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Artigo

$H_3PW_{12}O_{40}$ (HPA), AN EFFICIENT AND REUSABLE CATALYST FOR BIODIESEL PRODUCTION RELATED REACTIONS. ESTERIFICATION OF OLEIC ACID AND ETHERIFICATION OF GLYCEROL

Jorge H. Sepúlveda*, Carlos R. Vera, Juan C. Yori y Juan M. Badano
Instituto de Investigaciones en Catálisis y Petroquímica, Santiago del Estero 2654, 3000 Santa Fe, Argentina
Daniel Santarosa
Faculdade Química, Pontifícia Universidade Católica de Campinas, Rod. D. Pedro I, km 136, 13020-904 Campinas - SP, Brasil
Dalmo Mandelli
Faculdade Química, Pontifícia Universidade Católica de Campinas, Rod. D. Pedro I, km 136, 13020-904 Campinas – SP / Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Rua Santa Adélia, 166, 09210-170 Santo André - SP, Brasil

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In esterification of oleic acid with methanol at 25 °C HPA displayed the highest activity. Moreover the HPA could be reused after being transformed into its cesium salt. In the reaction of etherification of glycerol HPA and Amberlyst 35W showed similar initial activity levels. The results of acid properties demonstrate that HPA is a strong protonic acid and that both surface and bulk protons contribute to the acidity. Because of its strong affinity for polar compounds, HPA is also seemingly dissolved in both oleic acid and methanol. The reaction in this case proceeds with the catalyst in the homogenous phase.

Keywords: heteropolyacids; esterification; etherification.

INTRODUCTION

Heteropoly compounds are used both as heterogeneous solid catalysts and as homogeneous catalysts.[1] The acidic as well as the oxidizing properties of heteropoly compounds in the solid state are very sensitive to the kind of counter cation and to the constituent elements of the polyanions.[2] The acidity of concentrated aqueous and non aqueous solutions of heteropoly acids (HPA) is higher than that of $HClO_4$ and H_2SO_4 by about 0.3 or 1.5 units of the Hammett acidity function.[3] For this reason heteropoly acids are very active in reactions demanding high acid strength.[4-6] They also attract some interest because they can replace hazardous liquid acids, such as sulfuric acid or corrosive Lewis solid acids (aluminum chloride) currently used in organic synthesis. In this sense they are regarded as potentially environmentally friendly solid acid catalysts.[7-9]

In bulk form heteropolyacids have a low specific surface area (< 10 $m^2\ g^{-1}$) but they can alternatively be used in supported form when the reaction needs to be performed heterogeneously. A heterogeneous reaction advantageously enables the separation of the catalyst from the products and unreacted reactants. Several supports of adequate high specific surface area can be used, such as silica, activated carbon, alumina, MCM-41 aluminosilicates and zirconia.[10-13]

One great disadvantage of heteropoly compounds and hence of HPA, is their relatively high solubility in water and polar solvents. This makes them prone to leaching from the catalyst surface and into the reaction medium. Once in solution the heteropoly compound continues to catalyse the reaction homogeneously until it is removed from the reaction medium with the reaction products. Exchanging part of the protons of HPA with different cations results in the formation of the corresponding salts. Salts of HPA and cations, like Cs^+, Ag^+ or NH_4^+ are insoluble or scarcely soluble in polar solvents and have a fairly high surface area (> 100 $m^2\ g^{-1}$).[14] However these salts sometimes tend to form colloidal suspensions in polar media and may pose difficulties for catalyst separation. Centrifugation might be required in order to separate the catalyst for further use.

The use of non-soluble HPA heterogeneous catalysts for many acid catalyzed reactions is therefore attractive as far as the catalysts are easily separated from the reaction media and prove to be reusable. In this sense the heterogeneization of HPA has attracted much interest and many efforts have been devoted to the preparation of solvent tolerant HPA formulations.[15-17]

One possible use of this special HPA catalysts could be in the acid-catalyzed production of biodiesel. Biodiesel comprises a mixture of fatty acid alkyl esters of natural origin produced by transesterification of natural oils and fats with short chain alcohols such as methanol or ethanol. It is totally compatible with petrodiesel and can be used in Diesel motors almost without any modification. Due to the natural origin of biodiesel the feedstocks may contain many undesirable components. Typical impurities are free fatty acids (FFA) and other minor compounds.[18] FFAs are especially problematic in plants using homogeneous alkali-catalyzed transesterification reactors. They react with the dissolved alkaline catalyst and form soaps that plug pipelines and process vessels and that interfere with phase separation in some units. In order to run the process without plant upsets the FFA content must be reduced to less than 3% by caustic refining. This is a big loss for high acidity feedstocks (10-30% FFA) because raw materials account for about 80% of the cost of the finished fuel.

High FFA feedstocks for biodiesel manufacture can be processed with no waste if acid catalysts are used. In the past concentrated H_2SO_4 have been tried but they have proved to supply only a small reaction rate in comparison to alkaline catalysts. In the usual industrial practice the unreacted oil fraction is sent to an alkali-catalyzed reactor after the acid-catalyzed pretreatment, thus adding to the complexity and cost of the process.

Solid acid catalysts could be advantageously used for biodiesel manufacture from high FFA feedstocks. Not only they are not affec-

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*e-mail: jsepulve@fiq.unl.edu.ar

ted by the presence of acids but they can also be easily separated from the reaction products. Tungsten-zirconia,[19] sulfated-zirconia,[20] polyvinylsulfonic resins[21] and heteropolyacids,[22,23] have been recently used for the catalytic synthesis of biodiesel.

The performance of esterification catalysts for biodiesel production can be tested with real feedstocks or alternatively with model compounds. In this sense oleic acid and oleic triglycerides are useful model compounds because oleyl chains are the most common components of many natural oils. Esterification of the acid is especially difficult because water is formed as a by-product and tends to deactivate the catalyst acid centers.

Another problem in the biodiesel industry is that of the glycerol by-product. In the last years the market price of glycerol has plummeted due to the availability of great glycerol surpluses from the biodiesel industry.[24] This has motivated the interest in the valorization of glycerol by transformation into another product of low cost of manufacture. One such products is GTBE (Glycerol tertiary butyl ether). GTBE is an additive produced by etherification of glycerol with t-butanol or isobutylene that is used as Diesel fuel smoke, pour and cloud point depressant.[25] GTBE synthesis is a typical acid catalyzed reaction.[26] The reaction has been mainly studied using resins,[27] and supported acids.[28] No applications of heteropolyacid compounds as etherification catalysts have been yet reported.

This paper studies the acid-catalyzed esterification of oleic acid with methanol over $H_3PW_{12}O_{40}$ both in the homogeneous and heterogeneous phase. This reaction is used as a model reaction test for the production of biodiesel from high FFA feedstocks. The reutilization of the HPA by separation and precipitation into $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was specially studied. The results obtained with these HPA catalysts were compared with those achieved with a commercial Amberlyst 35W resin catalyst. The catalysts were further characterized by using them in the acid-catalyzed, liquid-phase etherification of glycerol with tert-butanol to form GTBE.

EXPERIMENTAL

Materials

$H_3PW_{12}O_{40}$ (HPA) was supplied by Merck. The Amberlyst 35W resin was supplied by Rohm and Haas. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, the cesium salt of $H_3PW_{12}O_{40}$ was prepared by precipitation from an aqueous HPA solution with a suitable amount of a Cs_2CO_3 solution as described elsewhere.[29] The latter salt was supplied by Sigma-Aldrich.

Catalysts characterization

The textural properties of the solid catalyst were measured in a Quantachrome Nova-1000 equipment by physisorption of N_2 at the temperature of -196.5 °C. The crystalline structure of the catalysts was determined by X-ray diffraction using a Shimadzu XD-3A diffractometer and CuKαradiation filtered with Ni. Spectra were recorded with a step size of 0.02° and a counting time of 1 s.

UV-Vis spectroscopy was used to determine the content of HPA in solution. Spectra were measured in a UV-1800 double beam Shimadzu spectrophotometer. The samples were measured with 10 mm optical path cells and the HPA content was determined with the aid of calibration curves.

Esterification of oleic acid

A two-necked round-bottom glass flask was used as reactor. It had a reflux condenser and a magnetic stirrer. In a typical run, 2.82 g (10 mmol) of oleic acid, 5 mL of methanol and 1.3 g (10 mmol) of di-n-butyl ether (internal standard) were added before starting the reaction. Three different values of catalyst mass were used, 0.03, 0.05 and 0.1 g, in order to see the influence of the catalyst-to-reactant ratio. Then the temperature was rapidly raised to the desired value and the catalysts were put into the solution. The products of the reaction were analyzed with an HP6890 gas chromatograph equipped with a poly-methyl-phenyl-siloxane capillary column (30 m, 0.53 mm ID, 1.5 µm film thickness). The analysis was performed with an injector temperature of 250 ºC and an oven temperature program with an initial value of 60 ºC (hold 5 min), a heating rate of 10 ºC min^{-1} and a final temperature of 220 ºC. The amount of each product was obtained with the aid of calibration curves. These curves were constructed by the analysis of standard solutions of methyl oleate and oleic acid of varying concentration.

Etherification of glycerol

The reaction was performed in the liquid phase in an autoclave stirred reactor. The vessel and all connections were made of stainless steel. In a typical run 19.9 g of glycerol (Gly) and 32.0 g of tert-butanol (tB) (molar ratio, tB/Gly:2) were charged to the reactor. The mixture was purged with nitrogen and then heated to 70 °C under vigorous stirring (1000 rpm were used in order to avoid interphase mass transfer restrictions related to the low solubility of tert-butanol in glycerol). The reaction was carried at the autogenous pressure of the closed system. In all cases a fixed amount of 0.5 g of catalyst ground to 35-80 meshes was used. The reaction was carried out at the specified temperature for a given time. Then the stirring and heating were stopped and the reaction was quenched by cooling the reactor in an ice bath. The unreacted tB concentration in the reaction products was determined by gas chromatography. The technique requires the use of an internal standard, isopropylic alcohol (IPA, Ciccarelli, >99%). The analysis were performed in a Varian Star 3400 CX chromatograph with a flame ionization detector. A 30 m long, 0.53 mm ID, 1 µm film thickness, fused silica Zebron ZB-5 (Phenomenex) capillary column, was used for the chromatographic analysis. An injector temperature of 250 ºC, an initial column temperature of 60 ºC (hold 5 min), a heating rate of 10 ºC min^{-1} and a final temperature of 250 ºC, were used in all the analysis.

Dehydration of 1,4 butanediol

Dehydration of 1-4-butanediol in the liquid phase was used for assessing the acidity of the catalysts.[30] The reaction was carried out in a Parr autoclave. In each run 1.8 g of 1-4-butanediol, 12 mL of 1-4 dioxane (solvent) and 0.12 g of catalysts were charged to the reactor. Then the mixture was heated to 100 °C under vigorous stirring to start the reaction. The products of the reaction were analyzed by gas chromatography, using calibration curves and di-n-butyl ether (10 mmol) as an internal standard. The chromatograph was a Varian 3400 CX equipped with a flame ionization detector and an HP-Innowax capillary column (30 m, 0.32 mm ID, 0.50 µm film thickness). The temperature of the injector was 270 ºC, the column oven initial temperature was 120 ºC (hold 5 min), the heating rate was 10 ºC min^{-1} and the final temperature was 250 ºC (hold 10 min).

Reuse of the catalyst

HPA dissolved in solution is recovered after the reaction and separated from other products by means of precipitation with a cesium salt (CO_3Cs_2). The salt reacts with HPA forming an insoluble solid of formula $C_{2.5}H_{0.5}PW_{12}O_{40}$ that can be separated by filtration once the reaction is completed. The salt is then dried in a stove at

110 ºC overnight and calcined in a muffle at 300 ºC in still air for 3 h. The Cs salt can then be used in the reactions of etherification and esterification by using the same procedure employed for HPA.

RESULTS AND DISCUSSION

Catalyst characterization

Table 1 shows some measured properties of the catalysts such as specific surface area as measured by nitrogen adsorption and acidity as measured by NH_3 temperature programmed desorption and conversion of 1-4-butanediol at 100 °C after 4 h of reaction.[31] The value of the specific surface area of the cesium salt was similar to other results reported elsewhere.[32] The acidity of each catalyst can be a priori indirectly estimated from the data of dehydration of 1,4-butanediol. These acidity values can then be compared with those obtained by ammonia desorption. However there is no good correlation between the acid amount per unit mass and the data of dehydration of 1,4-butanediol. There is a relatively good correspondence between the values for the HPA and its Cs salt but the data for the Amberlyst resin look like an outlier.

Table 1. Catalyst properties

Catalyst	BET area, $m^2\ g^{-1}$	Acidity, mmol $NH_3\ g^{-1}$	Acid density, mmol $NH_3\ m^{-2}$	Conversion[a] of 1,4-butanediol, %
HPA	6	0.316	0.0523	55
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	135	0.065	0.00045	16
Amberlyst 35W	45	4.8[b]	0.106[b]	44

[a] Conversion (mol %) to tetrahydrofuran after 4 h of reaction at 100 °C. [b] Not measured. Data supplied by the supplier (Rohm and Haas products division of Dow Chemical Co.).

Both HPA and the resin Amberlyst 35W are strong acids and they have been termed "superacids" because they have a surface acidity greater than 100% H_2SO_4 in the Hammet acidity scale. In this sense both have strong enough acid sites to perform the dehydration of 1,4-butanediol at relatively mild temperatures. The surface acidity of the resin is one order of magnitude higher than that of HPA and its cesium salt. The observed differences in the rate of butanediol dehydration can be possibly attributed to the "pseudoliquid" behavior of HPA compounds. In this state of the HPA related compounds all protons in the bulk of the solid contribute to the reaction.

If we compare the dehydration activity of HPA and its Cs salt we can see that the activity of HPA is higher. This is most likely related to the higher amount of acid sites per unit mass present in the HPA catalysts. Accessibility of the butanol to the surface seemed to have no impact on the activity results. The HPA catalyst for example had only 5 $m^2\ g^{-1}$ and its activity was the highest. The results seem to indicate that the global activity is proportional to the amount of strong acid sites per unit mass.

Some authors have postulated that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and HPA catalysts display superacidity. The Cs salt had an H^o value of ca. -13.6 Hammet units. This acid strength should be enough for dehydrating 1,4-butanediol to a great extent.[33] The results indicate that the conversion of the HPA catalyst was four times higher than the conversion of the Cs-salt. These results correlate with the lower amount of acid sites per unit mass of the Cs-salt.

The Amberlyst 35W resin and the HPA catalysts displayed a similar density of acid sites (0.5-1.0 mmol $NH_3\ m^{-2}$) and both had protonic acid sites. The absolute amount of acid sites was however much higher for the resin (4.8 mmol $NH_3\ m^{-2}$ compared to 0.3). In spite of this the conversion of 1,4-butanediol is higher on HPA. This is attributed a priori to HPA having a higher proportion of strong acid sites needed to catalyze the reaction. Another possible explanation is the higher affinity displayed by HPA for butanediol and other polar compounds in the homogeneous phase. Though being performed in batch mode, in one set of experiments, sampling was done continuously. These results are shown in Figure 1. The pattern of conversion of butanediol to tetrahydrofuran as a function of time of reaction is identical for both the HPA and the Amberlyst 35W catalysts. The high activity of HPA despite its low amount or density of acid sites in the solid state might be related to its solubility in alcoholic media. This solubilization would dramatically increase the amount of available acid sites. The solution of HPA appears completely crystalline when inspected visually. When analyzed by UV, Keggin structures in a true solution state can be detected both in aqueous and alcoholic media.[34]

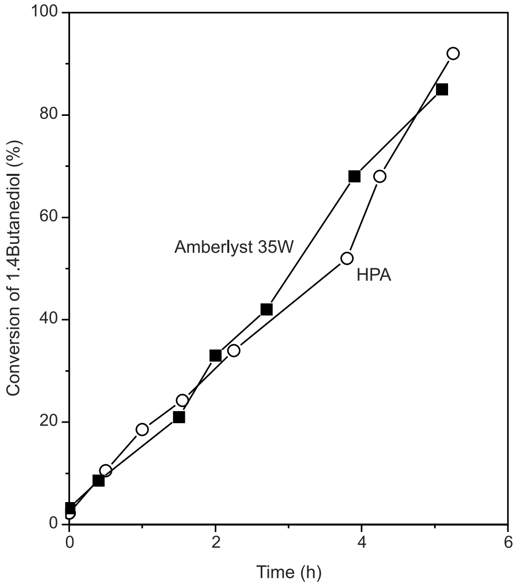

Figure 1. *Conversion (mol %) of 1,4-butanediol to tetrahydrofuran at 100 ºC as a function of reaction time. (■) Amberlyst 35W resin. (●) HPA*

The high activity of HPA is best explained by the affinity of polar molecules for HPA when this is present in the medium as a soluble or partly soluble species. Misono and coworkers[35] have coined the term "pseudo-liquid" to refer to the particular state of heteropolyacids in some media that enables them to have all their polyanions and protons, even those of the solid bulk, available for acting as active catalytic sites. This property gives HPA very high activity and unique selectivity features. The hiper active "pseudo-liquid" behavior has been found both in liquid-solid and gas-solid systems.

Catalytic esterification of oleic acid

In Figure 2 are shown the results of conversion oleic acid as a function of reaction time during its esterification with methanol as catalyzed by HPA at 25°C. It can be seen that for an oleic acid/HPA ratio of 94 g/g (0.03 g HPA) 40% conversion of the oleic acid into methyl oleate is achieved at 10 h reaction time. HPA is very efficient; when 0.1 g are used near 80% conversion is obtained at 10 h reaction time. Other results not shown in this figure stress the efficiency of HPA. For example when 0.2 g of HPA at 50 °C are used (oleic/HPA=14 g/g) 50% conversion is achieved in 2 h. In contrast when 0.1 or 0.2 g of the resin 35W and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are used at 25°C no conversion of the oleic acid can be detected after 10 h reaction time.

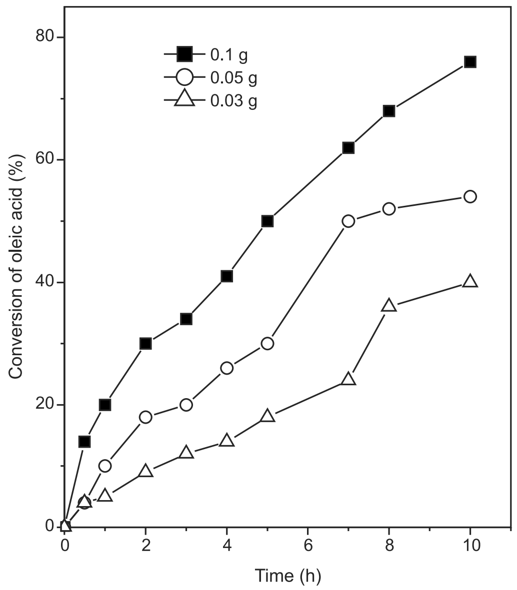

Figure 2. *Esterification of oleic acid (10 mmol) with methanol (24.6 mmol). Conversion as a function of reaction time.* $H_3PW_{12}O_{40}$ *catalyst, 25 °C*

The results of the esterification reaction using the cesium salt of HPA and the Amberlyst 35W resin are included in Figure 3. At low temperatures these catalysts cannot convert oleic acid into methyl oleate. A minimum temperature of 90-110 °C seems necessary to achieve a high value of conversion. The resin and the Cs salt show similar activity patterns at these reaction conditions when using the same catalyst/reactant ratio.

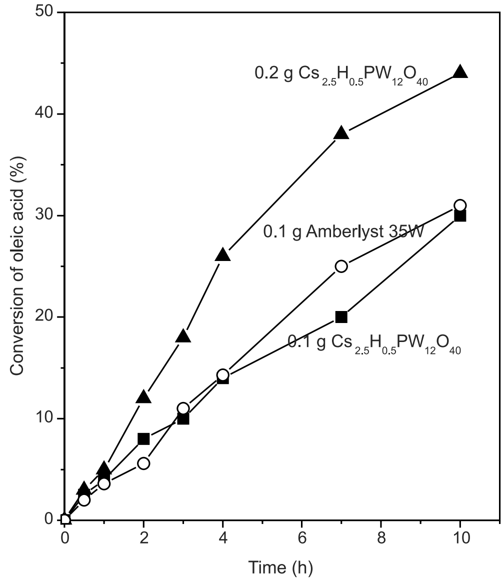

Figure 3. *Esterification of oleic acid (10 mmol) with methanol (24.6 mmol) at 110 °C. Conversion as a function of reaction time. (▲) 0.2 g* $Cs_{2,5}H_{0,5}PW_{12}O_{40}$*, (■) 0.1 g* $Cs_{2,5}H_{0,5}PW_{12}O_{40}$*, (○) 0.1 g 35W resin*

HPA and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ show remarkable differences in catalytic activity for the esterification of oleic acid with methanol. Both seem to have superacidity though HPA has a higher amount of Brönsted acid sites (Table 1). HPA cesium salts exhibit a a reportedly high catalytic activity in many reactions, like the hydrolysis of ethyl acetate,[36] the isomerization of n-butane,[37] or the alkylation of m-xylene and 1,3,5 trimethylbenzene with cyclohexane.[38] These reactions are likely catalyzed by the large number of surface acid sites of the HPA cesium salt or by surface acid-base pairs.

In some liquid phase reactions HPA and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ have shown very different reactivities.[39] In these reactions different substrates and solvents of different polarity were employed. Therefore the different reactivity can be explained by their different solubility, surface acidity and acid strength. For the esterification the catalytic activity does not show a correlation with the acidity (Table 1). In the case of the esterification of oleic acid with methanol the higher solubility of HPA in methanol is one main reason of its higher activity in comparison to that of the corresponding Cs salt; this reaction mostly took place in the homogeneous solutions.

Catalytic etherification of glycerol

The results for the HPA and Amberlyst 35W catalyst can be seen in Figure 4. At the beginning of the reaction, before the 2 h reaction time, the conversion increases with time of reaction more rapidly in the case of the resin catalyst. The resin yields 40% conversion at 1 h time of reaction while the same value is achieved by the HPA catalyst at 2 h reaction time. In the case of the resin an equilibrium value of about 55% is obtained after 3-4 h of reaction time. Conversely in the case of the HPA there seems to be no saturation value and the conversion increases steadily with reaction time and values of 80-90% conversion are obtained at the end of the reaction.

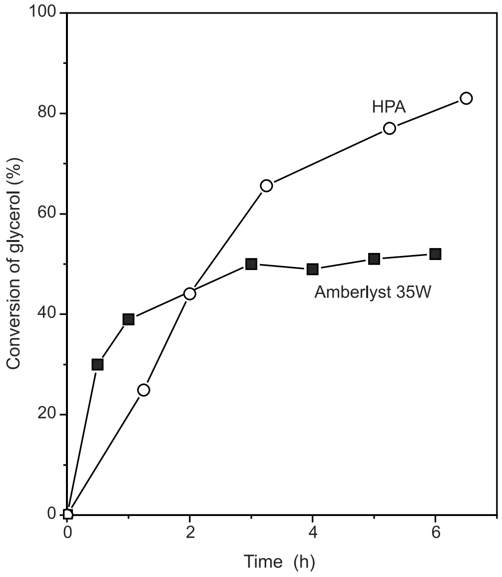

Figure 4. *Etherification of glycerol with tert-butanol at 90°C. Conversion as a function of time*

The reaction main products were mono-, di- and tri- glyceryl tert-buthyl ethers. The relative abundance of these products in the final solution was 3:1:1 (mass ratio) for both the HPA and the resin catalysts. Other products related to glycerol and tert-butanol were found in minor quantities but were not fully identified.

These results cannot be simply explained by resorting to the simple concept of reaction catalyzed over non-deactivating acid sites. The Amberlyst 35W has a higher protonic density than HPA but it does not yield a higher conversion value at high values of time of reaction. The plateau effect in the case of the resin can be due to the inhibiting effect of water. Etherification with the alcohol produces water as a by-product and this water becomes irreversibly adsorbed on the stronger acid sites. Hydration decreases the acid strength and hence the activity for etherification. Water acts as a weak base and indeed the hydrated Brönsted acid site has a lower acidity than the free one. Moreover the attachment of water molecules to protonic sites brings about some steric hindrance if the site is not easily accesible.

The inhibiting effect would be much stronger in the case of the resin and much milder in the case of the HPA catalyst.

HPA reuse

The reaction products of the HPA-catalyzed esterification of oleic acid with methanol were washed several times with water. Then the oil and aqueous phases were separately analyzed by gas chromatography. Oleic acid, methanol (0.021% w/w) and methyl oleate were present in the oil phase. Methanol, di-n-butyl ether and oleic acid (0.024% w/w) were present in the aqueous phase. UV-vis spectra were recorded and analyzed in order to detect the Keggin structure of HPA in these phases. No signals due to HPA were present in the spectrum of the oil phase. HPA was noticeably present in the aqueous phase (Figure 5). The position of the maximum of the UV-vis spectrum of HPA dissolved in water (curve A) is 260 nm. When dissolved in methanol (curve B) the maximum occurs at 265 nm. In the case of the spectrum of the HPA present in the aqueous phase of the reaction products the maximum appears at 264 nm (curve C). This shift is due to the influence of the pH of the solution that governs the relative equilibrium concentration of the different species in solution.[34,40,41]

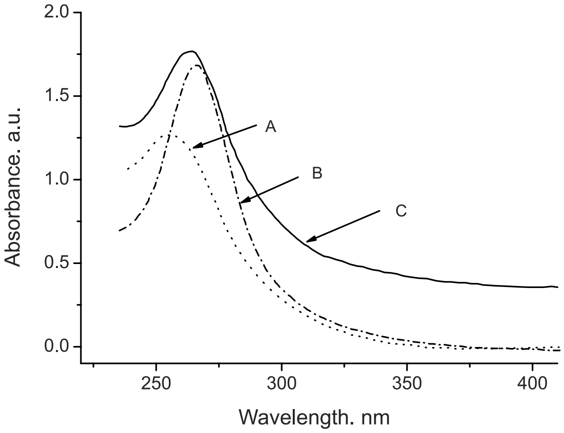

Figure 5. *UV-Vis absorbance spectra. (A) 10 mg of HPA dissolved in 100 mL of water. (B) 10 mg of HPA dissolved in 100 mL of methanol. (C) 2 mg of the reaction products dissolved in 10 mL of water*

The aqueous phase at the end of the esterification reaction was further used to test the reuse of the catalyst. For this purpose the Cs salt of HPA was prepared by adding a salt of Cs with a weak base in order to perform an acid-base reaction in which the carbonate anion is replaced by the heterepolyanion. Then the Cs salt can be used in a second esterification reaction. Despite the fact that the catalyst is not the original HPA solid, the activity of the Cs salt is similar to that of the resin and the reaction can proceed with good conversion.

The solution of Cs_2CO_3 was added dropwise and a white precipitate of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was formed. When precipitation was completed, the precipitate was filtered, dried at 100 °C in a stove and finally calcined at 300 °C in a muffle. The XRD spectrum of this powder, after it was used in the esterification reaction, is shown in Figure 6. The XRD spectrum of the Cs salt is similar to the spectrum of the free acid, thus confirming that the Keggin structure of the free acid is retained in the Cs salt.[42]

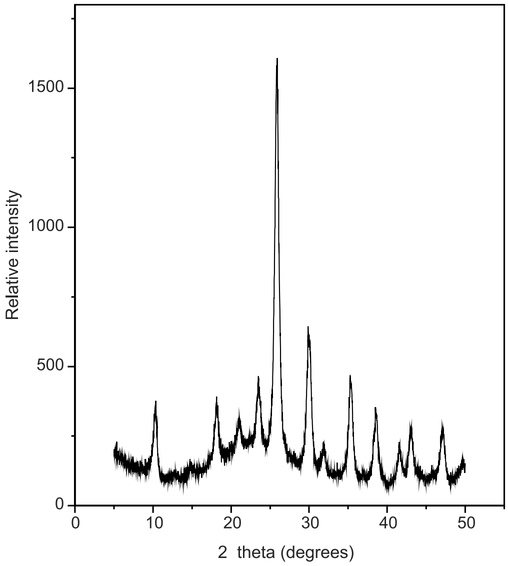

Figure 6. *XRD spectrum of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt*

CONCLUSIONS

The heteropolyacid $H_3PW_{12}O_{40}$ catalyst shows a higher activity than the Amberlyst 35W resin and its homologous Cs salt, in the reaction of oleic acid esterification with methanol. In the acid-catalyzed dehydration of 1,4-butanediol the activity of HPA is similar to that of the resin.

HPA shows a high efficiency for the esterification of oleic acid with methanol at 25 °C and it is possible to reuse it in the form of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, though this partially exchanged cesium salt is not as active as HPA itself. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ needs a reaction temperature of 90 °C to have a meaningful activity level.

HPA and Amberlyst 35W have a similar acid strength. However the resin is not active at 25 °C for the esterification of oleic acid with methanol and has an activity-temperature pattern similar to that of the cesium salt. HPA is active at room temperature and displays the highest esterification activity.

This result indicates that HPA is a strong protonic acid and that both surface and bulk protons contribute to the acidity. HPA is seemingly dissolved in polar oleic acid and methanol and the reaction proceeds homogenously. The Amberlyst 35W resin and the cesium salt are hardly soluble and in this case the catalytic action is constrained to the surface active sites.

In the case of the reaction of etherification of glycerol with tert-butanol both the Amberlyst 35W and HPA catalyst had similar initial activity levels. However at long reaction times the activity of the resin is limited likely because of the chemisorption of water on acid sities. Conversely HPA has a pattern of increasing conversion with reaction time.

The Cs salt of HPA proved to be a potential reusable catalyst for the trans/esterification of fatty materials and the etherification of glycerol, thus comprising a versatile material for the biodiesel production industry.

REFERENCES

1. Xiu-Kai, L.; Jink, Z.; Wei-Jie, J.; Zhi-Bing, Z.; Yi, C.; Chak-Tong, A.; Scott, H.; Hartmut, H.; *J. Catal.* **2006**, *237*, 58.
2. Rafiee, E.; Paknezhad, F.; Shahebrahimi, Sh.; Joshaghani, M.; Eavani, S.; Rashidzadeh, S.; *J. Mol. Catal. A: Chem.* **2008**, *282*, 92.
3. Misono, M.; *Catal. Rev.-Sci. Eng.* **1987**, *29*, 269.

4. Justus, J.; Vinu, A.; Devassy, B.; Balasubramanian, V.; Bohringer, W.; Fletcher, J.; Halligudu, S.; *Catal. Commun.* **2008**, *9*, 1671.
5. Dias, J.; Rangel, M. C.; Dias, S.; Caliman, E.; Garcia, F.; *Appl. Catal., A* **2007**, *328*, 189.
6. Okumura, K.; Yamashita, K.; Yamada, K.; Niwa, M.; *J. Catal.* **2007**, *245*, 75.
7. Blasco, T.; Corma, A.; Martínez-Escolano, P.; *J. Catal.* **1998**, *177*, 306.
8. Benaissa, H.; Davey, P.; Khimyak, Y.; Kozhevnikov, K.; *J. Catal.* **2008**, *253*, 244.
9. Devassy, B.; Halligudi, S.; *J. Catal.* **2005**, *236*, 323.
10. Rajasekar, K.; Pandurangan, A.; *Catal. Commun.* **2007**, *8*, 635.
11. Das, D.; Parida, K.; *Appl. Catal., A* **2006**, *305*, 32.
12. Rafiee, E.; Paknezhad, F.; Shahebrahimi, Sh.; Joshaghani, M.; Eavani, S.; Rashidzadeh, S.; *J. Mol. Catal. A: Chem.* **2008**, *282*, 92.
13. Jermy, R.; Pandurangan, A.; *Catal. Commun.* **2008**, *9*, 577.
14. Rao, P. M.; Wolfson, A.; Kababya, S.; Vega, S.; Landau, M.; *J. Catal.* **2005**, *232*, 210.
15. Okumura, K.; Yamashita, K.; Hirano, M.; Niwa, M.; *J. Catal.* **2005**, *234*, 300.
16. Yuan, C.; Zhang, F.; Wang, J.; Ren, X.; *Catal. Commun.* **2005**, *6*, 721.
17. Amini, M.; Seyyedhamzeh, M.; Bazgir, A.; Mozhdeh, A.; *Appl. Catal., A* **2007**, *323*, 242.
18. Ma, F.; Hanna, M.; *Bioresour. Technol.* **1999**, *70*, 1.
19. Furuta, S.; Matsuhashi, H.; Arata, K.; *Biomass Bioenergy* **2006**, *30*, 870.
20. Martín, D.; López, M.; Mariscal, R.; Yori, J. C.; Vera, C. R.; Grau, J. M.; *Proceedings XV CAC, IV MercoCAT*, La Plata, Argentina, November 12-16, 2007, ID-191.
21. Özbaya, N.; Oktar, N.; Tapana, N.A.; *Fuel* **2008**, *87*, 1789.
22. Caetano, C.; Fonseca, I.; Ramos, A.; Vital, J.; Castanheiro, J.; *Catal. Commun.* **2008**, *9*, 1996.
23. Sunita, G.; Devassy, B.; Vinu, A.; Sawant, D.; Balasubramanian, V.; Halligudi, S.; *Catal. Commun.* **2008**, *9*, 696.
24. Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C.; *Angew. Chem., Int. Ed.* **2007**, *46*, 4434.
25. Noureddini, H.; *US Patent 6,174,501* **2001**.
26. Dewattines, C.; Hinnekens, H.; *Zeolites* **1996**, *16*, 318.
27. Klepáčová, K.; Mravec, D.; Bajus, M.; *Appl. Catal., A* **2005**, *294*, 141.
28. Melero, J. A.; Vicente, G.; Morales, G.; Paniagua, M.; Moreno, J. M.; Roldán, R.; Ezquerro, A.; Pérez, C.; *Appl. Catal., A* **2008**, *346*, 44.
29. Yanyong, L.; Gaku, K.; Kyutae, N.; Misono, M.; *Appl. Catal., A* **1998**, *166*, L263.
30. Sepúlveda, J.; Texeira, S.; Schuchardt, U.; *Appl. Catal., A* **2007**, *323*, 242.
31. Balbinot, L.; Schuchardt, U.; Vera, C.; Sepúlveda, J.; *Catal. Commun.* **2008**, *9*, 1878.
32. Koyano, G.; Ueno, K.; Misono, M.; *J. Mol. Catal. A: Chem* **1994**, *86*, 319.
33. Liu, Y.; Koyano, G.; Misono, M.; *Top. Catal.* **2000**, *11/12*, 239.
34. Sepúlveda, J.; Yori, J. C.; Vera, C. R.; *Appl. Catal., A* **2005**, *288*, 18.
35. Kengaku, T.; Matsumoto, Y.; Na, K.; Misono, M.; *J. Mol. Catal. A: Chem.* **1998**, *134*, 237.
36. Nakato, T.; Kimura, M.; Nakata, S.; Okuhara, T.; *Langmuir* **1998**, *14*, 319.
37. Na, K.; Okuhara, T.; Misono, M.; *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 367.
38. Mizuno, N.; Misono, M.; *J. Mol. Catal. A: Chem.* **1994**, *86*, 319.
39. Koyano, G.; Ueno, K.; Misono, M.; *Appl. Catal., A* **1999**, *181*, 267.
40. Pizzio, L.; Caceres, C.; Blanco, M.; *Appl. Catal., A* **1998**, *167*, 283.
41. Kimura, H.; Nakato, T.; Okuhara, T.; *Appl. Catal., A* **1997**, *165*, 227.
42. Soled, S.; Miseo, S.; McVicker, G.; Gates, W. E.; Gutierrez, A.; Paes, J.; *J. Chem. Eng.* **1996**, *64*, 247.