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Conversion of CO_2 to Methanol on Cu/Zn/Zr, Pd/Zn/Zr or Cu/Zn/Zr+Pd/Zn/Zr catalysts

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The catalytic conversion of CO_2 to valuable products, as methanol for example, can strongly contribute to the mitigation of that extremely abundant greenhouse gas. In the CO_2 to methanol reaction, Cu- and Pd-based catalysts are the most commonly studied. Although Pd is more expensive than Cu, catalysts with Pd can convert CO_2 into methanol at atmospheric pressure. This could mean a significant industrial advance, since Cu-based materials allow the methanol production only at high pressures. However, in general, both Cu- and Pd-based catalysts show low activity and/or low selectivity to methanol[1]. Complementary, CuPd catalysts were also investigated and showed better results in the CO_2 conversion and methanol selectivity than those shown by the monometallic Cu or Pd catalysts[2]. It is still a challenge to understand how palladium interferes in the copper properties and the bimetallic active phase improves the catalytic performance. The difficulty to reach that knowledge have been mainly justified by the impossibility of characterizing the materials under high pressure. In order to clarify the role of Cu and Pd in the bimetallic catalyst to CO_2 hydrogenation, the use of physical mixtures of Cu and Pd catalysts can be an interesting alternative. In principle, in a physical mixture, the properties of the individual catalyst could be conserved and the contribution of modifications in the electronic properties by the addition of Pd to Cu catalysts could be excluded. In this way, these data may contribute to further understand the origin of the pointed synergistic effect between Cu and Pd and gain new insights into the reaction mechanism. Here, we propose to study the CO_2 hydrogenation to methanol applying Cu/Zn/Zr, Pd/Zn/Zr, and the their physical mixture in a 50/50 mass ratio. To simplify we will refer to Cu/Zn/Zr, Pd/Zn/Zr, and Cu/Zn/Zr+Pd/Zn/Zr as CZZ, PZZ, and $C_{50}P_{50}ZZ$, respectively. In this work, CZZ and PZZ were synthesized by a traditional co-precipitation method. The composition of PZZ and CZZ was set up to 5/30/65 and 30/40/40 (wt.%), respectively, as confirmed by X-ray fluorescence spectrometry. The CO_2 hydrogenation was carried out at 20 bar between 220 and 300 °C. The reactor was fed with a 60 mL min^{-1} flow of a $CO_2/H_2/N_2$ mixture with a molar ratio of 1:3:2. The investigated materials presented similar CO_2 conversion at 220, 240, 260, 280, and 300 °C. On the other hand, $C_{50}P_{50}ZZ$ was the best catalyst for the methanol production. For instance, at 240 °C, the space-time yield of methanol was 139 g kg_{cat}^{-1} h^{-1} for $C_{50}P_{50}ZZ$, while those for CZZ and PZZ were 109 and 37 g kg_{cat}^{-1} h^{-1}, respectively. These results were rationalized in terms of the physical and chemical properties of the Cu and Pd catalysts and their complementary functions in the CO_2 to methanol reaction mechanism.

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References
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