



Short Communication

Catalytic upgrading of levulinic acid to ethyl levulinate using reusable silica-included Wells-Dawson heteropolyacid as catalyst

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ABSTRACT

In this paper we report, for the first time, the direct incorporation of a heteropolyacid (HPA) with Wells-Dawson structure during the synthesis of silica by the sol-gel technique, in acidic media, using tetraethyl orthosilicate. The catalyst characterization was carried out by ³¹P MAS-NMR, FT-IR, XRD, N₂ adsorption-desorption measurements, and the acidic properties were determined through potentiometric titration with *n*-butylamine. The synthesized catalysts were used in the esterification of levulinic acid with ethanol, at 78 °C, to obtain ethyl levulinate. The synthesis of silica-included HPAs was satisfactory, and the samples kept their HPA structure intact after synthesis. The catalytic tests for the esterification reaction between levulinic acid and ethanol to produce ethyl levulinate have shown that the silica-included Wells-Dawson HPA is an active and selective catalyst for this reaction. It must be noted that silica-included HPAs also kept their structure and catalytic activity after three consecutive reaction cycles. These results indicated that these solid acids are promissory catalysts for the esterification reaction of levulinic acid and ethanol to ethyl levulinate.

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1. Introduction

Biomass is defined as any organic matter that is available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other waste materials [1,2]. The annual production of biomass is about 1.7–2.0 × 10¹¹ tons [3]; however, only 6 × 10⁹ tons is currently used for food and non-food applications. The biomass carbohydrates are the most abundant renewable resources available, and they are currently viewed as a feedstock for the Green Chemistry of the future [4–6].

Levulinic acid (LA), derived from the acid catalysis from lignocellulosic biomass, one of the top-twelve building blocks [2], is a potentially versatile building block for the synthesis of several chemicals for applications such as fuel additives, polymer and resin precursors [7–11]. Several reviews have been published describing the properties and potential industrial applications of LA and its derivatives [1,12,13]. There are numerous useful compounds derived from levulinic acid. For example, ethyl levulinate (EL), obtained by esterifying LA with ethanol, can be used as an oxygenate additive in fuels. EL and other levulinic acid esters can be obtained by esterification reaction in the presence of an acid catalyst, such as sulphuric, polyphosphoric or *p*-toluenesulfonic acid in homogeneous medium [14–16]. However, it

is well known that the use of conventional liquid acids has environmental problems associated with handling, containment, disposal and regeneration due to their corrosive and toxic nature. The use of solid acid (heterogeneous) catalysts in organic synthesis and in the industrial manufacture of chemicals is increasingly important since they provide green alternatives to homogeneous catalysts [17,18]. On the other hand, catalysis by heteropolyacids (HPAs) is a well-established area and it has the potential of a great economic reward and green benefits [19].

Although there are many structural types of heteropolycompounds, the majority of the catalytic applications use the most common commercial Keggin-type structure and then the Wells-Dawson one, owing to their availability and chemical stability [20,21]. However, the application of phosphotungstic acid with Wells-Dawson structure as catalyst is a field of growing importance in sustainable acid catalysis [22].

Catalytic processes using HPAs as solid acid catalysts have many advantages over homogeneous liquid acid catalysis. They are non-corrosive, cheap and environmentally friendly, presenting fewer disposal problems. However, their high solubility in water and polar solvents, as well as the low specific area of bulk HPAs, limits their application as heterogeneous catalysts. So attempts to stabilize HPAs by supporting them on several carriers such as silica, alumina, titania, among others, have been made [23,24]. The interaction of the acids with these supports has led to a sharp improvement of the catalytic properties; however, the supported HPA catalysts obtained by impregnation techniques are unsuitable for their use as catalysts

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in polar reaction media due to a continuous leaching of the HPAs. In order to avoid any HPA leaching, recently, Castanheiro's group has reported the esterification of free fatty acids with methanol using Keggin heteropolyacids immobilized on silica [25].

Moreover, Popa et al. [26] studied the synthesis of heteropolyacid-mesoporous silica composites, which was carried out in acidic media by different methods. The effect of incorporating heteropolyacids ($H_3PMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$) species into organized mesoporous silica was studied by using nonionic and cationic surfactants. Besides, these authors included a Keggin-type heteropolyacid in silica using a sol-gel technique by the hydrolysis of ethyl orthosilicate [27].

In this paper we report, for the first time, the direct incorporation of a heteropolyacid with Wells-Dawson structure during the synthesis of silica by the sol-gel technique, in acidic media, using tetraethyl orthosilicate. The catalyst characterization was carried out by ^{31}P MAS-NMR, FT-IR, XRD, N_2 adsorption-desorption measurements, and the acidic properties were determined through potentiometric titration with *n*-butylamine. In addition, the esterification reaction (in heterogeneous conditions) of levulinic acid with absolute ethanol at 78 °C, by incorporating the phosphotungstic HPA with Wells-Dawson structure (WD) as active phase in a silica framework (Scheme 1), is reported.

2. Experimental

2.1. Synthesis of silica-included Wells-Dawson HPA

The Wells-Dawson HPA included in silica was synthesized by the sol-gel technique. A mixture of *n*-butanol and Wells-Dawson acid (WD) and, finally, water was added to tetraethyl orthosilicate. The mixture was stirred under nitrogen atmosphere for 1 h, at room temperature. Then, this mixture was stirred at 40–60 °C for 24 h. The hydrogel obtained was dehydrated in an oven at 80 °C and the catalyst samples were used without calcination in the catalytic tests, because the acidity of this type of materials depends on their hydration state and on the treatment temperature [22,28].

We synthesized two catalysts with two different amounts of WD acid included in silica. For the catalyst named 20WD-S, 2.7 g of pure WD acid were included, and for 40WD-S catalyst, 5 g of pure WD acid. In both cases, the amount of pure silica was 14.7 g. By sol-gel technique, for each sample, the total amount of WD acid is incorporated in the silica framework. Before being incorporated in silica, the bulk pure Wells-Dawson acid was synthesized according to the method developed in our laboratory [28]. Keggin-structure HPAs included in silica catalysts were also synthesized by the sol-gel technique in order to compare them with the Wells-Dawson HPA. In this case, a commercial phosphomolybdic acid ($H_3PMo_{12}O_{40}$, sample 40K-S) was used. Wells-Dawson synthesized samples were characterized by ^{31}P MAS-NMR, FTIR, S_{BET} , and potentiometric titration by *n*-butylamine techniques.

^{31}P MAS-NMR spectra were recorded in Bruker MSL-300 equipment. Chemical shifts were expressed in parts per million with respect to 85% H_3PO_4 as an external standard. FTIR spectra were obtained in Nicolet IR.200 equipment. Pellets in KBr and a measuring range of 400–4000 cm^{-1} were used to obtain the FT-IR spectra of the solid samples at room temperature. Power XRD patterns were recorded in Phillips PW-1732 equipment with built-in recorder, using Cu K α radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and

scanning angle between 5 and 60° of 2 θ at a scanning rate of 2° per min. Specific surface areas (S_{BET}) and textural characteristics of the catalysts were determined by the nitrogen adsorption/desorption technique using Micromeritics ASAP 2020 equipment.

The acidic properties of the samples were determined by potentiometric titration using a solution of *n*-butylamine in acetonitrile in a Metrohm 794 Basic Titrimo apparatus. A 0.05 mL portion of *n*-butylamine (0.1 N), in acetonitrile, was added to a known mass of solid (between 0.1 and 0.05 g) using acetonitrile as solvent, and stirred for 3 h. Later, the suspension was titrated with the same base at 0.05 mL/min. The electrode potential variation was measured in a Metrohm 794 Basic Titrimo apparatus with a double junction electrode.

Catalytic tests were carried out in a stirred batch reactor at 78 °C. In a typical experiment, the reactor was loaded with 30 mmol of absolute ethanol, 250 mg of 40WD-S and 2 mmol of levulinic acid. The reaction was followed by TLC (thin layer chromatography until a reaction time of 10 h, using a 4:1 mixture of hexane:ethylacetate as solvent). TLC aluminum sheets (silica gel 60 F $_{254}$ Merck) were used. The catalyst was filtered off and washed twice with absolute ethanol, 2 mL each/with 2 mL absolute ethanol. The filtrate and the washing liquids were combined and concentrated in vacuum. The residue was dissolved in CH_2Cl_2 (10 mL) and the solution was washed with $NaHCO_3$ 5% (3 \times 2 mL) and water (1 \times 5 mL) to separate the levulinic acid. The organic phase was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford crude ethyl levulinate. The product was identified via comparison with an authentic sample of ethyl levulinate and mass spectra analysis. The reaction yield was expressed as the ratio of % moles of product to moles of initial substrate. *Ion impact mass spectrum of ethyl levulinate*: MS (EI), 70 eV, m/z (rel. intensity): 144 (4) [M^+], 129 (22), 99 (67), 74 (20), 43 (100), 29 (17) [29].

Stability tests of the silica-included HPA catalysts were carried out by running four consecutive experiments under the same reaction conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed with absolute ethanol (2 \times 2 mL), dried under vacuum and then reused. The filtrate was analyzed for W content via ICP, but no W traces were detected.

3. Results and discussion

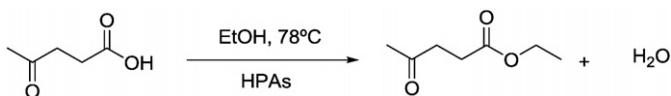
3.1. Catalysis characterization

3.1.1. S_{BET} measurements

Table 1 lists the surface area, average pore diameter and pore volume of the different synthesized samples and silica obtained by sol-gel. Bulk Wells-Dawson acid has a very low value of S_{BET} (2–4 m^2/g), and pure silica 507 m^2/g , respectively. For 40WD-S and 20WD-S, the S_{BET} are 531 and 580 m^2/g , with average pore diameter of 25.8 and 26.7 Å, respectively. The values of S_{BET} are higher than the pure silica because WD incorporated in framework of silica acts as a pore forming. This can also be observed in the pore volume values (Table 1). The difference between 20WD-S and 40WD-S may be due to the catalyst contains the highest amount of WD could be incorporated into the framework silica and, also, remains in the mouth of the pores, reducing the three measured parameters (Table 1).

Table 1
Surface area of different samples.

Sample	Surface area: S_{BET} , m^2/g	Average pore diameter, Å	Pore volume, cm^3/g
Bulk WD	2–4	–	–
Pure SiO_2	507	21.9	0.18
20WD-S	580	26.7	0.35
40WD-S	531	25.8	0.20



Scheme 1. Ethyl levulinate synthesis.

3.1.2. ^{31}P MAS-NMR of silica-included WD samples

In order to verify the incorporation of WD in the silica framework, the synthesized samples were characterized by ^{31}P MAS-NMR. This technique is the “fingerprint” of the HPA compounds. The pure bulk WD acid has two equivalent phosphorus atoms and consequently, it shows only one main peak in the ^{31}P MAS-NMR spectrum in the range of -12.8 , -13 ppm [30]. The spectra of ^{31}P MAS-NMR of WD included in SiO_2 catalysts with two different loadings of WD (40WD-S and 20WD-S, *a* and *b* curves, respectively), are shown in Fig. 1. The results indicated that silica-included WD samples display the main peak with a chemical shift at -13.2 ppm, which indicates that after the synthesis and drying, the acid maintains its Wells-Dawson heteropolyanion structure. Two new small signals at -12.4 and -11.7 ppm approximately are evident in the samples. These signals could be related to the presence of different Dawson species, such as $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ strongly interacting with the Si–OH groups of the support, and to species such as $\text{P}_2\text{W}_{21}\text{O}_{71}^{6-}$, respectively [30].

3.1.3. FT-IR measurements

On the other hand, the FTIR spectra (Fig. 2) also show that after synthesis the WD keeps its Dawson structure. This figure shows the spectra for the bulk WD and for the 40WD-S sample, after subtraction of the spectra that correspond to the support. The characteristic bands of the HPA with Dawson structure are 1091 (stretching frequency of the PO_4 tetrahedron), 963 ($\text{W}=\text{O}$ terminal bonds), 911 and 778 cm^{-1} (“inter” and “intra” W–O–W bridges, respectively) [30]. It can be observed that the acid included in silica displays the same characteristic bands. Nevertheless, for these samples a broadening of the band at 1091 cm^{-1} is observed. This fact can be due to a loss of tetrahedron symmetry [30] because of the interaction between WO_6 octahedral and sylanol groups of silica. A shift of the 778 cm^{-1} band (“intra” W–O–W bridges) can also be observed, which could be attributed to the same effect.

On the other hand, XRD measurements of the silica-included samples only showed a broad diffraction peak corresponding to the silica support, without the characteristic lines for WD acid as we reported in previous work for supported catalysts [30]. This indicates that WD HPAs are included as small particles not detectable by XRD. Similar results were obtained by Popa et al. [27]

Both ^{31}P MAS-NMR and FTIR measurements show that the Wells-Dawson acid keeps its Dawson structure after its incorporation in the silica framework.

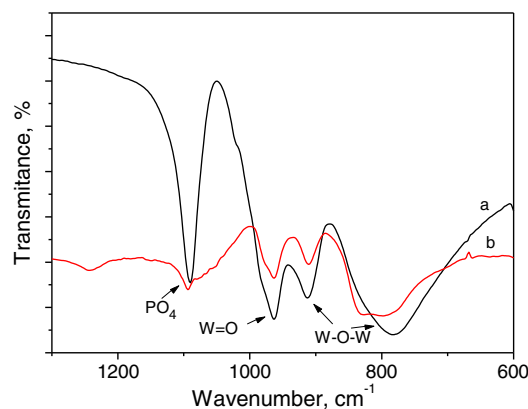
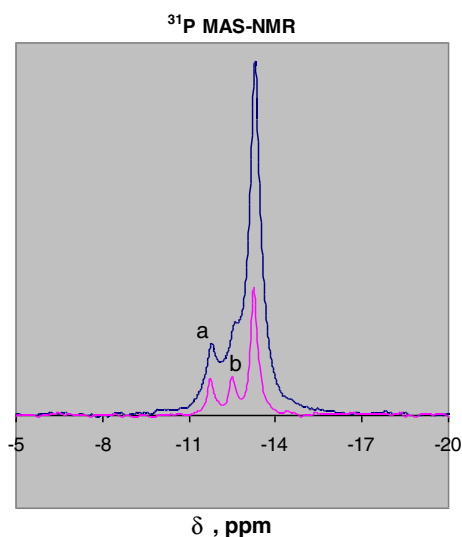


Fig. 2. FTIR spectra of bulk WD (curve a) and 40WD-S (curve b) samples.

3.1.4. Potentiometric titration measurements using *n*-butylamine

The *n*-butylamine is considered a strong base, so its adsorption on sites of different acid strength could be expected. The total solid acidity is titrated without distinguishing the type of acidity. At this point, it is interesting to comment that the development of a potentiometric method was thought of taking into account that the acid and basic functions of a solid are not properly defined thermodynamically. Moreover, an indicator test such as the Hammett method, though considered as a reference technique, is difficult to apply to certain solids. The method used here is based on the observation that the potential difference is mainly determined by the acidic environment around the electrode membrane. The measured electrode potential is an indicator of the acidic properties of dispersed solid particles. The acidic properties of the solid samples measured by this technique enable the evaluation of the number of acid sites and their acid strength. In order to interpret the results, it is suggested that the initial electrode potential (*E*) indicates the maximum acid strength of the surface sites, and the values (meq/g solid), where the plateau is reached, indicate the total number of acid sites. The acid strength of surface sites can be assigned according to the following ranges: very strong site, $E > 100$ mV; strong site, $0 < E < 100$ mV; weak site, $-100 < E < 0$ mV, and very weak site, $E < -100$ mV.

The acidity of bulk Wells-Dawson and Keggin HPAs is Brønsted in nature, and their initial electrode potential indicated that both are superacids [31,32]. Furthermore, the potentiometric curves obtained by titration of silica-included WD catalysts with *n*-butylamine and their comparison with that of the Keggin structure (40K-S) are summarized in Fig. 3. Silica-included HPA catalysts also show very

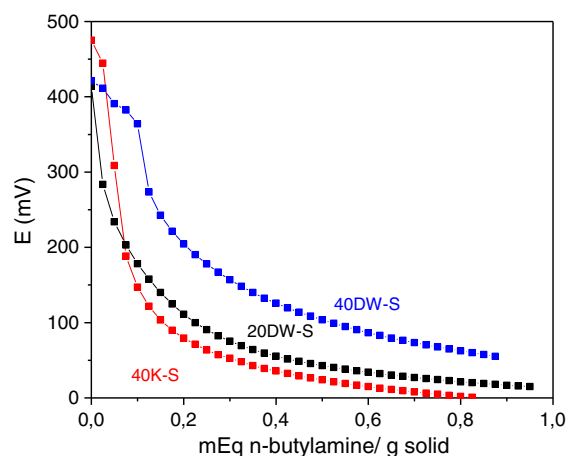


Fig. 1. ^{31}P MAS-NMR spectra of silica-included Wells-Dawson HPA samples, a) 40WD-S and b) 20WD-S.

Fig. 3. Curve of potentiometric titration of different silica-included samples: 40WD-S; 20WD-S; and 40K-S.

strong acid sites after their incorporation in the silica framework; this could be related to the proton mobility, which in part depends on the negative charge distribution in the heteropolyanion oxygen's. It is observed that the increase in the concentration of WD does not cause an important variation in the acidic properties but there is a variation of plateau start for both cases. Compared with the Keggin structure, this property shows a similar behavior when HPA is included in the silica network. It is possible that negative charges of WD anions are located on the external oxygen atoms, so the attraction of the ternary structure to protonated OH groups is probable. For each WD anion there are 6H^+ eventually capable of acting on OH groups of sol-gel silica.

If an interaction occurs between these OH groups and the protons, giving rise to OH^{2+} groups, there are probably enough OH groups to complete the interaction, but only a small amount of them (those that are sterically favorable) can be available for the interaction with both the WD anions and the protons. The acidity of these bulk compounds is higher than that of mineral acids and it depends on their hydration state, the strength of acid sites and proton accessibility [22].

3.2. Catalytic tests

3.2.1. Performance using different catalysts

This work describes, for the first time, the application of heteropolyacids with Wells-Dawson structure, included in silica for the direct esterification of levulinic acid, in heterogeneous conditions, with excess of ethanol. It must be noted that, if the WD active phase is deposited by impregnation, there will be always leaching during the reaction in polar solvent like ethanol due to WD is very soluble, and simultaneously there will be heterogeneous and homogeneous catalysis. Table 2 shows the obtained results for the yield% of EL using different bulk and silica-included catalysts. The catalytic tests were carried out in a stirred batch reactor at $78\text{ }^\circ\text{C}$, as has been described in the experimental section. The reaction yield was expressed as the ratio of % moles of product to moles of initial substrate. In our reaction conditions, EL was obtained as an only product (selectivity of 100%). Secondary products such as angelica lactone, 4-etoxy γ -valerolactone and/or aldehydes were no detected. Blank experiments, without catalyst and silica sol-gel (SiO_2) as catalysts, were performed under similar reaction conditions (Table 2, entries 1 and 2, respectively). No conversion of LA for both samples was detected. Besides, the esterification reaction of LA using two bulk catalysts with different structure, Wells-Dawson (WD) and Keggin (K) HPA, (Table 1, entries 3 and 5), were performed. In these conditions, both catalysts are very soluble in the reaction medium (homogeneous catalysis). The obtained yields were 93% and 92% for bulk WD and K HPA, respectively.

On the other hand, the yields (%) of EL using K and silica-incorporated WD heteropolyacids are also listed in Table 2, entries 4 and 6 to 10, respectively. It can be observed that for both types of

Table 2
Catalytic performance of different heteropolyacids in levulinic acid esterification at $78\text{ }^\circ\text{C}$.

Entry	Catalyst type	Catalyst	EL yield (%)
1		None	–
2	SiO_2	Support	–
3	Keggin HPA	K_{Bulk}	92
4		40K-S	38
5		WD_{Bulk}	93
6		40WD-S	76
7	Wells-Dawson HPA	40WD-S ^a	–
8		40WD-S ^b	72
9		40WD-S ^c	70
10		40WD-S ^d	79

Experimental conditions: 2 mmol of LA, 7.5 mL (128 mmol) of absolute ethanol (ratio ethanol/LA: 64/1); reaction time, 10 h, $78\text{ }^\circ\text{C}$. ^{a,b,c,d}Using 20, 100, 500 and 1000 mg of catalyst.

Table 3

Stability studies of the 40WD-S catalyst on the esterification of levulinic acid with ethanol. Reuse of the catalyst in four consecutive experiments.

Entry	Catalytic cycle	Yield to EL (%)
1	First use	76
2	1st re-use	68
3	2nd re-use	68
4	3rd re-use	68

Experimental conditions: 0.01 mmol catalyst, 2 mmol of levulinic acid, 7.5 mL (128 mmol) of absolute ethanol; 10 h, $78\text{ }^\circ\text{C}$, molar ratio ethanol/LA: 64/1.

HPA structures, the catalytic activity decreases from bulk HPA to the included ones. These results are in agreement with the acidity measurements explained in detail in Section 3.1.2.

Besides, experiences using different amounts of active 40WD-S catalyst (20, 100, 500 and 1000 mg) were performed (Table 2, entries 7 to 10). The results showed that an increase in the amount of catalysts from 100 to 1000 mg only produces a slightly increase in the yield to EL.

3.2.2. Catalyst recycling

As mentioned before, the disadvantages of HPAs as heterogeneous catalysts lie in their low specific area and high solubility in polar media, such as ethanol used as a reactant for the esterification reaction. After the direct incorporation in silica, WD samples have a higher specific surface area, but it is necessary to avoid any leaching of the WD acid during the reaction. In fact, the catalytic stability of the fresh synthesized 40WD-S catalyst was evaluated in the esterification reaction using a molar ratio of absolute ethanol/EL of 64:1, by performing consecutive batch reactions with the same samples, as is described in detail in the experimental section. After the first run the yield decreased, and after the second batch the catalyst activity stabilized during three reaction cycles. The EL yields to the four cycles were 76%, 68%, 68% and 68%, respectively (Table 3). The filtrate was analyzed for W content via ICP, but no W traces were detected. According to these results, an ethanol pretreatment of the fresh synthesized WD sample before the esterification reaction was done. The sample was refluxed in absolute ethanol, for 48 h, and then this washed sample was filtered and dried under vacuum. ICP analysis of the filtrate indicated that the 10% of WD active phase was lost after this pretreatment with ethanol. Catalytic tests using this ethanol-washed sample were done. The results indicated that after this

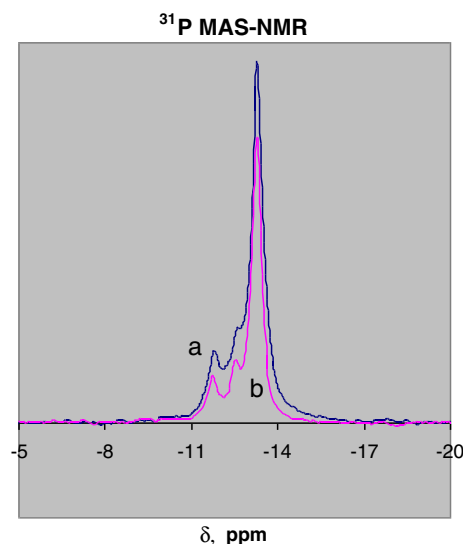


Fig. 4. ^{31}P MAS-NMR spectra of silica-included Wells-Dawson HPA. a) Fresh 40WD-S and b) the same sample after three reaction cycles.

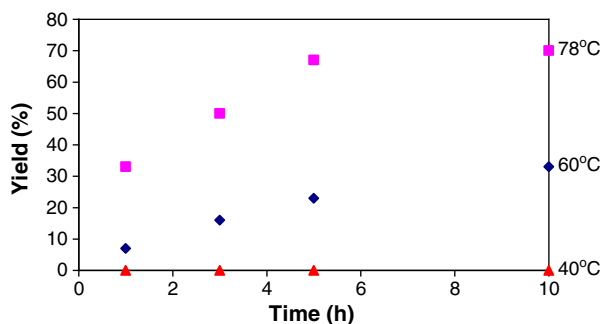


Fig. 5. Yield to ethyl levulinate (EL) vs. time, at different reaction temperatures: a) 40 °C; b) 60 °C and c) 78 °C.

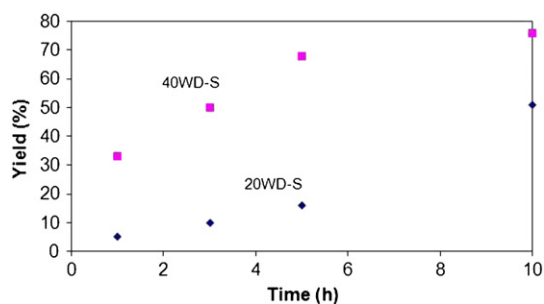


Fig. 6. Yield to ethyl levulinate (EL) vs. time, at two different loadings of included Wells-Dawson acid.

pretreatment the decrease in activity after the first cycle was not observed, and the catalyst kept the activity constant during four cycles.

The reused sample was characterized by ^{31}P MAS-NMR and compared with the fresh synthesized sample before the catalytic test, and the HPAs also kept their HPA structure after four reaction cycles (see Fig. 4a and b, respectively).

In order to verify heterogeneous conditions of the esterification reaction, additional catalytic experiments were done. The ethanol-

prewashed 40WD-S sample was put in contact with ethanol for 48 h at reflux, under stirring, without LA. After this time, the catalyst was separated from ethanol by centrifugation, and LA was added to the reaction mixture. The reaction was carried out for 10 h, and ethyl levulinate was not detected. This behavior indicates that the reaction only occurs heterogeneously.

3.2.3. Influence of the different operative conditions on the esterification reaction

In order to find the best reaction conditions for the esterification reaction, several experiences using different molar ratios of absolute ethanol to LA, reaction times, temperatures and different loadings of WD included in silica were done. For these tests, the ethanol-prewashed 40WD-S samples were used.

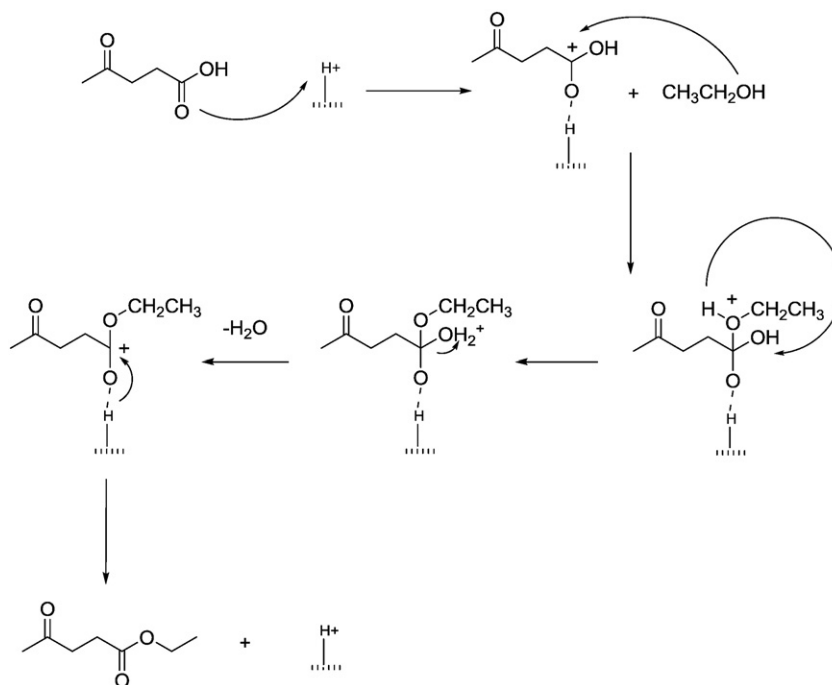
The molar ratio of ethanol to LA was varied from 64 to 3:1, and the results showed that a ratio of 3 is enough to obtain similar yields of ethyl levulinate at 78 °C and 10 h, 76% and 78%, respectively.

Fig. 5 shows the yield of EL versus time, at different reaction temperatures 40, 60 and 78 °C, using the ethanol-prewashed 40WD-S sample. In this case, a ratio of ethanol/LA of 3 was used, according to the results mentioned above. An increase of ethyl levulinate is observed as temperature and time increase.

On the other hand, Fig. 6 shows the effect of a lower loading of WD incorporated in silica, 40WD-S and 20WD-S samples, as a function of time, at 78 °C and an ethanol/LA molar ratio of 3. A diminution of the EL yield for the sample with the lowest WD loading with respect to the 40WD-S sample can be observed. It must be noted that the number of acidic sites for the 20WD-S sample is half that of 40WD-S, according to the titration measurements (see Fig. 3).

3.2.4. Proposal for a possible mechanism

The reaction mechanism for the esterification reaction of levulinic acid with ethanol can be described as a general Fischer esterification with several steps: first, an adsorption of levulinic acid on Brønsted sites on the catalyst surface, forming a protonated levulinic acid intermediate, increases the electrophilicity of carbonyl carbon. This carbonyl carbon would be attacked by the nucleophilic oxygen atom of ethanol leading to the formation of an oxonium ion. Then a proton transfer in



Scheme 2. Proposed mechanism for levulinic acid esterification with ethanol.

the oxonium ion gives a new oxonium ion and finally the loss of water from the latter oxonium ion, and subsequent deprotonation leads to the ester, with the acid site on the catalyst surface being regenerated [33,34] (Scheme 2).

4. Conclusions

For the first time, Wells-Dawson HPA structures were incorporated in the silica framework by the sol-gel technique. The synthesis of catalysts by the sol-gel technique was satisfactory and the samples kept their HPA structure intact after synthesis. The catalytic tests for the esterification reaction between levulinic acid and ethanol to produce ethyl levulinate using these silica-incorporated Wells-Dawson catalysts were done. It was observed that the esterification of levulinic acid with ethanol only occurs in the heterogeneous phase. It must be noted that silica-included HPAs also kept their structure and catalytic activity after three consecutive reaction cycles. These results indicated that these solid acids are promissory catalysts for the esterification reaction of levulinic acid with ethanol to ethyl levulinate and they would be active and selective catalysts for this reaction.

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