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Replacement of CuCr catalysts by environmentally benign CuZn catalysts - effect of the chemical composition and pre-treatment on hydrogenolysis performance

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PURPOSE OF THE ABSTRACT

Ester hydrogenolysis is a key reaction to produce fatty alcohols having wide range of applications. Currently, copper-chromium catalysts are used. Nonetheless, the use of chromium, particularly during catalyst production and disposal, has a significant negative environmental impact and contradicts the basic principles of the ?Green chemistry?. The main aim of the research is thus to investigate the properties of CuZn catalysts as an ecological alternative to CuCr catalysts used in hydrogenolysis of esters to alcohols.

A series of CuZn catalysts with Cu/Zn ratio of 0.5-2 was prepared by a co-precipitation method, calcined and characterized in detail to assess their phase composition, crystallite sizes and textural properties. Their catalytic performance was tested in dimethyl adipate (DMA) hydrogenolysis in batch or flow reaction conditions at T=175-210 °C and hydrogen pressure of 10 or 16 MPa.

It was found that starting Cu/Zn ratio affected the phase composition precipitates that consisted of different amounts of aurichalcite to zincian malachite. Nonetheless, calcination in air at 350 °C afforded mixtures of CuO and ZnO with the crystallite sizes of 4.0-5.7 nm and 6.3-6.9 nm, respectively. XPS results showed that the Cu/Zn surface ratio (0.29-0.48) was significantly lower than the Cu/Zn bulk ratio (0.5-2) determined by XRF. According to TEM, the CuO and ZnO distribution in the catalysts was homogeneous. Furthermore, both calcination temperature and atmosphere were found to affect phase composition of the catalysts as well as their crystallite sizes. In oxidizing atmosphere, the mixture of CuO and ZnO were produced and their crystallite sizes increased when increasing calcination temperature from 220 to 500 °C. Whereas in inert or reducing atmosphere both oxides were accompanied by Cu2O and Cu. The crystallite size of Cu2O and Cu was larger than the sizes of CuO and ZnO indicating a less intimate contact between Cu-phases and ZnO in catalysts calcined in nitrogen and hydrogen.

Catalysts obtained by calcination at 350°C (regardless the calcination atmosphere) converted DMA efficiently. The presence of zinc in the catalysts was essential for both the increase in turnover frequency (TOF) and the reaction activation energy (Ea). DMA conversion and product selectivity were, however, influenced by the choice of calcination parameters. The largest DMA conversion was observed over sample calcined in air at 350°C which was attributed to the small crystallite size and intimate contact between the CuO and ZnO phases prior to catalyst reduction. In contrast, DMA conversion notably decreased over samples prepared by calcination in N2 or H2 at higher temperatures. This was attributed to the lower number of active sites formed on the interfaces between CuO and ZnO domains after reduction and the lower stabilization of Cu crystallites in the ZnO matrix. The reaction over air-calcined samples yielded 1,6-hexanediol with high selectivity, while the catalysts calcined in nitrogen or

hydrogen exhibited high selectivity to transesterification products. The observed change in the catalytic performance of the differently pre-treated samples allowed suggesting that different active sites were responsible for hydrogenolysis and transesterification pathways and that the relative distribution of these sites changed in dependence on the calcination procedure used.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

CuZn catalysts | dimethyladipate | hexanediol | hydrogenolysis

BIBLIOGRAPHY