HYDROGENATION OF CO_2 CATALYSED BY Cu AND Pd NANOPARTICLES SUPPORTED ON ZnO AND CARBON

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INTRODUCTION

Cu/ZnO and Pd/ZnO nanoparticle catalysts have been widely studied for hydrogenations. In this work, ZnO supported Cu and Pd nanoparticle catalysts are used for CO_2 hydrogenation and the dependence on parameters such as temperature, pressure and reduction temperature were analyzed. Palladium is more active than copper and forms a PdZn phase at higher reaction temperatures. Alloying cannot be observed with copper. Sintering effects were observed by electron microscopy. Palladium initially has smaller particles than copper, but they sinter strongly. The long-term stability was also investigated and it was concluded that all catalysts have relatively good stability over the reaction time. At atmospheric pressure mainly CO was formed, whereas at a pressure of 20 bar also methane and traces of methanol were produced.

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

The increased use of CO_2 to produce higher quality chemicals may be a future approach for recycling CO_2. Cu and Pd particles on different supports (oxides) can serve for this purpose, with ZnO being frequently used. Cu is often commercially applied but has the disadvantage that it oxidizes and is less catalytically active than palladium. Palladium, on the other hand, is expensive. Therefore, a way should be found to combine the positive aspects of both metals and to minimize their disadvantages. For this purpose, besides monometallic catalysts (Cu/ZnO, Pd/ZnO), bimetallic PdCu catalysts, in particular, were produced, characterized and kinetic tests were performed for the hydrogenation of CO_2 to various products [1], [2].

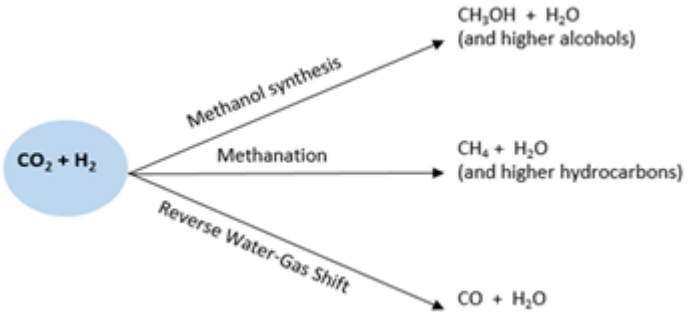

Figure 1. Main pathways for the hydrogenation of CO_2. These pathways are related to temperature, pressure and catalyst.

RESULTS AND DISCUSSION

The selectivity of the reaction depended on the reaction temperature, the pressure and the respective catalyst. Since CO_2 is a thermodynamically stable molecule, high temperatures but also the oxide are required for activation. The formation of PdZn alloys, which form in Pd/ZnO catalysts, also plays a role in the catalytic activity [3], [4]. It was found that at atmospheric pressure the palladium catalysts have a much higher catalytic activity than the copper nanoparticles. In contrast, no difference in activity could be observed at a pressure of 20 bar. Interestingly, the bimetallic PdCu catalysts are catalytically more active at 20 bar pressure than the monometallic Cu and Pd nanoparticles. Pressure is necessary for the production of methane gas. At atmospheric pressure, for example, no methane was formed, but at 20 bar the selectivity to methane increases. Measurements

have shown that pretreatment with hydrogen is not necessary for reactions at elevated pressures, which is of great industrial importance. Furthermore, Pd and Cu nanoparticles were also applied to graphene as support. Interestingly, even with these catalysts, there is an activity for CO_2 hydrogenation, although there is no oxide support.

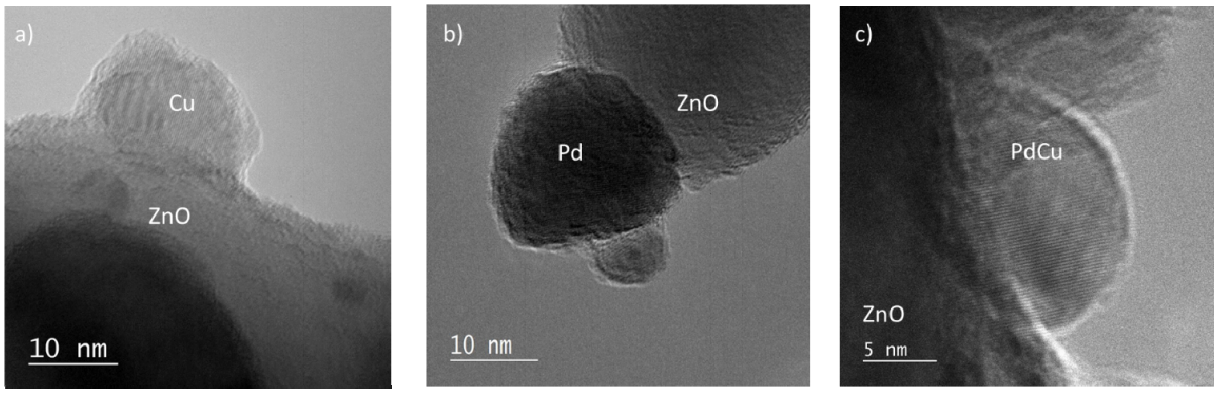

Figure 2. HR-TEM images of Cu/ZnO (a), Pd/ZnO (b) and PdCu/ZnO (c) nanoparticle catalysts

CONCLUSION

By combining different characterization methods the catalytic activity of monometallic and bimetallic copper and palladium nanoparticles supported on zinc oxide could be determined and the influence of the metal composition, the different synthesis methods and the behaviour of the particle distribution on catalysis could be investigated. These results can provide important insights into industrial applications (production of CO, CH_4 and CH_3OH), as it has been found that bimetallic catalysts actually provide higher catalytic activity than monometallic catalysts. Further spectroscopic measurements (especially in-situ) will be necessary for the future to complete the characterization.

ACKNOWLEDGEMENTS

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