Optimization of Cu-ZnO Laterally Condensed Catalysts for Methanol Synthesis: On the Influence of the Residence Time

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 CO_2 hydrogenation is a kinetically limited reaction, occurring exclusively at the catalyst surface. ¹ To achieve satisfactory catalytic conversions, it is essential to form a reactive interface that facilitates the adsorption of CO_2 and its subsequent conversion to the desired products, in this case, methanol. Reducing the bulk of the catalyst is a promising approach to lowering production costs, concentrating the material primarily on the reactive and functional interfaces. Although the surface area of a laterally condensed catalyst (LCC) is restricted by its geometric dimensions, its catalytic performance can be enhanced due to the higher density of active centers on the surface.



Figure 1. CO_2 conversion (L) and methanol selectivity (R) for the performed series of catalytic tests

The industrially established system for methanol production via CO_2 hydrogenation is $Cu/ZnO.^2$ To identify the most active surface, the performance of LCC systems in four major configurations was studied, with either ZnO or Cu as a top layer (3 or 20 nm) or as a bottom layer (20 nm), deposited on a Si (100) wafer. Catalysts with ZnO as the top layer, particularly the 3 nm variant, exhibited enhanced catalytic performance compared to their counterparts with Cu on the surface. This observation aligns with available literature, where ZnO often forms a graphitic-like overlayer on Cu crystallites³. As a powder reference, a catalyst with a comparable composition was synthesized, consisting of silica-supported Cu_2O nanocubes covered with a layer of ZnO, with a Cu/ZnO mass ratio of 5.6. To better understand the relationship between gas flow rate and the mass of the powder catalyst, different weight hourly space velocities (WHSV) were applied, ranging from 30,000 ml/gh to 3,000,000 ml/gh, to approximate the conditions of



the LCC measurement (constant total flow 50 ml/min, 250°C, 40 bar). Given the LCC mass is around 0.1 mg, the WHSV during measurement, with a total gas flow of 22 ml/min, is approximately 13,000,000 ml/gh.

Despite the extremely high WHSV during LCC sample measurement, the observed catalytic activity was comparable to the powder tested at WHSVs of 600,000 - 3,000,000 ml/gh (Fig. 1). This indicates that the development of new reactors dedicated to thin films is necessary to reduce the ratio between gas flow rate and LCC mass, thereby enabling higher system yields.

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