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Effect of Ni Metal Content on Emulsifying Properties of Ni/CNTox Catalysts for Catalytic Conversion of Furfural in Pickering Emulsions

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Abstract: Ni/CNTox catalysts with variable metal content have been prepared to investigate their emulsifying and catalytic properties for the liquid-phase conversion of furfural. The solid catalysts and emulsions were analyzed by several characterization techniques. The catalytic activity linearly increased with increasing Ni content (up to 10 wt.%) before dropping down again for a Ni content of 15 wt.%. The loss of catalytic activity was attributed to larger emulsion droplets formed by the inhibition of hydrophilic sites. All Ni/CNTox catalysts were highly selective to cyclopentanone as a main product, while several changes regarding secondary product were observed. Ni/CNTox catalysts with a Ni content up to 10 wt.% favor the formation of levulinic acid, while catalysts with a Ni content of 15 wt.% were selective to tetrahydrofurfuryl alcohol. This was attributed to an inhibition of the acid sites thus favoring the catalyst's hydrogenating capacity.

Introduction

The catalytic production of fuels, fuel additives and chemicals from biomass, which is known as biorefinery, has received considerable attention regarding the replacement of petroleum-based production and the reduction of greenhouse emissions.^[1-3] Moreover, it has been reported that biomass with a high

proportion of cellulose is suitable as a source for making components for electronic and energy devices.^[4] Biomass has gained notable importance since it can be considered as a renewable, abundant, and low-cost raw material for the production of biofuels and add-value chemicals.^[5,6] An important product obtained from fast pyrolysis of biomass is the so-called bio-oil.^[7,8] However, due to its complex composition, bio-oil displays several undesirable characteristics such as chemical and thermal instability, corrosivity and low calorific values.^[9–11] Consequently, catalytic process such as hydrogenation (HY) and hydrodeoxygenation (HDO) ^[12,13] are the most widely studied for improve the fuel properties of bio-oil and to produce value-added chemicals.^[11]

It has been reported that several lignocellulosic biomass derivates including levulinic acid, sorbitol, glucose, guaiacol, 5-hydroxymethylfurfural and furfural can be converted to obtain add-value chemicals and renewables plastics over different eco-friendly catalysts.^[14–18] Recently, Liao *et al.* ^[19] reported on the selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid over engineered catalysts, which consisted of Au-Pd alloy nanoparticles (NPs) and cobalt oxide supports using a metal-organic framework (MOF) as a precursor prepared via *de novo* synthesis.

According to the US Department of Energy, furfural (FAL) has been selected as one of the top 30 building blocks obtained from biomass,^[20] which can be converted directly or indirectly to more than 80 chemicals due to its high chemical reactivity.^[21,22] The relevance of FAL catalytic conversion comes from the large number of chemicals and biofuels that can be obtained from its transformation.^[23–27] FAL can be converted to long-chain products by C-C coupling condensation reaction,^[28,29] valuable fuel additives such as 2-methyltetrahydrofuran (2-MTHF)^[30] and furfuryl ether (FFE),^[31,32] and to value-added compounds such as furan by decarbonylation,^[33] furfuryl alcohol by hydrogenation^[34,35] and by hydrogenation/ring rearrangement to cyclopentanone (CPO).^[36–40]

Particular focus has been put on the transformation of furfural to aliphatic cyclic molecules such as cyclopentanone and cyclopentanol because they are important intermediate in fine chemical industry with a broad range of application in the perfume, medicine, and agriculture field.^[40,41] Several catalytic studies (**Table S1**, supplementary material) have been focusing on the effect of the active phase,^[42–44] metal content,^[34] nature of the catalytic support ^[34,45–47] and the reaction media,^[48] among others. In this regard, Jia *et al.*^[49] studied the aqueous phase hydrogenation of furfural to cyclopentanone over NiFe-supported catalysts. The author found that the addition of Fe to Ni inhibited further hydrogenation of the furan ring to tetrahydrofurfuryl alcohol and enhanced CPO selectivity.

Currently, single liquid-phase conversion of furfural often hinders the separation of the key products. Moreover, this does not represent the real conditions, in which this platform molecule would be found in the biphasic bio-oil.^[50] Therefore, the most appropriate approach for the conversion of biomass-derived molecules is over a new amphiphilic catalysts capable to disperse at the liquid-liquid interface thus forming stable emulsion droplets.^[51]

In phase-transfer catalysis, an emulsifier is added to the biphasic mixture of two immiscible solvents with the purpose to enhance the interfacial surface area.^[52] However, the main disadvantage of using homogeneous emulsifiers is their difficult separation from the reaction media.^[53] This drawback can be overcome by replacing the molecular surfactants with solid particles that possess amphipathic character.^[54,55] The catalytic properties of Pickering emulsions has gained tremendous attention due to many advantages of using emulsions, such as enhancement of the rate of mass transfer between phases based upon an increased interfacial area.^[56] However, the concept of solid stabilized emulsions has not been widely used in the catalytic upgrading of biomass derivatives.

The formation of amphiphilic catalysts can be realized by the fusion of two solid particles with opposite properties. For instance, the fusion of carbon materials and oxide nanoparticles^[57] generates a material with adjustable amphiphilic properties. Crossley *et al.*^[58] deposited Pd nanoparticles onto carbon nanotube-silica hybrid catalyst for water-oil HDO of vanillin. They demonstrated that the vanillin hydrogenation over the nanohybrid catalyst took place at the aqueous interface of the emulsion droplets forming vanillin alcohol. Then, as the reaction proceeded, reaction products such as 2-methoxy-4-methylphenol and 2-methoxyphenol were obtained, which migrated to the organic phase of the emulsion due to their relative solubility. Another approach of tuning amphiphilic properties of a solid particle is to modify their surface chemistry during synthesis or by a simple

post-synthesis treatment. For instance, carbon materials such as graphene, fullerene, carbon onions, carbon nanotubes among others, are mostly hydrophobic. However, it is possible tailor/decrease their hydrophobic character by chemical functionalization using acids (such as HNO_3 and H_2SO_4), which allows for the incorporation of hydrophilic sites on their surface. This procedure favors the formation of solid particles with amphiphilic character.^[59,60]

Regarding the final emulsion properties, it has been reported that parameters such as particle's wettability, organic/aqueous solvent ratio and sonication time can modify the emulsion type, droplet size and emulsion fraction formed.[61] All these studies point to the fact that the wettability of the catalysts plays a key role in the HDO of biomass-derived molecules and it should be carefully designed to obtain the desired catalytic performance. Despite of the encouraging results reported, the use of theses nanohybrid materials has been limited to the hydrogenation of vanillin (biomass-derived polvol compounds)[62,63] and some C-C coupling reactions over supported-Pd catalysts.^[54,64] Only a few reports in the literature can be found addressing the application of these nanohybrid materials, which make use of cheaper and more abundant element such as Ni regarding the conversion of furfural in emulsion systems. Recently, Herrera et al.[65] modified CNT with different acidic treatments to study the effect on the amphiphilic-catalytic properties of Ni/CNTox catalysts for furfural upgrading. They verified that a more severe acid treatment notably increased the hydrophilic character of the solid particles. thus decreasing the catalytic activity. It is worth to emphasize that this study has been performed with a constant Ni content. In single-phase catalytic conversion, the metal loading is a crucial parameter that significantly changes the activity and the products' selectivity.^[66] A detailed look at the existing research literature reveals that there is no study published addressing the effect of the metal content on the wettability of the solid particles and their catalytic activity in emulsions system. Therefore, this study aims at investigating the effect of the Ni content (2, 7, 10 and 15 wt.%) on the amphiphilic properties of solid catalysts and their performance for catalytic conversion of furfural at the interface of Pickering emulsions.

Results and Discussion

Characterization of the catalysts

The results of the XRD analysis for all xNi/CNTox nanohybrid catalysts (x = 2, 7, 10 and 15 wt.%) are depicted in Fig. 1. All the catalysts displayed diffraction peaks at 25.9 and 42.7° (20) corresponding to the (002) and (100) diffraction planes of graphite, respectively (ICDD N°01-075-0444).^[67] Additionally, the xNi/CNTox catalysts showed diffraction peaks at 44.2 and 51.7° (2θ) , which correspond to the characteristic peak of (111) and (200) crystalline planes of Ni⁰ (JCPDS 04-0850). Moreover, the diffraction peak located at 43.1°, which partially overlaps with the (100) reflection of graphite, can be assigned to NiO. It can be observed that the peak intensity of the diffractions observed at 44.2 and 51.7° (corresponding to Ni⁰) gradually increased with increasing Ni content, which is consistent with Ni loading in the catalysts. The presence of NiO in the catalysts could be attributed to some nickel oxide species that interact strongly with the support or to the passivation layer.

FULL PAPER



Figure 1. XRD pattern of oxidized CNTs and the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%).

Fig. S1 shows the N2 physisorption isotherms recorded at -196 °C of the oxidized (CNTox) support and the calcined xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%). It can be observed that both the CNTox support and the impregnated Ni/CNTox catalysts exhibit a type II isotherm, which is typical for macroporous solids according to the IUPAC classification.[68] Additionally, their BJH plots are shown in Fig. S1 (inserts in the graphs). All xNi/CNTox catalysts displayed an average pore size in the range of mesoporosity with minor macroporous contributions. The surface area (SBET), estimated surface area (S^*_{BET}) , total pore volume (V_p) and pore diameter (d_p) of the support and the catalysts are summarized in Table 1. The comparison of the S_{BET} and S^*_{BET} values of the xNi/CNTox catalysts indicates that these values did not significantly change with the Ni content (considering an experimental error in the SBET results of 10 %). This statement holds true for Ni contents up to 10 wt.%. In contrast, the 15%Ni/CNTox catalyst displayed a significant decrease of SBET value, which may suggest a partial pore blockage. This observation agrees well with the results determined for the total pore volume. As can be seen Table 1, all catalysts displayed a similar averaged pore diameter, which implies that this parameter was not significantly modified by the Ni content.

 H_2 -TPR profiles of the xNi/CNTox nanohybrid catalysts (x = 2, 7, 10 and 15 wt.%) are shown in **Fig. 2**. It can be observed that all xNi/CNTox catalysts show three main reduction peaks at around 290, 376 and 482 °C. In published research work, Suhong *et al.* have observed different H_2 -TPR profiles depending on the surface chemistry, particle size and/or location of the metal

particles for CNT-supported nickel catalysts.^[69] Therefore, the reduction peak observed at 376 °C can be assigned to the reduction of NiO nanoparticles located in the exterior wall of the CNTs.^[70,71] Regarding to the reduction peak observed at 290 °C, it can be attributed to the reduction of NiO nanoparticles with different strengths of interaction with the support or to the reduction of NiO particles inside of the CNT channels.^[72]

catalysts quantified by N_2 physisorption.				
Catalyst	S _{BET} S [*] _{BET} ^[a]		V _p ^[b]	d _p ^[c]
	(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)
CNTox	224	-	1.27	38
2%Ni/CNTox	187	219	1.09	38
7%Ni/CNTox	198	208	1.01	34
10%Ni/CNTox	184	202	0.88	32
15%Ni/CNTox	144	190	0.65	32

[a] Estimated specific surface area calculated based on support contribution (S_{BET} value of CNTs). [b] Recorded at a relative pressure of 0.96. [c] Estimated by 4V/A from BET. Where V is referred to total pore volume and A to surface area.



Figure 2. H_2 -TPR profile of the xNi/CNTox (x = 2, 7, 10 and 15 wt.%) catalysts.

These results suggest that the metal nanoparticles located inside of the tubes can be reduced more easily than those deposited on the external surface ^[66,70] since the inner surface is less reactive than the defective external surface. It is important to mention that

FULL PAPER

previous chemical functionalization of CNTs with nitric acid tends to increase the number of surface oxygen groups (defects).[65,73] Furthermore, the following oxidation step may have partially opened the ends of the nanotubes, which can be a possible explanation of the peak observed at lower reduction temperatures. This agrees well with results published by Iglesias et al.^[74]. Moreover, it can be observed that an increased Ni content produces a shift of the reduction peak of NiO located at 290 °C to lower reduction temperature. This result suggests a lower interaction of metal particles with the support at high Ni contents induced by the location of the Ni particles in the less reactive inner channel of the CNTs. It has been reported that the H₂ consumption peak observed at higher temperatures around 487 °C can be associated to the reduction of the CNT support.^[75] Total and partial H₂ uptake and reducibility of the xNi/CNTox catalysts are summarized in Table 2. These results were determined by deconvoluting the respective H₂-TPR profiles (Fig. **S2**). Based upon these data, a significant increase of the total H_2 uptake with increasing Ni content can be observed. Moreover, the H₂ uptake associated to the reduction of Ni nanoparticles at 280 °C is greatly enhanced for all catalysts than that observed at 370 °C. This behavior is associated to a preferential deposition of Ni nanoparticles inside of the nanotubes due to capillary forces of the tubes.^[76] Moreover, the reducibility of all catalysts was similar (85-90%), which suggests a strong interaction of some NiO species with the support, which is in concordance with the XRD results.

Table 2. Total and partial hydrogen uptake (mmol g^{-1}) and reducibility (%) of xNi/CNTox (x = 2, 7, 10 and 15 wt.%) obtained by Gaussian deconvolution of the H₂-TPR profiles.

Catalyst	H ₂ uptake (mmol g ⁻¹) ^[a]			NiO ^[b]	Reducibility
	Peak 1 Peak 2		Total	(mmol g ⁻¹)	(%)
	(280 °C)	(370 °C)			
2%Ni/CNTox	0.212	0.029	0.241	0.268	90
7%Ni/CNTox	0.672	0.123	0.795	0.937	85
10%Ni/CNTox	0.891	0.288	1.178	1.339	88
15%Ni/CNTox	1.569	0.219	1.788	2.008	89

[a] Estimated by Gaussian deconvolution H₂-TPR profiles. [b] Estimated by the amount of NiO impregnated in the catalyst.

TEM micrographs of the amphiphilic xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%) and their corresponding histograms of the size distribution of the Ni particles are depicted in Fig. 3. It can be seen in this figure that the CNTox support consists of long graphitic walls with defects created during the acid functionalization. Moreover, it can be observed that most of the ends of the oxidized CNTs are opened (as indicated by red arrows), which enabled the deposition of Ni nanoparticles in the interior channels of the CNTs, which agrees well with the results of H₂-TPR. Moreover, the histograms of the size distribution of the Ni particles of the 2, 7, 10 and 15%Ni/CNTox catalysts show mean values at around 9.2 ± 0.3 nm, 6.7 ± 0.1 nm, 7.4 ± 0.1 nm and 7.2 ± 0.2 nm, respectively. Based upon these results, there is not significant change in the size of the Ni nanoparticles with increasing Ni content, which suggests a homogeneous distribution of Ni nanoparticles over the support.

In order to estimate the Ni metal dispersion in the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%), CO chemisorption was performed (**Table 3**). It can be observed that the CO uptake increased with increasing Ni content. Furthermore, the dispersion expressed as CO/Ni atomic ratio is given in **Table 3**. The CO/Ni ratio demonstrated that the calculated dispersion did not significantly change with an increasing Ni content. This, in turn, implies that Ni nanoparticles are homogeneously dispersed over the CNTox support. The average Ni particle size of 10.2 nm matches fairly well with the results obtained by TEM.

Table 3. Measurement of the CO chemisorption over the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%).			
Catalyst	CO uptake	CO/Ni	Particle size
	(cm ³ g ⁻¹)		(nm)
2%CNTox	0.49	0.09	11.5
7%Ni/CNTox	1.87	0.10	9.6
10%Ni/CNTox	2.44	0.10	10.6
15%Ni/CNTox	4.19	0.11	9.2

Fig. S3a-d show the spectra of the Ni $2p_{3/2}$ region of the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%) measured by XPS. Curve fitting of the spectra revealed two partially overlapping contributions and a satellite peak for all catalysts. **Table 4** summarizes the binding energies (BE) of the most intense Ni $2p_{3/2}$ component, their relative proportion (shown in parenthesis) and the Ni/C atomic surface ratio. It can be observed that all catalysts exhibited a peak located at $852.8 \pm 0.1 \text{ eV}$, which can be assigned to Ni⁰ and a contribution of BE at $855.9 \pm 0.1 \text{ eV}$, which correspond to NiO species.^[72,77] Additionally, all catalysts display a satellite peak with a BE of $860.0 \pm 0.1 \text{ eV}$, thus confirming the presence of Ni²⁺.^[77]

Table 4. Binding energies (eV) and atomic surface ratio of the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%).

Catalyst	C 1s (eV)	O 1s (eV)	Ni 2p _{3/2} (eV)	Ni/C
				(atom/ atom)
2%Ni/CNTox	284.8 (79)	531.3 (24)	852.8 (87)	0.0011
	286.1 (17)	532.6 (35)	855.9 (13)	
	288.0 (4)	533.8 (41)		
7%Ni/CNTox	284.8 (81)	531.3 (20)	852.8 (86)	0.0026
	286.1 (16)	532.6 (36)	856.0 (14)	
	287.9 (3)	533.8 (44)		
10%Ni/CNTox	284.8 (78)	531.3 (27)	852.7 (85)	0.0037
	286.2 (18)	532.6 (34)	856.0 (15)	
	288.0 (4)	533.8 (39)		
15%Ni/CNTox	284 8 (80)	531 3 (23)	852 8 (88)	0 0050
	286.2 (15)	532.6 (35)	856.0 (12)	0.0000
	288.0 (5)	533.8 (42)		





Figure 3. TEM micrographs and corresponding particle size distribution of nickel metal of the different xNi/CNTox (x = 2, 7, 10 and 15 wt.%) catalysts.

The XPS data also demonstrate that the relative proportion (shown in parenthesis) of Ni⁰ is much higher than that of Ni²⁺. This holds true for all catalysts, which suggests that some Ni species strongly interact with the support. This in turn, goes hand in hand with the observed degree of the reducibility degree (85-90 %) obtained by H₂-TPR and XRD. Additionally, Table 4 also summarizes the observed peaks regarding the C 1s and O 1s regions of the catalysts (spectra not shown). For all catalysts, it can be seen that the C 1s peak consisted of three contributions located at 284.8, 286.2 and 288.0 ± 0.1 eV. The O 1s peak had also three contributions located at 531.3, 532.6 and 533.8 ± 0.1 eV. Concerning the C 1s region, the contribution with BE of 284.8 eV represents graphitic carbon.^[71,78] The C 1s contribution located at 286.2 eV and the O 1s signal at 532.6 eV correspond to the C-O bonds in phenolic and/or ether groups.^[66,79] Carboxyl/carbonyl groups can be correlated with the contribution located at 287.8 eV (C 1s signal) and 531.4 eV (O 1s signal).^[80] The contribution located at 533.8 eV of the O 1s signal can be assigned to C-O bonds in carboxylic anhydride groups. Additionally, the relative ratios (C 1s region, shown in parentheses) indicate the predominant existence of graphitic carbon on the surface of all samples. Moreover, it can be deduced from this table that the relative proportion (O 1s region) did not change with increasing Ni content and confirm the generation of different surface oxygen groups during the chemical functionalization using nitric acid. The Ni/C atomic surface ratio is a direct measure of the Ni nanoparticles distribution over surface of the support. Fig. 4 shows the relationship between Ni/C atomic surface ratio and Ni content over the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%). It can be observed that the Ni/C atomic surface ratio linearly increases with the Ni content. This result indicates that the Ni homogeneously dispersed over nanoparticles are the functionalized surface of the CNTox support, which is in good agreement with the observed tendencies in TEM and CO.

 NH_3 -TPD/MS were conducted to evaluate the effect of the Ni content on the acidity strength of the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%). The corresponding profiles are depicted in **Fig. 5**.



Figure 4. Relationship between the Ni content of the xNi/CNTox catalysts and the Ni/C atomic surface ratio obtained by XPS.

Although ammonia desorption does not allow to discriminate between Brønsted and Lewis acid sites, the amount of desorbed NH₃ is an indirect measure of the material's overall acidity. According to previous studies, the acid strength can be classified as weak acid sites (T < 300 °C), medium acid sites (300 °C < T < 500 °C) and strong acid sites (T > 500 °C).^[81] In terms of acid strength, it is observed that most of acid sites presented in the catalysts are weak (under 300 °C) with minor contributions of medium acid sites (300 - 500 °C). These acid sites present in the Ni/CNTox nanohybrid catalysts arises from different surface oxygen groups formed during the chemical functionalization. Furthermore, as can be seen in Fig. 5, the ammonia amounts desorbed decrease in the following order 2%Ni/CNTox > 7%Ni/CNTox > 10%Ni/CNTox > 15%Ni/CNTox. It has been reported that surface functional groups played a key role over the final properties of catalysts. Bowden et al.[82] proved that surface functional groups act as anchoring centers for metal nanoparticles. The experimental trend indicates that an increase of Ni content reduces the density of superficial acid sites. This implies that Ni nanoparticles are preferably anchored and dispersed over the

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surface oxygen groups thus producing a decrease in the acid site density.



Figure 5. NH₃-TPD/MS profile of the xNi/CNTox (x = 2, 7, 10 and 15 wt.%) catalysts.

To evaluate the effect of the Ni content on the wettability of the xNi/CNTox nanohybrid catalysts (x = 2, 7, 10 and 15 wt.%), the static contact angle (θ) was measured on the catalysts' surface (**Fig. 6** and **Fig. S4**). For particles stabilizing Pickering emulsions, θ is the equivalent of the HLB (hydrophilic-lipophilic balance) of surfactants.^[83] It is well accepted that when $\theta < 90^{\circ}$, particles are considered to be hydrophilic and can stabilize oil-in-water emulsions (o/w). In contrast, in case of $\theta > 90^{\circ}$, particles are mainly hydrophobic and favor the stabilization of water-in-oil emulsion droplets (w/o).^[54] Concerning carbon materials, they are well-known to be mainly hydrophobic. However, it is possible to incorporate hydrophilic sites (represented by surface oxygen

groups) on the surface of solid materials through oxidative functionalization.^[60,84] **Fig. S4** shows that, after oxidative treatment, the CNTox support presents a reduced contact angle of 117.9 ° in comparison with the pristine CNT with a contact angle of 138.1 °. As can be seen in **Fig. 6**, the Ni-based catalysts with a Ni content of 2, 7, 10 and 15 wt.% display a contact angle of 119, 123, 127 and 135 °, respectively. These results indicate that an increase of the Ni content tends to increase the hydrophobic character of the catalysts, thus reducing the amphiphilic character of the solid particles. The preferentially anchored of the Ni nanoparticles at the created surface oxygen groups (hydrophilic sites) produce a partial blocking of theses hydrophilic centers. Therefore, these results together with the results obtained by NH₃-TPD/MS points towards the fact that high Ni content reduce the acid and amphiphilic character of Ni-based catalysts.

In Pickering emulsions, fine amphiphilic solid particles adsorbed at the water/oil interface sterically hinder the coalescence of droplets and effectively stabilize the emulsion.^[56] In Fig. 7a-d. optical micrographs of the emulsion droplets stabilized over the xNi/CNTox nanohybrid catalysts (x = 2, 7, 10 and 15 wt.%) are shown. When the water-dodecane mixture was sonicated in presence of the Ni/CNTox catalysts, amphiphilic particles were dispersed at the liquid-liquid interfaces and an effective formation of emulsion droplets was observed. However, several differences can be observed with respect to the size of the resulting droplets. Based upon Fig. 7a-d. it can be seen that the Ni-based catalysts with a Ni content of 2, 7, 10 and 15 wt. % display average droplet sizes average of $20 \pm 6 \mu m$, $28 \pm 8 \mu m$, $29 \pm 7 \mu m$ and $44 \pm 2 \mu m$, respectively. Ruiz et al.[85] demonstrated that an increase of the concentration of the solid particles may lead to an increase of stabilized emulsion fraction and a decrease of the size of the emulsion droplets, thus producing stable emulsions. The amphiphilic character of the nanohybrids makes them segregate naturally to the water/oil interface, thus becoming suitable for the stabilization of emulsions with small droplet sizes and remarkable stability.^[54] Therefore, for Ni contents below to 10 wt.% emulsions with small droplet size can be formed, whereas the emulsion droplets are bigger and, therefore, less stable for a Ni content of 15 wt.%.



Figure 6. Static water contact angle measurements for the xNi/CNTox (x = 2, 7, 10 and 15 wt.%) catalysts. The photos were captured after the deposition of the water droplet on the surface of the self-supporting pressed sample disc.

FULL PAPER



Figure 7. Optic/fluorescent microscope images of w/o emulsion stabilized over a) 2%Ni/CNTox, b) 7%Ni/CNTox, c) 10%Ni/CNTox and d) 15%Ni/CNTox catalysts.

Claire et al. verified that the wettability of the particles is essential to control the emulsion type (o/w or w/o, simple or multiple) and the droplet's size.[55] After the addition of a fluorescent and watersoluble dye, it became possible to identify the type of emulsions formed over the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%). In Fig. 8, it can be observed that the internal area of the emulsion droplets presented fluorescence, which proved that the nanohybrid catalysts were capable to effective form w/o emulsion droplets. These results are in good agreement with the measured contact angle.



Figure 8. Optic/Fluorescent microscope image of w/o emulsion droplets stabilized by 2%Ni/CNTox catalyst. A water-soluble and fluorescent dye (green color, fluorescent Na salt) was added to identify the emulsion's type.

Catalytic activity

Since bio-oil derived from biomass is a complex liquid that is partially soluble in either water or hydrocarbon solvents, the hydrogenation reaction in water-oil systems are more desirable from a practical point of view. Therefore, catalytic conversion of furfural (FAL) in water-dodecane emulsions stabilized over xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%) were investigated. Fig. 9 shows the specific catalytic activities based upon the initial reaction rates (x 10⁻⁶ mol_{FAL} g_{cat}⁻¹ s⁻¹) obtained from Fig. S5. It can be observed that the initial rate linearly increases with a Ni content up to 10 wt.% before following a more curved trend (dotted line in Fig. 9) for higher contents (15 wt.% of Ni). The increase in the catalytic activity can be generally related with an increased number of active sites on the surface (dispersion) and, therefore, a loss of linearity at high metal contents could be associated to the formation of agglomeration.^[66,86] The increase of the catalytic activity up to Ni content of 10 wt.% can be well related to the surface accessibility of Ni sites as suggested by TEM, CO chemisorption and XPS results. However, for higher Ni contents (15 wt.%), the observed results cannot be connected with a loss of dispersion since the characterization results of this catalysts show the opposite. This implies that there are other parameters affecting the catalytic activity in emulsion system, such as the wettability of the solid nanoparticles and the size of the emulsion droplets. Large emulsion droplets generate less stable drops and are prone to coalescence process.^[85,87] The optical micrographs confirmed that the small droplet size did not change significantly with an increasing Ni content up to 10 wt.%. In contrast, when a 15 wt.% of Ni were incorporated over the support surface, the droplet average size increased notably (factor of 2). This reduced the accessibility of hydrophilic sites (surface oxygen groups) and changed the wettability of solid particles, thus forming larger emulsion droplets, which tend to be less stable. Therefore, the loss of the catalytic activity for catalysts containing more than 10 wt.% of Ni could be attributed to the increased droplet's size and the reduced stability of larger droplets. Fig. S5 shows the conversion of FAL and the yield of products as a function of time over the xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%). The main product obtained over all catalysts was cyclopentanone (CPO). Minor amounts of 2-methyltetrahydrofuran (2-MTHF) and cyclopentanol (CPOL) were observed. Concerning the detected

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Figure 9. Initial rate of furfural conversion as a function of the Ni content over the different xNi/CNTox catalysts. The dotted line represents the theorical linear trend.

secondary products, several changes were observed as a function of the metal content. When FAL conversion was performed over the Ni-based catalysts with a Ni content up to 10 wt.%, levulinic acid (LA) was mainly formed. In case of 15%Ni/CNTox catalyst, tetrahydrofurfuryl alcohol (THF-OH) was the second mayor product. These results indicate that at high Ni content (15 wt.%) the dehydrating ability of acid sites is minimized, while the hydrogenating capacity was increased, according to the **Scheme 1**. This could be explained by a modification of the active sites as inferred by the characterization results. **Scheme 1** shows the main products obtained in aqueous hydrogenation of furfural in presence of hydrogen and metal/acid-functionalized catalysts.^[42,48] It can be seen that FAL can be initially converted to FUR-OH through a direct hydrogenation of C=O bond over

metal sites.^[42] The formation of CPO takes place via furanic ring rearrangement of FUR-OH through Piancatelli reaction,^[48] under reduced atmosphere in aqueous medium, while CPOL is obtained by consecutive hydrogenation of CPO. Moreover, THF-OH can be obtained via direct hydrogenation of FUR-OH. Hydrogenolysis of FUR-OH allows for the formation of 2-methylfuran (2-MF),[88] which is further hydrogenated to 2-MTHF. Finally, LA is obtained via direct ring opening through acid hydrolysis reaction.[89] It has been reported that several parameters can affect the FAL rearrangement towards CPO.[48] Hronec et al. studied the aqueous FAL conversion towards CPO over Pd-Cu/C catalysts.^[40] They found that the higher catalytic activity displayed for these catalysts was related to the proper distribution of Pd⁰ and Cu⁺ species. Furthermore, CPO formation was studied by Bradley et al.,[90] who demonstrated that the strong FAL adsorption over groups 8-10 metals is connected to the interaction between the orbital π and the orbitals d of the metals. This interaction weakens the C-O bond, thus helping to stabilize the n^2 -(C-O) aldehvde complex.^[90] The same behavior could potentially explain the ring opening and the FAL rearrangement to CPO over xNi/CNTox (x = 2, 7, 10 and 15 wt.%). In Scheme 2 the reported catalytic rearrangement of FAL to CPO is depicted.^[47] Initially, FAL is hydrogenated towards FUR-OH over the active sites of the metal. Afterwards, the water molecules attack via the fifth position of the furan ring to form the oxycation.^[38] Then, under acidic conditions, the rearrangement of the formed oxycation to 4-hydroxycyclopentenone (4HCPTO) happens through Piancatelli rearrangement. Finally, further dehydration of 4HCPTO, catalyzed by acid sites, give rise to very unstable intermediate 2cyclopentanone (2CPTO) before being further hydrogenated to CPO.

Fig. 10 shows the products' selectivity calculated at a furfural conversion of 10 %. It can be observed that all catalysts display a fairly similar selectivity to CPO (about 63% aprox.) at lower FAL conversion.



Scheme 1. Main products during the hydrogenation of furfural in water under hydrogen atmosphere and metal-acid catalysts.^[40,48]

8

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I = Intermediary; II = 4-hydroxi-2-cyclopentenone (4HCPTO); III = cyclopentedienone; IV = 2-cyclopentenone (2CPTO)

Scheme 2. Catalytic rearrangement of furfural (FAL) to cyclopentanone (CPO) showing hydrogenation, rearrangement, and dehydration reactions over amphiphilic Ni/CNTox catalysts.^[47]

Moreover, it can be observed that the selectivity of secondary products is strongly modified for higher Ni contents. The Ni-based catalysts with a Ni content up to 10 wt. % showed the highest selectivity to LA (> 20%) with a lower selectivity to THF-OH (about 10%). In contrast, the 15%Ni/CNTox catalyst displayed the highest selectivity towards THF-OH (35%) with a lower selectivity to LA (5%). These results clearly demonstrate that an increase of Ni content to 15 wt.% decreased the dehydrating ability of acid sites, thus leading to a modification of the reaction mechanism. It has been reported that selectivity changes towards specific products depends on the properties of the acid-base support (acid strength and amount of acid sites).^[91-93] Mellmer et al. reported on the selective production of LA from FUR-OH over H-ZSM5 catalysts.^[94] In a first catalysts' screening, they found that the solid catalysts with weak-medium Brønsted acid sites, produced the lowest yield to LA.



Figure 10. Distribution of obtained products at a furfural conversion of 10% over the *x*Ni/CNTox catalysts (x = 2, 7, 10 and 15 wt.%) at 200 °C, 2.0 MPa of H₂ and water/dodecane ratio 1:1.

This suggests that catalysts with strong Brønsted acid sites were essential to obtain LA as a primary product. According to experimental results, Ni-based catalysts with a Ni content below 10 wt.% display a higher concentration of acid sites (with weak acidity) compared to the catalyst with 15%Ni/CNTox (**Fig. 5**), which favors the formation of LA as a secondary product. The preferential THF-OH formation was influenced by the deposition of the Ni. The metal nanoparticles would preferably deposit over the surface functional groups. However, in case of higher Ni content (15 wt.%), an inhibition of the surface groups can be achieved, thus minimizing the acid function of the catalyst. Consequently, changes in the selectivity were observed. Moreover, the modification of Ni nanoparticles, produced by large emulsion droplets cannot be ruled out.

In order to highlight the promising advantages of performing a catalytic reaction in an emulsion system, the conversion of FAL and the yield of products as a function of the reaction media over the nanohybrid 10%Ni/CNTox catalyst after 1 h of reaction are depicted in Fig. S6. It can be observed that the FAL conversion in emulsion system is much higher than in the individual single aqueous and organic phases. This result indicates that the reactivity can be increased in emulsion systems due to a generation of a higher interfacial areas. This behavior enhances the rate of mass transfer between the involves phases, which enables the diffusion of reactant to active sites. A similar behavior was reported by Jimare et al.[95] for the HDO of vanillin over Pd/CNT-SiO₂ nanohybrid in emulsion systems. These authors demonstrated that the formation of stable emulsions remarkably increased the value of the volumetric global mass transport coefficients due to the growth of the interfacial area. Therefore, the reaction rate can be greatly enhanced by increasing the mass transport coefficient with solid-particle stabilized emulsions. Additionally, it can be observed that the catalytic conversion of FAL in non-polar solvents (dodecane) is eighteen times higher than that in aqueous media. This result suggests that the presence of non-polar solvents in either single or emulsion

phases hinders the deactivation of active sites through the formation of a hydrophobic film at the interface of the emulsion droplets. This helps to avoid the irreversible adsorption of water on the active sites.^[96] A clear dependence of the yield of reaction products on the reaction media can be also observed in Fig. S6. Furfuryl alcohol (FUR-OH) and 2-methyltetrahydrofuran (2-MTHF) were the main products observed with dodecane only, while tetrahydrofurfuryl alcohol (THF-OH) was a minor product. This result suggests that furfural hydrogenation products were obtained only in absence of water. In contrast, cyclopentanone (CPO) was the main product observed in the aqueous medium, while FUR-OH was detected in traces, which implies that the presence of water inhibits to a certain extent the hydrogenation capacity of the nanohybrid catalyst. In contrast, important CPO and levulinic acid (LA) were produced in a high amount using an equal proportion of solvent (emulsion), whereas FAL hydrogenation products were only obtained in low concentrations. The difference in the vield of CPO in w/o emulsion indicates that the rearrangement reaction of FUR-OH is dominant in the CPO formation, which is consistent with previous study.[62] Therefore, the results obtained suggest that equal amounts of organic and aqueous phase favor the catalytic conversion of FAL and the production of cyclopentanone. These results display a better catalytic performance (greater activity and high selectivity to cyclopentanone) in comparison to others catalytic systems reported in the literature (Table S1) for the liquid conversion of furfural, which is a clear indication of the potential of this catalytic system.

Conclusion

Amphiphilic Ni/CNT particles with different metallic content have been prepared in order to study their emulsifying properties for the conversion of furfural (biomass-derived furan compound) at the water-oil interface. It was found that the wettability of the catalysts and the size of emulsion droplets are key parameter to enhance the catalytic activity. The catalytic activity linearly increased with increasing Ni content (up to 10 wt.%) before dropping down again for a Ni content of 15 wt.%. The increase of catalytic activity was related to the increase of active Ni sites. In contrast, the loss of the catalytic activity observed for higher Ni contents (15 wt.%) was attributed to the enlarged droplet's size and their resulting instability, which was produced by the inhibition of hydrophilic sites in this catalyst. All catalysts were highly selective towards the formation of cyclopentanone. However, several changes were observed regarding to secondary products formed. Ni-based catalysts with a Ni loading up to 10 wt.% were selective to levulinic acid, while the 15%Ni/CNTox catalyst was mainly selective to tetrahydrofurfuryl alcohol as a second major product. Ni nanoparticles were anchored over the surface oxygen groups, thus inhibiting the acid sites. The catalyst is less dehydrating and more hydrogenating thus favoring the formation of THF-OH.

Experimental Section

Synthesis of catalysts

Prior to the synthesis of the Ni-based catalysts, 1.0 g of pristine CNT was oxidized using 10.0 mL of a HNO₃ solution at 65% during 3 h at 110 °C. Then, the solid was filtered and washed with deionized water until reaching a neutral pH. Finally, the functionalized support was dried at 110 °C for 12 h. The nanohybrid xNi/CNTox catalysts (x = 2, 7, 10 and 15 wt.%) were prepared by incipient impregnation of an aqueous solution of Ni(NO₃)₂ x 6H₂O with different Ni contents. The catalysts were dried overnight at 110 °C, and then, calcined in air for 1 h at 300 °C. Finally, the catalysts were reduced in H₂ (flow rate of 60.0 mL min⁻¹) for 4 h at 400 °C and passivated in 1% O₂/N₂ flow (60.0 mL min⁻¹) for 1 h with the reactor immersed in a liquid nitrogen/isopropanol bath. Afterwards, the catalysts were kept for 1.5 h at room temperature.

Characterization of the catalysts

X-ray diffraction (XRD) was carried out using a Bruker D2 powder diffractometer (radiation source Cu-K α (λ = 1.5406 Å) operated at 30 kV/10 mA and a LinxEye solid-state detector. BET Surface area (S_{BET}) and textural properties of CNTox supports and xNi/CNTox catalysts (x= 2, 7, 10 and 15 wt.%) were determined from N₂ physisorption at -196 °C using a Micromeritics 3Flex equipment. The BJH method was used to calculate the distribution of the pore sizes. Temperature-programmed reduction (H₂-TPR) studies were obtained using a Micromeritics 3Flex equipment equipped with a thermal conductivity detector. In each experiment, 0.035 g of the sample were heated under 5% H₂/Ar with a flow rate of 100 mL min⁻¹. The sample was heated at a rate of 10 °C min⁻¹ from 25 to 900 °C. The degree of reducibility of the catalysts was calculated according to **Equation (1)**:

reducibility (%) = $\frac{mmol H_2}{mmol NiO} \times 100$

where the mmol of H₂ was estimated by Gaussian deconvolution of the H₂-TPR profiles (Fig. S2, the H₂ uptake was calibrated previously) and the moles of NiO was estimated from the percentage of NiO impregnated on the catalysts. Transmission electron microscopy (TEM) images of xNi/CNTox were acquired using a JEOL Model JEM-1200 EXII microscope. Samples were ground and dispersed in methanol and, then, transferred to a copper grid (methanol dispersion method). To obtain the Ni particle size, histogram plots for over 300 particles of the reduced-passivated xNi/CNTox catalysts were depicted using the software Image Tool 3.0 software. The metal dispersion was estimated from CO chemisorption using a Micromeritics 3Flex apparatus. The catalysts (0.05 g) were reduced in-situ under H_2 flow using the same reduction conditions as described for the synthesis of catalysts. Ni dispersion was calculated by assuming a CO:Ni stoichiometry of 1:1. X-ray photoelectron spectroscopy (XPS) of in-situ reduced catalysts was realized using a VG Escalab 200R electron spectrometer with a MgKa (1253.6 eV) photon source. All binding energies (BE) were referenced to the C 1s level of the carbon support at 284.8 eV. An estimated error of ± 0.1 eV can be assumed for all measurements. The intensities of the peaks were calculated from the respective peak areas after background subtraction and spectrum fitting by the standard computer based statistical analysis. The acidity of xNi/CNTox catalysts was determined by temperature-programmed desorption of ammonia (NH₃-TPD/MS) using a 3Flex (Micromeritics) equipment. The sample was pre-treated in flowing He (flow rate of 50 mL min⁻¹) at 40 °C for 0.5 h and, then, saturated with NH₃ using He (flow rate of 50 mL min⁻¹) as a carrier gas. The samples were purged with He for 0.5 h to remove physically adsorbed NH3 and, subsequently, cooled to ambient temperature in He. Once the TCD baseline was restored. NH₃-TPD/MS was performed with a heating rate of 10 °C min-1 up to 900 °C and He flow (flow rate of 50 mL min⁻¹). The wettability of the xNi/CNTox catalysts were determined by measuring the static contact angles (θ) with distilled water (droplet's volume of 2 µL) under ambient conditions on a self-supporting pressed sample using a drop shape analyzer DSA-25-E (Krüss GmbH). The optical/fluorescent micrograph were obtained in an Axiostar plus Zeiss microscope equipped with a HBO 50 mercury vapor lamp.

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(1)

50% for 15 minutes.

Hydrogenation of furfural

Preparation of the emulsions using the nanohybrid catalysts

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To prepare the water/oil emulsions with the different xNi/CNTox [4] nanohybrid catalysts (x = 2, 7, 10 and 15 wt.%), deionized water and dodecane were used as aqueous and organic phases, respectively. In [5] each experiment, 50 mg of the catalyst was dispersed in 8 mL of water by sonication with a horn sonicator (UP50H, Hielscher) at 25% of amplitude for 15 minutes. Afterwards, 8 mL of dodecane was added (water:dodecane ratio equal to 1:1) before sonicating the final mixture at an amplitude of 105397 [6] The catalytic conversion of furfural was carried out in a Batch Parr [7] reactor. In each experiment, 0.232 mol L⁻¹ of furfural, 50 mg of the xNi/CNTox catalyst (x = 2, 7, 10 and 15 wt.%) and 16 mL of the emulsion (water and dodecane mixture) were used. Before to reaction, the vessel [8] reactor was purged using a N₂ flow for 15 minutes to remove the oxygen content inside of the reactor. Afterwards, the reactor was heated up to the [9] reaction temperature (200 °C) and the H₂ pressure was adjusted (2.0 MPa). To obtain the furfural conversion as a function of the time reaction, consecutive reactions were carried out at different times. After each [10] reaction, the reactor was cooled down and the H_2 flow was replaced by a N2 flow. Once the reactor reached room temperature, the emulsion was [11] broken by filtering the catalyst's particles out. Both liquid phases were C. Herrera, I. T. Ghampson, K. Cruces, C. Sepúlveda, L. Barrientos, [12] separated and analyzed individually by GC using flame-ionization detector

(FID) and an Elite-1 column (Perkin Elmer, 30 m x 0.53 mm x 3.0 μm film thickness). The products were identified by their column retention time in comparison with available standards. The specific rate r_s (mol g_{cat} ⁻¹ s⁻¹) [13] was calculated from the initial slope of the plot of furfural conversion as a function of time, according to Equation (2): [14] $r_s = \frac{[b \times n]}{r_s}$ 2018, 6, 13628-13643. (2) [15] where b is the initial slope of conversion vs. time plot (s⁻¹), n is the initial number of moles of furfural in the solution (mol), and *m* the amount of the Sci. 2020, 565, 96-109. catalyst (g). The selectivity (%) for each product was calculated at a furfural [16] conversion of 10 %, according to Equation (3): 2017. 5. 2421-2427. [17]

selectivity
$$(\%)_i = \frac{X_i}{X_T} \times 100$$
 (3)

where X_i is the percentage of product *i* and X_T is the percentage of furfural converted (10 %).

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12

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Graphical Abstract



Furfural conversion into add-value chemicals has been investigated at the interface of emulsion droplets. Special attention has been focused on the effect of Ni content over the emulsifying properties. It was found that enlarged droplet's size, which was at higher Ni content, disfavor the activity and stability of catalytic system. Moreover, it was found that the products selectivity can be tuned in function of metal content.