Application of In2O3-catalysts for Slurry Phase Hydrogenation of CO_2 to Methanol: Influence of Reaction Conditions, Support and Catalyst Preparation

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Abstract

To reduce greenhouse gas emissions the development of novel storage and transport technologies for renewable produced electrical power is necessary. In comparison to conventional energy, renewables are highly dependent on the availability of primary energy sources like wind and sunlight. One concept to overcome this challenge is to convert electrical to chemical energy, e.g. by electrolysis of water to hydrogen and oxygen in an electrolysis cell. Yet storage and transport of hydrogen is a challenging task requiring the subsequent conversion to base chemicals like methanol.

Due to the deactivation of the industrial $Cu/ZnO/Al_2O_3$-catalysts by stoichiometrically produced water [1], novel water resistant catalysts for the CO_2 hydrogenation to methanol are required. Recently, it has been shown that heterogeneous In_2O_3-catalysts supported on semiconductor metal oxides presents a promising alternative [2], but require further catalyst development.

In this work we follow two different synthesis approaches, namely wet-chemical impregnation and laser-based catalyst preparation. The latter represents a novel technique to individually study the catalytic activity in terms of nanoparticle purity, functional properties (size, morphology, oxidation state) and support properties (e.g. defect densities) [3]. Nanoparticles are synthesized by scalable pulsed laser ablation in a liquid under surfactant-free conditions and subsequent adsorption in chosen weight loading, onto various oxidic support materials. Due to subsequent processing, nanoparticle properties (e.g. nanoparticle size) are adjusted independently of the nanoparticle load or the used support [3]. Furthermore, the gained nanocatalyst is active without high temperature calcination further maintaining preadjusted support properties (e.g. defect structure of dopant distribution).

To quantify the activity of the catalysts for methanol synthesis a slurry reactor with suspended catalyst in a high boiling liquid phase was used. Advantages of this concept are the applicability of catalysts in the size of nanometers without inducing high pressure drops. To examine the influence of the catalyst morphology on the catalytic performance, several analytical techniques were used. The Indium-loading of the catalyst was checked by ICP-OES. BET-sorption measurements and CO_2-TPD were applied for the characterization of the catalyst supports concerning their total surface area and CO_2 binding capacity. Via XPS measurement the oxidation state of the Indium-and Zirconia-species were analysed before and after the reaction. Furthermore, the catalyst surface was examined by electron microscopy and XRD.

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[2] O. Martin, “Indium Oxide as a Superior Catalyst for Methanol Synthesis by CO_2 Hydrogenation,” *Angewandte Chemie*, vol. 55, no. 21, pp. 6261–6265, 2016.
[3] D. Zhang, “Laser Synthesis and Processing of Colloids: Fundamentals and Applications,” *Chemical reviews*, vol. 117, no. 5, pp. 3990–4103, 2017.