

Communication

Aqueous Phase Hydrogenolysis of Bio-Derivable Furfuryl Alcohol to Pentanediols Using Copper Catalysts

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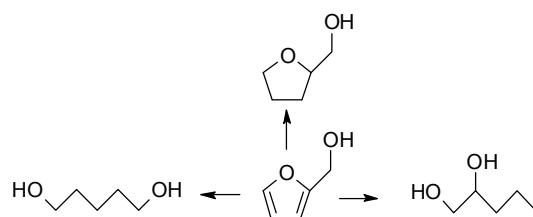
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Abstract: In the context of sustainable production processes based on bio-derivable feedstocks, the hydrogenolysis of furfuryl alcohol gives access to two important diols. This work evaluates the performance of commercial copper catalysts in the aqueous phase hydrogenolysis reaching a selectivity towards 1,2-pentanediol of up to 34%. In contrast to noble metal catalysts such as supported ruthenium, the selectivity of the hydrogenation product, tetrahydrofurfuryl alcohol, is significantly lower, so the desired diols are now the main products of this reaction. Catalysis experiments show that the performance is correlated to the catalyst composition rather than the free copper surface, indicating a strong influence of the supporting material. Although the formation of oligomeric and polymeric side products is still perturbing, copper catalysts represent promising candidates for this reaction due to their low cost and wide availability.

Keywords: furfuryl alcohol hydrogenolysis; 1,2-pentanediol; 1,5-pentanediol

1. Introduction

Renewable feedstocks are receiving increasing interest in the modern chemical industry. The use of platform chemicals in analogy to the current petrochemical-based value chains is especially desirable for a flexible production [1]. However, novel platform chemicals such as furfural or furfuryl alcohol increase the need for new processes and catalytic systems [2,3]. The hydrogenation and hydrogenolysis of furfuryl alcohol are giving access to a variety of different chemicals, such as tetrahydro furfuryl alcohol or pentanediols [4,5]. The production of pentanediols via bio-based routes is of interest because of their various applications; for example, they can be used as monomers of resin [6], intermediates for pesticides [6] or as ingredients of cosmetic products [7]. A sustainable route for the production of 1,2-pentanediol (1,2-PeD) is of special interest, because this diol is currently produced via a cost-intensive multistep route by selective oxidation of petrochemically derived pentene-to-pentene oxide and a subsequent hydrolysis [8,9]. Scheme 1 gives a brief overview on the desired products available by hydrogenation and hydrogenolysis of furfuryl alcohol.



Scheme 1. Schematic overview on the products available via hydrogenolysis or hydrogenation of furfuryl alcohol.

Although there has been interest in the conversion of furfuryl alcohol for more than a few decades, most of the catalysts have disadvantages regarding their environmental impact (e.g., chromium containing catalysts); necessity for special solvents or additives (e.g., Adam's catalyst [10]); or at least the price of the catalyst, as in the case of platinum-based catalysts. Early research mainly focused on copper chromite-based catalysts [11–13]. Although these catalysts exhibit good selectivity towards the desired products, the environmental impact of chromium-based catalysts is not desirable. The use of noble metal-containing catalysts such as ruthenium [14–17] or platinum [10,18–21] is a promising alternative, but noble metals have a higher price and limited availability. The use of copper-containing catalysts seems to be a promising alternative due to copper's low price and the wide industrial availability. Liu et al. have shown that copper catalysts exhibit good selectivity values towards the desired products, reaching up to 51% of 1,2-pentanediol and 31% of 1,5-pentanediol using self-prepared catalysts and ethanol as a solvent [22,23]. In a former publication, our working group was able to show the performance of commercial copper catalysts for the hydrogenolysis of glycerol to 1,2-propanediol [24]. This work evaluates the performance of these commercial copper catalysts in the hydrogenolysis of furfuryl alcohol. Processes for the conversion of biomass and bio-derived platform chemicals often use water as a solvent, so instead of using ethanol as a solvent as did Liu et al., this work uses water.

2. Results and Discussion

In order to evaluate the performance of the copper catalysts for the conversion of furfuryl alcohol, various different catalyst compositions have been tested. Table 1 gives an overview of the results.

Table 1. Overview of the selectivity and conversion of different commercial copper catalysts after 6 h reaction time.

Cat. #	Catalyst Composition (%)	X ^a (%)	1,2-PeD (%)	1,5-PeD (%)	1,4-PeD (%)	THFA (%)	Others (%)	Sum. (%)
1	60 CuO 40 ZnO	12	16	5	2	22	13	58
2	47 CuO 46 Cr ₂ O ₃ 7 BaO	8	5	1	1	25	12	44
3	40 CuO 40 ZnO 20 Al ₂ O ₃	13	16	4	2	19	10	51
4	70 CuO 30 SiO ₂	14	2	0	1	8	5	16
5	89 CuO 9 SiO ₂ 2 CaO	6	6	2	1	24	9	42
6	36 CuO 48 ZnO 16 Al ₂ O ₃	16	27	8	3	12	10	60
7	53 CuO 47 MgO/SiO ₂	13	9	4	2	29	9	53
8	50 CuO 20 ZrO ₂ 30 ZnO	13	23	8	2	25	11	69
9	60 CuO 40 ZrO ₂	22	26	8	2	18	8	62
9 ^b	60 CuO 40 ZrO ₂	100	0	0	0	0	44	44
- ^c	-	5	5	1	1	25	7	39

Reaction conditions: 150 mL of 5 wt. % FA in H₂O, 300 mg Na₂CO₃, p_{H₂} = 5 MPa, T = 443 K, 6 h. PeD: Pentanediol, THFA: Tetrahydro furfuryl alcohol, ^a X: furfuryl alcohol conversion. ^b reaction without Na₂CO₃ after 4 h. ^c reaction without catalyst.

The activity and selectivity of the catalysts tested in this work clearly vary when changing the composition. In particular, catalysts containing zinc oxide or zirconia exhibit good selectivity and activity towards 1,2-pentanediol. In order to discriminate this from the different copper loadings of the

catalysts, Table 2 shows the copper-specific reaction rates regarding these two products. These reaction rates underpin the high activity of the zinc oxide or zirconia-containing catalysts, confirming a strong influence of the catalyst support on the performance.

Table 2. Specific reaction rates referred to the copper mass.

Cat. # ^a	Copper Specific Reaction Rate (10^{-2} mmol·min ⁻¹ ·g _{Cu} ⁻¹)		Copper Surface (m ² ·g _{cat.} ⁻¹) from [24]
	1,2-PeD	THFA	
1	0.64	0.82	16.2
2	0.10	0.63	12.0
3	1.01	0.94	4.7
4	0.03	0.22	8.5
5	0.06	0.28	5.1
6	3.09	1.06	11.9
7	0.51	1.47	-
8	1.26	1.19	-
9	2.21	1.39	-

Reaction conditions: 150 mL of 5 wt. % Furfuryl alcohol in H₂O, 300 mg Na₂CO₃, p_{H2} = 5 MPa, T = 443 K, 6 h,

^a catalyst code in Table 1.

Unlike the hydrogenolysis of glycerol where a clear correlation between copper surface and catalyst activity was observed [24], such a correlation is not observed in the case of the hydrogenolysis of furfuryl alcohol. The influence of the catalysts' composition on the catalyst performance is presumably caused by an interaction between copper and the supporting material at their interface. Liu et al. [22,23] proposed an interaction of the hydroxy group of furfuryl alcohol with the support at the interface, leading to a favored cleavage of the C–O bond of the furfuryl alcohol ring. In this context, the amphoteric character of zirconia and zinc oxide could be a reason for the good performance of these catalysts, but further investigations are needed to prove this in detail.

Interestingly, the amount of 1,5-pentanediol, accessible via breaking the opposite C–O bond in the furan ring, is comparatively low with regard to 1,2-pentanediol. A more pronounced but similar relation in the selectivity distribution between the two diols is observed when using ruthenium catalysts. The preferred cleavage of the C–O bond forming the 1,2-diol again indicates differences in the stability of adsorbates or reaction intermediates which could also be influenced by the supporting material. However, in contrast to ruthenium-based catalysts, the selectivity towards tetrahydrofurfuryl alcohol is significantly less pronounced in the case of the copper catalysts, which makes them interesting alternatives to produce pentanediols. However, the low carbon balance found in the GC analysis is striking, although sodium carbonate has been added to the reaction to reduce the amount of polymer formed by acid-catalyzed side reactions in the aqueous solution. Experiments excluding the addition of sodium carbonate show that polymers are rapidly formed in aqueous conditions while no hydrogenation or hydrogenolysis products are formed (see Table 1). A further increase of the sodium carbonate amount did not lead to a change in conversion or selectivity values. To exclude volatile or gaseous components, the reactor gas phase was also analyzed using a gas phase infrared spectrometer after 6 h reaction time, but only traces of carbon containing components have been found. This leads to the presumption that the missing carbon is bound in oligomeric and polymeric structures of furfuryl alcohol which cannot be detected by GC due to their high boiling point.

Due to the sensitivity of the copper surface on oxidation caused by short air contact, the influence of a hydrogen atmosphere during the heat-up of the reactor was investigated in catalytic experiments by heating up under argon atmosphere. Furthermore, to discriminate from the reactions during heat-up, additional experiments were done by quickly adding the substrate after reaching the desired reaction conditions. Results in Table 3 show a significantly higher selectivity towards 1,2-pentanediol in the case where the reactor was heated up under hydrogen atmosphere, even if the substrate is added after the reactor has reached the desired temperature. These negative effects regarding the formation of 1,2-pentanediol are possibly caused by the formation of oligomeric or polymeric compounds during

the heat-up, which partially block the active sites, hence decreasing the catalytic activity and favoring the polymerization reactions.

Table 3. Selectivity and conversion under variation of the heat-up procedure.

Heat-up Gas	X ^b (%)	1,2-PeD (%)	THFA (%)	1,5-PeD (%)	1,4-PeD (%)	Others (%)	Sum. (%)
hydrogen	22	26	18	8	2	8	62
argon	21	18	14	5	3	10	50
argon ^a	33	18	24	5	2	6	55
hydrogen ^a	32	28	12	9	2	6	57

Reaction conditions: 1 g catalyst 9, 150 mL of 5 wt. % FA in H₂O, 300 mg Na₂CO₃, p_{H2} = 5 MPa, T = 443 K, 6 h.

^a Subsequent substrate addition via storage tank after heat-up. ^b X: furfuryl alcohol conversion.

To estimate the influence of reaction conditions on the catalytic performance, the catalyst containing copper and zirconia (cat. 9) was selected for further experiments because of its good selectivity towards the main products while exhibiting a high activity in the screening experiments. When increasing the reaction temperature, the furfuryl alcohol conversion rises up to about 54% after 6 h, but the formation of byproducts (mainly cyclopentanol and its derivatives) significantly increases at the expense of the selectivity of the main products. Hence, raising the reaction temperature must be done carefully to avoid incurring side reactions with high reaction barriers such as isomerization and polymerization reactions. On the other hand, increasing the hydrogen pressure from 5 MPa to 9 MPa has only a small effect on the conversion but a slightly positive effect on selectivity of the main products (Table 4), by enhancing the hydrogen-dependent reactions.

Table 4. Selectivity and conversion under variation of the reaction parameters.

T/K	p _{H2} (MPa)	X ^a (%)	1,2-PeD (%)	1,5-PeD (%)	1,4-PeD (%)	THFA (%)	Others (%)	Sum. (%)
443	5	22	26	8	2	18	8	62
443	7	24	30	9	3	18	7	67
443	9	28	34	10	3	18	10	75
473	5	54	10	2	3	7	35	57

Reaction conditions: 1 g catalyst 9, 150 mL of 5 wt. % FA in H₂O, 300 mg Na₂CO₃, 6 h. ^a X: furfuryl alcohol conversion.

Due to the low activity of the catalyst, the conversion achieved in the experiments after 6 h is relatively low. To gain a better insight into the reaction network, the reaction was studied during a period of about 28 h. Figure 1 shows the temporal evolution of the three main product concentrations.

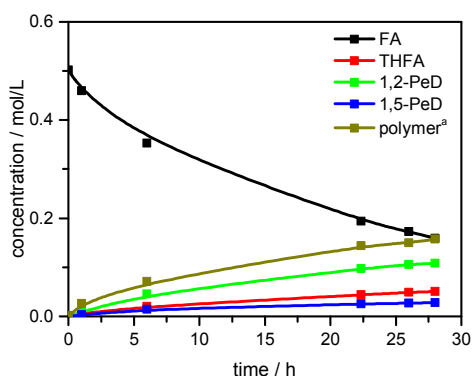


Figure 1. Temporal evolution of the concentrations during 28 h reaction time. (Reaction conditions: 1 g catalyst 9, 150 mL of 5 wt. % FA in H₂O; 300 mg Na₂CO₃; p_{H2} = 5 MPa, T = 443 K) ^a amount of polymer is calculated from the mass balance of the gas chromatographic analyses.

The curves in Figure 1 indicate a parallel reaction mechanism with regard to the three main products. Additionally, experiments using the main products as a substrate did not show any conversion, so there is no evidence of a consecutive reaction in this reaction network. The selectivity of the main products stays almost constant during the reaction.

3. Materials and Methods

Catalysis experiments are carried out using a 300 mL stainless steel batch reactor (Parr Instruments, Moline, IL, USA). Catalysts are supplied by KataLeuna GmbH Catalysts/CRI. Details on the catalysts and characterization are published elsewhere [24]. The copper surface of the catalysts differs in the range of 4.7 m²/g to 16.2 m²/g, but no clear correlation between the copper surface area and the copper content of the catalysts is observed. Prior to each experiment, the catalyst was grinded and sieved so that the catalyst particles were smaller than 63 µm. The catalyst powder was then reduced in flowing hydrogen at 533 K for 2 h. After cooling down to room temperature, the catalyst was suspended in water and transferred to the reactor in order to prevent oxidation of the copper surface. To minimize rapid polymerization of furfuryl alcohol, 300 mg sodium carbonate was added to the solution. The reactor was pressurized with hydrogen at 0.5 MPa before the catalyst slurry was heated to the desired temperature. After reaching the temperature, the pressure was increased to the desired value and held constant during the experiment. During the reaction, liquid phase samples were taken and analyzed by gas chromatography (Shimadzu GC-2010 Plus, Shimadzu Corporation, Kyoto, Japan, Optima WaxPlus column, Macherey Nagel, Düren, Germany). The reaction products were identified by GC-MS (Shimadzu GC-MS 2010 Plus, Shimadzu Corporation, Kyoto, Japan, Optima WaxPlus column, Macherey Nagel, Düren, Germany).

4. Conclusions

The present work shows that commercial copper catalysts are promising alternatives to noble metal-based catalysts. Although copper catalysts show a rather low activity in comparison with noble metal catalysts such as ruthenium, they show a high selectivity towards 1,2-pentanediol of up to about 34% while only a relatively small amount of tetrahydrofurfuryl alcohol is formed. The hydrogenolysis rate seems to strongly depend on the catalyst composition, while no clear correlation between the copper surface and activity was observed. In particular, catalysts containing zirconia or zinc oxide show a good performance regarding the production of 1,2-pentanediol. Future studies on the mechanism, especially at the interface of copper and supporting material, will be of particular interest for understanding the influence of the support on the catalytic performance and thus the targeted modification. However, the high diols and rather small tetrahydrofurfuryl alcohol selectivity make copper catalysts promising candidates, even under aqueous conditions.

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Author Contributions: D.G. designed and performed experiments, analyzed data and wrote the paper. M.L. and P.C. designed the experiments and gave technical support and conceptual advice.

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