Highly Dispersed Cu Species over Al-TUD-1 for CO_2 Hydrogenation

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$CuO-ZnO-ZrO_2$ (CZZ) composite is intensively investigated at CO_2 hydrogenation to methanol due to its high CO_2 activation and water tolerance abilities [1]. In this work, highly dispersed metallic Cu^0 species from the $CuO-ZnO-ZrO_2$ catalyst have been prepared with the assistance of the mesoporous aluminosilicate support Al-TUD-1. The amorphous 3D-structured Al-TUD-1 presents high surface area (> 600 $m^2\ g^{-1}$) and abundant Brønsted acid sites that play a role for Cu^0 partial incorporation into the support structure and for anchoring Cu^0 nanoparticles [2]. As a result, the Cu^0 surface area of the hybrid CZZ@Al-TUD-1 catalysts has been increased to the maximum value of 49.0 $m^2\ g_{copper}^{-1}$, which is higher than the value for the initial pure CZZ (38.7 $m^2\ g_{copper}^{-1}$). Theoretical DFT simulation confirms that the Al atoms in the aluminosilicate support's framework form hydroxyl sites for anchoring efficiently metallic Cu^0 species, thus creating highly dispersed and stable Cu^0 nanoparticles in the CZZ@Al-TUD-1 hybrid materials. The catalytic results obtained over the hybrid CZZ@Al-TUD-1 (Si/Al atomic ratio of 25) catalyst in the CO_2 hydrogenation into methanol are following: the methanol production over 840 g $kg_{Cu}^{-1}\ h^{-1}$ or 180 g $kg_{cat}^{-1}\ h^{-1}$ at 280 °C and 20 bar (*figure 1*), and 1820 g $kg_{Cu}^{-1}\ h^{-1}$ or 383 g $kg_{cat}^{-1}\ h^{-1}$ at 280 °C and 50 bar.

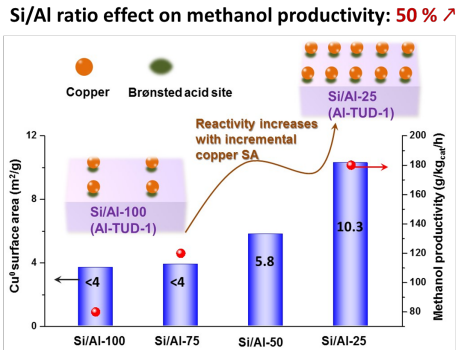

Fig. 1. Metallic Cu^0 surface area and catalytic results of the CZZ@Al-TUD-1 catalyst with different Si/Al ratio in the support

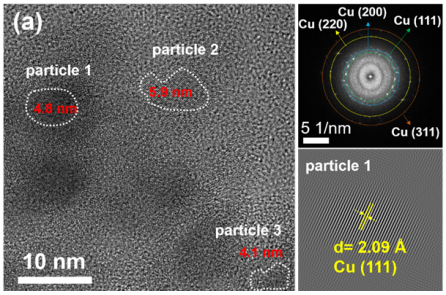

Fig. 2. Metallic Cu^0 surface area and catalytic results of the CZZ@Al-TUD-1 catalyst with different Si/Al ratio in the support

In order to understand the microstructure and the chemical state evolution of the hybrid catalysts during the reaction, reduced and spent materials were analyzed. XRD results show only the characteristic diffraction peaks for the Cu^0 phase. Surprisingly, there is no big change for the crystallite size of Cu^0 before and after the reaction: 4.6 nm for the reduced and 4.3 nm for the spent CZZ@Al-TUD-1 catalyst (Si/Al = 25) (*figure 2*). That means that there is no severe agglomeration of Cu^0 particles during reaction and the anchoring over the Al functions in the support is beneficial for improving the stability of such copper-based catalysts. The HR-TEM images for the spent catalyst with the corresponding FFT show the diffraction points attributed to different planes of metallic copper. The shape of the particles is irregular instead of the round metal particles probably indicating the strong interaction between Cu^0 with ZnO, ZrO_2 and additionally with the support Al-TUD-1 [3].

The results herein provide an understanding of the nature of the strong metal-support interactions and give new insights into designing the Cu-based catalysts for CO_2 hydrogenation reactions [4].

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[2] R. Anand *et al*, J. Catal. 242 (2006) 82-91
[3] L.Y. Zhang *et al*, Angew. Chem. Int. Edit. 54 (2015) 15823-15826
[4] Q. Jiang *et al*, Appl. Cat. B 269 (2020) 118804