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Effect of the support on a new metanethole synthesis heterogeneously catalyzed by Keggin heteropolyacids

María del Rosario Torviso [a], Elba N. Alesso [a], Graciela Y. Moltrasio [a], Patricia G. Vázquez [b], Luis R. Pizzio [b], Carmen V. Cáceres [b], Mirta Noemí Blanco [b,*]

[a] *Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires,*
Junín 956, 1113 Buenos Aires, Argentina
[b] *Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr Jorge J. Ronco" (CINDECA), Departamento de Química,*
Facultad de Ciencias Exactas, Universidad Nacional de La Plata-CONICET, 47 No. 257, 1900 La Plata, Argentina

Abstract

Keggin heteropolyacids, supported on solids of different nature and textural characteristics, were used in the reaction of anethole dimerization in order to obtain metanethole. The characterization by Fourier transform infrared spectroscopy showed that all catalysts present the Keggin structure of the heteropolyanions without degradation. Besides, all the obtained solids have strong acidity, as determined by potentiometric titration. The results of anethole conversion show that the activity of the catalysts is strongly dependent on the textural properties of the supports used to obtain the catalysts, particularly their mean pore size.
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1. Introduction

Metanethole is a natural compound that has been extracted from *Spheciospongia vesparia* sponges [1]. This cyclodimer can be obtained from its monomer derived from styrene, anethole, by means of acid catalysis through the use of Brønsted acids such as sulfuric acid [2] or Lewis acids such as Cl_4Ti [3].

The replacement of the classic homogeneous catalysts by acid solids is attempted, due to the advantages involved. Among them, the process and workup simplicity, the reuse or regeneration of the catalysts, the decrease of corrosion problems, and waste disposal in an environmentally friendly way can be mentioned.

The heteropolyacids with Keggin structure (HPA) possess special characteristics that allow their use as catalysts in acid reactions, as they have a very high intrinsic acidity [4]. However, due to the low surface area of the bulk HPA, it is advisable to support them on a carrier with high surface area such as silica, zirconium dioxide, activated carbon, or siliceous materials such as MCM-41 [5–8]. The use of a support that leads to a good dispersion of the HPA on a high surface area can result in an increase of the catalytic activity [9].

In the design of this type of supported catalyst, the porous structure is an aspect to be taken into account. The pore size must be adequate in order that the molecule transport to or from the active sites can be made easier. Besides, a good HPA immobilization in the support is a subject to be carefully considered for the use of the catalysts in liquid-phase reactions. Izumi and Urabe [10] have used HPA supported on activated carbon for the intermolecular dehydration of butanol and *t*-butyl alcohol in liquid phase, and proposed that carbon is an excellent carrier to immobilize the HPA as a loss of the active component does not take place during the reaction.

In previous studies [5,6], it was proved that silica is a support with suitable properties to obtain HPA-based catalysts for acid reactions. In particular, the catalytic behavior of the tungstophosphoric acid (TPA) or molybdophosphoric acid (MPA) supported on silica, after washing with the solvent used as

* Corresponding author. Tel.: +54 221 4211353; fax: +54 221 4211353.
E-mail address: mnblanco@quimica.unlp.edu.ar (M.N. Blanco).

reaction media, was studied in the dehydration of 1,2-diphenylethanol, 1-3,4-dimetoxyphenyl-2-phenylethanol, and cholesterol, obtaining very good conversions [11].

On the other hand, in previous work [12], we studied the dimerization of styrenes and stilbenes employing the catalysts based on the HPA mentioned above. In most of the cases, styrenes with a different type of substitution in the aromatic ring gave cyclodimers with indanic structures as main products.

The aim of the present work is to study anethole dimerization, catalyzed by TPA or MPA supported on solids with different surface and textural properties. A new contribution to the field of acid reactions catalyzed by Keggin heteropolyacids is presented, and the results are discussed in relation to the catalyst characteristics.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using solutions of tungstophosphoric acid (Fluka, p.a.) or molybdophosphoric acid (Merck, p.a.). The solutions were used to impregnate supports with different characteristics. The solids employed as supports were silica Grace (S_G), silica Ralt-Chemie (S_R), and two commercial activated carbons from wood (C1 and C2). The characteristics of these supports are shown in Table 1.

For the preparation of the TPA/S_G and MPA/S_G catalysts, the equilibrium impregnation technique was employed using an impregnation time of 72 h. The solvent used for preparing the impregnating solutions of TPA and MPA was a mixture of demineralized water and ethanol 96% (Soria), in a volumetric ratio 1:1.

The preparation of the TPA/S_R and MPA/S_R catalysts was carried out by impregnating spheres of S_R. The pore filling impregnation technique was utilized, with impregnating solutions of TPA or MPA prepared in the same solvent mentioned above.

Catalysts based on TPA supported on carbon (TPA/C1 and TPA/C2) were also prepared. Both carbons were previously subjected to an acid and a basic treatment to remove impurities. The catalysts were prepared by the pore filling impregnation technique with TPA solutions in a mixture of water–ethanol, in the same volumetric ratio mentioned above.

Table 1
Textural properties of the supports and catalysts

Support	Specific surface area (m^2/g)	Pore volumen (cm^3/g)	Mean pore diameter (nm)
S_G	311	1.70	5–10
S_R	253	1.04	11.3
C1	804	0.74	<3
C2	478	0.82	<3 and 4
TPA/S_G	249	0.86	10.0
MPA/S_G	218	0.80	10.0
TPA/S_R	190	0.49	10.4
MPA/S_R	206	0.58	11.3
TPA/C1	153	0.07	<3
TPA/C2	272	0.14	<3

After the impregnation, all the catalysts were dried at room temperature for 24 h, calcined at 200 °C for 3 h, and washed with chloroform for three periods of 24 h, in a device with continuous stirring. Subsequently, the catalysts were thermally treated again under the same conditions.

2.2. Support and catalyst characterization

The textural properties of the supports and the catalysts were determined by the nitrogen adsorption/desorption technique at 77 K using Micromeritics Accusorb 2100E equipment.

The infrared with Fourier transform spectra (FT-IR) of the solids were recorded using a Bruker IFS 66 spectrometer, with pellets in KBr, in the range between 400 and 1500 cm^{-1}.

The acidity of the catalysts and supports was measured by potentiometric titration. A known mass of solid was suspended in acetonitrile and was stirred for 3 h. Then, the suspension was titrated with a 0.05N solution of *n*-butylamine in acetonitrile at a flow of 0.05 cm^3/min. The electrode potential variation (mV) was measured in an Instrumentalia SRL digital pH meter, with an Ag/AgCl electrode.

2.3. Anethole dimerization

The reaction was carried out in a glass batch reactor at atmospheric pressure. Anethole was dissolved in chloroform and then the solid catalyst was added to the solution in an anethole:MPA(TPA) molar ratio of 1:0.03. The resulting mixture was heated to reflux, and the reaction was followed by chromatography (TLC). Finally, the catalyst was separated by filtration and the solvent was removed in vacuum. The reaction products were purified by *p*-TLC using chloroform:hexane (7:3) as solvent, and identified by means of physical and spectroscopic data.

The possible catalyst solubilization was also tested, by following the reaction after the filtration of the catalyst.

The anethole conversion was followed by HPLC, using Konik-500-A equipment, with UV detector (wavelength 294 nm (anethole) and 205 nm (metanethole)), C-18 column, and acetonitrile–water (75:25) solvent at 1.5 cm^3/min flow. The retention times for anethole and metanethole are 4.05 and 12.50 min, respectively.

The conversion was calculated as the ratio between millimoles of transformed reagent and 100 mmol of initial reagent, and the product yield as the ratio between milligrams of metanethole and 100 mg of initial reagent.

3. Results and discussion

3.1. Support and catalyst characterization

The catalysts based on the molybdophosphoric or tungstophosphoric acids were prepared by supporting them on silica or carbon. It can be observed from the support textural properties shown in Table 1 that both silicas possess a BET specific surface area lower than those of the carbons of vegetable origin, while the pore volume as well as the mean

pore diameter are higher. The specific surface area of the silica-supported catalysts was 50–80 m^2/g lower than that of the supports. However, the values corresponding to the catalysts supported on carbons were considerably lower than that of the support (Table 1). These materials were chosen to observe if there is an influence either of the texture or of the surface nature of the support. The surface groups differ, since hydroxyl groups are present on the silicas, while in the carbons a variety of surface groups can be present in addition to hydroxyl groups, such as carbonyl, lactonic, aromatic groups, among others. On the other hand, the different textural characteristics can be reflected in the catalytic behavior, as was proved in alcohol dehydration reactions using different carbons [13].

The FT-IR spectra of the catalysts based on MPA showed bands at 1056, 958, 870, and 791 cm^{-1}, and those corresponding to TPA presented bands at 1079, 983, 891, and 800 cm^{-1}, which are characteristic of the molybdophosphate and tungstophosphate anions, respectively [11,13,14]. However, some bands were overlapped with those of the supports. The FT-IR spectra of the silica supports (S$_G$ and S$_R$) exhibited bands at 1100, 800, and 470 cm^{-1}. On the other hand, C1 and C2 showed bands at 1250, 1100, 1030, and 900 cm^{-1}. Fig. 1 shows the spectra of the HPA supported on S$_G$ and C1. The spectra of the catalysts based on the HPA supported on S$_R$ and C2 are similar to those supported on S$_G$ and C1, respectively. Thus, the characterization by FT-IR showed that, in all the prepared catalysts, the corresponding anion is present with undegraded Keggin structure.

The acidity of the solids was characterized by potentiometric titration with *n*-butylamine. By this technique, it is possible to estimate the strength and the number of acid sites present in the solids. It is considered that the initial electrode potential (E_i) indicates the maximum strength of the acid sites, and the value from which the plateau is reached (meq amine/mmol HPA) indicates the total number of acid sites that are present in the titrated solid. The strength of the acid sites can be classified according to the following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ mV (weak sites), and $E_i < -100$ mV (very weak sites) [15].

The curves of the electrode potential as a function of meq amine/mmol HPA of the catalysts are shown in Fig. 2. It is observed that, according to the previous scale, all the catalysts present very strong acid sites. The solids obtained by supporting the heteropolyacids on S$_R$ have slightly stronger acid sites, with $E_i = 730$ and 714 mV for MPA/S$_R$ and TPA/S$_R$, respectively, than those of the HPA supported on S$_G$, which presented $E_i = 690$ and 601 mV for MPA/S$_G$ and TPA/S$_G$, respectively. Besides, both HPA supported on S$_R$ showed a similar number of sites between each other, though lower than that of the S$_G$-supported heteropolyacids. The fact that MPA presents a stronger acidity than TPA when supported on S$_G$, apparently contrary to literature, is fundamentally due to the catalyst preparation method. These catalysts were obtained by the equilibrium impregnation technique and their content after leaching with chloroform was 0.217 mmol MPA/(g cat.) and 0.133 mmol TPA/(g cat.). In previous reports [5,6], equilibrium adsorption isotherms of both HPA from solutions in water–ethanol were determined on the same support used in this work. It was found that the amount adsorbed on the support surface is 0.067 mmol MPA/(g cat.) and 0.025 mmol TPA/(g cat.). So the washed catalysts preserve a considerable fraction of both HPA occluded in the pores of the support, higher for MPA/S$_G$. This HPA fraction occluded in the pores should be interacting more weakly and less dispersed on the surface of the support than the adsorbed fraction leading to a higher amount of protons less engaged to the surface groups of the support. As a consequence, the S$_G$-supported molybdophosphoric anion is interacting more strongly and it is more dispersed on the surface of the support presenting a higher acidity than the tungstophosphoric anion.
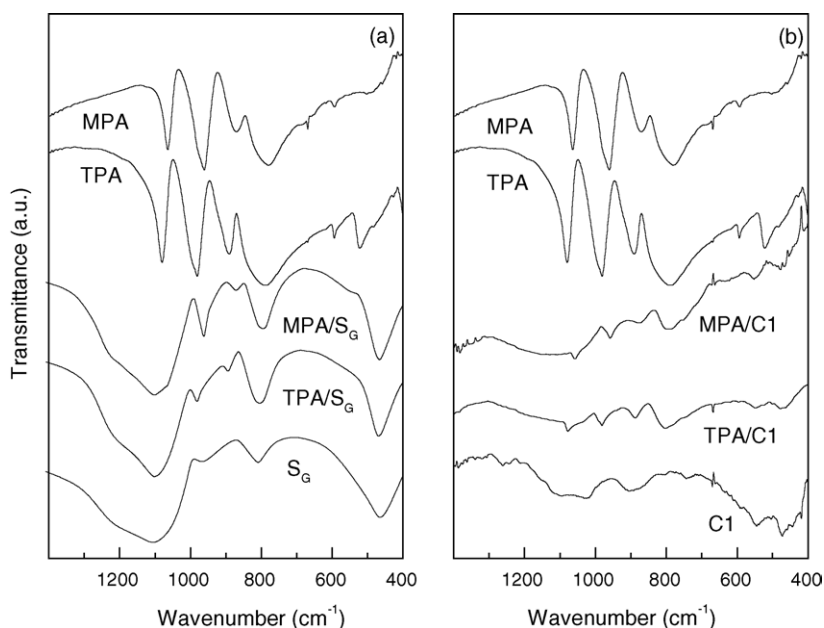

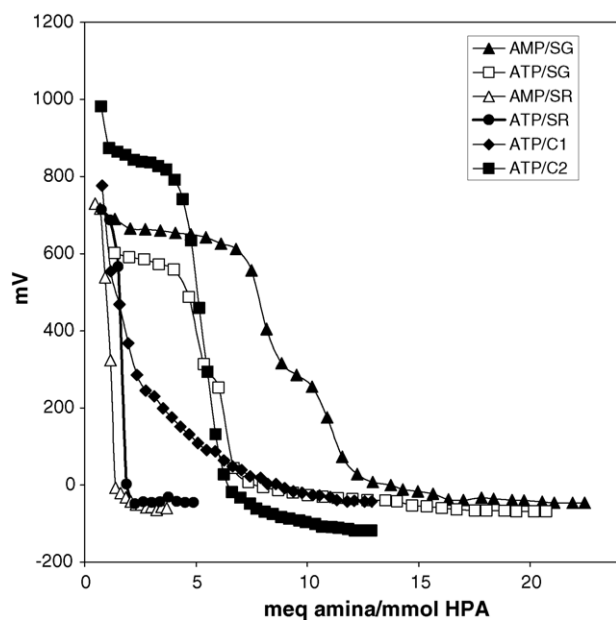Fig. 1. FT-IR spectra of the supports, the bulk acids, and the catalysts supported on S$_G$ (a) and on C1 (b).

Fig. 2. Potentiometric titration curves of the supported catalysts.

Scheme 1. Possible diasteroisomeric racemic mixtures in anethole cyclodimerization.

On the other hand, the TPA/C2 catalyst presented the strongest acid sites of all the prepared catalysts, with $E_i = 982$ mV, while for TPA supported on C1 the E_i value was 776 mV. It may be pointed out that the acidity of the HPA may substantially change when they are supported on different solids due to their interaction with the supports. So, the interaction of HPA with carbon is higher than that with silica. The adsorbed amount is 0.10 mmol and 0.053 TPA/(g cat.) for TPA/C1 and TPA/C2, respectively [13], leading to lower and slightly lower TPA occluded amount than for TPA/S$_G$. Also, the HPA acidity is influenced by the HPA dispersion on the support surface which depends on the textural properties of the supports and the preparation method.
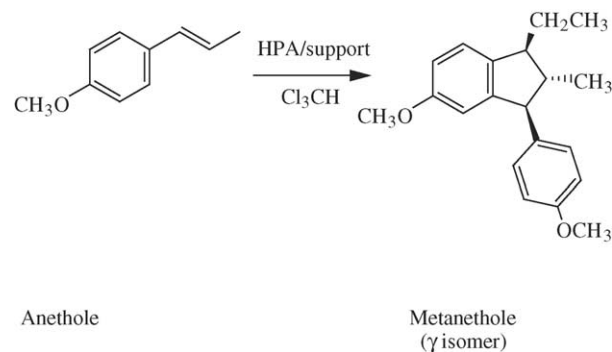
3.2. Anethole dimerization

Anethole dimerization was first carried out using TPA/S$_G$ and MPA/S$_G$ as catalysts. As three stereogenic centers are formed in the anethole cyclodimerization, four diasteroisomeric racemic mixtures can be obtained, α, β, γ, and δ (Scheme 1). Nevertheless, only one of the possible diasteroisomers (γ) was obtained and the physical properties of this dimer coincided with those of the natural product metanethole, which is shown in Scheme 2. The γ-configuration of the cyclodimer was determined by ^{1}H NMR, ^{13}C NMR spectroscopy, and bidimensional experiments (HMQC and NOESY).

The same reaction was carried out using other catalysts based on the same heteropolyacids supported on solids with different specific surface area and pore size, as S$_R$ and two commercial carbons. In all cases, a molar ratio of anethole:catalyst of 1:0.03 was employed.

The anethole conversion obtained using MPA supported on the two studied silicas as a function of time is shown in Fig. 3. It can be observed that the reaction kinetics is scarcely affected by the support used. On the contrary, the support leads
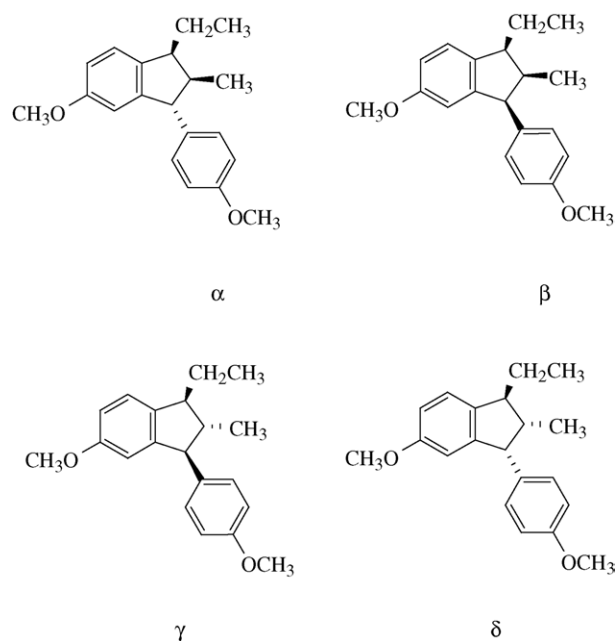
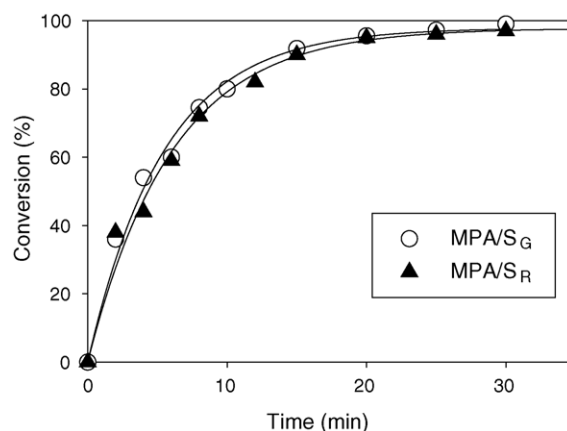Scheme 2. Anethol dimerization to metanethole.

Fig. 3. Anethole conversion as a function of time using MPA/S$_G$ and MPA/S$_R$ as catalysts.
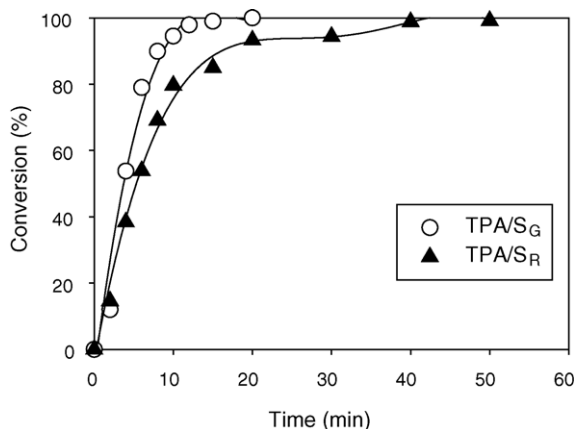
Fig. 4. Anethole conversion as a function of time using TPA/S_G and TPA/S_R as catalysts.

Table 2
Reaction time required for reaching the maximum anethole conversion

Catalyst	Time (min)	Anethole conversion (%)
TPA/S_G	15	99
MPA/S_G	30	99
TPA/S_R	40	99
MPA/S_R	40	99
TPA/C2	120	50
TPA/C1	120	8

to a difference in the behavior of TPA. When it is supported on S_G, it allows reaching high conversion faster than when it is supported on S_R. In this case, TPA behaves in a similar way to MPA (Fig. 4).

When carrying out the reaction using carbon-supported TPA, the TPA/C2 catalyst was less efficient than the silica-supported catalyst using the same reagent:catalyst molar ratio as in the previous tests, and even if a higher amount of catalyst was used (reagent:catalyst molar ratio = 1:0.05) (Fig. 5). When the TPA/C1 catalyst was tested, a significant conversion was not observed, even after 120 min under reaction.

It is interesting to point out that no further conversion was observed in the reaction medium after the catalyst filtration at reaction temperature, so the HPA catalysts do not leach during reaction.

The reaction time required for reaching the maximum conversion with all the studied catalysts is included in Table 2. In all the tests, metanethole was obtained with yields between 60 and 70%. Several other products with unknown structure were obtained in a very low yield.

It can be observed that the reaction time required to reach a 99% conversion employing silica-supported catalysts is significantly lower than that using TPA supported on C2 to
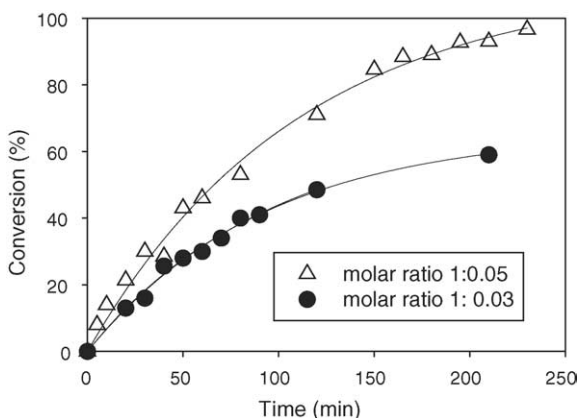
attain 50% conversion or on C1 to reach only 8% conversion. Among the factors that might have an influence, the acid strength of the catalysts, the nature of the surface groups of the support, and the textural properties can be mentioned. As it is observed in Fig. 2, the acid strength of TPA/S_G is lower than those corresponding to the other catalysts; nevertheless, this catalyst is the one that allowed obtaining the maximum anethole conversion (99%) in the shortest time (15 min). On the other hand, TPA/C2 is the catalyst with the highest acid strength, but it only converted 50% in 120 min. Then, it is evident that the observed behavior is not determined by the acid strength (Fig. 2). This conclusion is similar to that obtained by Adams et al. [16] using cation-exchanged montmorillonite clays as catalysts. In turn, the nature of the surface groups of the support can lead to an adequate HPA dispersion in the case of the silicas and better accessibility of the protons to act in the reaction. Nevertheless, it can be stated that the main factor is the higher pore size of the silica-supported catalysts than that of the catalysts supported on carbons (Table 1), which allows the dimer molecule to be formed easily. Also, it is important to point out that the pore volume of the catalysts based on carbon decreased in a greater extent than those based on silica, during the impregnation with HPA. The TPA/C1 catalyst gave a very low conversion since it has the smallest pore size and pore volume.

Similar conclusions were drawn when the anethole conversion obtained at 15 min is compared for each one of the catalyst (Fig. 6). In this case, the great difference in conversion attained
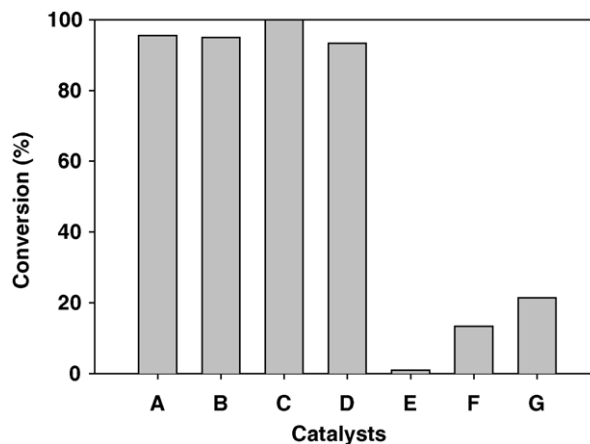

Fig. 5. Anethole conversion using TPA/C2 catalyst at different reagent:catalyst molar ratios.

Fig. 6. Anethole conversion at 15 min under reaction with different catalysts: (A) MPA/S_G, (B) MPA/S_R, (C) TPA/S_G, (D) TPA/S_R, (E) TPA/C1, (F) TPA/C2 (reagent:catalyst molar ratio 1:0.03), and (G) TPA/C2 (reagent:catalyst molar ratio 1:0.05).

with the silica-supported catalysts with respect to the carbon-supported HPA is well illustrated. It may be pointed out that the nature of the support has a high influence on the catalyst performance. As a result, the maximum anethole conversion varied from 99 to 8%, though the yield to metanethole only changed between 60 and 70%.

In a previous paper [13], it was found that in alcohol dehydration reactions, the heteropolyacid-supported catalyst performance also depends on the mean pore diameter of the carbon used as support. The conversion is quantitative in the dehydration reaction of 3,4-dimethoxyindan-1-ol catalyzed by TPA(MPA) supported 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 a smaller mean pore diameter and subsequent lower dimer formation, allowing alkene to become the main product.

With regard to the anethole dimerization catalyzed by silica-supported HPA, it was found out that the reaction time required for reaching the maximum anethole conversion using the TPA(MPA)/S_R catalysts is higher than that corresponding to the catalysts supported on S_G (Table 2). It may be suggested that the lower number of acid sites of the former catalysts (Fig. 2) has also an influence. In addition to the catalyst acidity, the behavior of the TPA(MPA)/S_R catalysts may be due to the fact that these catalysts were employed as spheres with approximately 4 mm diameter and, though the S_R support has a higher pore size, the effective diffusivity of reagents and products is lower than in the case of the TPA(MPA)/S_G catalysts, which have a smaller particle size.

In relation to this subject, the influence of the particle size on the conversion was evaluated. For this purpose, tests were performed using MPA/S_R catalyst ground in a mortar. It can be observed that the particle size has an important influence on the catalyst performance (Fig. 7). The conversion using different solid fractions obtained by grinding and sieving the MPA/S_R catalyst was also determined. For a reaction time of 2 min, conversions that vary between 55 and 99% for particle sizes between 840 and 100 μm were obtained (Fig. 8). So, the decrease of the diffusional control, when the particle size decreases, is well observed. Nevertheless, it may be mentioned
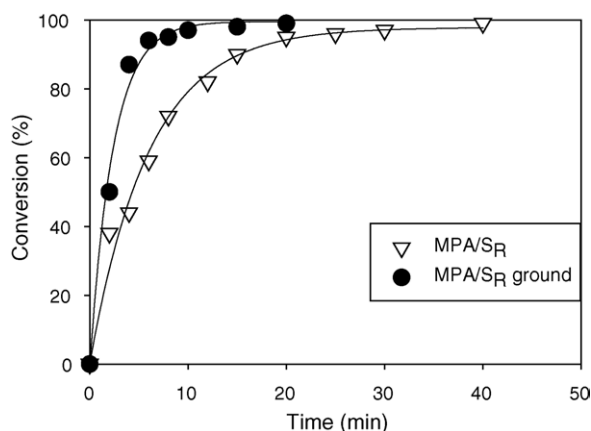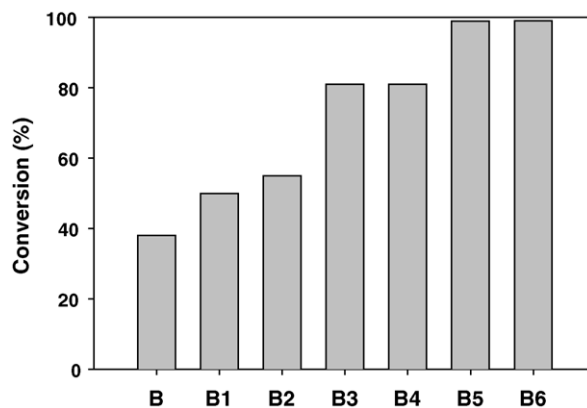
Fig. 8. Anethole conversion at 2 min under reaction using different ground fractions of MPA/S_R catalyst: (B) spheres, (B1) ground in a mortar, (B2) sieve 20 (>840 μm), (B3) sieve 20–30 (840–590 μm), (B4) sieve 30–40 (590–420 μm), (B5) sieve 40–140 (420–105 μm), and (B6) lower than sieve 140 (<105 μm).

that, with this catalyst and in this fast reaction, this effect does not become evident for higher reaction times. For example, at 6 min under reaction, high and close conversion values, between 95 and 99%, were obtained with the different fractions.

The results are interesting because the silica-supported HPA lead to high anethole conversion at low temperature (60 °C) and low reaction time (less than 40 min). They gave 99% conversion with a 60–70% yield in metanethole. One of the few results found in the literature for the heterogeneously catalyzed anethole dimerization reaction was obtained with cation-exchanged montmorillonites [16]. These authors have obtained 90–95% conversion with 32–44% recoverable metanethole yield, but working at 126 °C and with a reaction time of 1 h. Baker and Enderby [17] reported another method for such cyclodimerization catalyzed by sulfuric acid, and obtained metanethole with 24% yield at 7 h under reaction.

To the best of our knowledge, the present work is a new contribution to the field of Brønsted acid reactions heterogeneously catalyzed by Keggin heteropolyacids because it is the first time that supported HPA are used to synthetically obtain metanethole. In addition, it was carried out by an ecofriendly technology, thus contributing to environmental protection.

4. Conclusions

All the prepared catalysts, based on HPA supported on solids with different textural properties and surface groups, presented undegraded Keggin structure and strong acid characteristics.

The results of anethole dimerization showed that the best catalysts are those obtained by supporting the HPA on silica, since anethole quantitative conversions were obtained in shorter times, lower temperature, and with better yields to metanethole than those reported in literature.

The conversions are lower using the two tested carbons, this effect being mainly related to the small pore size of these supports. The use of different supports had an influence on the conversion but not on the yield to metanethole.

Fig. 7. Anethole conversion as a function of time for the MPA/S_R catalyst in the original sphere shape and the ground catalyst.

On the other hand, with the supported acids, the recovery of the catalyst is easier. Besides, the production of effluents harmful to the environment is avoided.

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