

Influence of the alcohol molecular size in the dehydration reaction catalyzed by carbon-supported heteropolyacids

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The catalytic performance of tungstophosphoric and molybdophosphoric acids supported on two commercial carbons, for dehydration reactions of several alcohols, was studied. The alcohol conversion depended on their molecular size, while selectivity to alkenes was also related to cyclodimer molecular size formed by certain alkenes in acidic medium. Acidity and mean pore diameter of the catalysts showed an influence on the conversion degree of the alcohols into alkenes and also into alkene cyclodimerization.

KEY WORDS: supported catalysts; heteropolyacids; carbon; alcohol dehydration; cyclodimerization.

1. Introduction

Heteropolyacids with Keggin-type structure (HPA) have higher Brønsted acidity than conventional solid acids, so that their use is possible as catalysts in various industrial acid reactions [1]. The set of liquid phase reactions, in which HPA can be employed in place of conventional inorganic and organic acids, is quite extensive [2–8].

In previous papers [9,10], our research group showed that the catalytic activity of tungstophosphoric (TPA) and molybdophosphoric (MPA) acids for isopropanol dehydration in gaseous phase increases when HPA are dispersed on carbon.

As it was previously studied [11], and also reported in the literature [12], carbon is an excellent support to attach firmly the HPA. As a result, carbon-supported HPA will not be appreciably dissolved when used as acid catalysts in water and organic solvents. Besides, heteropolyacids supported on solids have many advantages over homogeneous catalysts, as their easy separation from liquid products, as well as their non-corrosive properties and the fact that they are environmentally benign.

The diverse biological origin of the carbon support implies a great variability in the properties required for catalyst preparation, as surface area, surface functional groups, pore shape and size distribution. The features of the interaction established between the heteropolyanion and surface functional groups exert a crucial influence on HPA dispersion [13] and on the nature of the species present on the solid surface [9]. Schwegler *et al.* [14]

assumed that the interaction between HPA and carbon is due to electrostatic attraction, caused by proton transfer to the carbon. On the other hand, catalyst pore size may affect catalytic activity due to the steric hindrance of reagents and/or products penetrating or leaving the catalyst pores. Moreover, the presence of diverse functional groups on carbon surfaces, related to the carbon origin, leads to differences in their acidity.

With regard to the conversion of alcohols into alkenes [15,16], several methods may be used. However, most of them involve the use of strong acids, high temperatures or transformations in their esters, in some cases harmful for sensitive molecules. Besides, some alkenes form cyclodimers in acidic medium, which makes it difficult to obtain them as a single product. In a previous paper [17], the catalytic performance of silica-supported TPA and MPA (TPA/S and MPA/S) in dehydration reactions of 1,2-diphenylethanol, 1-(3,4-dimethoxyphenyl)-2-phenylethanol and cholesterol, was studied. Highly satisfactory activity and selectivity results were observed. The dehydration reaction of other secondary as well as tertiary alcohols was also carried out [18]. On the other hand, the efficiency of silica-supported HPA catalysts in stilbene and styrene dimerization [19] and alkylation reactions [20] has been reported.

Taking into account the above-mentioned statements about the advantages of HPA supported catalysts, two carbons with dissimilar texture and acidity were used in the present paper, as supports for TPA and MPA. The HPA based catalysts on carbon were characterized by physicochemical techniques. The aim was to study the effect of such differences on the performance of these catalysts in dehydration reactions of several secondary alcohols with different molecular size.

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2. Experimental

2.1. Catalyst preparation

The used supports were two commercial wood-based activated carbons, named C1 and C2 hereinafter. Before being impregnated, these materials were successively washed with solutions of NaOH (0.1 mol/dm³) and HCl (0.1 mol/dm³). Then chemically treated in a solution of HNO₃ (30% w/v), heated by reflux for 2 h, and washed with distilled water up to neutral pH. Their textural features are shown in table 1.

Catalysts were prepared by pore filling impregnation with solutions of H₃PW₁₂O₄₀·*n*H₂O (Fluka) or H₃PMo₁₂O₄₀·*n*H₂O (Merck) in ethanol (Soria)-water. After impregnation, they were dried at room temperature for 24 h, and then calcined at 200 °C for 3 h. In order to assure that HPA will not become dissolved during reaction, the solids were washed with chloroform for three 24-h periods, in a system with continuous stirring and at the temperature in which the reaction will be carried out (60 °C), till any HPA leaching was observed.

Lastly, the catalysts were thermally treated in the same conditions above-mentioned and will be hereinafter named TPA/C1, TPA/C2, MPA/C1 and MPA/C2.

2.2. Quantitative analysis in solution

Molybdenum or tungsten concentrations in impregnating and washing solutions were 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 hollow monochromator lamps as light source. 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).

2.3. Solid characterization

2.3.1. Textural properties

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

2.3.2. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of solid samples were recorded using a Bruker IFS 66 FT-IR spectrometer, with pellets in KBr and a measuring range of 400–1500 cm⁻¹.

2.3.3. X-ray diffraction (XRD)

XRD patterns of solid samples were recorded. To obtain these graphs, a Philips PW-1732 device with built-in recorder was used. Conditions were as follows: CuK_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° per minute.

2.3.4. Acidity measurements

Catalyst acidity was measured by means of potentiometric titration. A known mass of solid suspended in acetonitrile was stirred for 3 h. Later, the suspension was titrated with a solution of *n*-butylamine in acetonitrile (0.05 N) at a flow of 0.05 cm³/min. The electrode potential variation was measured with an Instrumentalia S.R.L. digital pH meter. It must be pointed out that another organic solvents were tested, but acetonitrile was found to be one of the more suitable solvent.

2.4. Dehydration reactions

Reactions were carried out in a glass batch reactor at atmospheric pressure. The alcohol chosen to be dehydrated (0.3 meq) was dissolved in chloroform (3 × 10⁻³ dm³) and the catalyst (molar ratio *R* = 0.10 or 0.15 meq HPA/meq alcohol) added to the solution. The resulting mixture was heated to reflux (60 °C) and the reaction followed by thin layer chromatography. This technique was carried out using TLC aluminum sheets with silica gel 60F₅₅₄, benzene for the elution and the initial alcohol as reference. On completion, the catalyst was separated by filtration and the solvent removed *in vacuo*. Reaction products were suitably purified and identified by physical and spectroscopic data. Conversion was calculated as mmoles of transformed alcohol by every 100 mmol of initial reagent and the yield for each product as number of mmoles of the product for every 100 mmol of reagent. The selectivity to a product is defined as mmoles of the product by 100 mmol of converted alcohol. It can be pointed out that blank experiments carried out with the supports did not present any significant catalytic activity.

The conversion percentage was determined by HPLC, with a Konik-500-A device, fitted with an UV detector, 5 mm × 25 cm C-18 column, 70:30 acetonitrile–water solvent at 2 cm³/min flow rate, using the calibration curve method with the alcohols and the products.

The studied alcohols (1–6) are shown in figure 1, as well as alkenes (7–12) and corresponding dimers (13–19).

Table 1

Surface area, pore volume and mean pore diameter of the supports

Support	Surface area (m ² /g)	Pore volume (cm ³ /g)	Mean pore diameter (nm)
C1	804	0.74	<3
C2	478	0.82	<3 and 4

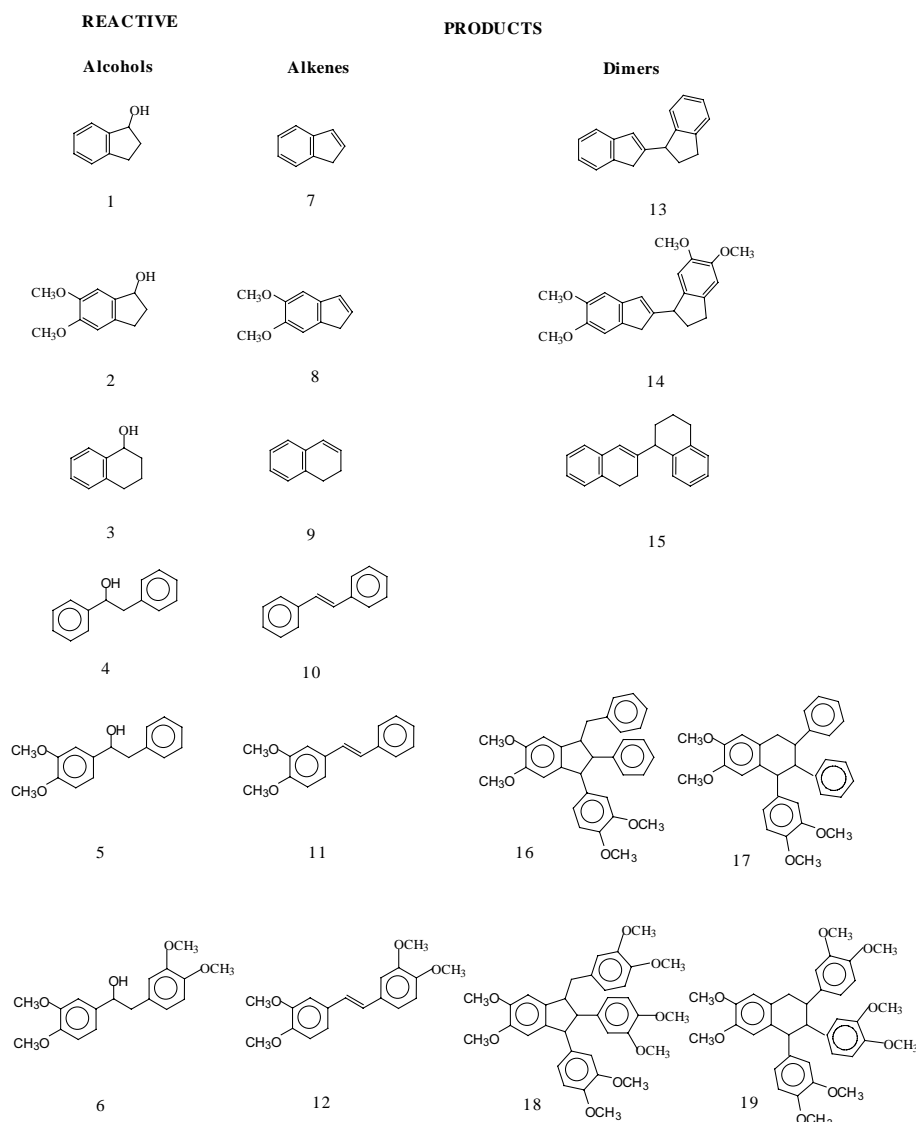


Figure 1. Studied alcohols (1–6) and the products of the dehydration reaction, alkenes (7–12) and dimers (13–19).

3. Results and discussion

3.1. Support and catalyst characterization

Studies on the textural properties of the supports used for catalyst preparation showed that C2 has a lower surface area than C1 and a higher mean pore diameter in a bimodal distribution (table 1).

After washing with chloroform, HPA contents of the catalysts were 0.128 and 0.136 mmol TPA/g catalyst, for TPA/C1 and TPA/C2, respectively. The concentration value of MPA on C1 was 0.214 and on C2 was 0.227 mmol MPA/g catalyst. The observed HPA leaching was in all cases lower than 0.4% of the initial HPA amount in the catalysts. On the other hand, the HPA leaching in the reaction systems in the presence of alcohol was not detected. The use of these washed catalysts allowed the reaction to be heterogeneously catalyzed.

HPA interaction with carbon surface groups is more complex than in the case of other carriers [21] and the nature of the interaction between the active metal species and the surface functional groups of carbon is still poorly understood [22]. By means of FT-IR spectroscopy, C1 and C2 showed five main bands, placed at 1640, 1250, 1100, 1030 and 900 cm^{-1} . According to Boehm [23], the 1640 cm^{-1} band may be assigned to carbonyl groups situated near hydroxyl groups (enols). The bands at 1250, 1100–1030 and 900–800 cm^{-1} have been assigned by Arriagada *et al.* [24] to C–O–C bonds of lactonic groups, the presence of ethers or phenols and aromatic groups, respectively.

In the catalysts based on MPA and TPA supported on C1 and C2, FT-IR bands of the support were observed. However, the intensity of the maximum at 1030 cm^{-1} decreased considerably as a result of interaction between the precursor and surface groups of the support.

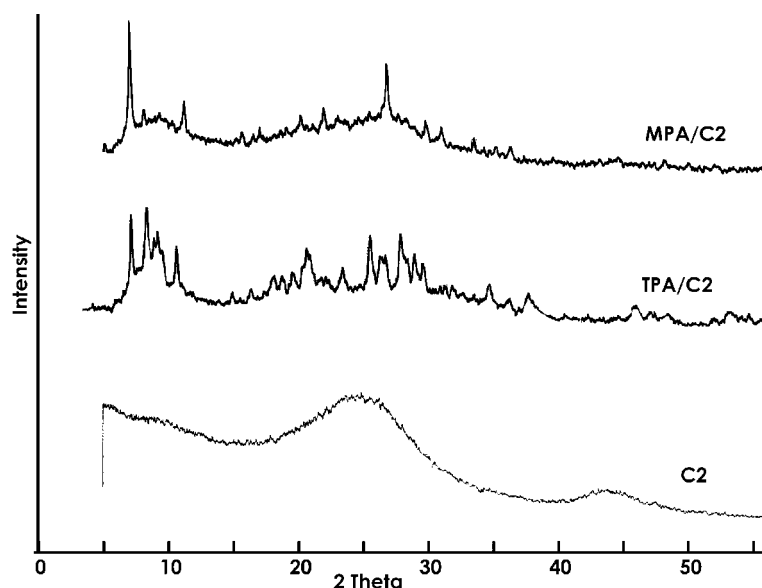


Figure 2. XRD patterns of MPA/C2 and TPA/C2 catalysts and C2 support.

FT-IR spectra of the TPA based catalysts also showed bands at 1079, 983, 891 and 800 cm^{-1} , and those based on MPA at 1056, 958, 870 and 791 cm^{-1} , in agreement with those previously reported for bulk acids [25]. Therefore, in the catalysts prepared on both supports, TPA and MPA were present with undegraded Keggin structure.

In the XRD pattern of C2 (figure 2), diffraction lines corresponding to crystalline structures were not observed. A similar pattern was obtained for C1 carbon. These results indicate that both supports possess amorphous structure. Nevertheless, by means of XRD, differences between the prepared catalysts were found. While TPA (MPA)/C2 patterns showed the diffraction lines of bulk heteropolyacids (figure 2), those of TPA (MPA)/C1 only presented small or poorly defined lines assigned to bulk TPA or MPA. This behavior is related to the lower surface area of C2, which leads to lower dispersed HPA on the support surface.

Moreover, for TPA based catalysts, a significant dependence of their acidic features on the support nature may be observed (figure 3). The obtained results indicated that TPA/C2 is a solid with higher acidity than TPA/C1, both in acid strength (initial electrode potential) and in the total number of acid sites (meq/g solid where the plateau is reached). Although the acidic properties of both supports are similar (figure 3), the observed behavior may be due to lower TPA interaction with the C2 support surface groups, which leads to a lower HPA dispersion and therefore greater proton availability. Similar results were observed for MPA/C2 and MPA/C1 catalysts (figure 4).

Previous adsorption isotherm studies of TPA and MPA solutions on both carbons have shown lower interaction of HPA with C2 than with C1 [10, 26, L.

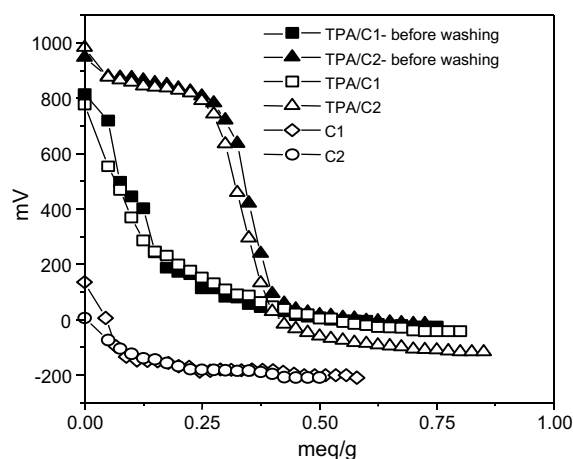


Figure 3. Titration curves of TPA/C1 and TPA/C2 catalysts, before and after washing with chloroform, and of supports C1 and C2.

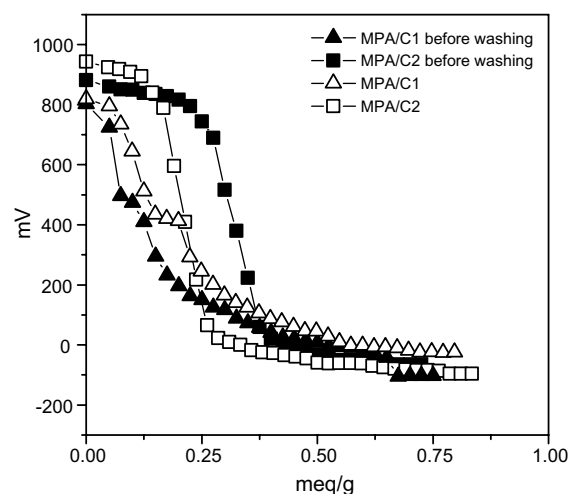


Figure 4. Titration curves of MPA/C1 and MPA/C2 catalysts, before and after washing with chloroform.

Table 2
Alcohol dehydration products and unconverted alcohol for TPA/C2 as catalyst

Reagent	Time (min)	Alkene (%)	Dimer (%)	Alcohol (%)
Indan-1-ol (1)	110	11	89	0
3,4-Dimethoxy-indan-1-ol (2)	110	2	98	0
1-Tetralol (3)	30 110	93 90	7 10	0 0
PhCHOHCH ₂ Ph ^a (4)	1920	99	0	1
VERCHOHCH ₂ Ph ^b (5)	110	80	20	0
VERCHOHCH ₂ VER ^c (6)	540	14.5	0	85.5

Note: $R = 0.15$ meq TPA/meq alcohol.

^a 1,2-diphenylethanol; ^b 1-(3,4-dimethoxyphenyl)-2-phenyl-ethanol;

^c 1,2-(3,4-dimethoxyphenyl)-ethanol.

Pizzio *et al.*, unpublished results]. Within the studied range of impregnating solution concentration (5–100 mg W(Mo)/cm³), the maximum number of adsorption sites occupied by HPA per gram of carbon was estimated. Values calculated were 8.5×10^{19} molecules/g support for TPA/C1 [26] and 3.8×10^{19} molecules/g support for TPA/C2 (L. Pizzio *et al.*, unpublished results). With regard to MPA adsorbed on C1 and C2, values were 6.5×10^{19} [10] and 3.6×10^{19} (L. Pizzio *et al.*, unpublished results) molecules/g support, respectively. These results indicate that the amount adsorbed of both HPA on C1 is roughly twice as that on C2, according to carbon surface areas (table 1).

On the other hand, the acidic characteristics of the catalysts were not affected by the leaching with chloroform, as shown in figures 3 and 4.

3.2. Dehydration reactions

3.2.1. Influence of the alcohol molecular size

The yield values of the several alcohols to alkenes are shown in tables 2 and 3, using TPA/C2 and TPA/C1 as catalysts, respectively. The alkene dimer yield, due to dimerization reactions of certain alkenes in acidic medium, and unconverted alcohol values, are also displayed. The cyclodimerization, whose mechanism was previously reported [17], makes difficult to obtain only the corresponding alkene.

When dehydration reactions of the studied alcohols (figure 1) were carried out with the TPA/C2 catalyst, the reaction was quantitative in almost all cases, except for VERCHOHCH₂VER (6) (table 2). For this alcohol, the reaction was followed during a long time in order to observe a change in the conversion, but the objective was not reached. Such behavior is related to the molecular size of this alcohol, greater than the others,

Table 3
Alcohol dehydration products and unconverted alcohol for TPA/C1 as catalyst

Reagent	Time (min)	Alkene (%)	Dimer (%)	Alcohol (%)
Indan-1-ol (1)	90 120	12 17	26 33	62 50
3,4-Dimethoxy-indan-1-ol (2)	120	79	21	0
1-Tetralol (3)	240	22	9.5	68.5
PhCHOHCH ₂ Ph (4)	180 2700	17 28	0 0	83 72
VERCHOHCH ₂ Ph (5)	300 140	17 30	0 0	83 70
VERCHOHCH ₂ VER (6)	780	4	0	96

Note: $R = 0.15$ meq TPA/meq alcohol.

and its steric hindrance to penetrate within catalyst pores for the reaction to occur.

Another feature to be considered is the amount of formed dimer, which was lower for alcohols 3, 4, 5 and 6 than for indan-1-ol (1) and 3,4-dimethoxyindan-1-ol (2), as shown in table 2. It should be emphasized that alcohol PhCOHCH₂Ph (4) does not form cyclodimers because it lacks active groups for ring closure. The behavior of alcohols 3, 5 and 6 is due to their higher molecular size and/or that of their dimers, which prevented dimers to be formed within catalyst pores. Thus, high selectivity to alkene was achieved for these alcohols. It is interesting to point out that a similar result is not feasible when H₂SO₄ [19] or *p*-toluenesulfonic acid [27] are used as catalysts, since mainly cyclodimerization products are obtained.

Regarding the catalytic performance of TPA/C1 (table 3), due to its acidic properties and its mean pore diameter, alcohol conversion was lower than the value obtained when TPA/C2 is used. However, a similar influence of alcohol molecular size on the reaction conversion and dimer formation was observed. As the alcohol molecular size is higher, the conversion decreased and simultaneously selectivity to alkene formation was higher. The 3,4-dimethoxyindan-1-ol behaves different because, due to its methoxy groups, it is more reactive than indan-1-ol, without substituents, and for that reason conversion was total. The difference between both alcohols, as a result of their molecular size, is that 3,4-dimethoxyindan-1-ol allowed the alkene to become the principal product (79:21; alkene:dimer), whereas indan-1-ol afforded a mixture of alkene and dimer (17:33; alkene:dimer) with a higher selectivity to dimer.

These results were compared with those corresponding to alcohol dehydration reactions using silica-supported TPA as catalyst [17,18], which are shown in table 4. Alcohol conversion in dehydration reactions catalyzed by TPA/S was total and dimers were mainly

Table 4
Alcohol dehydration products and unconverted alcohol for TPA/S as catalyst

Reagent	Time (min)	Alkene (%)	Dimer (%)	Alcohol (%)
Indan-1-ol (1)	90	14	86	0 ^a
3,4-Dimethoxy-indan-1-ol (2)	90	10	90	0
1-Tetralol (3)	15 180	60 7	38 93	2 ^a 0
PhCHOHCH ₂ Ph (4)	30	99	0	1 ^b
VERCHOHCH ₂ Ph (5)	120	0	99	0 ^b
VERCHOHCH ₂ VER (6)	300	10	90	0

Note: *R* = 0.10 meq TPA/meq alcohol.

^aFrom Ref. [18]; ^bfrom Ref. [17].

formed, as a consequence of the higher mean pore diameter (>5.4 nm). As mentioned above, alcohol PhCOHCH₂Ph (4) does not form cyclodimers.

It may thus be concluded that the conversion of dehydration reactions depends on alcohol molecular size, while the selectivity to alkenes is also related to dimer molecular size.

3.2.2. Influence of the catalyst characteristics

Yield values of 3,4-dimethoxyindan-1-ol to alkene and its dimer, and also unconverted alcohol values, using different catalysts, are shown in table 5, highlighting that the conversion was total when the dehydration reaction is catalyzed by TPA on C2, C1 and S. However, selectivity to alkene depended on the catalyst characteristics. The dehydration of alcohol 2 with TPA/C1 catalyst was more selective to alkene than with the other TPA based catalysts. The lower dimer formation is a result of lower mean pore diameter of C1 (table 1). On the other hand, alcohol conversion was also total when the catalysts are MPA/C2 and MPA/C1. The latter is more selective to alkene in the same way as the similar catalyst based on TPA.

Table 5
3,4-Dimethoxyindan-1-ol (2) dehydration products and unconverted alcohol with different catalysts

Catalyst	Time (min)	Alkene (%)	Dimer (%)	Alcohol (%)
TPA/C2	110	2	98	0
TPA/C1	120	79	21	0
TPA/S	90	10	90	0
MPA/C2	100	60	40	0
MPA/C1	120	76	24	0

Note: *R* = 0.15 meq HPA/meq alcohol.

Table 6
PhCHOHCH₂Ph (4) dehydration products and unconverted alcohol with different catalysts

Catalyst	Time (min)	Alkene (%)	Dimer (%)	Alcohol (%)
TPA/C2	192	99	0	1
TPA/C1	180	17	0	83
TPA/S	30	99	0	1
MPA/C2	192	99	0	1
MPA/C1	180	24	0	76

Note: *R* = 0.15 meq HPA/meq alcohol.

Table 6 displays the results of PhCOHCH₂Ph alcohol dehydration using different catalysts. For the catalysts prepared by impregnation of MPA and TPA on C2 it may be concluded that alcohol conversion is almost total. Besides, selectivity to alkene was higher for these catalysts. Since this compound, as above-mentioned, does not form any dimer, the main cause of this behavior is that they have a higher acidity than the catalysts prepared with C1 as support (figures 3 and 4). Though the TPA/S catalyst has a lower acidity, with 600 mV initial electrode potential [17], than TPA/C2 and TPA/C1, the obtained conversion was also almost total. This is due to its higher mean pore diameter (>5.4 nm), which affords readier reagent accessibility to the catalyst active sites.

Results achieved show that catalyst features, as acidity and mean pore diameter, exert an important influence on the conversion degree of alcohols into alkenes and also in alkene cyclodimerization.

4. Conclusions

Alcohol molecular size was found to exert a marked influence on the heterogeneous dehydration reactions catalyzed by heteropolyacids supported on two commercial carbons. The larger the alcohol molecule, the lower the conversion and the higher the selectivity to alkene formation. Nevertheless, the 3,4-dimethoxyindan-1-ol shows a different behavior. Due to the presence of methoxy groups, it is more reactive than indan-1-ol without substituents. On the other hand, the selectivity to alkene depends on dimer molecular size, whose formation decreases with larger dimer size.

Catalyst performance in the studied dehydration reactions also depends on the properties of the carbon used as support. These characteristics, fundamentally the mean pore diameter, are determining factors of the catalytically active material dispersion on the support surface, its interaction with the carbon surface groups and therefore of the catalyst final acidity.

The conversion is quantitative in the dehydration reaction of 3,4-dimethoxyindan-1-ol, catalyzed by TPA (MPA) on C2 as well as on C1. However, with the TPA

(MPA)/C1 catalysts there is a higher selectivity to alkene than with the other catalysts, due to lower mean pore diameter and subsequent lower dimer formation, allowing alkene to become the main product.

Regarding PhCOHCH₂Ph alcohol dehydration using MPA (TPA)/C2, total alcohol conversion is observed. Both conversion and selectivity to alkene are higher than when using catalysts based on C1. This is a consequence of the higher acidity of HPA supported on C2. As this alcohol cannot form dimers, the effect of the properties of the catalysts, mainly the acidic characteristics, in the selectivity to alkene formation are clearly observed.

The main goal is to demonstrate the effect of the molecular size of the studied alcohols on the conversion and selectivity towards the possible reaction products, in the heterogeneously catalyzed dehydration reaction. In addition, the importance of the properties of the ecofriendly heterogeneous catalysts used, particularly their pore size, on their performance is proved.

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