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Investigation of environmentally-friendly Cu-based hydrogenolysis catalysts

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PURPOSE OF THE ABSTRACT

Ester hydrogenolysis is the reaction of choice for alcohol production from a wide range of esters. Early in the 20th century, Cu-Cr-based catalysts, called Adkins catalysts, were developed for this process [1]. The catalyst consists of CuO.CuCr2O4 and some promoters such as BaO or Pd [2]. The hydrogenolysis is performed on reduced metallic particles, while the Cr2O3 plays a structural role in increasing the copper dispersion and affecting the copper particle size. This synergic effect enhances the catalyst activity and stability. Nonetheless, the presence of Cr2O3 brings besides the positive effect also a negative environmental effect due to the toxicity of chromium ions. The use of this type of catalyst is also restricted by European Union, which raises the importance of catalyst replacement. Therefore, we search for a suitable replacement that will be as active and selective as the CuCr-based catalyst, but more environmentally-friendly.

For this purpose, we have investigated various promoted catalysts that were compared with unpromoted Cu and CuCr catalysts, used as a benchmark [3, 4]. Cu nanoparticles were promoted using ZnO, Al2O3 and MgO with different Cu/promoter ratio and their effect was evaluated. Co-precipitation was used as a synthesis method. The promoter incorporation increased Cu dispersion and those nanoparticles became less prone to sintering at higher temperatures compared to single-phase Cu catalysts. Then, all catalysts were tested in dimethyl adipate (DMA) hydrogenolysis. Catalytic parameters such as DMA conversion, selectivity or hydrogenolysis activity (TOFH) were evaluated and together with characterization data revealed the promoter effect. The unpromoted Cu catalyst quickly deactivated and its performance in DMA hydrogenolysis was the lowest. As the addition of a promoter improved Cu dispersion, it directly influenced the DMA conversion that increased. More interestingly, the promoted catalysts outperformed the commercial CuCr catalysts in terms of DMA conversion. The selectivity was found to depend strongly on the acid-base character of the catalysts that was investigated by adsorption techniques. Simultaneously, we understood the formation of transesterification by-products and discussed their importance as their selectivity can reach up to 50 %. To sum up, CuZn and CuZnAl catalysts were observed to be the most promising catalysts to replace the CuCr catalyst.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

CATALYSIS | HYDROGENOLYSIS | COPPER | ESTER

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