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Copper-based catalysts prepared from hydrotalcite precursors Hfor shift reaction at low temperatures

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Abstract

CuO/ZnO/Al$_2$O$_3$ catalysts were prepared from calcination of hydrotalcite-like compounds obtained by co-precipitation of Cu, Zn and Al nitrates. The characterization of the hydrotalcite-derived catalyst by XRD showed the formation of CuO and ZnO, with small contribution of spinel phase and diameter of CuO crystallite of about 10 nm; TPR analysis showed a higher reduction temperature due to the higher interaction of copper species with support. The commercial and synthesized catalysts were tested in the low temperature shift reaction. In the activity test, the commercial catalyst showed a higher conversion. On the other hand, in the stability test at 250 °C, the 30CuHTc catalyst showed the lower decrease in the activity, which can be attributed to its higher resistance to sinterization since the interaction of copper with the support helps to maintain the metallic dispersion with time on stream.
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1. Introduction

Hydrogen is forecast to become a major source of energy in the near future due to its availability, production flexibility (it can be produced from different feedstocks and production processes) and versatility of utilization (electricity generator, energy carrier in stationary and portable applications), besides being non-toxic and non-pollutant.

Hydrogen is basically produced from fossil fuels, mainly natural gas, which accounts for almost 50% of the world production [1]. Currently, the largest and generally the most economical way to produce hydrogen is steam reforming of methane, which produces a mixture of hydrogen and carbon monoxide (synthesis gas) [2]. In order to increase H$_2$ yield and promote CO conversion, the water–gas shift reaction is largely employed in industrial scale on refineries and commercial plants of hydrogen and ammonia [3,4]:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41 \, kJ/mol$$
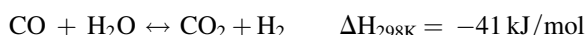
For maximum H$_2$ yield, the shift reaction is usually conducted in two-bed system, with the first bed operating at high temperatures (340–400 °C), over Fe$_2$O$_3$/Cr$_2$O$_3$ catalyst, and the second one at low temperatures (180–250 °C), over CuO/ZnO/Al$_2$O$_3$. The copper-based catalysts present high activities and CO exit concentrations as low as 0.1–0.3% can be achieved, however, they are highly sensitive to poisoning and thermal sintering.

Although these copper-based catalysts have been widely employed commercially since the early 1960s, there are still controversies concerning the nature of active sites and the role of ZnO promoting the catalytic activity [5–7]. It is well-known that the composition and the method of preparation of the copper-based precursors is crucial in determining the final properties of the catalyst [8]. The CuO/ZnO/Al$_2$O$_3$ catalysts are commonly prepared by coprecipitation technique [4,5], but other methodologies are being studied, as caustic leaching of Cu–Zn–Al alloys [7] or impregnation of the alumina support with copper and zinc precursors [9,10].

On the other hand, the use of mixed oxides derived from hydrotalcite-like compounds (HTLCs) presents great potential for application in the water–gas shift reaction since the highly-dispersed and homogeneously distributed metal

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