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Hydrodeoxygenation of furfural-acetone condensation adducts to tridecane over platinum catalysts

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ABSTRACT

The total hydrodeoxygenation of furfural-acetone condensation adduct (F_2A) for obtaining tridecane is studied in this work. Three different Pt catalysts (using alumina, activated carbon, and graphite-MgZr oxide composite as supports) were tested using acetone as solvent (4.5 mmol/L of adduct) in a stirred batch reactor at 493 K and 5.5 MPa. Best results were obtained with Pt/Al₂O₃, yielding 21.5% of n-tridecane after 24 h reaction time, with carbon balances close to 96%. The performance of the carbon supported catalysts was poorer (both in terms of conversion, tridecane selectivity and carbon mass balance closure) mainly because of the strong adsorption of reactants and reaction intermediates, whereas the MgZr-HSAG also present activity for the undesired cleavage of C—C bonds of the condensation adducts. A kinetic model, considering serial-parallel reaction steps and first order dependence on the organic reactant has been successfully applied for modelling the results obtained with the three catalysts. The dependence of the kinetic constants on the catalyst properties suggest that metal dispersion and the concentration of weak acid sites are the main parameters affecting catalyst performance.

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1. Introduction

Production of renewable liquid fuels from biomass resources is nowadays of key interest, especially the promising aqueous-phase routes [1]. Among them, the process suggested by *Dumesic and coworkers*, proposing a catalytic process that allows obtaining diesel from biomass, is specially promising, since it does not require high temperatures, improving the global economy of the process [2,3]. The process sequence is summarized in Scheme 1. As it can be observed, it is a sequence of four steps with different catalysts at different reaction conditions: the hydrolysis of the sugar polymers; followed by the dehydration of sugars yielding aldehydes; the condensation of these compounds using a linking molecule (usually acetone); and the total hydrodeoxygenation of these condensation adducts to the final lineal hydrocarbons, with similar properties as the mineral diesel.

Considering the promising results of these first studies, the efforts to improve this process have grown exponentially. In good agreement, the mechanism of sugar hydrolysis and dehydration has been deep studied, developing active and selective heterogeneous catalysts that allow optimizing the reaction conditions under the green-chemistry principles [4–6]. In the same way, the

http://dx.doi.org/10.1016/j.cattod.2015.09.055 0920-5861/© 2015 Elsevier B.V. All rights reserved. activity of different mixed oxides and other basic catalysts in the aldol condensation of furfural and acetone is the topic of many papers, concluding that Mg-Zr mixed oxide is one of the most promising materials, reaching condensation yields higher than 80% at mild conditions [7,8]. Besides, this material yields higher selectivities to C13, increasing the quality of the resulting drop-in fuel upon hydrogenation of the resulting adducts.

The combustion enthalpy of these condensation adducts is very low because of the high oxygen content, which markedly decreases its quality as fuel and promotes corrosion problems [9]. Hydrodeoxygenation (HDO) is the most effective technology for increasing this combustion enthalpy by hydrogenation of double bonds and removing the oxygen as water at medium pressure and temperature [10]. This reaction was previously applied to oilderivatives, and the references of applying this process to biomass upgrading have increased in the last ten years [11]. However, the hydrodeoxygenation of the furfural-acetone condensation adducts is much more difficult because of the complexity of the parent molecules, with different functional groups. Different successive steps are required for removing oxygen atoms (ketonic and cyclic ones), to hydrogenate the aliphatic chain and the furan-ring unsaturations as well as to open these rings. In addition, these steps must take place without breaking the carbon chain. The complexity of these individual reactions is even higher due to steric interactions among the different functional groups. As consequence, a very limited number of studies about the total HDO of these compounds

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2

ARTICLE IN PRESS

L. Faba et al. / Catalysis Today xxx (2015) xxx-xxx



Scheme 1. General mechanism for biodiesel synthesis from hemicellulosic biomass by dehydration-aldolization-hydrogenation/deoxygenation [3].

have been published [12–14]. Despite of the few references, noble metals (mainly Pt, Pd and Ru) seem to be the optimum catalysts for these reactions. However, each individual step is controlled by different parameters, so the role of acidity and metal dispersion in the global process is not negligible [15]. The reaction conditions must be well defined when these noble metals are used, in order to prevent side-reactions such as decarboxylation and decarbonylation [16] that would decrease the carbon chain length, decreasing the diesel quality.

Previous works of our research group are focused in the hydrodeoxygenation of the first condensation adduct (C8) obtained by the reaction between furfural and acetone. Pt was identified as the most active noble metal, obtaining more than 25% of n-octane after 24 h of reaction [17]. The reaction mechanism, the kinetic and the stability were also studied, identified the role of different morphological and surface catalytic properties in each reaction step. Consequently, different supports were tested concluding that the metal dispersion is the key parameter of this reaction, obtaining good results with supports as different as alumina, active carbon and high surface area graphites [15].

The aim of this paper is to study the hydrodeoxygenation of the second adduct: the C13-condensated (1,5-bis(2-furanyl)-1,4pentadien-3-one), which presents the highest practical interest. Reaction conditions were chosen considering the best results obtained in the HDO of the first adduct (493 K; 2.0 MPa of H₂ with a total pressure of 5.5 MPa, 24 h) using Pt catalyst. Despite the higher complexity of this molecule, there are same functional groups in both cases, so it could be predicted that main effect of this complexity should be in the reaction time but not in the reaction temperatures. Besides, good results obtained at these conditions could be useful to consider the hydrodeoxygenation of both adducts (real mixture obtained after the condensation step) without any purification. The differences and similarities between the HDO of C8 and C13 condensated adducts are also discussed. Results obtained are used to corroborate the mechanism and the kinetic model, relating the results to the catalytic properties.

2. Experimental methodology

2.1. Catalytic preparation

Three different catalysts have been tested in this work: Pt/Al_2O_3 ; Pt/AC and Pt/MgZr/HSAG. 0.5% Pt/Al_2O_3 catalyst was a commercial sample supplied by BASF. High surface area graphites (HSAG-500)

and active carbons (AC, GF 40) were stocked by Timcal S.A. and Norit, respectively. In order to study the possibility of implement the condensation and hydrodeoxygenation as one-step process, Pt/MgZr/HSAG500 was also prepared, by impregnation of Pt over the MgZr/HSAG prepared by co-precipitation, as it is detailed in previous work [8]. The possibility of carry out the condensation and hydrodeoxygenation steps as on-pot process was previously studied, leading to important economic and technical improvements [18].

Pt-catalysts were prepared by ion exchange, using metal chlorides as precursor ($Pt(NH_3)_4Cl_2$, supplied by Aldrich). The solutions were prepared considering a final metal loading of 1%. The ion exchange was carried out in a rotavapor at 343 K for 24 h, after which the solvent was removed using a vacuum system. Resulting solids were washed, filtered, dried at 373 K and heating in He flow at a temperature rate of 5 K/min until 873 K, holding this temperature during 2 h. All the materials were activated before any characterization or activity test at 473 K for 2 h under flowing hydrogen gas.

2.2. Catalysts characterisation

The surface, morphological and physical-chemical properties of all the materials have been determined by N_2 physisorption (surface area, pore volume and diameter), XRD and TEM (metal dispersion), ICP-OES (metal loading) and NH₃-TPD (acid sites strength and concentration). Details about each procedure and instruments have been reported in our previous works [15,17]. In order to better understand the catalytic activity of each catalyst, main characterisation results are summarised in Section 3.

2.3. Reaction studies

Reactions were carried out in a 0.5 L stirred batch autoclave reactor (Autoclave Engineers EZE Seal) equipped with a PID temperature controller and a back pressure regulator. The reactor was loaded with 0.25 Lof a acetone solution of 0.45 g of 1,5-bis(2-furanyl)-1,4-pentadien-3-one (labelled as "A" to better identified it) (Alfa Aesar, 98%). Considering the low aqueous solubility of this compound, acetone was used as solvent. This solvent was chosen taking into account economic reasons as well as the fact that acetone is already presented in the condensation reaction. Preliminary experiments using other solvents, including water and linear alkenes, show very low solubility of the C13 condensation adducts.

L. Faba et al. / Catalysis Today xxx (2015) xxx-xxx



Scheme 2. Chemical structures of the compounds identified in the hydrodeoxygenation (HDO) of C13-condensated adduct identified with the capital letter used in the manuscript.

70 mg of the catalyst were added (with an average particle diameter of $50-80 \,\mu$ m) and air was purged out by adding nitrogen up to 1.5 MPa for three times before starting reaction. The C13 loading and the reactant/catalyst ratio were chosen considering the previous results obtained in the aldolization studies [7]. The reactor was pressurized to 2.5 MPa of H₂, stirred at 1000 rpm and heated to 493 K, reaching a final pressure of 5.5 MPa. This hydrogen pressure is large enough to consider that reaction is carried out in an excess of hydrogen in comparison to the stoichiometrically needed. According to the theoretic calculations, a complete hydrogenation of all the C13 molecules would imply a consumption of 0.0252 mol of H₂ (0.24 MPa at 293 K).

Samples were withdrawn from the sampling port, filtered and analysed by capillary GC-FID in a Shimadzu GC-2010, using a CP-Sil 5 capillary column as a stationary phase. Peak assignment was performed by GC-MS and responses were determined using standards and the effective carbon number theory [19]. Each sample has been analysed at least three times with deviations below 4% in all the cases. The structure of the different intermediates can be observed in Scheme 2. Due to the difficult of the nomenclature of each compound, they were labelled with a capital letter, as it is summarized in this Scheme.

3. Results and discussion

Considering the complex structure of the reactants, a preliminary study to choose the optimum solvent was needed. The solubility on water is not enough to guarantee high precision in the analyses. Same drawback is presented when non-polar organic solvents are used (hexane, diethyl-ether). Higher solubility was obtained using aprotic polar organic solvents, such as ethyl acetate, tetrahydrofuran (THF) and acetone, increasing its solubility at increasing dielectric constant values. Best behaviour was observed with acetone. Before been chosen as solvent, a blank test was carried out, discarding any acetone hydrogenation product after 24 h. These analytic results are also supported by other technical and economic reasons: acetone is one of the reactants in the previous step of the biomass to biofuels process (aldol condensation), so there is not a new compound. Considering all these points, acetone is chosen as solvent for this process.

Batch experiments at 493 K and 5.5 MPa were performed with the selected catalysts in order to identify the most active material and to analyse if reactivity trends are similar in the HDO of C8 and C13 condensation adducts. Reaction conditions are chosen considering previous results obtained in the HDO of the C8 adduct [17]. The most active catalyst was selected considering both, the selectivity for n-tridecane and the carbon balance. Selectivities are calculated as the ratio between the concentration of each compound and the concentration of C13 adduct converted.

Fig. 1 shows the evolution of the selectivity of different reaction intermediates as function of the C13 conversion for the three tested catalysts. The catalytic activity of all the supports (before impregnation with Pt) has been tested, obtaining negligible concentration of any reaction product. These results corroborate that a noble metal is needed at least for the first steps of the reaction. However, in the case of carbonaceous materials, there is a decrease in the carbon balance, indicating a relevant influence of reactant adsorption. Concerning to the metal modified catalysts, same tendencies were obtained with all the materials, despite that there are important differences in the values. Compounds labelled as "B" and "C" show a typical profile of primary reaction product, with a significant selectivity at zero conversion and a decreasing profile due to the subsequent steps. The decrease is more significant in the case of the "B" intermediate, indicating that the following HDO steps start mainly from this intermediate. By contrast, "D" intermediate follows the typical pattern of a secondary reactive product, with negligible selectivity at the initial time and reaching a maximum after which its selectivity decreases, yielding the final product (n-tridecane). Considering the fast conversion of the C13 condensation adduct (mainly in the case of Pt/Al₂O₃ and Pt/AC), the region of higher conversion is magnified in the right part of each graph, making easier the analysis of evolution at these values.

According to these results, C=C double bonds are firstly hydrogenated, but this reaction is so fast that there is not a clear sequence between the hydrogenation of aliphatic and cyclic unsaturations. Consequently, the intermediate in which the furanic rings are reduced is also observed since the first moments. This behaviour was already observed in the hydrogenation of other compounds containing multiple conjugated carbon-carbon double bonds [20]. It should be highlighted that the identification of reaction compounds was carried out using GC-MS without observing intermediates corresponding to the hydrogenation of only one of the aliphatic or cyclic C=C. Considering the symmetry of this molecule, there is not any apparent reason that justifies a preferential attack to one of them. Contrary to the results observed in the case of the HDO of the C8 condensation adduct, the hydrogenation of the ketonic group is clearly observed. Next steps between this intermediate and the final n-tridecane are so fast that the resulting intermediates are not detected. Thus, these steps are omitted, considering directly the transformation of this intermediate (D) into n-tridecane.

Considering the similar tendencies observed with all the materials, main differences are better analysed as function of the distributions of all the compounds at 50% and 90% of C13 conversion, considering also the time needed to reach these conversions

3

4

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Fig. 1. Evolution of the selectivity with C13 reactant conversion in the HDO of C13-condensation adduct catalyzed by (a) Pt/Al₂O₃; (b) Pt/AC; (c) Pt/MgZr/HSAG. Symbols: (\diamond) B; (\blacklozenge) C; (\blacktriangle) D; (\blacksquare) n-tridecane (E).

as well as the final distribution obtained after 24h of reaction. These selectivities are summarised in Fig. 2. Results at 50% of conversion indicate a higher activity of Pt/Al₂O₃. In addition to differences in the selectivities, the differences in the times needed to reach this conversion must be highlighted. In the case of Pt/Al₂O₃ and Pt/AC, this conversion is reached after only 2 h reaction time, whereas more than 6h reaction time are needed in the case of Pt/MgZr/HSAG500. Results of carbonaceous materials are conditioned by the low carbon balances, lower than 50% in the case of Pt/AC and 72% in the case of Pt/MgZr/HSAG500. As opposite, the carbon balance of Pt/Al₂O₃ is higher than 98%. This material shows the highest activity, highest yields for "C" and "D" intermediates and almost 10% of n-tridecane selectivity after only 2h of reaction. On the contrary, only significant amounts of the first intermediate are observed when active carbon is used and Pt/MgZr/HSAG500 shows an intermediate behaviour, with 3% of n-tridecane.

At 90% of conversion, products distribution obtained with the three catalysts are very similar. In all the cases, the highest selectivity corresponds to the first intermediate, indicating that the hydrogenation of aliphatic unsaturations is the first and fastest step. More than 90% of conversion is reached after 8 h with Pt/Al_2O_3 , after 6 h with Pt/AC and after 20 h with the basic materials. Concerning to

the carbon balance, value obtained with Pt/Al_2O_3 (97.6%) discards any adsorption or side-reaction, whereas the values of the active carbon and the graphite (55 and 67%, respectively) justify the low selectivities of the different intermediates. As a consequence, the selectivity to n-tridecane only reaches values higher than 10% in the case of Pt/Al_2O_3 .

Considering the long time needed to reach the 90% conversion when Pt/MgZr/HSAG500 is used, the distribution of the final selectivities after 24 h is not significantly different. Despite of this fact, it must be highlighted the soft increase in the selectivity of the last intermediate and the n-tridecane, reaching a final value of 11.2%. These results discard a negative effect of basicity on the whole process and suggest that increasing reaction time would have a positive effect in the n-tridecane yield. Concerning to the Pt/Al₂O₃, 21.5% selectivity for n-tridecane was reached after 24 h, being this alumina supported catalyst the most active one, with full conversion and more than 95% of final carbon balance. This results is in good agreement with the good activity observed in the hydrodeoxygenation of the C8 adduct [15], suggesting that the higher complexity of the reactant has not a significant effect in the catalytic parameters that play a key role in this process. As in the other cases, results obtained with Pt/AC are strongly conditioned by the low carbon balance (44.5%). Most significant evolution of the reaction

L. Faba et al. / Catalysis Today xxx (2015) xxx-xxx



Fig. 2. Distribution of the different reaction intermediates in the HDO of C13-condensated adduct catalyzed by Pt/Al_2O_3 (white); Pt/AC (gray) or Pt/MgZr/HSAG (black). Results obtained at (a) 50%; (b) 90% of conversion and after (c) 24 h of reaction.

is related to the complete conversion of the reactant, despite that almost negligible evolution of the final product is observed.

Taking into account these data, a deep study to justify the low values of carbon balances obtained with HSAG and AC supports is needed for clarifying the reasons of this behaviour. The retrocondensation was the only side-reaction observed, and its products were only detected when Pt/MgZr/HSAG500 was used as catalyst, but they were not detected neither for Pt/Al₂O₃ nor Pt/AC. The existence of this reaction has been previously demonstrated [21], yielding acetone and furfural. No signals corresponding to the first condensation adduct (C8) or its hydrogenated derivatives were detected. The strong reaction conditions are suggested as the responsible of this complete retroaldolization. Considering that acetone is the solvent, only furfural (or its hydrogenated derivatives) would be identified. The basic sites of MgZr mixed oxide [7] justify the presence of this side reaction, questioning the viability of this material as good catalyst for the C13 HDO.

In good agreement to this hypothesis, Fig. 3 shows the evolution of the C5 compounds identified by GC-MS whereas Fig. 4a illustrated their influence on the carbon balance values. As it can be observed in Fig. 3, there are significant selectivities of furfural and the partial hydrogenated adducts (similar adducts as those identified in furfural hydrogenation [22]), reaching a maximum global selectivity of 16%. Furfural appears since the first reaction times but its selectivity never reaches values higher than 3% because of



Fig. 3. Evolution of the different furfural hydrogenation products with reaction time when using Pt/MgZr/HSAG as catalyst: (\blacklozenge) furfural; (\bigcirc) furfuryl alcohol; (\blacktriangle) methylfurane and (\blacksquare) tetrahydromethylfurane.



Fig. 4. (a) Evolution of the carbon balance as function of the reaction time when Pt/MgZr/HSAG is used as catalyst: (\blacklozenge) considering only the main reaction; and (\blacksquare) considering also the C5's products obtained as side reaction. (b) Evolution of the carbon balance as function of the reaction time when Pt/AC is used as catalyst.

its fast hydrogenation to furfuryl alcohol. Contrary to the behaviour of C8 and C13 condensation adducts, the aromatic cycle is more stable than the carbonyl group (aldehyde for furfural; ketone for the adducts), so this functionality suffers the hydrogenation firstly. In fact, the methyltetrahydrofurane (MTHF) only appears in the last part of the reaction, with almost negligible selectivity.

Once this side reaction is taken into account, the evolution of the carbon balance obtained with this material improves, being over 70% during all the reaction (Fig. 4a). However, this value is still much lower than the value obtained with Pt/Al₂O₃ (constant between 100 and 96%), suggesting the presence of additional causes. At this point, two different zones of carbon balance decrease are identified for the Pt/MgZr/HSAG, catalyst: the first one in the first two hours of reaction time, and the other one between the eighth and

L. Faba et al. / Catalysis Today xxx (2015) xxx-xxx

6

Table 1

Summary of the main morphological al chemical properties of the catalysts used in this work [15].

	N ₂ Physisorption			Metal loading, ICP-OES (%)	TEM		NH ₃ -TPD		
	$S_{\text{BET}}(m^2/g)$	<i>d</i> _p (nm)	<i>v</i> _p (cm ³ /g)		Metal dispersion (%)	Metal particle size (nm)	Weak acidity (µmol/g)	Medium acidity (µmol/g)	Total acidity (µmol/g)
Pt/Al ₂ O ₃	116	17	0.49	0.5	24	4	789	119	908
Pt/AC	1716	1.9	0.59	0.59	21.3	4.7	18	71	89
Pt/MgZr/HSAG	234	10.1	0.5	0.58	13.1	8.4	243	230	473



Scheme 3. Reaction mechanism proposed to the hydrodeoxygenation of the C13-condensated adduct catalyzed by different Pt materials.

the tenth hour. This pattern suggests that the first one is caused by the reactant itself, whereas the other one is caused by a product. Considering the chemical structures of reactant and some intermediates, a strong interaction between these compounds and the catalytic support (adsorption) can be assumed as the reason of the first carbon balance decrease. In order to corroborate this hypothesis, an adsorption test was carried out, with same concentration of reactant and catalyst as in the reaction, and analysing the evolution of C13-condensated adduct in the liquid phase when this solution is heated to 493 K (reaction temperature) but in an inert atmosphere (in order to prevent the reaction). The C13-condensated adsorption capacity of Pt/MgZr/HSAG was calculated analysing the liquid phase with GC-FID, obtaining a value of 1.23 mmol/g. This value is high enough to justify the initial decrease in the carbon balance by this adsorption (the value obtained with Pt/Al₂O₃ was 0.04 mmol/g). This adsorption can be explained considering the high number of unsaturations of this molecule and the high affinity between these functionalities and carbonaceous supports [23]. The second decrease in the carbon balance corresponds with the time at which the concentration of the first intermediate reaches a maximum with this catalyst. Considering the similar structure, it is assumed that this second decrease corresponds to the adsorption of this molecule. TPO analyses were carried out but results are not conclusive because of the similar oxidation temperature of all these compounds. These adsorptions cause a partial blockage of the active sites, making slower the reaction but without causing a complete deactivation.

In the case of Pt/AC, the presence of side reactions is discarded because no C5 products were detected by the GC-FID. Observing the evolution of the carbon balance (Fig. 4b), the strong adsorption of the reactant seems to be not enough to justify these results and the negligible activity of this catalyst. Same adsorption analyses were carried out with this material, obtaining an adsorption capacity of 2.36 mmol/g, much higher than the obtained with the other catalysts. This fact justifies the decrease of the carbon balance in the first hours of reaction. However, the continuous decreasing tendency suggests that adsorption on active carbon affects not only to the reactant but also to all the reaction intermediates. The high surface area of this material (main characterization results are summarized in Table 1 and deeply discussed in our previous work [15]) and the different functionalities justifies the high relevance of this complex process when this catalyst is used.

3.1. Kinetic results

Results obtained are better explained considering a kinetic analysis. These profiles are congruent with the reaction mechanism previously proposed for the HDO of C8-condensation adducts [17]. According to this mechanism, this process is the result of different series-parallel steps with a first-order dependence on the reactant and partially hydrogenated condensation adducts and apparent zeroth order on H₂ concentration. This hypothesis is based on the large excess of this reactant (observing a maximum decrease of 0.4 MPa after 24 h of reaction). Considering the experimental results, the previous mechanism can be directly adapted in order to analyse the behaviour of Pt/Al₂O₃. However, in the case of carbonaceous materials, two adsorption steps (corresponding to the reactant and the first intermediate) are also considered, as well as a side reaction of retroaldolization in the case of Pt/MgZr/HSAG. Considering that the hydrogenation of furfural is not the aim of this work, in order to simplify the mechanisms, all the C5 compounds are considered as a single lumped compound. With these assumptions, the HDO of C13-adduct follows the scheme showed in Scheme 3. As in our previous works, the presence of mass transfer effects was discarded by ensuring small catalytic particle size (sieved from 50 to $80 \,\mu$ m) and by carrying out the reactions under high stirring speed (1000 rpm). Consequently, the kinetics of this process is controlled by the rate of the chemical steps. The temporal evolution of all the species with reaction time was modelled

L. Faba et al. / Catalysis Today xxx (2015) xxx-xxx

Table 2

Kinetic constants $k_1 - k_6$ ($1 s^{-1} mol_{exp} Pt$) and adsorption constants $k_{A1} - k_{A2}$ ($m s^{-1}$) for the fitting experimental data at 493 K to the proposed kinetic model.

	Kinetic and adsorption constants									
Catalyst	k_1	k_2	k_3	k_4	k_{-4}	k_5	k_6	k _{A1}	k _{A2}	r^2
Pt/Al ₂ O ₃	17.5	9.79	13.4	3.17	2.99	11.1	-	0	0	0.991
Pt/AC	16.3	6.32	5.63	2.55	53.6	25.1	-	$9.0 imes10^{-9}$	$1.1 imes 10^{-9}$	0.98
Pt/MgZr/HSAG	15.4	7.39	9.42	3.10	18.6	21.3	2.44	2.9×10^{-8}	5.8×10^{-9}	°0.96

using the SCIENTIST[®] software, applying the Burlich-Stoer approximation and the following differential equations:

$$\frac{dA}{dt} = -k_1 \cdot A - k_2 \cdot A - k_7 \cdot A - k_{AL} \cdot A \tag{1}$$

$$\frac{dB}{dt} = -k_1 \cdot A - k_3 \cdot B - k_4 \cdot B + k_{-4} \cdot C - k_{A2} \cdot C$$
(2)

$$\frac{dC}{dt} = k_2 \cdot A - k_4 \cdot B - k_{-4} \cdot C \tag{3}$$

$$\frac{dD}{dt} = k_4 \cdot B - k_S \cdot D \tag{4}$$

$$\frac{dE}{dt} = k_{\rm S} \cdot D \tag{5}$$

$$\frac{dF}{dt} = 2 \cdot k_6 \cdot A \tag{6}$$

Values of the kinetic constants obtained are reported in Table 2. In order to better comparison of the results, values are normalized considering that kinetic constants are function of metal loading and metal dispersion whereas adsorptions are surface processes:

$$k'_{A} = \frac{k_{D}(s^{-1}) \cdot V(m^{3})}{M_{cat}(g) \cdot S_{BET}(m^{2} \cdot s^{-1})}$$
(7)

$$k' = \frac{k(s^{-1}) \cdot V(L)}{M_{cat}(g) \cdot (\% metal/100) \cdot (1/A_{Pt}) \cdot d}$$
(8)

Where "V" is the reaction volume; " $M_{cat''}$ is the mass of catalyst used in each reaction; " $S_{BET''}$ is the specific surface area measured by nitrogen physisorption; " $A_{Pt''}$ is the atomic mass of Pt; and "d" is the metal dispersion calculated by TEM. All these morphological parameters have been measured in our previous work [15] and main results are summarized in Table 1.

As it can be observed in Table 2, good fits were obtained with the three materials, with a correlation coefficient higher than 0.95 in all the cases. In good agreement, there is a good fit between experimental and theoretical values, as it is illustrated in Fig. 5. In general, kinetic constants values are lower than those previously proposed for the C8-adduct HDO, but they follow the same trend, mainly in the first steps of the process, with higher values when Pt/Al_2O_3 is used as catalyst [15]. These values are congruent with the higher complexity of both, the reactant molecule and the process. As to the adsorption constants, values obtained in the C13 HDO are two orders of magnitude higher than those obtained during the C8 HDO, in good agreement with the influence of the molecule size in adsorption processes. Values of kinetic constants have been analysed in terms of the main characterization parameters of the three catalysts, observing that each step of the process is conditioned by different parameters, in such a way that a good balance among different catalytic properties is needed to maximize the n-tridecane yield. Most significant trends are shown in Fig. 6. According to these graphs, the hydrogenation of the aliphatic C=C (controlled by the k_1 and k_2) is slightly structure-sensitive, increasing its value at decreasing metal particle size (Fig. 6a). This behaviour has been previously observed in the hydrogenation of other complex molecules [24]. The role of acidity is not clear, observing positive and negative effects as function of the step analysed. If only the weak acidity is considered (Fig. 6b), a positive influence of the concentration of



Fig. 5. Comparison between evolutions of experimental concentrations (symbols) and results predicted by the kinetic model proposed (broken lines). Results corresponding to (a) Pt/Al_2O_3 ; (b) Pt/MgZr/HSAG; and (c) Pt/AC. Symbols: (\times) A; (\blacklozenge) B; (\spadesuit) C; (\blacksquare) D; (\blacktriangle) E.

this acid sites on the kinetic constant is observed in almost all the direct steps. Acidity is needed to favour the complete hydrogenation of all C–C double bonds (conditioned by the value of k_2) and the hydrogenation of ketonic group (related to the k_3 constant). Concerning to the equilibrium between the first and the second intermediate, the global effect of weak acidity is also favourable. The acidity has a negative effect in the evolution of this constant, so it can be concluded that higher weak acidity prevents the formation of intermediate "C" (this product is not directly related to the n-tridecane formation). The weak acidity is not good to promote the cyclic breakups (k_5). However, analysing the final values, it can be concluded that this step does not control the whole process and

8

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L. Faba et al. / Catalysis Today xxx (2015) xxx-xxx



Fig. 6. Evolution of different kinetic constants as function of different catalytic properties: (a) metal particle size; and (b) weak acidity. Symbols: $(\bigcirc) k_1$; $(\diamondsuit) k_2$; $(\bigcirc) k_3$; $(\bigstar) k_4$; $(\bigsqcup) k_5$; $(\bigstar) k_4$.

this step is fast enough if the previous intermediate is obtained. In good agreement to this hypothesis, the highest n-tridecane selectivity is obtained with Pt/Al_2O_3 , despite of its acidity. If same kinetic constants are analysed as function of the medium strength acidity, this tendencies are not so clear, suggesting that an increase in the strength of these sites can have an opposite effect.

Considering that same parameters condition the hydrodeoxygenation of both condensation adducts (C8 and C13), and that best activity results were obtained with Pt/Al₂O₃ in both cases; this material is proposed as the most promising one for the hydrodeoxygenation of real mixtures of condensated adducts in order to obtain diesel from (hemi)cellulose wastes by aqueous-phase reactions.

4. Conclusions

The HDO of the C13-condensation adducts was studied, analysing the catalytic activity of different materials that have been successfully tested for HDO of similar compounds. All the experimental results were used to propose a reaction mechanism and a kinetic model, identifying the role of catalytic parameters in each step of the process. This analysis corroborates the complexity of this reaction, with different contributions in each step, but highlighting the role of the metal dispersion. In good agreement, best results were obtained with Pt/Al₂O₃, yielding more than 22% of n-tridecane after 24 h of reaction at 493 K and 5.5 MPa. The presence of basic sites on the catalyst leads to undesired C--C cleavage yielding furfural, which can be subsequently hydrogenated. On the other hand, the presence of strong adsorption and side reactions limit the activity of catalysts supported on active carbon and high surface area graphites, discarding these materials as catalysts for this reaction.

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