chemistry proceedings

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Proceedings

The Effect of Cu Content on the Hydrodeoxygenation Performance of $Cu_{(x)}MgFeO$ Ex-LDH Mixed Oxide Catalysts †

Adriana Urdă [1,*], Tudor Toderaşc [1], Irina Atkinson [2], Daniela Culiţă [2], Florica Papa [2], Gabriel Crăciun [3] and Ioan-Cezar Marcu [1]

[1] Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12, Blvd. Regina Elisabeta, 030018 Bucharest, Romania; tudortoderasc@yahoo.com; ioancezar.marcu@chimie.unibuc.ro

[2] "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, 060021, Bucharest, Romania; irinaatkinson@yahoo.com; danaculita@yahoo.co.uk; floricapapa@gmail.com

[3] National Institute for Research and Development in Microtechnology – IMT Bucharest, 126A Erou Iancu Nicolae Street, 077190, Voluntari, Romania; craciunster@gmail.com

* Correspondence: adriana.urda@chimie.unibuc.ro;

† Presented at the 2nd International Electronic Conference on Catalysis Sciences—A Celebration of *Catalysts* 10th Anniversary

Abstract: $Cu_{(x)}MgFeO$ mixed oxides (with Mg/Fe = 3 and 2.5 ≤ x ≤ 20 at. % Cu with respect to cations) were obtained through coprecipitation and thermal decomposition of layered double hydroxides (LDH) precursors, characterized and tested in the hydrodeoxygenation (HDO) reaction of benzyl alcohol. The solids were characterized by XRD, N_2 adsorption-desorption, H_2-TPR, CO_2-TPD and SEM-EDX techniques. The influence of Cu loading, reaction temperature (150 – 230 °C), and reaction time (15 min – 5 h) were investigated. With 94 % alcohol conversion and 94 % selectivity for toluene, $Cu_{(10)}MgFeO$ was the best catalyst in this series. The catalytic performances of the $Cu_{(x)}MgFeO$ catalysts were correlated with their physico-chemical characteristics.

Keywords: hydrodeoxygenation, Cu-Mg-Fe-O mixed oxides, benzyl alcohol

Citation: Urdă, A.; Toderaşc, T.; Atkinson, I.; Culiţă D., Papa F.; Crăciun G.; Marcu I.-C.. The effect of Cu content on the hydrodeoxygenation performance of $Cu_{(x)}MgFeO$ ex-LDH mixed oxide catalysts . *Chem. Proc.* **2021**, *3*, x. https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

Nowadays, hydrodeoxygenation (HDO) is employed for converting oxygenated compounds into hydrocarbons through treatment at moderate temperatures and pressures [1,2]. HDO of benzyl alcohol has been less investigated until now compared to other substrates, and mostly on noble metal catalysts [3-5]. Copper-containing mixed metal oxides seem to be interesting catalysts for this kind of reactions due to their significant hydrogenolysis activity and limited tendency for complete hydrogenation of aromatic ring [1,6]. These materials can provide a cheaper, efficient alternative to noble metal catalysts or to typical sulphided hydrotreatment catalysts commonly used for converting biomass into biodiesel [7]. In this work, several $Cu_{(x)}MgFeO$ mixed oxides, with x between 2.5 and 20 at. %, were prepared, characterized and tested in the HDO reaction of benzyl alcohol.

2. Methods

Catalysts preparation: The $Cu_{(x)}MgFe$-LDH precursors (x = 2.5; 5; 7.5; 10; 15; 20 at. % Cu with respect to cations, and Mg/Fe = 3) were prepared from the corresponding nitrates by co-precipitation with a 2M NaOH solution, at constant pH = 10. After maturation at 80 °C overnight, they were washed until pH = 7 and separated by centrifugation, followed by drying at 80 °C overnight. The corresponding mixed oxides, denoted $Cu_{(x)}MgFeO$, were obtained by calcination at 500 °C for 5 h.

Catalysts characterization: The structure and phase composition of the catalysts were examined by XRD, performed on a Rigaku Ultima IV diffractometer using a CuKα (λ = 1.5406 Å) monochromatic radiation source. The textural properties were determined from the adsorption-desorption isotherms obtained with a Micromeritics ASAP 2020 apparatus. The reducibility of the calcined samples was investigated by H_2-TPR on a Quantachrome ChemBET-3000 analyzer, using 5 % H_2 in Ar. The basic properties were determined by CO_2-TPD on a Quantachrome ChemBET-3000 analyzer. EDX analysis has been performed on a FEI Nova NanoSEM 630 scanning electron microscope.

Catalytic tests: The catalytic reactions were performed in a 16 mL magnetically stirred stainless steel autoclave reactor (HEL Limited), at 230 °C, using 1 mL of benzyl alcohol and an initial H_2 pressure of 5 atm. The product analysis was done by gas chromatography on a Trace GC instrument (ThermoFinnigan) equipped with a FID detector and a DB-5 column.

3. Results and Discussion

The LDH structure with hexagonal lattice and R3m rhombohedral symmetry was identified in all the precursors. In the sample with 20 % Cu, CuO side phase was also observed, typical for LDH systems with high Cu loadings [1,8]. The average crystallite size, estimated from the Debye-Scherrer equation, had only small variations between 6.1 and 7.1 nm. The mixed oxides showed, besides the periclase phase, the presence of $MgFe_2O_4$, with diffraction lines partially superposed on those of the periclase phase (Figure 1). In the case of the $Cu_{(20)}$MgFeO sample, the segregated phase of CuO was again observed. The average crystallite size had values around 6.3 nm for 5-15 % Cu, decreasing to 5.7 nm for the sample with 20 % Cu.

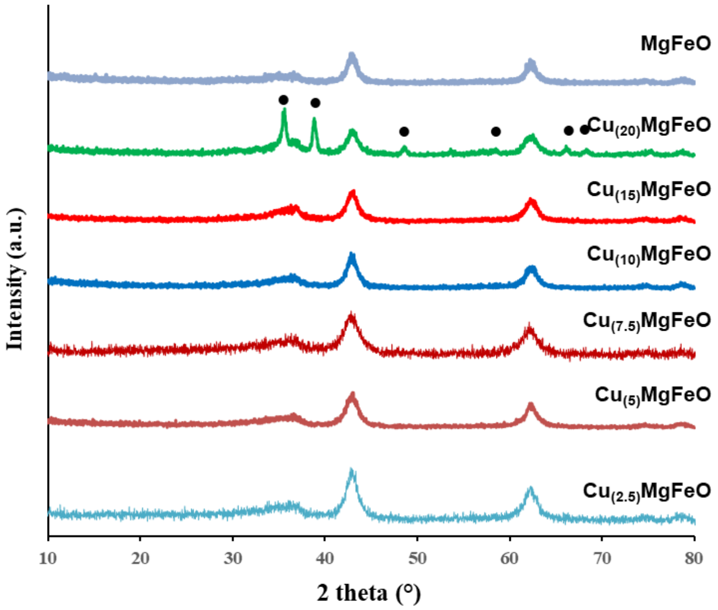

Figure 1. XRD patterns of the $Cu_{(x)}$MgFeO calcined catalysts. ● – CuO phase.

All mixed oxide catalysts showed high specific surface areas and mesoporous structures. The BET surface areas increased from 107 $m^2\ g^{-1}$ for MgFeO to 146 $m^2\ g^{-1}$ for $Cu_{(5)}$MgFeO, then decreased to 97 $m^2\ g^{-1}$ for $Cu_{(20)}$MgFeO, probably due to the formation of the CuO phase.

EDX measurements showed for all samples Mg/Fe ratios between 3 for $Cu_{(5)}$MgFeO and 4.5 for $Cu_{(10)}$MgFeO, and also higher Cu content than the nominal value (e.g. 11.9 for $Cu_{(10)}$MgFeO).

The reduction of both Fe and Cu species was observed in H_2-TPR measurements (Figure 2), with hydrogen consumption increasing with Cu loading. The low temperature reduction peak was attributed to the reduction of Cu^{2+} dispersed in the periclase matrix, while at higher temperatures the reduction of Fe^{3+} takes place. The peak above 600 °C was attributed to the reduction of spinel mixed oxides. The MgFeO sample (not shown) showed only one reduction peak at 400-600 °C, corresponding to the reduction of Fe^{3+} species.

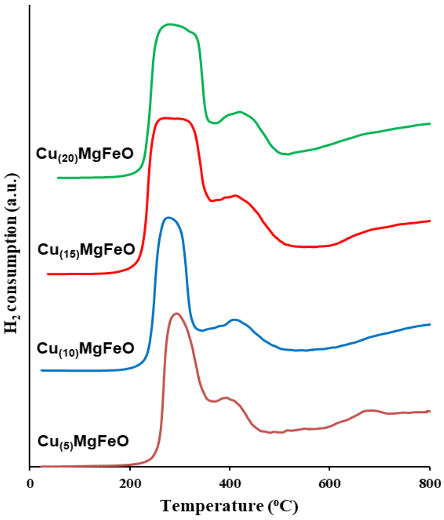

Figure 2. H_2-TPR profiles for the Cu_xMgFeO catalysts.

CO_2-TPD confirmed the presence of low and medium-strength basic sites. With increasing Cu loading the number of these sites – both low and medium-strength – increases up to 15 % Cu, then it decreases, probably due to the formation of the separate CuO phase.

The influence of the Cu loading on the catalytic activity of $Cu_{(x)}MgFeO$ catalysts in the HDO of benzyl alcohol is summarized in Table 1.

Table 1. Influence of the Cu loading on the catalytic activity of $Cu_{(x)}MgFeO$ catalysts in HDO of benzyl alcohol (50 mg catalyst, 230 °C, 5 atm H_2, 3 h reaction time)

Catalyst	Alcohol conversion (%)	Selectivity (%)			
		Toluene	Benzaldehyde	Benzyl benzoate	Benzene
$Cu_{(2.5)}MgFeO$	68.5	77.2	19.0	3.6	0.2
$Cu_{(5)}MgFeO$	79.4	81.3	15.6	3.0	0.1
$Cu_{(7.5)}MgFeO$	84.0	83.6	13.2	3.0	0.1
$Cu_{(10)}MgFeO$	**93.8**	**93.8**	**6.2**	**0.0**	**0.0**
$Cu_{(15)}MgFeO$	81.8	74.1	19.1	6.6	0.1
$Cu_{(20)}MgFeO$	86.4	70.1	10.4	19.4	0.1
MgFeO	7.7	57.6	42.4	0.0	0.0
CuO	92.3	72.3	19.9	7.8	0.0
Cu^{2+}	53.8	65.7	27.3	6.1	0.8

MgFeO sample shows very low conversion, that strongly increases upon Cu loading, reaching almost 94 % for the $Cu_{(10)}MgFeO$ catalyst, but at higher Cu loading it decreases. High conversion was obtained on a CuO sample prepared by the same method, and even $Cu(NO_3)_2$ crystals disolved in benzyl alcohol led to 54 % conversion. Toluene was always the main reaction product, with 94 % selectivity for $Cu_{(10)}$MgFeO, while benzaldehyde was identified as reaction intermediate [1], with benzyl benzoate and benzene as side products. Cu^{2+} was investigated as a potential homogeneous catalyst for the reaction, and the results prompted an ongoing reasearch on the stability of the $Cu_{(10)}$MgFeO catalyst. These results are correlated with the reducibility and basicity of the catalysts: alcohol conversion and toluene selectivity increase with the Cu loading (higher basicity and amount of reduced Cu sites). At too high copper amounts the specific surface area decreases due to the formation of CuO, leading to a lower selectivity to toluene.

Since $Cu_{(10)}$MgFeO showed the best results, we investigated the influence of the reaction temperature and reaction time on this sample. The reaction temperature was varied between 150 and 230 °C, with conversion values increasing with temperature from 4 to 94 %. The reaction time was investigated from 15 min to 5 h, and conversion increased from 40 to 97 %. Toluene was in all cases the main reaction product.

The spent catalyst from HDO of benzyl alcohol (at 230 °C) was investigated by XRD after drying in He at 200 °C, and then again after being recalcined at 500 °C, for possible reuse in HDO. The spent sample consisted of Cu_2O phase and a partially reconstructed LDH phase, probably containing organic anions from the reaction environment, such as benzoates and benzylates. After recalcination, besides the periclase-like phase, the sample contained Cu_2O, CuO and $MgFe_2O_4$ phases, suggesting that the stability of the catalyst could be affected. Currently, the stability of the $Cu_{(10)}$MgFeO catalyst is under investigation.

Conclusions

$Cu_{(x)}$MgFeO mixed oxides (with Mg/Fe = 3 and $2.5 \le x \le 20$ at. % Cu with respect to cations) were prepared, characterized and tested in the HDO reaction of benzyl alcohol. The Cu loading had a strong influence on the catalytic properties, $Cu_{(10)}$MgFeO showing the best results (94 % alcohol conversion and 94 % selectivity for toluene). The catalytic performances of the catalysts were correlated with the reducibility and basicity of the catalysts. After recalcining the $Cu_{(10)}$MgFeO spent catalyst its structure showed some modifications, therefore the stability of the catalyst is currently investigated.

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