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Hydrogenation of Furfural to Cyclopentanone in Tert-Butanol-Water Medium: A Study of the Reaction Intermediates Reactivity Using Cu/ZnO/Al₂O₃ as Catalyst

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Abstract: The catalytic transformation of furfural to cyclopentanone has been investigated using two different liquid phases as solvent: water and 30 wt.% tert-butanol in water. When using neat water at 160 °C, 40 bar of H₂, and after 2 h of reaction time, furfural polymerizes, and the yield of cyclopentanone is just 42% with a low carbon balance, indicating that furfural is transformed to non-detected by-products, likely heavy resins. When using 30 wt.% tert-butanol in water, the yield of cyclopentanone is ca. 20%, and the major product is furfuryl alcohol with a 47% yield. We have studied the catalytic transformation of the most relevant reaction intermediates in the overall conversion of furfural to cyclopentanone. In the presence of tert-butanol, two steps are inhibited in the overall pathway: (i) the Piancatelli rearrangement of furfuryl alcohol and (ii) the transformation of cyclopentenone. This inhibition is attributed to the neutralization of protons from water dissociation by surface sites on the catalyst, preventing their participation in the overall reaction. To counteract these inhibitions when tert-butanol is present, higher H₂ pressure (60 bar) and temperatures (200 °C) are required. We have been able to obtain productivities per gram of catalyst and mols of Cu basis of 411 g_{prod}·h⁻¹·g_{cat}⁻¹ and 14 g_{prod}·s⁻¹·mol_{Cu}⁻¹, respectively, which is substantially above that found for other copper-based catalysts.

Keywords: cyclopentanone; furfural; hydrogenation; Cu/ZnO/Al₂O₃; reaction intermediates



Citation: Orozco-Saumell, A.; Mariscal, R.; Vila, F.; López Granados, M.; Alonso, D.M. Hydrogenation of Furfural to Cyclopentanone in Tert-Butanol-Water Medium: A Study of the Reaction Intermediates Reactivity Using Cu/ZnO/Al₂O₃ as Catalyst. *Catalysts* **2023**, *13*, 1394. <https://doi.org/10.3390/catal13111394>

Academic Editor: Karine De Oliveira Vigier

Received: 2 October 2023

Revised: 20 October 2023

Accepted: 23 October 2023

Published: 25 October 2023



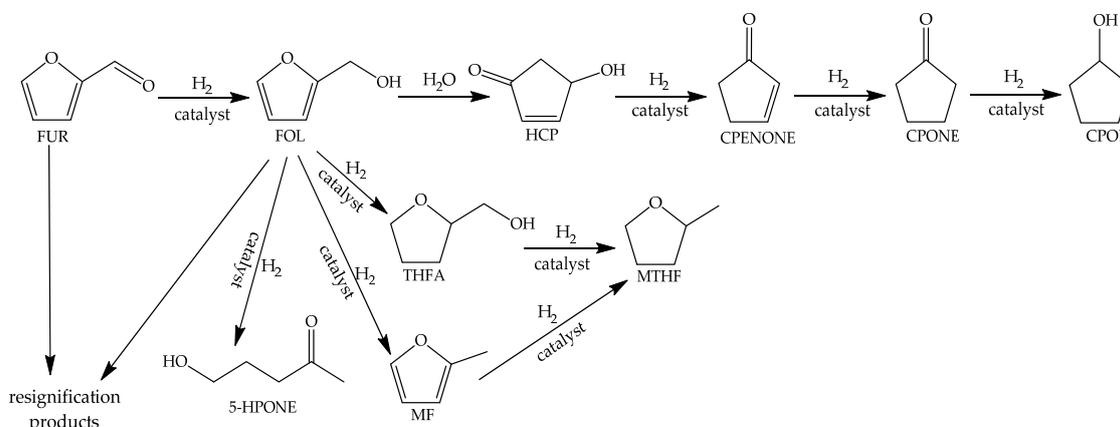
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1. Introduction

The depletion of fossil resources and the problems associated with climate change are encouraging research on deploying biorefineries to obtain chemical products, plastics, and biofuels from biomass. Lignocellulosic biomass is a renewable and abundant resource composed of lignin, cellulose, and hemicellulose; the latter may be fractionated into C5 and C6 sugars [1–3]. Furfural (FUR) is a compound derived from the C5 fraction, featuring two C=C double bonds, a furanic ring, and a functional C=O group. It finds applications in the chemical and polymer industry [4]. One important field of research is the hydrodeoxygenation (HDO) of furfural, such as the production of cyclopentanone (CPONE). HDO is an important reaction that aims to efficiently remove oxygen while minimizing hydrogen consumption using selective catalysts [5]. CPONE is a high-value product used for the synthesis of various industrial chemicals, including fragrances, cosmetic products, solvents, and agrochemicals [6].

FUR can undergo various reactions, including C-C cleavage, C-O hydrogenolysis, C=O hydrogenation, reorganization, and hydrogenation of the furanic ring, as well as polymerization. Some of these reactions are illustrated in Scheme 1. The choice of catalyst and reaction conditions influences the product distribution. During the hydrogenation process, FUR is initially converted to furfuryl alcohol (FOL) by reducing the C=O bond. Subsequently, FOL can follow different pathways. The furan ring can be further hydrogenated

to yield 2-methyl furan (MF), tetrahydrofurfuryl alcohol (THFA), methyltetrahydrofuran (MTHF), or 5-hydroxy-2-pentenone (5-HPONE) [7,8]. Wang et al. reviewed the catalytic hydrogenation of FUR for these products [9].



Scheme 1. Reaction scheme. Hydrodeoxygenation of FUR to CPONE.

Since 1976, the reorganization of FUR, has been extensively studied. Piancatelli et al. first observed this phenomenon in an acidic aqueous system, sparking increasing interest in this route due to the possibility of obtaining intermediates from natural resources. The synthesis of CPONE involves the Piancatelli-type rearrangement of the furan-ring conjugate system (C=C-C=C), followed by dehydration and hydrogenation reactions. In comparison to monometallic catalysts, heterogeneous bimetallic catalysts have shown higher catalytic activity [10]. In López's review [11], various heterogeneous catalysts used in the hydrogenation of FUR were compared. Recently, the importance of bimetallic catalysts has grown, and more studies have been conducted utilizing this type of catalyst. To achieve high selectivity to CPONE, the active sites should promote the hydrogenation of the intermediate FOL to obtain CPONE. Several studies have investigated the hydrogenation of FUR to CPONE in batch mode using metals such as Ni, Pd, Cu, or Fe. Copper, as a transition metal, has gained increasing attention in the scientific community due to its affordability, accessibility, and satisfactory selectivity in catalytic hydrogenation processes [9]. For this study, we have chosen a commercial catalyst Cu/ZnO/Al₂O₃ due to the acid capacity provided by copper, which allows FUR to bind on the catalyst's surface and undergo hydrogenation to CPONE and the acidity of alumina that facilitates the Piancatelli rearrangement. Copper metal particles exhibit high activity in hydrogenation reactions, making them valuable catalysts for in situ hydrogen synthesis in methanol-reforming, showing exceptional catalytic performance [12]. Furthermore, they have been used for the HDO of glycerol [13,14], FUR [8], and the hydrogenation of esters to alcohols [15], demonstrating remarkable catalytic efficiency in these processes as well.

There is limited research on the catalytic production of CPONE in water and co-solvents. The presence of water as a solvent favors the reorganization towards the formation of CPONE. However, the use of co-solvents could avoid side reactions and increase the yields of desired products. Hnorec et al. investigated the hydrogenation of FUR using different alcohols, such as n-decanol and 2-propanol, as solvents, and they found that the furan ring rearrangement did not occur [16]. Jia et al. conducted a study using a water-methanol co-solvent system. In this case, methanol inhibited the formation of CPONE and resulted in the production of THFA [17]. Another study utilized toluene as a co-solvent with water, which resulted in high yields of CPONE and suppressed the side reactions from FUR and FOL that are more likely to occur in an aqueous medium [18]. Tert-butanol (t-BuOH) was selected because it is the best co-solvent for the further transformation of CPONE into cyclopentanone oxime [19], an intermediary in the synthesis of Nylon-5. So, no purification of the CPONE would be necessary if t-BuOH could be used as solvent for the hydrogenation of FUR. The aim is to provide insights into the key steps and factors

that influence the efficiency and selectivity of the hydrodeoxygenation reaction. A detailed analysis of catalysts used in the hydrodeoxygenation process is provided in this work, using water and t-BuOH-water mixtures as reaction media. The use of t-BuOH could help avoid undesirable polymerization of FOL and improve the carbon balance in this reaction. The potential involvement of intermediate species and their transformation pathways were also explored in order to study why the progress to CPONE does not occur as described in other works.

2. Results and Discussion

Catalytic Activity

The solvent has an important role in the hydrogenation of FUR to CPONE to avoid the polymerization in the transformation of FUR to FOL and FOL to 5-Hydroxy-2(5H)-furanone, HCP (see Scheme 1). Dohade et al. suggest that a biphasic toluene-water mixture enhances the catalytic activity toward CPONE because it suppresses the side reactions of FUR and FOL, which are more likely to occur in a water medium [19]. In our case, these secondary reactions could also be avoided by adding a co-solvent. We have studied the effect of adding different amounts of t-BuOH on the product's selectivity (Figure 1). Increasing the amount of t-BuOH improved the carbon balance and prevented the polymerization of FUR or FOL. However, it was observed that the rate of CPONE production was slower with higher amounts of t-BuOH. This finding indicates that adding alcohols prevents the FOL polymerization, but at the same time, the solvent prevents the CPONE production. Figure 1 shows that the rate of FOL transformation decreases along with the concentration of t-BuOH (line red). It should be noted that the experimental error, calculated by repeating several experiments, was below $\pm 5\%$ for neat water experiment and below $\pm 3\%$ for experiments with t-BuOH; consequently, the yields obtained are statistically different.

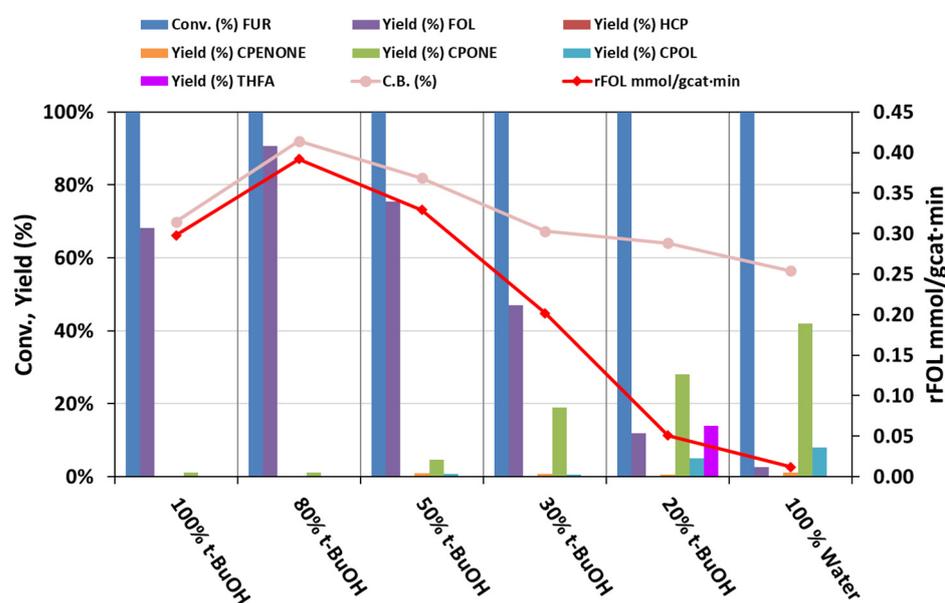


Figure 1. Effect of different amounts of t-BuOH in water. Reaction conditions: 1 wt.% catalyst, 5 wt.% FUR, 160 °C, 40 bar H₂, 2 h, overall volumen (weigh) = 5 g. C.B. stands for carbon balance, and rFOL for the rate of formation of FOL).

The reaction conducted in 20% t-BuOH in water resulted in a higher yield of CPONE but also obtained THFA (12% yield), which is formed via hydrogenation of the furanic ring and not through Piacantelli rearrangement. This suggests that low solvent concentrations help FOL to hydrogenate the furanic ring. In addition, if all FOL were transformed into CPONE, the maximum yield achievable would be around 40%. However, utilizing 30% t-BuOH in water, the FOL yield is still ca. 45%, and it is still possible to attain

approximately 70% yield of CPONE if all FOL is successfully converted. Therefore, in order to perform a more comprehensive study of the polymerization and reaction rate of the different intermediates produced during the hydrodeoxygenation of FUR to produce CPONE, considering the best scenario to achieve the maximum yield of CPONE, we selected 30% t-BuOH in water as the reaction mixture.

We have carried out a study of the different intermediates of the reaction (Figure 2). The data confirms that the reaction using water as solvent was faster than using water/tert-butanol, but the carbon balance was better when the co-solvent was added. We have observed that the main issue in our system was the polymerization of FUR and FOL. We first compared the conversion of FUR and product distribution after 1 h in neat water and a 30% t-BuOH-water mixture. As for the results in Figure 2, the carbon balance was better when t-BuOH was added to the reaction, but the reaction was slowed down, and the main product was FOL instead of CPONE (see Figure 2a). The presence of dark solid product observed during neat water reactions suggests the polymerization of FUR/FOL as the most effective side reaction and, consequently, the cause of the lower carbon balance. In the case of the FUR reaction, an unknown product was observed in both cases by HPLC, which was not present in the other reactions. This unknown product could be a result of polymerization. Kim et al. studied the acid-catalyzed oligomerization of FOL, and they deduced the formation of conjugated diene structure from difurfuryl furan (a product obtained from FOL polymerization) [20]. The carbon balance reported in this work does not take into account this unknown product.

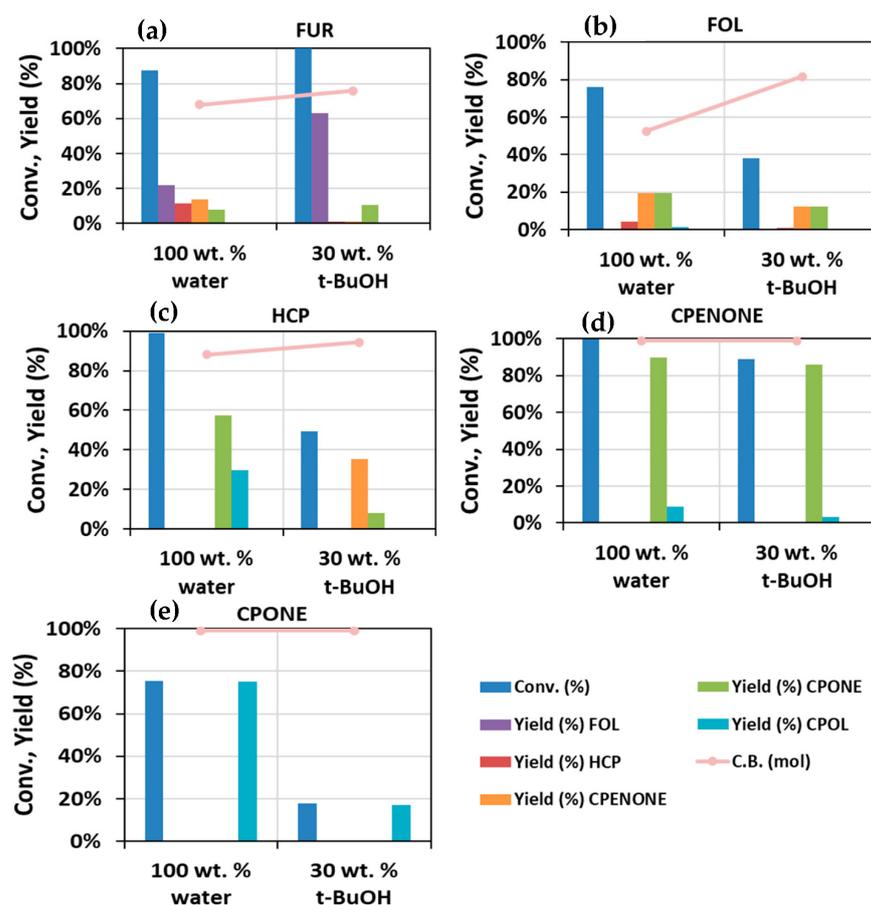


Figure 2. Study of intermediates of reaction in 100 wt.% H₂O and 30 wt.% t-BuOH in water. Hydrodeoxygenation: (a) FUR; (b) FOL; (c) HCP; (d) CPENONE; and (e) CPONE. Reaction conditions: 1 wt.% catalyst, 5 wt.% FUR, 160 °C, 40 bar H₂, 1 h, overall volumen (weigh) = 5 g.

To better understand the t-BuOH effect in each reaction step, an activity study with every reaction intermediate and also with the final product was carried out: FOL, HCP,

2-cyclopentenone (CPENONE and CPONE (Figure 2b–e, respectively). Table 1 displays the intrinsic reaction rates of all the intermediates involved in the reaction (margin of error of ca. 10%). The rate of FOL conversion in water was 0.23 mmol/g_{cat}·min (carbon balance of ca. 53%), whereas with t-BuOH, the rate was 0.14 mmol/g_{cat}·min (carbon balance of 82%). This shows that the presence of t-BuOH also reduced the conversion of FOL, both to desired products and degradation products, whereas when in only water, the decomposition rate was higher, and the carbon balance was lower.

Table 1. Reaction rates of different intermediates. 100 wt.% water and in brackets 30 wt.% t-BuOH in water. In black, the conversion rate of the molecule.

Reactions Rate (mmol/g _{cat} ·min)	FUR	FOL	HCP	CPENONE	CPONE
rFUR	0.48 (0.65)				
rFOL	0.19 (0.54)	0.23 (0.14)			
rHCP	0.10 (0.01)	0.04 (0.01)	0.77 (0.37)		
rCPENONE	0.12 (0.01)	0.02 (0.02)	0.00 (0.30)	0.84 (0.75)	
rCPONE	0.07 (0.09)	0.16 (0.11)	0.51 (0.07)	0.77 (0.72)	0.63 (0.15)
rCPOL	0.00 (0.00)	0.01 (0.00)	0.26 (0.00)	0.07 (0.03)	0.63 (0.15)

The reaction of HCP to CPONE in water was extremely rapid (Figure 2c), resulting in the production of CPONE and cyclopentanol (CPOL). The conversion rate of HCP in water was 0.77 mmol/g_{cat}·min (the conversion was complete), while the formation rates of CPONE and CPOL were 0.51 and 0.26 mmol/g_{cat}·min (yields of 57 and 29%), respectively. In contrast, the same reaction in t-BuOH did not progress significantly, with only 49% of HCP being transformed and a yield of 37% CPENONE (see Figure 2c), showing a much lower hydrogenation rate. In this latter case, the conversion rate of HCP was 0.37 mmol/g_{cat}·min, and the formation rates of CPENONE and CPONE were 0.30 and 0.07 mmol/g_{cat}·min, respectively. For the CPENONE hydrogenation (Figure 2d), in both reaction media, the hydrogenation rate of CPENONE and the formation rate of CPONE were very rapid, and there was no difference because of the presence of t-BuOH. Figure 2e shows the hydrogenation of CPONE to CPOL. When using water as a solvent, 75% of CPONE was transformed into CPOL with a selectivity of 100% within 1 h, indicating that the reaction occurs very rapidly. However, CPOL was not present in the hydrogenation process of FUR and FOL. This absence can be attributed to the possibility that CPENONE reacted with other compounds derived from FOL (or its oligomers), and these CPENONE derivatives, along with the polymers of FOL, inhibited the transformation of CPONE into CPOL [21,22]. In contrast, when t-BuOH was used as a co-solvent, CPONE was not hydrogenated to CPOL. Only 17% of CPONE was converted to CPOL, and the selectivity in this reaction, the same as that in water, was 100%. This can be an advantage of using t-BuOH if we do not want to obtain CPOL.

Based on these observations, even with an increased reaction time when using t-BuOH, the yield of CPONE would not significantly increase. This suggests that less solvent can be used, but the key step is the rearrangement of FOL to HCP, as it determines the progress of the reaction. This is the limiting step of the reaction due to the slow transformation of FOL in both water and t-BuOH. The poor carbon balance when water was used as the solvent suggests that the main issue in this step was the polymerization. In conclusion, the results of Figure 2 and Table 1 indicate that although t-BuOH prevents the polymerization of FOL and the hydrogenation of CPONE to CPOL, unfortunately, these advantages are overcome by the inhibition of the Piancatelli rearrangement of FOL (the rate-determining step of the overall process) and the HCP hydrogenation, both responsible of the factual low yield of CPONE in t-BuOH solutions.

We have also investigated the effects of different concentrations of FOL (Figure 3) on the yields of different products. As expected, at high FOL concentrations (10 wt.%), the reaction rapidly proceeded to form unknown products, which were likely the result of

polymerization, as confirmed by the presence of a dark solid residue. When the reaction was conducted with 5 wt.% FOL in water, CPONE was formed. From Figure 2b, we can observe that at 1 h of reaction time, CPENONE and CPONE were obtained, and after 2 h, CPENONE was transformed into CPONE, but the transformation of FOL did not progress further. In contrast, when using the same concentration of FOL with 30 wt.% t-BuOH in water as the solvent, the conversion of FOL decreased, leading mainly to the formation of unknown products, as we have seen above. Lastly, as expected, using a lower concentration of FOL, the carbon balance improved. However, an unknown product was still present, and the carbon balance was not close to 100% in any case. When performing the reaction with 1 wt.% FOL using water as the solvent, besides the formation of unknown products by oligomerization, there was an over-hydrogenation, and CPOL was formed. This may be due to the fact that, at high concentrations of FOL, the polymerization rate increased faster than the rearrangement rate of the furanic ring. Therefore, using low concentrations of FOL leads to higher selectivity to CPONE and CPOL while effectively avoiding polymerization [21].

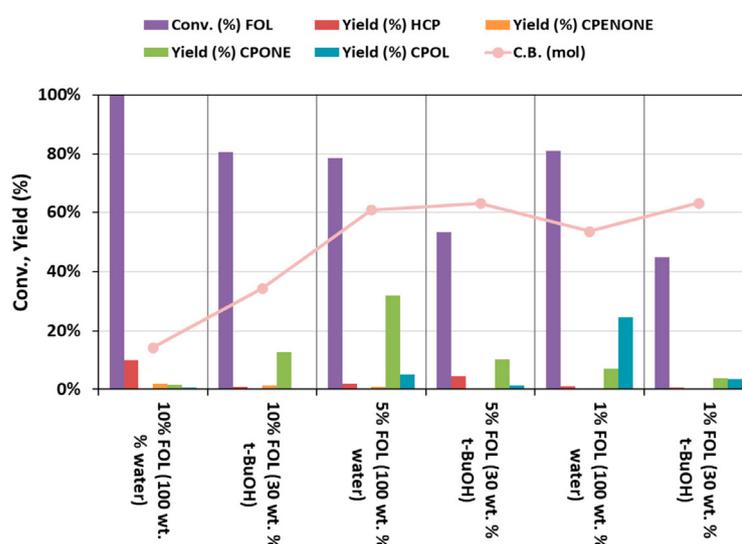


Figure 3. Different concentrations of FOL, in 100 wt.% water and 30 wt.% of t-BuOH in water. Reaction conditions: 1 wt.% catalyst, 10, 5 and 1 wt.% FOL, 160 °C, 40 bar H₂, 2 h, overall volumen (weigh) = 5 g.

To gain more information on the relevant steps in FOL transformation to CPONE in aqueous tert-butanol, several experiments without H₂ pressure were conducted (Figure 4). In the absence of H₂, only Piancatelli and polymerization reactions can take place, and any further hydrogenation of HCP and other intermediates was prevented. For the sake of comparison, additional experiments without a catalyst and with 40 bar of H₂ were also carried out. When using 1 wt.% of the catalyst and increasing the reaction time (0.5, 1, and 2 h), both the conversion of FOL and yield of HCP increased, as expected. However, remarkably, when no catalyst was used after 2 h of reaction, FOL was fully converted, largely to FOL-derived humins and also, at a non-negligible rate, to HCP. This indicates that acid-homogeneous species (protons from water dissociation) were involved both in the polymerization and in the Piancatelli rearrangement. The fact that the conversion was the same when 40 bars of H₂ were fed in the absence of a catalyst (next set of columns in Figure 4) reinforces the hypothesis of the involvement of water protons. In the presence of the catalyst, the FOL conversion and the HCP yield were smaller than with the Cu catalyst-free experiments, which indicates that these active protons were, in practice, neutralized by the surface sites in the catalyst. Basic sites or unsaturated Lewis acid sites present on the surface of ZnO and Al₂O₃ [23] can react with the aqueous protons, removing active homogeneous species. Finally, the last experiment feeding 40 bar of H₂ in the presence of

Cu catalyst (last columns) shows that, after 2 h of reaction, the conversion was even smaller than without H₂ and that HCP was almost converted partially to CPONE and CPOL but also in a large extension to unknown products. The latter suggests that the polymerization to heavy products affects not only FOL but also the subsequent intermediates, and that the presence of tert-butanol could not prevent these undesirable products. The possibility that t-BuOH can be involved in a Meerwein-Ponndorf-Verley (MPV) hydrogenation of the substrates was ruled out, because when testing FOL without pressure of H₂ (Figure 4), the reaction only advanced to HCP. If the t-BuOH had been significantly involved in the MPV reduction of FOL, we would have obtained CPENONE or CPONE, and this was not the case.

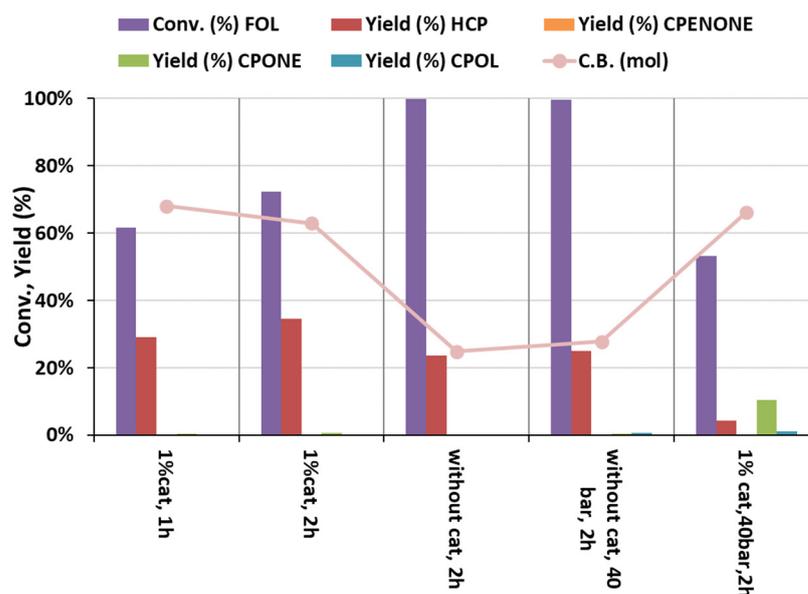


Figure 4. Study of FOL reactivity in the absence of H₂. Reaction conditions: 5 wt.% FOL, 160 °C, 30 wt.% t-BuOH in water, overall volumen (weigh) = 5 g. The amount of catalyst and time of reaction were modified. The two last columns of the reaction have pressure (40 bar H₂).

To give more support for the participation of the water-derived protons in the Piancatelli rearrangement of FOL and their neutralization by the catalyst surface, three more H₂-free experiments were conducted in the presence of an increasingly larger concentration of catalyst in the reaction. The results were summarized in Table 2 and showed a significant inhibition of the rate of transformation of FOL as more catalyst was incorporated, a direct consequence of the neutralization of protons available in the solution. Accordingly, the lower activity when using t-BuOH diluting the presence of water is just the result of having less active homogeneous protons to catalyze the reaction: the lower the water concentration, the smaller the amount of unneutralized protons left after contact with the catalyst. In conclusion, the catalyst was needed for the reaction to proceed further in the subsequent steps to yield CPONE but interfered with the very active sites capable of conducting the determining step: the Piancatelli rearrangement.

Table 2. Reactions rate of FOL transformation in the absence of H₂ varying the amount of catalyst. Reactions conditions: 5 wt.% FOL, 160 °C, 0.5 h, 30 wt.% t-BuOH in water, overall volume (weight) = 0.5 g.

Reactions Rate (mmol/g _{cat} ·min)	3 wt.%	2 wt.%	1 wt.%
rFOL	0.08	0.14	0.34
rHCP	0.04	0.07	0.17

To counteract the lower CPONE yields obtained using tert-butanol/water medium, derived from the inhibition of the rearrangement of Piancatelli and the HDO of HCP to CPONE, we have investigated the effect of the H₂ pressure and the reaction temperature on the course of the reaction. Figure 5 illustrates different kinetic studies conducted at temperatures of 160, 180, and 200 °C. The reaction carried out at 160 °C (Figure 5a) was allowed to proceed for a longer period of time because the rate was much slower than at higher temperatures. As the reaction time increased, a decrease in the carbon balance was observed, indicating the formation of undetected products and polymerization of FOL, as previously observed. This experiment confirms that both FUR and FOL polymerize at high temperatures. To address this issue, studies were carried out at 180 °C (Figure 5b) and 200 °C (Figure 5c) with shorter reaction times. At 180 °C, the highest yield of CPONE, 35%, was obtained after 2 h, with a carbon balance of 43%, whereas at 200 °C, CPONE yields close to 40% was obtained after 1 h of reaction with a similar carbon balance). Interestingly, at 200 °C and 0.5 h of reaction, the yields of HCP, CPENONE, and CPONE were 33%, 20%, and 24%, respectively, totaling ca. 77% of selective hydrogenation, but after 1 h of reaction, HCP transformed, into another unknown product not detectable using HPLC, very likely via polymerization.

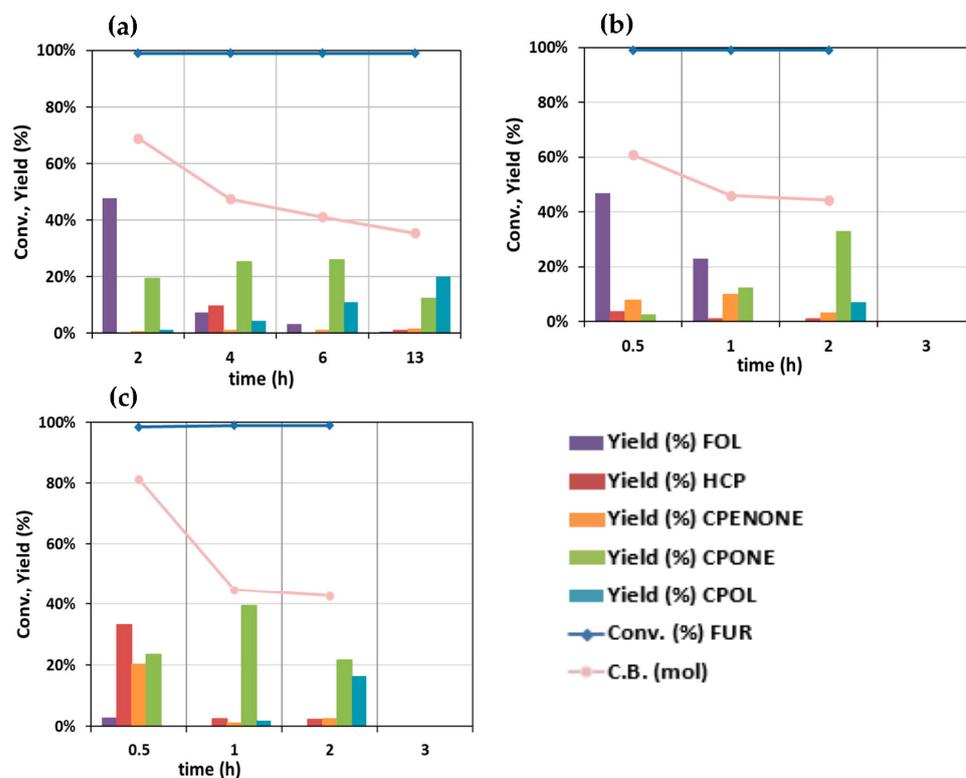


Figure 5. Study of the reaction kinetics in 30 wt.% of t-BuOH in water. Reaction conditions: 1 wt.% catalyst, 5 wt.% FUR, 40 bar H₂, overall volumen (weigh) = 5 g. (a) 160 °C; (b) 180 °C and (c) 200 °C.

The study of reaction pressure was also conducted, yielding promising results, as depicted in Figure 6. Increasing the pressure to 60 bar of H₂ resulted in a CPONE yield of 47% after 0.5 h of reaction. This yield was above the highest yield achieved in only water, which was ca. 41%, with a quite similar carbon balance (Figure 1). When we used 80 bar of H₂, we obtained yields of CPONE and CPOL of 15 and 17%, respectively, and observed that the carbon balance decreased. This suggests that the polymerization of the products or other intermediates of reaction as alkoxide and/or hydroxyalkyl species can be obtained with such high pressure of hydrogen [17]. Moreover, CPOL was obtained, which was not a product of interest in this research.

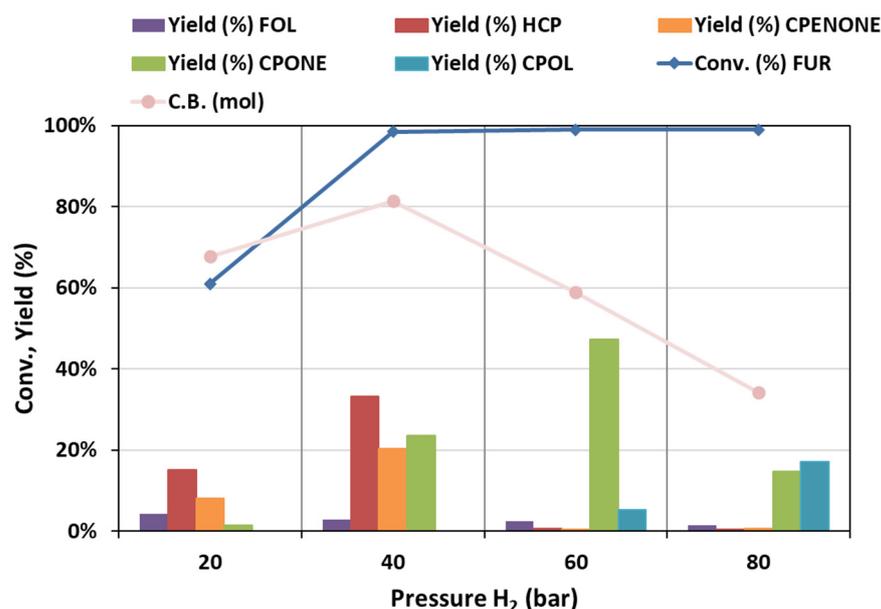


Figure 6. Study of the reaction pressure in 30 wt.% of t-BuOH in water. Reaction conditions: 1 wt.% catalyst, 5 wt.% FUR, 200 °C, 0.5 h, overall volumen (weigh) = 5 g.

In practice, this yield at 60 bar of H₂ is equivalent to a productivity of 411 g_{prod}·h⁻¹·g_{cat}⁻¹, which was significantly higher than those achieved with other catalysts, including other Cu catalysts, as summarized in Table 3. Entries 1–3 investigated the hydrogenation of FUR using Ni₅Cu₁₅/m-SiO₂, NiCu/SiO₂-AE-450, and CuNi/Al-MCM-41 catalysts. In the first two cases, the yield of CPONE was above 90%, while in the third case, it was 68%. However, the productivities per gram of catalyst did not exceed 100 g_{prod}·h⁻¹·g_{cat}⁻¹, except for Entry 2, which achieved 106 g_{prod}·h⁻¹·g_{cat}⁻¹ and 7 g_{prod}·s⁻¹·mol_{Cu}⁻¹. The study concluded that copper species on the catalyst surface adsorbed the C=O bond, inhibiting the hydrogenation of the C=C bond. The productivities of Entry 1 and 3 were 58 and 95 g_{prod}·h⁻¹·g_{cat}⁻¹ and 7 and 38 g_{prod}·s⁻¹·mol_{Cu}⁻¹, respectively. While these copper catalysts were effective in achieving high CPONE yields, the productivity per gram of catalyst was limited due to the need for extended reaction times or high catalyst-to-FUR ratios. When we compare the productivity mols of Cu basis, Entry 3 was the highest value obtained [4,24,25].

Table 3. Summary of the catalytic properties and productivities with Cu catalysts tested in the hydrogenation of FUR to CPONE.

Entry	Catalyst	FUR (wt.%)	cat./FUR (wt.%)	P (MPa)	T (K)	Time (h)	X _{FUR} (%)	Y _{CPONE} (%)	Prod. (g _{prod} ·h ⁻¹ ·g _{cat} ⁻¹)	Prod. (g _{prod} ·s ⁻¹ ·mol _{Cu} ⁻¹)	Ref.
1	Ni ₅ Cu ₁₅ /mSiO ₂	3	34	3	413	4	100	90	58	7	[24]
2	NiCu/SiO ₂ -AE-450	4	13	2	423	6	100	95	106	7	[4]
3	CuNi/Al-MCM-41	5	13	2	433	5	98	68	95	38	[25]
4	CuCo _{0.8} @C-500	1	35	0.5	423	9	100	90	25	2	[26]
5	Cu _{0.4} Mg _{5.6} Al ₁₂	4	67	0.2	453	5	100	98	26	24	[27]
6	CuZn/CNT	5	40	4	413	10	95	85	19	2	[28]
7	Cu-4-F	1	34	2	413	2	100	87	110	-	[29]
8	Cu/ZrO ₂ -500	3	10	1.5	423	4	100	91	192	13	[30]
9	Cu/Zn/Al ₂ O ₃	5	20	6	473	0.5	100	47	411	14	pw

pw: present work.

Entry 4 reported a bimetallic Cu–Co catalyst supported on a 3D carbon matrix derived from glucose. The catalyst exhibited a productivity of 25 g_{prod}·h⁻¹·g_{cat}⁻¹ and 2 g_{prod}·s⁻¹·mol_{Cu}⁻¹, requiring a loading of 35 wt.% catalyst relative to FUR, a reaction time of 9 h and low H₂ pressure [26]. In Entry 5, selective hydrogenation of FUR was carried out using Cu catalysts supported on basic hydrotalcite. The Cu_{0.4}Mg_{5.6}Al₁₂ catalyst achieved a yield of 98% but required a loading of 67 wt.% catalyst relative to FUR. However, the

productivity was not as high as in other cases, reaching $26 \text{ g}_{\text{prod}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. It was found that Cu^{2+} ions replaced Mg^{2+} ions in the hydrotalcite structure, and Cu^{2+} particles formed on the surface of the catalyst from CuO , subsequently reduced to Cu^0 and Cu^+ .

The productivity mols of Cu basis was $24 \text{ g}_{\text{prod}} \cdot \text{s}^{-1} \cdot \text{mol}_{\text{Cu}}^{-1}$, so the catalyst is very active when compared to the amount of copper. The high activity and selectivity of copper played a crucial role in converting FUR into CPONE or other products [27]. The high load of catalyst and the low pressure of H_2 used could confirm that the protons of water are involved in the reaction. Entries 6 and 7 investigated the hydrogenation of FUR with Cu and Zn catalysts, both achieving CPONE yields of over 80%. However, a high catalyst loading was required. Entry 6 showed a productivity of $19 \text{ g}_{\text{prod}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ after 10 h of reaction, and the productivity mols of Cu basis ($2 \text{ g}_{\text{prod}} \cdot \text{s}^{-1} \cdot \text{mol}_{\text{Cu}}^{-1}$) was one of the smallest, while Entry 7 demonstrated $110 \text{ g}_{\text{prod}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. Productivity in base to the mol cannot be obtained from this entry because the amount of Cu used is not shown. This productivity was one of the highest in this work because the pressure, temperature, and time were moderate (2 MPa, 423 K, and 2 h). The concentration of FUR was low (only 1 wt.%), but the loading of the catalyst relative to FUR was high (34%). Notably, in the latter case, the high catalytic activity was attributed to highly dispersed and surface-acidic Cu species, along with strong interface interactions between Cu^0 particles and the ZnAl-MMO component within surface-active nanosheets [28,29]. Entry 8 confirmed the synergistic effect of surface Cu^+ in CPONE formation, acting as a Lewis acid promoting the reorganization of the furanic ring. The Cu/ZrO₂-500 catalyst achieved a yield of 91%, productivity per gram of catalyst and mols of Cu basis of $192 \text{ g}_{\text{prod}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ and $13 \text{ g}_{\text{prod}} \cdot \text{s}^{-1} \cdot \text{mol}_{\text{Cu}}^{-1}$, respectively, and good stability over five consecutive cycles. Strong metal-support interactions (SMSI) facilitated the formation of surface Cu^+ , leading to favorable acidity and high catalytic efficiency. Cu^0 atoms on the surface facilitated H_2 dissociation, while Cu^+ atoms were responsible for C=O bond absorption and activation, promoting furanic ring reorganization [30]. In the present work, a productivity per gram of catalyst and basis in mol of Cu was $411 \text{ g}_{\text{prod}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ and $14 \text{ g}_{\text{prod}} \cdot \text{s}^{-1} \cdot \text{mol}_{\text{Cu}}^{-1}$, respectively, with a CPONE yield of 47% was achieved after 0.5 h, at 6 MPa and 473 K. This productivity was the highest reported for the hydrogenation of FUR to CPONE using copper as a catalyst. In all the works where copper has been used as a catalyst, it has been observed that while the catalyst is necessary for the reaction, it somehow interferes with the Piancatelli rearrangement, requiring specific reaction conditions such as low furfural loading, high catalyst loading, high temperature, etc.

3. Materials and Methods

3.1. Reagent and Materials

Furfural (98%), furfuryl alcohol (98%), cyclopentenone (98%), cyclopentanone (99%), cyclopentanol (98%), tetrahydrofurfuryl alcohol (98%), methyl furan (98%) and methyl tetrahydrofuran (98%), 2-propanol (99.5%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Furfural was purified using vacuum distillation and stored in the refrigerator before the experiments. 4-Hydroxy-2-cyclopentenone (98%) was purchased from Ambeed. Tert-butyl alcohol (99%) was supplied from Thermo Scientific (Waltham, MA, USA). A copper-based methanol reforming catalyst, HIFUEL R120, was purchased from Alfa Aesar.

In this work, we have focused on the effect of t-BuOH on the catalytic properties of a well-known and studied commercial catalyst. Further details about the textural, chemical, and surface properties can be found elsewhere [12,31].

3.2. Catalytic Experiments

Catalytic hydrogenation of furfural was performed in a 20 mL stainless steel reactor equipped with a magnetic stirrer. For a typical reaction, 0.05 g of catalyst, 0.25 g of furfural, and 4.7 g of water or 30 wt.% t-BuOH in water were added to the reactor vessel. The final volume was 5 g. After loading and closing the reactor, it was flushed five times with nitrogen, then flushed five times with hydrogen, and then pressurized with hydrogen to the

corresponding pressure. The reactor was heated to the desired temperature by inserting it in a bore practiced in an aluminum block heated in a heating plate. The stirring speed was fixed to ca. 1000 rpm to eliminate diffusion problems. At the end of the reaction, the reactor was cooled to room temperature by immersion in a water bath. The liquid was analyzed by HPLC. 2-propanol was incorporated as internal standard (0.3 g) into the reaction mixture and, after being filtered through a 0.22 μm syringe filter, was analyzed in an Agilent 1200 HPLC chromatograph equipped with a refraction index detector and a Bio-Rad Aminex C-18 column (300 mm \times 7.8 mm). A 10 wt.% methanol mobile phase was employed at 323 K and a 0.6 mL $\cdot\text{min}^{-1}$ flow rate. FUR conversion and product yields were calculated according to the following formulas:

$$\text{FUR conversion (mol\%)} = \frac{m_{\text{FUR}}^0 - m_{\text{FUR}}}{m_{\text{FUR}}^0} \times 100 \quad (1)$$

$$\text{Product yield (mol\%)} = \frac{m_{\text{prod}}}{m_{\text{FUR}}^0} \times 100 \quad (2)$$

where m_{FUR}^0 refers to the mol quantity of FUR initially loaded into the reactor, and m_{FUR} and m_{prod} refer to the mol number of FUR and products, respectively, in the reaction mixture. The HPLC chromatographic factor of the organic products was calculated by analyzing solutions with known concentrations of the different organic products (FOL, HCP, CPENONE, CPONE, CPOL, THFA, MTHA, MF).

The mass balance of carbon was estimated as the sum of the moles of products determined using standard compounds and unconverted FUR. The mass loss was ascribed to other not-identified compounds analyzed using HPLC and mostly to the water-soluble oligomers formed during the reaction. The intrinsic reaction rate was defined as a ratio between mmol of product obtained per gram of catalyst and per minute. In all cases, activity results at 60 min were used.

4. Conclusions

The catalytic transformation of FUR to CPONE has been investigated using two different liquid phases: water and 30 wt.% of tert-butanol in water. The hydrodeoxygenation of FUR is a promising route for the sustainable production of CPONE from renewable sources. Using water as a solvent, FUR polymerized, and only a fraction was converted to CPONE (42% yield). When 30 wt.% tert-butanol was added the major product was instead FOL (yield 47%), with a minor yield of CPONE (20%). This indicates that the pathway to obtain CPONE was inhibited when using the co-solvent compared to using water alone. It was found that this was due to the inhibition of the transformation of intermediate products such as FOL and HCP and the transformation of CPENONE. This inhibition was ascribed to the neutralization of protons, resulting from water dissociation, by basic surface sites of the catalyst, preventing their involvement in the overall reaction.

Lastly, using higher hydrogen pressures (60 bar) and temperatures (200 $^{\circ}\text{C}$) than those used for only water medium can overcome the inhibition of CPENONE and result in higher yields of CPONE than those accomplished in only water. In this study, productivity per gram of catalyst was 411 $\text{g}_{\text{prod}}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$, and mols of Cu basis of 14 $\text{g}_{\text{prod}}\cdot\text{s}^{-1}\cdot\text{mol}_{\text{Cu}}^{-1}$ have been achieved, significantly larger than those observed for other copper-based catalysts.

Future research is suggested to further improve the efficiency and economic feasibility of this process. To this end, different copper loadings and supports will be investigated, and subsequently deactivation in a continuous liquid phase fixed bed system will be investigated. In addition, further research is needed to investigate if t-BuOH results in better stability properties of the catalyst with respect to deactivation issues. The deactivation of the catalyst is actually ignored and overlooked in many of the investigations related to the synthesis of CPONE from furfural, and the prevention of the formation of heavy oligomers/polymers from FOL and other intermediates because of the t-BuOH presence may have a positive impact in the robustness of the catalyst.

Author Contributions: Conceptualization, A.O.-S., M.L.G. and D.M.A.; Formal analysis, M.L.G.; Funding acquisition, R.M., M.L.G. and D.M.A.; Investigation, A.O.-S. and F.V.; Methodology, A.O.-S., M.L.G. and D.M.A.; Project administration, D.M.A.; Supervision, R.M., M.L.G. and D.M.A.; Validation, F.V.; Writing—original draft, A.O.-S., M.L.G. and D.M.A.; Writing—review and editing, A.O.-S., R.M., F.V., M.L.G. and D.M.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Spanish Ministry of Science, Innovation, and Universities (projects RTI2018-094918-B-C41, -C42 and -C44). AOS also acknowledges financial support for a contract financed by the Biobased Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation program under grant agreement No. 101023202. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio-based Industries Consortium.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: A.O.-S., due to the CSIC-UAM framework agreement, thanks to Ph.D. Program in Applied Chemistry of Doctoral School of Autonomous University of Madrid.

Conflicts of Interest: The authors declare no conflict of interest.

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