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Influence of the Cu particle size and oxidation state on the activity and selectivity of Cu_xO/ZnO catalysts in HMF hydrodeoxygenation reaction

AUTHORS

Magdalena BRZEZINSKA / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO 116, LODZ

Jacek GRAMS / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO 116, LODZ

Nicolas KELLER / CNRS/UNIVERSITÉ DE STRASBOURG, ICPEES, 25 RUE BECQUEREL, STRASBOURG

Agnieszka RUPPERT / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO 116, LODZ

PURPOSE OF THE ABSTRACT

5-hydroxymethylfurfural (HMF) is one of the most important products of lignocellulose hydrolysis. It can be further converted into 2,5-dimethylfuran (DMF) which is considered as a biofuel additive or into 2,5-dihydroxymethylfuran (DHMF) which can be used in 'green' polymers production [1] (Fig.1).

Due to high functionalization of HMF, designing a catalyst for HMF hydrodeoxygenation process remains a challenge. Literature reports that ZnO supported Cu catalyst can be a promising system due to moderate zinc oxide acidity which can positively affect DMF formation. What is more, Cu shows high affinity to C=O bond, which promotes its hydrogenation, remaining C=C bond intact [2]. Thus, the aim of this work was to synthesize Cu/ZnO catalysts and to study the influence of copper particle size and its oxidation state on both activity and selectivity in HMF hydrogenolysis.

Investigated catalysts containing 10wt.% of copper, were synthesized using two methods. Beside a standard impregnation method (with Cu(NO₃)₂ used as a precursor), a solar light photon-assisted synthesis method was additionally developed for preparing Cu/ZnO catalysts, taking advantage from the redox photo-activity of the ZnO semi-conductor support to proceed Cu photo-assisted deposition process at room temperature. This strategy allows to skip thermal treatment and reduction step using hydrogen or any other chemical reductant, and further to tune the copper oxidation state. In this method two different Cu precursors were used, (ie. Cu(NO₃)₂ and Cu(acac)₂) with two different solvents (H₂O and THF-H₂O (2:9 v/v)). Progress of the process was followed by in situ UV-Vis measurements. The physico-chemical properties of the Cu/ZnO catalysts were investigated using different techniques, such as X-ray diffraction (XRD), electron microscopy (SEM, TEM). Further, the activity of the Cu/ZnO catalysts was evaluated in the HMF hydrodeoxygenation.

In a first approach, the performance of the catalysts synthesized via the impregnation method was investigated (Tab.1).

As it is shown in table 1, DHMF was observed as the main product using catalysts prepared via the impregnation method. What is more, it can be seen that the lower the reduction temperature, the higher the activity of the catalyst, and the catalyst after calcination - so without any reductive treatment - showed the highest activity with almost 100% HMF conversion towards DHMF. XRD measurements performed after test confirmed that the most active sample contained Cu on the highest oxidation state (Fig.2). Interestingly, during recycling tests, the most active sample remained at a high activity (Tab.2), although a change in the product distribution was noted.

The observed change in the product distribution during catalyst recycling tests may be connected with many factors, such as a material morphology change or the solvothermal reaction conditions which can be beneficial for the tested system.

Similar observations were noted for the catalysts prepared by the photon-assisted synthesis method (Tab.3). Catalyst with Cu on higher oxidation state, confirmed by XRD measurements (Fig.3), showed higher selectivity to DMF. This is tantamount to higher activity of CuO/ZnO, since larger amount of hydrogenolysis final product was obtained.

What is more, the choice of the preparation method directly impacted on the reaction selectivity while maintaining a complete HMF conversion. Indeed, the catalyst prepared via the photon-assisted synthesis method showed a strongly higher selectivity to the final HMF hydrogenolysis product - DMF, than that obtained via the impregnation method. This phenomena may be connected to the existence of different Cu_xO-ZnO interactions, particle size or morphology, with a more pronounced impact in the CuO-based sample.

Acknowledgements:

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FIGURES

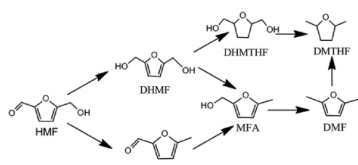


Fig. 1 HMF hydrodeoxygenation pathway

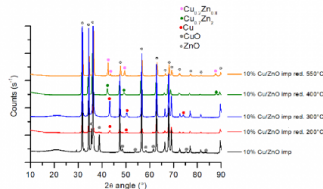


Fig. 2 XRD measurements for catalysts prepared via the impregnation method

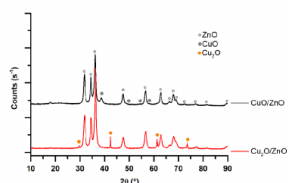


Fig. 3 XRD measurements for catalysts prepared via the solar light photon-assisted synthesis method

catalyst	HMF conversion [%]	Y_{DMF} [%]	Y_{5-MF} [%]	Y_{5-MFA} [%]	Y_{DMTHF} [%]
Blank test	3	0.1	1.8	1.2	0
10%Cu/ZnO imp. red.550°C	4	0.2	1.2	0.2	2.3
10%Cu/ZnO imp. red.400°C	12	0.2	1.8	0.2	6.2
10%Cu/ZnO imp. red.300°C	16	0.2	1.5	0.2	7.0
10%Cu/ZnO imp. red.200°C	41	0.3	1.9	0.9	36.0
10%Cu/ZnO imp. not reduced	97	0.4	1.4	2.5	92.7

Tab. 1 Activity of the catalysts prepared by the impregnation method in HMF hydrogenolysis, with influence of the reduction temperature.

number of cycle	catalyst mass	pretreatment	HMF conversion [%]	Y_{DMTHF} [%]	Y_{DMF} [%]	Y_{5-MF} [%]	Y_{5-MFA} [%]	Y_{DMTHF} [%]	Y_{DMF} [%]
1 st	0.300g	calcination in 300° C after each cycle	98	0	0.3	1.8	2.3	0.3	91.0
2 nd	0.300g		95	0.8	34.4	6.8	14.4	7.8	30.8

Tab. 2 Recycling tests for not-reduced 10%Cu/ZnO prepared by impregnation.

catalyst	HMF conversion [%]	Y_{DMTHF} [%]	Y_{DMF} [%]	Y_{5-MF} [%]	Y_{5-MFA} [%]	Y_{DMTHF} [%]	Y_{DMF} [%]
CuO/ZnO	100	11.0	85.0	0.6	2.9	0.4	0.0
Cu _x O/ZnO	96	2.5	50.0	1.7	7.1	0.2	23.0

Tab. 3 Activity of the Cu_xO-ZnO catalysts prepared by the photon-assisted synthesis method in HMF hydrogenolysis.

FIGURE 1

Figures

HMF hydrodeoxygenation scheme,
XRD measurements for the catalysts

FIGURE 2

Tables

Activity of the catalysts in HMF hydrodeoxygenation

KEYWORDS

copper | zinc oxide | hydroxymethylfurfural | hydrodeoxygenation

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