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Cu,Zn-ZSM-5 catalysts for CO_2 hydrogenation by reverse water gas shift (RWGS)

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Resumo-Abstract

Replacing fossil fuels with clean energy is essential to achieve the energy transition to low-carbon technology. One way to use CO_2 is to convert it into platform molecules (building blocks) or sustainable fuels. Hydrogenation by reverse shift reaction (RWGS) activates CO_2 into CO, which can be used as intermediate in the preparation of new products of interest, such as methanol, dimethyl ether (DME), among others. Cu/ZnO-Al_2O_3 catalysts are commonly studied for reverse shift reaction (RWGS) and have been shown to be quite active for this reaction, however, its CO_2 conversion can still be improved, since its conversion obtained values of 56,1% under the conditions studied. In this work, Cu,Zn-ZSM-5 catalysts were prepared by the ion exchange method (simultaneously or successively), introducing Cu and/or Zn contents of 1.5%. The materials were characterized and tested in the RWGS reaction with a catalyst mass of 0.2 g, total gas flow rate of 50 mL min^{-1} and a H_2:CO_2:Ar ratio of 6:1:3 (F/W = 15000 mL g^{-1} h^{-1}). The active phase for the reaction is the finely dispersed metallic Cu in the zeolitic support. The Cu-ZSM-5 catalyst reached 45,5% conversion with 100% selectivity to CO at 800°C, while showing low conversions at 400°C. The catalyst containing only Zn did not show significant activity, only at 800°C, reaching CO_2 conversions of 35,5% and selectivity of 98% to CO. The material prepared by successive ion exchange, when Zn was added first than Cu, presented higher CO_2 conversion, reaching 81% CO_2 conversion and 99.9% CO selectivity at 800°C. On the other hand, when Cu was exchanged prior to Zn, conversions of 40,3% and 99.6% CO selectivity were observed. The material obtained by simultaneous exchange presented 31,9% conversion with 99.7% CO selectivity at 800°C. This shows that the order of exchange of Cu^{2+} and Zn^{2+} ions significantly influences the catalyst activity in the RWGS reaction. These materials were also compared with the Cu/ZnO-Al_2O_3 catalyst, which presents higher CO_2 conversions in the temperature range of 300 to 600°C, but at higher temperatures no significant increase in conversion is observed, reaching a maximum conversion of 56,1% at 800°C with 99,9% of selectivity. The best performing Cu,Zn-ZSM-5 catalyst achieved better CO_2 conversion results and very close selectivity when compared to Cu,Zn-Al_2O_3.At low temperatures, generally below 500°C, the formation of CH_4 and, eventually, methanol is observed, which decreases with increasing temperature, favoring greater selectivity to CO from 500°C. The Cu,Zn-ZSM-5 catalysts presented a satisfactory catalytic performance under the conditions investigated, achieving high CO_2 conversions and high selectivity to CO at higher temperatures. The introduction of Zn^{2+} ions prior to the Cu^{2+} ions causes a significant increase in the catalytic activity, emphasizing its role as a promoter. The RWGS may be a preliminary reaction in the synthesis of methanol, as the formation of methanol was observed at low temperatures, this fact will be investigated in the future.

Keywords: CCUS, RWGS, Zeolitic catalyst, Cu,Zn-ZSM-5.

References

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