Use of ternary Cu/Zn/La mixed oxides for the hydrogenation/hydrogenolysis of hexyl hexanoate to 1-hexanol aimed at overcoming the issues of chromium-based systems

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Significance and Relevance

Cu-based catalysts are really attractive for the hydrogenation/hydrogenolysis of the esters to the corresponding alcohols, given their low cost and robustness, which make them already attractive for the methanol synthesis. In this work, hexyl hexanoate (HexHex) hydrogenolysis to 1-hexanol (HexOH) with different Cu-based catalysts was studied, e.g. binary Cu/Zn and ternary Cu/Zn/La catalyst mixed-oxides. For these evaluations, Cu/Zn/Cr mixed oxides were considered as benchmarks for the catalytic evaluations of our Cr-free catalysts. It was found that lanthanum effectively acted as a promoter, helping to improve the activity of the Cu active metal, and reducing the sinterization issue (35 mol% of conversion for the Cu/Zn versus 90 mol% for the Cu/Zn/La, working under the best reaction conditions). The catalytic performances of the Cu/Zn/La catalyst are comparable with those of the ternary Cu/Zn/Cr system (91 mol%), working under the same best reaction conditions, thus confirming the possibility of using our Cr-free catalytic systems for improving the sustainability of the HexOH synthesis.

Preferred and 2nd choice for the topic: (preferred topic) Green chemistry and biomass transformation, renewable resources conversion; (2nd choice) Fundamental advances in understanding catalysis. *Preferred presentation*: Oral only.

Introduction and Motivations

Hydrogenation/hydrogenolysis of esters to the corresponding alcohols is industrially attractive, given the relevance of these latter for the production of jet-fuels, diesel additives, lubricants and plasticisers. [1] The first catalyst employed for this reaction was copper chromite ($CuCr_2O_4$, Adkins catalyst), which is prone to give Cr^{6+}, nowadays undoubtedly recognized for its toxicity to the man and environment. To overcome this relevant issue, several Cr-free catalysts have been developed over the past years, mainly based on noble metals, such as Pt, Re, Pd and Ru, showing high catalytic activity towards the hydrogenation of medium-chain esters (C_4-C_8) to the corresponding alcohols. [2] Anyway, the high cost of these noble-based catalysts makes difficult their further use on the industrial scale, a bottleneck that shifts the attention towards the development of new, cheaper non-noble catalysts, in particular those based on Ni, Co and Cu metals. Regarding the Cu-based ones, binary Cu-Zn-mixed oxides are effective towards the hydrogenation of esters, Cu representing the active species, whilst ZnO stabilises Cu, reducing its sintering, at the same time affecting the acid-base properties of the bulk catalyst.[2]In this work, a ternary Cu/Zn/La catalyst, which was proposed by us for the methanol synthesis reaction from alkyl formates[3], has been now proposed for the hydrogenation/hydrogenolysis of HexHex to HexOH. Lanthanum acts as a promoter, further improving the resistance to sintering, at the same time affecting the acid-base properties of the bulk catalyst, both factors that synergistically play a key role in the involved reaction mechanism. [4]

Materials and Methods

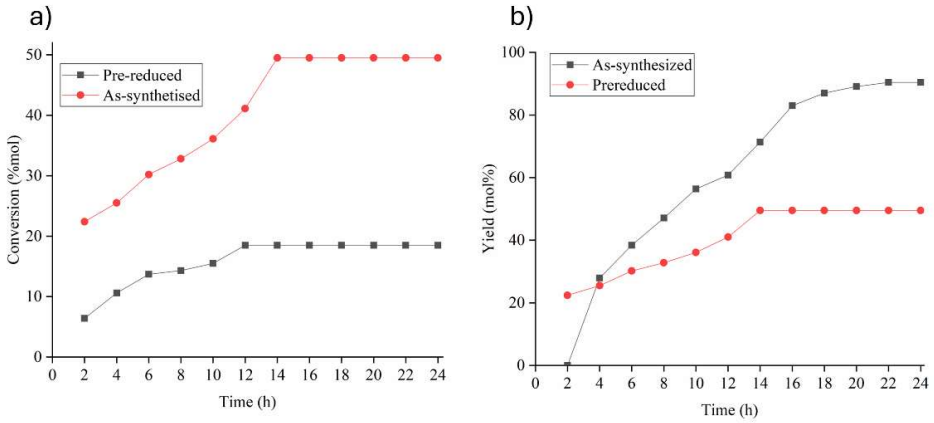
The syntheses of the Cu/Zn/Cr, Cu/Zn and Cu/Zn/La catalysts were carried out by co-precipitation technique, according to the detailed procedures available in the literature. [3,5] The corresponding compositions were confirmed by the Inductively Coupled Plasma (ICP) spectroscopy technique. Hydrogenation reactions were carried out in a 300 mL stainless steel Parr 4560 autoclave, equipped with a P.I.D. controller (4848). The analytical determinations were performed by GC-FID

analysis, using a DANI GC1000 DPC gas chromatograph. Further analytical details are reported in a previous work of us. [6]

Results and Discussion

First, Cu/Zn/Cr catalyst was tested for the hydrogenolysis reaction of model HexHex (pH_2: 100 bar, T: 230 °C, catalyst loading 5 wt%), monitoring the kinetics for 24h, whereas the corresponding HexHex conversion of 82.6 mol% was obtained. In the attempt of improving to the best the activity of the pristine catalyst, a wet pre-reduction step was included (pH_2= 100 bar, time: 5h, T: 200 °C in MeOH). [5] In this case, only a moderate improvement of the conversion was achieved (92 mol% after 24 h), always keeping the complete selectivity to HexOH. Then, the Cu/Zn-based catalyst was tested, working under the same reaction conditions, ascertaining a much lower conversion (35 mol%), which was stable already after 6h of reaction, demonstrating the unsatisfactory performances of this binary system towards HexOH production. Instead, the Cu/Zn/La catalyst allowed a much higher conversion (about 90 mol% after 24 h), demonstrating the positive effect of lanthanum towards the reduction of copper sintering, at the same time affecting the acid-base properties of the bulk catalyst, both factors that synergistically play a key role in the involved reaction mechanism. [4] Remarkably, a worsening of the HexHex conversion was ascertained by including the pre-reduction step of the ternary catalyst (only 50 mol% after 24 h, see Figure 1), highlighting that excessive reduction of the Cu species is not effective for the hydrogenolysis stage. [7] Further characterizations of all pristine and spent catalysts are in progress, to deepen the role of metal oxidation state and acidity/basicity of the species involved in the reaction mechanism.

Figure 1 Kinetics of HexHex hydrogenation to HexOH using as-synthesized and pre-reduced Cu/Zn (1a) and Cu/Zn/La (1b) catalysts.



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