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Fructose transformations in ethanol using carbon supported polyoxometalate acidic solids for 5-Etoxymethylfurfural production

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Abstract: A series of carbon supported polyoxometalates have been prepared and studied as acid catalysts for the fructose dehydration. The catalytic supports, microporous activated carbon (AC, S_{BET} = 1190 m²/g) and high surface area graphite (HSAG, $S_{BET} = 400 \text{ m}^2/\text{g}$), were loaded with 15wt% of polyoxometalates: phosphotungstic acid (TPA) or tungstosilicic acid (STA). The four resulting catalysts were tested in the fructose reaction at moderate temperature 140°C, using water and ethanol solvents. Catalytic properties have been compared with those of an acidic resin, Amberlyst 15. As relevant findings the specific interactions of carbon supports and polyoxometalaltes let the inhibition of active phase lixiviation. An improved catalyst (STA-HSAG) in terms of selectivity to valuable products (ethoxymethylfurfural and ethyl levulinate) and high specific catalytic activity using ethanol as solvent has been developed. This catalyst can be reused after regeneration by washing with organic solvents.

Introduction

Biomass derived compounds are possible sources for substitution of petroleum based products because they have a high content of carbons. In particular sugars (fructose and glucose mixtures), which are easily obtained after a cascade of operations from biomass, can be converted into platform molecules through acidic catalysed reactions.^[1-3] For instance 5hydroxymethylfurfural (HMF) and levulinic acid (LA) products are interesting platform molecules for the bio-refinery industry. Thus by dehydration of hexoses (i.e. glucose or fructose) can be produced HMF and later LA. For these catalyzed processes new high performance acid solids are required. Furthermore, the reaction media is also important, water as a green solvent should be desirable against organic liquid. Alternatively, bioethanol (another platform compound or raw material) may be used as reaction medium being possible to obtain other valuable products, instead of HMF and LA, ethoxymethylfurfural (EMF) and ethyl levulinate (ELA) will be formed.

Solvents used for biomass processes may lead to different

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quality products and even serve as reactants themselves. Thus, depending on the solvent employed, fructose dehydration reaction goes through different reaction routes, as illustrated in the Scheme 1.

When the solvent is water, there is only one possible way: fructose is dehydrated to HMF (1) and later a second hydration occurred to obtain LA (2) and formic acid. On the other hand, if ethanol (EtOH) is used as solvent, the reaction involves two possible pathways. One of this consists firstly in the dehydration of fructose to HMF (1) and subsequently HMF is ethylated to EMF (4) or 5-(diethoxymethyl)2-furanmethanol (DEFM) (5). Both of these could be ethylated to 5-ethoxymethylfurfural diethyl acetal (EMFDA) (7,8) or hydrated to ELA (9,10). Finally ethylated products (EMFDA) could be hydrated to produce ELA (11) and ethyl formate. Notice that this scheme is rather similar to the reported in the reference.^[4] Following the second possibility of fructose dehydration in ethanol medium, this is transformed into E-fructose by ethylation (3), thus this compound goes to its dehydration to obtain EMF (6). The next steps starting from EMF to yield DEMF, ELA and EMFDA are also displayed in the Scheme 1.



Scheme 1. Some possible pathways when fructose reacts over acid solids in the presence of ethanol or water.

The requirement of developing new solid acidic catalysts for the bio-refinery can be rationalized considering that at present used catalysts in the petroleum industry (typically zeolites) could not be efficient enough with biomass compounds, which can be related with the higher content of oxygen in this second group of raw materials.^[5] In addition, due to the relatively low thermal stability of the biomass feedstocks, compared with compounds resulting from petroleum industry, lower reaction temperatures have to be applied for biomass processing and consequently stronger acid sites are required.

lon exchange resins and zeolites are typically heterogeneous acidic catalysts used for dehydration reactions.^[6] Taking into account the acidity of the ion exchange resins, i.e. commercial Amberlyst-15, these protonated ion exchange solids appear to be a suitable alternative^[4,7]. As reported in different publications, using ion exchange resin higher catalytic performances than on zeolites can be achieved.^[8,9] Of course, solved inorganic acid can also be used in these reactions but their environmental negative impact implies less sustainability.

On the other hand, heteropolyacid solids or polyoxometalates (POMs) are another type of eco-friendly acid solids, and furthermore with stronger acidic sites than mineral acids.^[10,11] Many applications of POM as catalysts for hydrocarbon transformation processes have been reported^[12-15] and some excellent reviews have been devoted to these acid solids.[16-19] However, less extensive are the reports where POM are used as catalysts for transformations of biomass derived compounds. In this line Palkovits et al.^[20] have reported conversions of 90% and HMF's selectivity between 40-50% in fructose dehydration reaction, using both commercial or modified POMs. Also, dehydration of fructose has been studied by Chen et al.^[21] over cesium and vanadium modified POMs for whom conversions up to 99% and HMF vields near 70% were reported. Unfortunately many of these experiments were carried out with DMSO (dimethyl sulfoxide) as solvent, giving rise to less green processes. Relevantly, Ueda et al.^[22] have reported the dehydration of biomass raw material (i.e. cellulose) in an aqueous medium employing POM molecular wires based on tungstotellurate and tungstoselenate oxides as catalysts. Under the reaction conditions of this latter study high cellulose conversions and high glucose yields were achieved. As for the solvents used in these processes catalyzed by POMS, it should be remarked that commercial POMs are in general water soluble. Therefore, to these acid materials be employed as viable heterogeneous catalysts, anchoring of these structures over stable metal oxide solids (i.e. silica, alumina or metal oxides) or supporting them over highly hydrophobic materials (i.e. carbonaceous materials) would be necessary. So, for example, two phosphotungstic acids supported over silica (HPW/SiO2 and HSiW/SiO₂) were used by Yang et al.^[23] for fructose dehydration achieving conversion values of 70% and HMF yields near 37%. Recently we synthesized POM catalysts supported on activated carbon and high surface area graphite which were applied as solid acids for the vapour phase dehydration of bioethanol^[24], as well as bifunctional (by adding Ru nanoparticles) catalysts for the ethylene glycol and propylene glycol production from cellulose.[25]

Herein, we report new catalyst series based on two commercial POMs for studying fructose dehydration reaction. Seeing that in previous reports organic solvents were often used, our first objective is to do this reaction with green solvents (i.e. water or bioethanol). Secondly, as the possibility of lixiviation exits when supported POMs are employed as heterogeneous acid catalysts, the stability and recyclability of these new acidic materials was tested. The two commercial POMs ($H_3PW_{12}O_{40}$ (TPA) and $H_4[W_{12}SiO_{40}]$ (STA)) were supported over two different carbonaceous materials (high surface area graphite (HSAG) or

activated carbon (AC)) and compared with another acidic material of different nature (i.e. ion exchange resin). For this study Amberlyst-15 (Amb-15) was selected as reference catalyst due to its extensive use for dehydration biomass reactions.

Results and Discussion

All the catalytic experiments were carried out in a batch reactor and the kinetic data were obtained at a constant reaction temperature of 140 °C and a pressure of 30 bar of inert gas. These conditions were selected after different previous experiments without catalyst exploring fructose reactivity at higher reaction temperatures. We found that the reactive fructose is intensively decomposed in the empty reactor with increasing temperature (thermal degradation). Under the indicated reaction conditions blank experiments with the carbon supports, AC and HSAG, were performed to verify their intrinsic catalytic activity. Less than 10% of fructose conversion was obtained, mainly due to thermal decomposition, because only a yield lower than 1% toward interest products was observed after 6 h in reaction. Consequently the yield of desirable products using carbon support materials can be considered negligible.

In a first set of experiments, we have compared two catalysts, Amberlyst-15 (Amb-15) and $H_{40}SiW_{12}O_4 \cdot nH_2O$ (STA) supported over a high surface area graphite HSAG (STA-HSAG), in order to evaluate the effects of the solvents, water and ethanol. The results are presented in Figure 1. In these experiments fructose conversions and product yields evolution with the reaction time are compared for both catalysts (Amb-15 and STA-HSAG).



Figure 1. Comparison of the conversion of fructose and the yields toward main products when the catalysts are Amb-15 (a,c) or STA-HSAG (b,d) and solvents are water (a,b) or ethanol (c,d).

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Two main aspects can be featured: fructose is significantly more rapidly transformed in the ethanol media and the product selectivity (see Figure 1) changes from HMF (obtained by reaction 1 of the Scheme 1) in the case of water to EMF and EMFDA with ethanol, so reactions numbered as 1 or 3, and 4 or 6 followed of 7 in Scheme 1 are taking place. In Figure 2 yields to the main products and other products (formic, acetic and lactic acids in the case of water and ethyl formate and E-fructose with ethanol) are compared at the end of the reaction time (6 h). Clearly the best yield to EMF is achieved with ethanol and using STA-HSAG as catalyst. Interestedly this preliminary comparison with the Amb-15 reveals that our catalysts based on POMs can be competitive for fructose transformation.



Figure 2. . Comparison of catalytic yields to main products (Scheme 1) when water or ethanol are used as fructose solvents. The studied catalysts were: Amb-15 and STA-HSAG.

From Figures 1 and 2 we have selected ethanol as solvent media for the subsequent reaction studies. Also we are interested in the comparison of Amb-15 with the two POMs (STA and TPA) supported over activated carbon and HSAG. At this point it is necessary to remark that we have selected this commercial Amb-15 catalyst just due facility of acquisition, so we have not considered an improved acidic resin.^[26] Given the high solubility of the POM in the two solvents used in reaction (water and ethanol), some leaching of the supported acid POM into the reaction solution under the applied reaction conditions could be envisaged. In order to check the extent of this lixiviation effect, two complementary set of experiments were performed. First the liquid after finishing the reactions was analysed by inductively coupled plasma mass spectrometry to detect the presence of solved POMs. When water is the solvent the amount of POM lixiviated to the solution was of 50% (Table S1) while in ethanol was lower than 15 % of the initial loading in the catalyst. The second set of experiments was done to verify the leached POMs (working as homogeneous catalyst) give place to conversion and selectivities rather lower than our heterogeneous catalysts. For instance, with pure STA in the fructose dehydration in ethanol, we obtain conversions of 20%, with carbon balances near 90%, but with yields of 3% of DEFM and 7% of E-fructose. These data correspond to 3 h reaction in an experiment where a concentration of STA 3x10⁻⁵ molar has been used, with an initial 0.01 molar concentration of fructose in

ethanol (total volume in the batch reactor 90 ml). These results suggest that the dispersion of the POM on the carbon support may influence its catalytic behavior. In addition, as we will discuss below these solid materials can be reused in an ethanol medium. The reasons for the improved catalytic performance and stability can be associated to the tight anchoring of POMs over the carbon support surfaces. So Qi et al.^[27] demonstrated that heteropolyacids can be efficiently dispersed on N functionalized carbon nanotubes achieving active and stable catalysts in water media. Very recently, following this investigation line, some different interactions have been proposed to explain the anchoring of POMs over carbon nanotubes surfaces [28] These authors suggest that electrostatic interactions of POMs with the surface pyridinic N groups of the carbon nanotubes are one of the reasons for their irreversible immobilization on the carbon nanotubes. In our catalysts, the carbon supports are not functionalized with basic species, but the delocalized p-electrons present on the basal planes of carbons are assumed to have basic nature.^[29] On the other hand, the anchoring of POMs would take place at the graphite crystallite edges or with defective carbon surface sites will be inhibited by the oxygen surface groups, with acid character, that exit in such as defective sites. So an effective interaction of POMs with the basal graphitic surfaces would lead to a good dispersion of the POM on the support, i.e., low sizes of crvstallites.

In order to determine the sizes of POM crystallites in the fresh samples we have applied two techniques, Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). In Figure S2, the diffractograms of the four catalysts prepared as well as the two commercial POMs used in their preparation are displayed. It is clear that diffraction lines stemming from POM phases in the carbon supported POMs are broad and practically undetectable. The absence of significant peaks of POMs in the diffraction patterns of the catalysts, in spite of their high 15wt% loadings, reveals that crystallites are rather small, surely in the nanometric scale. These facts are confirmed from the SEM images of the four POM supported catalysts, which are shown in Figure 3 and Figure S3.



Figure 3. Representative SEM images of samples: HSAG (a), STA-HSAG (b), AC (C) and STA-AC (d).

For HSAG supported samples practically the POM crystallites are not distinguished from the bare support. In samples supported on AC some big POM particles can be observed (Fig. 3-d) on the external surface, but the amount of such particles seems to be rather low, so possibly the majority of POM particles are trapped in the micropores or small mesopores of the AC support, which are inaccessible to the SEM technique. These smaller crystallite sizes are indicative of specific interactions between carbon supports and POMs, which can justify the hindered solubility of these supported POM samples. Additionally, the sample STA-AC was studied by SEM after being used in reaction, some representative images are given in the Fig. S4. Interestingly most of the crystallites of STA with higher sizes have disappeared likely by dissolution in the ethanol reaction medium. The smaller POM crystallites remain stabilized by interaction with the carbon supports.

In order to gain information about these specific interactions a series of thermogravimetric analysis under inert gas flow have been performed. In Figure 4 are represented the thermogravimetric analysis curves and the differential scanning calorimetry (DSC) profiles for the bulk POMs (STA or TPA) and the supported catalytic systems. Moreover in the supplementary information, Figure S5, are displayed the differential thermal analysis (DTG) of all the samples and in Figure S6 the TG, DTG and DSC of the supports (HSAG or AC).



Figure 4. Thermogravimetric analysis (TG) black lines and scanning differential calorimetry (DSC) red lines of supported POMs, carbon supports and POMs.

In the case of pure POMs two weight losses can be distinguished: the first about 100°C, where the loss of hydration water molecules takes place, and the second between 160 °C and 260°C, corresponding to the removal of hydroxyl groups, as previously discussed.^[24] These weight losses are endothermic processes. In addition, for STA and TPA DSC exothermic signals at temperatures above 550 °C are evidenced, which are not accompanied of weight losses. These may probably correspond to POM decomposition into single metal oxides.^[24] In all supported catalysts this exothermic decomposition at higher temperatures is not observed, probably because parasite contributions of the carbon supports. Relevantly the weight loss associated to dehydration reactions are very diminished in the supported catalysts. In particular the peak due to dehydroxylation (near to 200 °C) is practically undetectable (see Fig. S5 where DTG profiles are presented). This fact can be indicative of existing specific interactions among carbon supports and POMs, which stabilize the properties of supported POMs versus the bulk crystalline material, in particular with regard to the hydroxyl group stability. These interactions of POMs with carbon supports can probably be related, as discussed above, with basal graphitic surface sites. In fact, though small these peaks of dehydroxylation can be appreciated for TPA and STA supported on AC whereas they entirely disappear when POMs are supported over HSAG. According XRD and SEM results, it seems that the smaller POM nanoparticles in interaction with graphitic surfaces (HSAG) are more stabilized in their hydroxylated forms than bigger POM crystallites supported over AC. Unfortunately the first weight loss associated to the dehydration of POMs can not be differenced of desorption of water from the supports (see also Fig. S6).

In order to compare all the synthesized catalytic materials, they were tested in the same reaction conditions: ethanol as solvent, 140°C of reaction temperature, a pressure of 30 bar of inert gas and a weight ratio of 15 of active phase to 100 of fructose. Figure 5 shows the fructose conversion values at different reaction times. Clearly from this Figure 5 and from data collected in Fig. S7 can be seen that POMs supported on HSAG and AC behave differently. In the presence of the POMs supported on HSAG, fructose reacts slower than over AC supported POMs but the production of target products seems to be quicker with HSAG supported catalysts. Probably the adsorption of fructose is more rapid over the higher sized crystallites of POM located at the external surfaces of AC. Also the production of byproducts, such as humic acids, is favored over the microporous AC support in comparison with HSAG, so the production of desirable products is delayed in the case of STA-AC and TPA-AC samples. This behavior about the formation of non-desirable products will be discussed below. As before mentioned under these reaction conditions a maximum of fructose conversion of 10% is achieved after 6 hours in reaction and the production of interest compounds is not significant for the bare supports.

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Figure 5. Evolution of fructose conversion with the reaction time over different catalytic materials.

By the extrapolation of the conversion rates in Fig. 5 to time zero it is possible to confirm that all the POM derived catalysts have comparable initial activities. However, the commercial Amb-15 sample has a diminished catalytic activity. In order to check the acidic properties of the different catalysts an additional test, the decomposition of isopropanol (IPD) reaction, was performed. For all the catalysts, the only detected product in this test was propylene, which is derived from the dehydration reaction catalyzed by acidic surface centers. Therefore, from the determination of specific activities for IPD, we have been able to obtain a direct and quantitative measure of acid sites. These results are reported in Table 1. It is noteworthy that during this IPD gas phase reaction no deactivation phenomena were observed, so both catalytic activity and propylene selectivity remain constant.

 Table 1. Specific catalytic activities determined for the different catalysts in the gas phase isopropanol decomposition reaction.

Catalyst	Activity (µmol conv./g·s)
Amb-15 STA-AC STA-HSAG TPA-AC TPA-HSAG	1.5 1.7 3.0 2.0 1.8

From this Table 1 is apparent that the density of acid surface sites exposed on Amb-15 material is slightly lower than on the POM supported samples, but this slight difference could explain the lower initial catalytic activity of this commercial material for the fructose dehydration reaction. However, in the case of Amb-15 catalyst is particularly relevant to note that the fructose transformation reaction and IPD test are performed in different media. The former process is studied in a batch reactor with ethanol as solvent, while the second is a gas phase continuous flow operation. It is well known that Amberlyst materials can suffers swelling phenomena in liquid medium modifying their accessible surface area as well as the amount of exposed acid sites.^[30]

In general, from Figure 5, it appears that POMs supported on AC are more active for the fructose transformation than when supported on HSAG. At least two aspects could contribute to these slight differences. As previously demonstrated by XRD and SEM, POM crystallites are smaller in size when supported over HSAG, which could explain the maximum of IPD activity (Table 1) detected for STA-HSAG. On the other hand, in the fructose dehydration reaction we could assume that some diffusional effects can be occurring. In fact small POM crystallites in the catalysts supported over HSAG are practically invisible in the corresponding SEM images, thus on these samples the smaller crystallites could be placed inside the nanometric hollows (inter graphite particle spaces) and suffer a restricted accessibility of fructose in comparison with the POMs supported over AC which presents crystallites with higher dimensions observable by SEM.

Also relevant is the comparison of catalytic yields to significant reaction products. In Figure 6 are reported as bar diagrams the vield values to different interesting compounds obtained from fructose using ethanol as solvent-reactant. These values correspond to 3 h under reaction. In the supplementary information is represented (Figure S7) the evolution of reaction products with the time for all studied catalytic materials. Interestingly, the yields to EMF+EMFDA depend on the active acid component. Clearly these yield values are higher over STA derived catalysts in comparison with TPA ones. Amb-15 sample can be placed in an intermediate position from this point of view of EMF productivity. In particular with the catalyst STA-HSAG, which exposes the maximum of acidic site density (Table 1), is possible to obtain up to near 50% yield to EMF+EMFDA under our soft experimental conditions.



Figure 6. Interest products yield (%), carbon balance and fructose conversion of all catalysts using EtOH as solvent.

A preliminary comparison with published data, for the same reaction and at comparable experimental conditions, evidences that our catalytic results agree in terms of catalytic activities and selectivities^[31] So, using zeolites and unsupported Amberlyst similar catalytic yields have been reported.^[32] Thus, our best (STA-HSAG) catalytic system, based in supported POM, achieves similar yields but in our case the ratio of substrate/active catalytic phase is noticeably higher.

Apparently HMF+DEFM selectivity values, these two compounds being intermediate reaction products (see Scheme 1), are higher when using Amb-15 or supported TPA catalysts. Contrarily the production of final products, EMF+EMFDA, is favoured with the STA derived catalysts. Taking into account that the total number of acid sites (Table 1) cannot directly be related with these findings, we could propose that the particular property of the supported STA smaller crystallites combines their surface acid sites and the neighbor atomic arrangements surrounding them. The cooperative action of both types of sites leads to EMF+EMFDA production. But we have no further evidences on the nanostructure of these special surface sites. On the other hand, it is relevant to compare fructose conversions and carbon balances for the different studied catalysts, these parameters are depicted in Fig. 6. Apparently catalysts supported over AC give place to poor carbon balances, comparing STA-AC and TPA-AC with the corresponding STA-HSAG and TPA-HSAG counterparts. For a tentative explanation of this support effect, we may consider that activated carbon support possesses a rather high contribution of micropores in its porous structure, and that these micropores can act as recipient (by irreversible adsorption) of humic acid byproducts, where they can polymerize or block the acid sites of POMs. Also the carbon balances, or the production of desirable products, seems to be higher with the catalytic samples prepared from STA versus TPA. As significant conclusions, we have been able to distinguish among two POMs, showing that comparing STA versus TPA the former produces less quantity of byproducts (humic acids) and it is better as catalyst for the fructose conversion with regard to the yield to final products. Furthermore, the comparison of two carbonaceous supports evidenced that carbon balances (or carbon deposits) are worse in the case of activated carbon. So we have been able to develop an improved catalyst in terms of yield to desirable products, for the fructose dehydration in ethanol media: STA-HSAG sample. Finally, this new synthesized catalytic material exhibits catalytic performance superior to commercial Amb-15 under the reaction conditions studied. Another important aspect to be considered for the application of this catalytic material (STA-HSAG) is its reusability. In Figure 7 the performances (fructose conversion, catalytic activities, selectivities and carbon balances) of the fresh catalyst and after regeneration under different treatments are shown. It can be seen that when the filtered catalytic material from the reaction media was directly reused the activity was considerably depleted (named D.Reuse). Therefore, as the spent catalyst becomes severely deactivated, we have treated aliquots of the used catalyst with three different activation protocols. First, the solid was washed sequentially with cyclohexane and diethylether (sample W.Activ) in order to remove humic acids

from the catalytic surfaces, as previously suggested in the literature.^[33,34] Second and third consist of thermal treatment under air flow at 300°C (T3.Activ) and 400°C (T4.Activ) for two hours.[35] As can be observed in Fig. 7 the only efficient regeneration treatment is the one which involves washing. These findings support our supposition that probably deactivation is due to humic acids as deactivating species. Moreover, humic acid byproducts cannot be eliminated by thermal desorption but can be removed by dissolution in organic solvents. Furthermore, the regeneration of the spent STA-HSAG catalyst means that STA does not lixiviated either under reaction condition or during the washing treatment. On the other hand, it should be noted that the commercial Amberlyst-15 material also suffers from deactivation by humic acid deposition, which is apparent from the change in its color turning to dark brown, and cannot be regenerated applying the washing treatment.



Figure 7. Catalytic properties of the reused STA-HSAG catalyst after regeneration of the spent material by applying different treatments.

Conclusions

Polyoxometalate acid catalysts supported on two carbon materials, activated carbon and high surface area graphite, have been studied in the fructose dehydration reaction. From the analysis and discussion of the catalytic performances and from the concurrent characterization of the synthesized catalytic materials, some relevant conclusions can be stablished. Under moderate reaction temperature and using ethanol as solvent, instead of water, increased values of yield to desirable products can be obtained. Interestingly the anchoring of POM to basal planes of graphite crystallites seem to takes place, thus these solids are quite stable again lixiviation. Also as a consequence of these interactions the resulting POM crystallites are rather low in dimensions (nanometric scale).

The systematic study of these composite materials as catalysts for the fructose transformation reaction reveals that product yields depend on the selected carbon support and on the POM active component. So it has been concluded that between the two studied POMs, STA and TPA, STA is more suitable for the ChemCatChem

fructose conversion to desirable final products. Furthermore, the comparison of two carbonaceous supports evidenced that carbon balance are worse in the case of activated carbon due to higher accumulation of carbon deposits during reaction on this support.

Summarizing, an improved catalyst (STA-HSAG) in terms of selectivity to valuable products (ethoxymethylfurfural and ethyl levulinate) and specific catalytic activities using ethanol as solvent has been developed. Furthermore, the generation of undesirable sub-products, such as humic acids, detected firstly by the loss of reaction carbon balances, causes severe deactivation of the catalytic materials. In fact regeneration of this more selective and active catalyst, STA-HSAG sample, can be achieved by washing treatments with organic solvents to remove strongly adsorbed sub-products. Comparison of STA-HSAG catalytic properties with those of an acidic resin, Amberlyst 15, reveals that our improved STA-HSAG catalyst is superior in activity and yields to desired products. In addition acid resin cannot be regenerated, either by thermal treatment or by washing with organic solvents.

Experimental Section

Catalyst preparation

Two carbon materials were studied as catalyst support: a commercial activated carbon (AC), produced from olive stones by Oleicola el Tejar, Córdoba Spain, and a commercial high surface area graphite HSAG-400 (HSAG) provided by TIMCAL.^[24] The activated carbon (AC) was sieved to 1.25–0.8 mm of grain sizes. This raw material was subjected to a treatment with hydrochloric acid solution 10% (v/v) at 100 °C for 24 h, in order to remove residual inorganic components, and after filtering and washing with distilled water until complete removal of detectable Cl- ions. The BET areas of the supports were: 1190 m2 g-1 (AC) and 400 m² g⁻¹ (HSAG).^[36]

The supported catalysts, with a 15 wt% POM loading, were prepared by incipient impregnation of the supports, with an ethanol/water solution of the solid acids $H_3PW1_2O_4$ · H_2O (TPA) and $H_{40}SiW_{12}O_4$ · nH_2O (STA) as reported previously.^[24] Finally, commercial acid resin (Amberlyst-15) catalyst was obtained from Alfa-Aesar.

Catalyst characterization

X-ray diffraction (XRD) was use to study the structural properties of the synthetized catalysts. The patterns were obtained on a Polycrystal X'Pert Pro PANalytical instrument, with Ni-filtered CuK α X-rays (λ = 1.54 Å). Bragg's angles between 5 and 95 were scanned at a rate of 0.058 degree per second.

The catalytic activity and selectivity in the decomposition of isopropanol (IPD) was taken as model reaction test for acid sites. The reaction was performed in a fixed-bed tubular glass reactor working at atmospheric pressure. The 2-propanol was fed into

the reactor by bubbling a flow of nitrogen ($80 \text{ cm}^3 \text{ min}^{-1}$) through a saturator-condenser maintained at 16,5°C, which allowed a constant isopropanol flow of 3 cm³ min⁻¹ or 130 mmol min⁻¹. In a typical experiment, an aliquot of sample of 70 mg (sized at 0.35-0.5 mm) was pre-treated inside the reactor at 140°C during 1 h under continuous flow of N₂. After cooling at 100°C in inert flow, the reaction was started at this temperature by feeding the 2propanol mixture (vaporized alcohol and N₂ gas). The reaction products were analyzed by an on-line gas chromatograph provided with a thermal conductivity detector or FID at 150°C and a Chromosorb W-HP column at 50°C for the separation of products.

In order to obtain information on morphological characteristics of the acidic solids supported over carbonaceous materials, the catalysts were subjected to a detailed scanning electron microscopy (SEM) study. Two equipments were employed, one of them was FE-SEM Hitachi S-4700 and the other apparatus was Hitachi TM-1000. Through energy dispersive X-ray spectroscopy (EDX) studies in both equipments, the presence of metals (Si, P and W), as well as the atomic ratio between these metals (1:12 – Si:W or P:W) of supported POMs were corroborated. Some of these results are presented in the supplementary information, Figure S1. The supported POM samples were studied without previous metallization treatment.

Thermogravimetric Analysis (TG) studies were carried out on a model SDTQ600 5200 TA apparatus. Each sample were heated from room temperature to 700 °C, at heating rate of 10 °C min⁻¹ under helium flow (100 cm³/min). These measures involved the weight loss (TG), derivative weight loss curves (DTG) and the differential scanning calorimetry (DSC) analysis. In order to detect the possible leaching of POM metals (i.e. tungsten and silicon or phosphorus) during reaction, the final reaction mixture was analyzed by inductively coupled plasma mass spectrometry (ICP-OES Optima 3300 DV Perkin Elmer). Determining tungsten concentration made possible to know the percentage (%) of POM is dissolved into the reaction medium.

Catalytic study of fructose dehydration

The dehydration of fructose was studied in a 100 ml Teflon-lined stainless steel autoclave reactor (Parr 4072, Parr Instrument Co.). Fructose, solvent and catalyst were mixed and loaded in the reactor that was flushed with He to exclude air. Then, the autoclave was heated to the reaction temperature while stirring the mixture (500 rpm). The reaction time was set to zero when the reaction temperature was reached, and data were recorded thereafter. Typical catalytic tests were carried out at 140°C and 30 bar of inert He, using 90 ml of solvent (ethanol or water), and a mass catalyst loading of 15 wt% of acid sites based on fructose, mass/mass. Comparisons of the catalytic results were made on the basis of similar mass of the catalysts. Liquid samples were taken periodically, filtered (0.2 µm-PTFE membrane) and analyzed. Quantitative analyses of fructose, Efructose, HMF, DEFM and LA were performed by HPLC with an Agilent system equipped with a Hi-plex H column, eluting with an

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aqueous solution of 0.005 M sulphuric acid (rate 0.6 mL/min) as mobile phase and an index refraction detector. Standard solutions covering the concentration range of the samples were used to obtain the calibration curve for the compounds of interest. The yield to EMF, EMFDA and ELA was determined by gas chromatography with a Varian 3350 system equipped with a capillary column SPB-5 and a FID detector using decane as internal standard.

The specific results were expressed as:

$$X_{fructose}(\%) = \frac{C_{fructose}^0 - C_{fructose}}{C_{fructose}^0} \times 100$$

$$Y_i(\%) = \frac{C_i}{C_{fructose}^0} \times 100$$

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Keywords: fructose transformation • heterogeneous catalytic reaction • polyoxometalates • ethoxymethylfurfural • ethyl levulinate

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A new acid catalyst is developed by anchoring a polymetalate to basal surfaces of graphite, with applicability for the transformation in ethanol solvent of fructose into ethoxymethylfurfural and ethyl levulinate.



Nadia García-Bosch, Belén Bachiller-Baeza, Inmaculada Rodríguez-Ramos and Antonio Guerrero-Ruiz*

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Fructose transformations using carbon supported polyoxometalate acidic solids as heterogeneous catalysts