of moles of the product for every 100 mol of reagent.

A thorough study of reaction time and optimal catalyst proportion was carried out in the case of 1,2-diphenylethanol. The conversion percentage was determined by HPLC, with a Konik-500-A device, fitted with an UV detector (wavelengths: 223 nm (1,2-diphenylethanol), 296 nm (stilbene)), 5 mm × 25 cm C-18 column, 70:30 acetonitrile–water solvent, with a 2 ml/min flow rate, retention times of stilbene and of 1,2-diphenylethanol were 5.54 and 2.25 min, respectively.

3. Results and discussion

3.1. Catalyst characterization

Catalysts based on MPA and TPA acids supported on silica were prepared by means of the equilibrium impregnation technique. They were then washed with the solvent in which the reaction was carried out, in order to avoid HPA solubilization during the reaction. Thus, it is possible to observe the behavior of the supported HPAs as heterogeneous catalysts, without masking effects due to homogeneous catalysis.

MPA and TPA contents of the catalysts after leaching with chloroform or toluene were 2.6 and 1.6 mmol Mo(W)/g catalyst, respectively. In a previous report [16], adsorption isotherms of both HPAs from solutions in water-ethanol were determined on the same support used for the preparation of the present catalysts. It was observed that the amount adsorbed on the support surface was 0.8 mmol Mo/gcat and 0.3 mmol W/gcat, that is to say that even after washing, catalysts preserved a considerable fraction of both HPAs occluded in the pores of the support. This result is not coincident with the conclusions found in previous papers [17,18], in which catalysts based on both HPAs on different supports were leached using ethanol-water as sol-

vent. It was observed that a fraction of adsorbed HPA was leached, besides the HPA occluded in the support pores. Furthermore, this last behavior was verified in another previous experiments [19] carried out with the catalysts prepared in this work and leached only with water. The observed difference with respect to the catalysts leached with chloroform or toluene is due to the insolubility of the HPA in solvents of low polarity. It should be pointed out that the HPA fraction occluded in the pores of the support may be interacting more weakly and less dispersed on the surface of the support than the adsorbed fraction.

The electronic absorption spectra of most non-reduced heteropolyanions appear in the 200–500 nm region and the bands may be ascribed to ligand to metal charge transfer. Catalyst characterization by means of DRS showed that their spectra presented a pattern similar to those of bulk acids. The latter have a band at 220 nm and another that extends up to 470 nm for TPA and up to 500 nm for MPA. MPA/S and TPA/S catalysts presented this second band sufficiently extended (Fig. 1a and b), both after washing with chloroform and with toluene (lines 1 and 2, respectively), confirming that the intact Keggin-type heteropolyanions are the species mainly present.

By means of FT-IR, it may be observed that the spectra of the catalysts exhibit bands coinciding with those of bulk acids, although some overlapped with those of the support, which has bands at 1100, 800 and 470 cm^{-1} . The bulk TPA spectrum shows bands at 1081, 982, 888, 793, 595 and 524 cm^{-1} , which coincide with those referred to in the literature for the acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [20]. The first five bands are assigned to the stretching vibrations P-Oa, W-Od, W-Ob-W, W-Oc-W, and to the bending vibration Oa-P-Oa, respectively. The subscripts indicate oxygen bridging the W and the heteroatom (a), corner-sharing (b) and edge-sharing oxygen (c) belonging to octahedra WO_6 and terminal oxygen (d). For MPA, the bands were found at 1064 (P-Oa), 962 (Mo-Od), 869 (Mo-Ob-Mo), 787 (Mo-Oc-Mo), 378 and 342 cm^{-1} (bending vibrations).

The TPA/S catalyst shows the bands at 982 and 793 cm^{-1} as an increase in transmittance of support bands, while the band at 888 cm^{-1} is observed without overlapping (Fig. 2a). MPA/S shows masking in

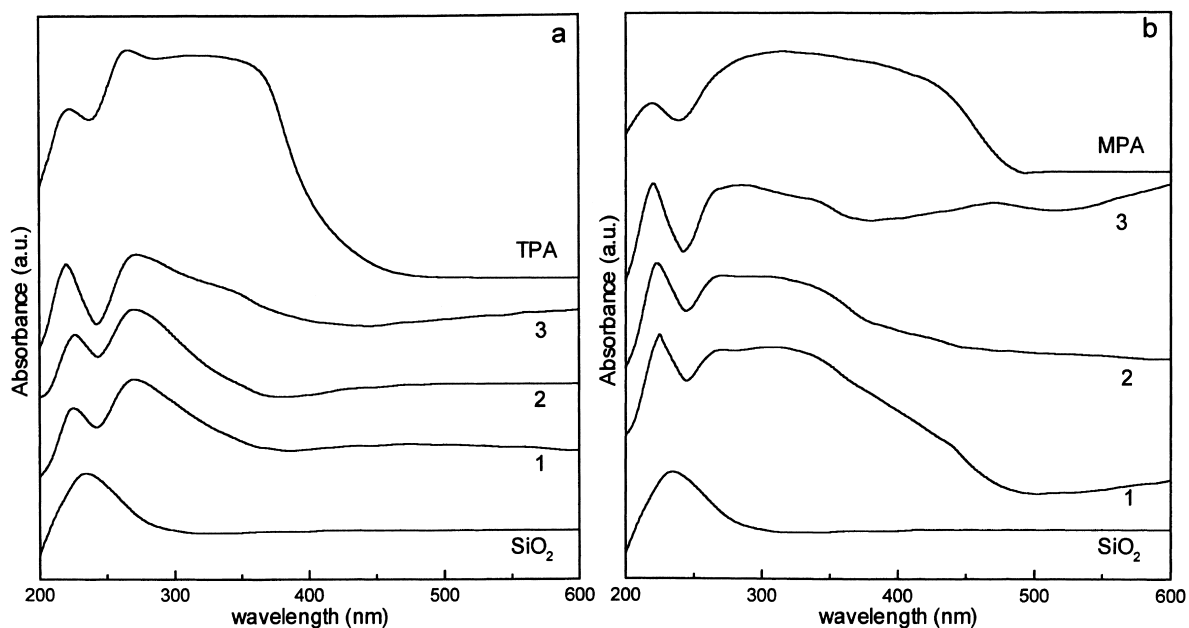


Fig. 1. DRS spectra of bulk acids and of TPA/S (a) and MPA/S (b) catalysts, washed with chloroform (1) or with toluene (2), and after being used in the reaction (3).

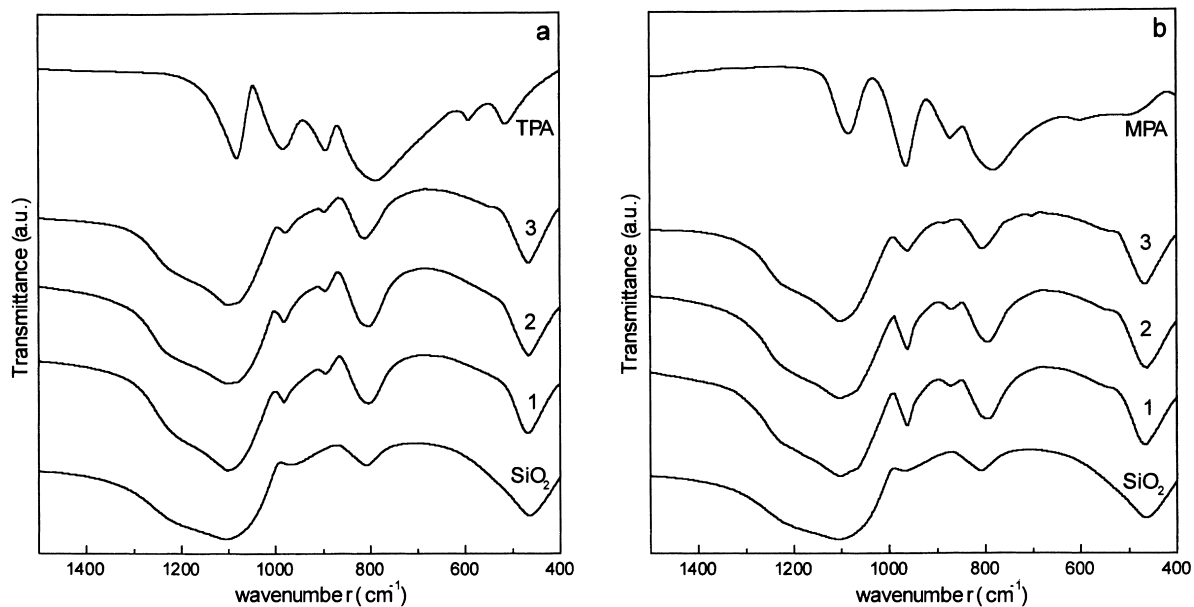


Fig. 2. FT-IR spectra of bulk acids and of TPA/S (a) and MPA/S (b) catalysts, washed with chloroform (1) or with toluene (2), and after being used in the reaction (3).

the 1100 cm^{-1} zone, the band at 962 and 787 cm^{-1} as an increase in intensity and a non-overlapping band at 869 cm^{-1} (Fig. 2b). These results corroborate those observed by DRS, that is the presence of the heteropolyacids with undegraded structure.

After their use in the reaction, catalysts were characterized by DRS and FT-IR. DRS spectra (Fig. 1a and b, line 3) show features similar to those of the original catalysts, although they present an absorbance increase in the 600 nm zone, indicative of partial Mo or W reduction. In FT-IR spectra (Fig. 2a and b, line 3), the heteropolyanion bands are observed.

XRD patterns of the catalysts are similar to that of the support, lacking diffraction lines corresponding to heteropolyanions. This indicates that the acids are highly dispersed on the support surface or present as non-crystalline species.

Also, the acidity measurements of the catalysts by means of potentiometric titration with *n*-butylamine

were carried out. This method enables the determination of the total number of acid sites and their distribution.

As a criterion for interpreting the results obtained, it is suggested that the initial electrode potential (E) indicates the maximum acid strength of the sites, and the value (meq amine/g solid) where the plateau is reached indicates the total number of acid sites [21]. The acid strength of these sites may be classified according to the following scale: $E > 100\text{ mV}$ (very strong sites), $0 < E < 100\text{ mV}$ (strong sites), $-100 < E < 0$ (weak sites) and $E < -100\text{ mV}$ (very weak sites). Fig. 3 shows that the catalysts present very strong acid sites, E in the range of 600 – 700 mV , having an acid strength considerably greater than that of the support. In the latter, an initial potential of -72 mV reaches a value of -100 mV for 0.2 meq/g , so that only weak acid sites are present. Also, the number of acid sites present in the catalysts is greater. The differences between the acid charac-

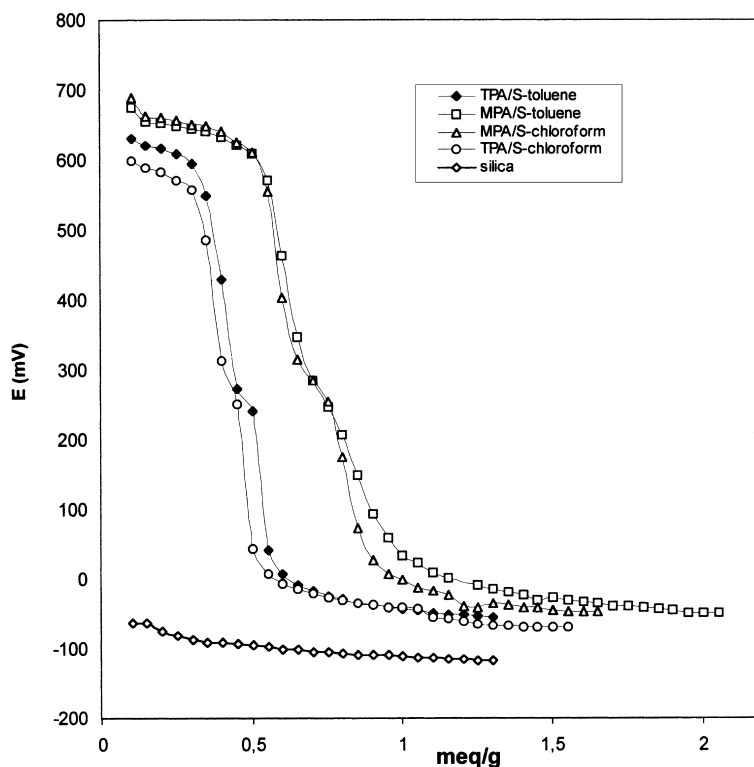


Fig. 3. Potentiometric titration of silica and TPA/S and MPA/S catalysts, washed with chloroform or with toluene.

teristics of the obtained catalysts are not appreciable, since E as well as the number of meq/mmol Mo(W) have similar values.

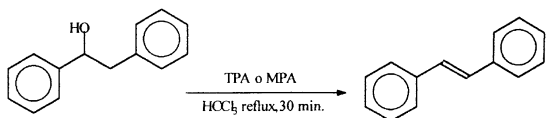
Lastly, in Fig. 3 it may be observed that the catalyst leaching with chloroform or with toluene does not affect their acidity.

3.2. Dehydration reactions

In a first stage, the chosen alcohol were secondary as 1,2-diphenylethanol, 1-(3,4-dimethoxyphenyl)-2-phenylethanol and cholesterol.

In ordinary heterogeneous catalysis of gas–solid reactions, the reactions take place on the two-dimensional surfaces of solid catalysts, both on the outer surface and on the surface of pore walls. In contrast, the reactions of polar molecules in the presence of heteropoly catalysts often proceed not only on the surface but also in the bulk phase. This is called ‘pseudoliquid phase’ behavior. Because of the flexible and hydrophilic nature of the secondary structures of the acid forms and group A salts, polar molecules like alcohols and amines are readily absorbed into the solid bulk by substituting for water molecules and/or by expanding the distance between polyanions. The rate of absorption of molecules is primarily determined by the basicity (or polarity) and secondarily by the molecular size. It was reported that the initial rates of alcohol absorption greatly decrease as the molecular size increases from 20 \AA^2 (methanol) to 35 \AA^2 (1-butanol); in the last case the rate value is close to zero [22]. This fact leads up to suppose that for the studied alcohols, due to their high molecular size, the dehydration reactions take place on the surface of solid catalysts.

Dehydration of 1,2-diphenylethanol was carried out at reflux in chloroform (61°C). It was found that the reaction is very selective when supported HPAs are used as catalysts, since only stilbene is obtained. Moreover, using both TPA/S and MPA/S catalysts only one of the two possible stereoisomers was obtained, *trans*-stilbene.

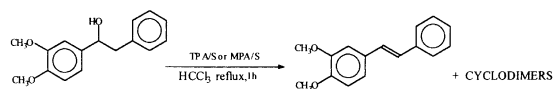


Besides, it was observed that the reaction proceeds at a very fast rate; the yield is practically quantitative in 30 min of reaction with either catalyst studied (Table 1). Nevertheless, some difference was observed at shorter times when the conversion achieved is greater with TPA/S. Quite likely, such dissimilar behavior is due to the fact that TPA is more highly dispersed on the silica surface in comparison with MPA. This is a consequence of the greater concentration of the MPA occluded within the pores of the catalyst.

Experiments have also been carried out by reducing the amount of catalyst used but this leads to lower percentage conversion (Table 2). Likewise, in this case some difference is observed in the behavior of supported TPA and MPA, achieving improved results with the former. Nevertheless, by employing 0.05 meq cat/meq 1,2-diphenylethanol, conversions only slightly higher than 50% are obtained with both catalysts.

In order to evaluate the behavior of silica-supported HPAs with respect to that of conventional acids, comparison was made with data from the literature. Thus, Noyce et al. [23] have reported similar results for the 1,2-diphenylethanol dehydration carried out in 50% sulfuric acid. Nevertheless, with the new catalysts the reaction was faster, environmentally clean and, as was performed in organic media, the compound was completely soluble.

On treating 1-(3,4-dimethoxyphenyl)-2-phenylethanol, besides the corresponding stilbene, cyclodimerization products were isolated.



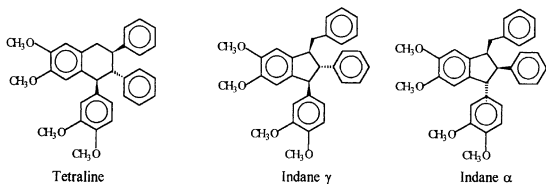
Conversion was also quantitative for this reaction, which yielded 3,4-dimethoxystilbene (12%) and cyclodimers (88%), after 1 h of reaction. The presence of electron-donor groups in the aromatic ring favors the conversion to cyclodimers. After 2 h of reaction only cyclodimers could be isolated. The mixture of cyclodimers proved to consist of 1,2,3,4-tetrahydronaphthalene (tetraline), γ -indane and α -indane in a 3:3:1 ratio. These same cyclodimers were obtained with a 41% yield by treatment of 3,4-dimethoxystil-

Table 1
Influence of reaction time on percentage conversion^a

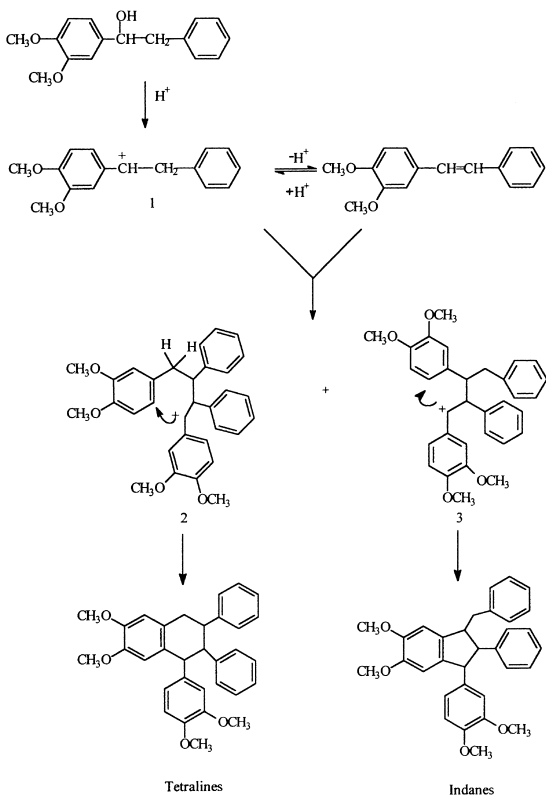
Reaction time (min)	Percentage conversion	
	TPA/S	MPA/S
15	91.9	53.9
30	99.6	99.8

^a Catalyst amount: 0.1 meq/meq alcohol.

bene with ethyl polyphosphate as catalyst at 80°C for 8 h [24].

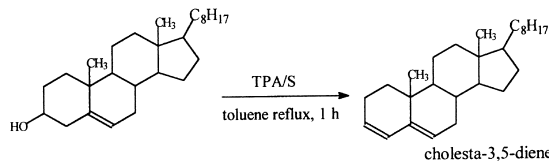


A probable mechanism for the dehydration and cyclodimerization reaction is represented in the following scheme:



The dehydration of alcohol occurs mainly on strong acid sites on catalyst surface [25], as reported by other authors [26,27]. Other studies [28] also described a dependence of the dehydration activity on strong Brönsted sites. The catalysts act as proton donors. Alcohol protonation and a water molecule release leads to the formation of carbocation **1** that transform into the corresponding stilbene by loss of a proton. In cases where at least one of the phenyl moieties is substituted by an electron-donor group, carbocation **1** may react with the stilbene giving rise to two new carbocations **2** and **3**, which induces the formation of tetralines and indanes through intramolecular aromatic electrophilic substitution, depending on aryl group substituents.

Another studied reaction was the dehydration of cholesterol in cholesta-3,5-diene, carried out at reflux in toluene (100°C) during 1 h. For this reaction, the conversion reached 70% when using either TPA/S or MPA/S. The absence of other possible dienes, such as 2,5 or 2,4, was confirmed by ¹H-NMR analysis. In the literature, there are mentioned other methods to prepare cholesta-3,5-diene, from cholesterol or *epi*-cholesterol, with similar or lower yield [29–34].



It is outstanding to point out that in each of the above reactions, the TPA/S and MPA/S catalysts were used several times without observing activity

Table 2
Influence of catalyst amount on percentage conversion^a

Catalyst amount (meq/meq alcohol)	Percentage conversion	
	TPA/S	MPA/S
0.1	99.6	99.8
0.08	94.0	60.0
0.05	56.1	52.6

^a Reaction time: 30 min.

loss. This behavior is in agreement with the characterizations carried out on the used catalysts, which show that they have similar structure and acidity to the original catalysts, previous to their utilization in the dehydration reactions.

On the other hand, no further conversion was observed in the resulting solution after the catalysts filtration at reaction temperature, then it is possible to assume that the catalytic reaction is really heterogeneous.

4. Conclusions

Equilibrium silica impregnation with TPA or MPA solutions in ethanol–water as solvent enables catalysts with undegraded primary acid structure to be obtained. Besides, it is shown that such structure remains after using the catalysts in the studied reactions.

As regards to the studies on their catalytic behavior in dehydration reactions of secondary alcohols, it was firstly found that maximal conversion in the case of 1,2-diphenylethanol is reached after 30 min of reaction with either catalyst, using 0.1 meq cat/meq alcohol. It was also observed that at briefer times conversion is greater with TPA/S than with MPA/S. Similar conversion values were previously described in the literature, but the reaction was carried out in 50% sulfuric acid. With these new catalysts, based on heteropolyacids, the reaction is faster, environmentally clean and, as the reaction is carried out in organic media, starting compound dissolution is total.

In the case of 2-(3,4-dimethoxyphenyl)-1-phenylethanol, the presence of aromatic groups substituted with electron-donor groups favors the cyclodimerization of the resulting stilbene, yielding indane- and tetraline-like structures. Such cyclodimerization is observed concomitantly with the formation of the corresponding 3,4-dimethoxystilbene. On the other hand, it was obtained a process for the direct dehydration of cholesterol.

Moreover, the possibility of catalyst reutilization and the simple reaction work-up are noteworthy advantages in comparison with traditional catalysts, as well as the raised yields.

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