

Cu/ZrO₂ catalysts for methanol steam reforming: structure activity correlations

A. Szizybalski¹, H. Purnama¹, F. Girgsdies¹, J.H. Schattka², Y. Wang², T. Ressler¹, R.A. Caruso², R. Schlögl¹

¹*Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany;*

²*Colloid Department, Max-Planck-Institute of Kolloid- und Grenzflächenforschung, Am Mühlenberg, Haus 2, 14476 Golm, Germany*

Conventional Cu/ZnO catalysts that can be used to produce hydrogen for fuel cell applications exhibit an unsatisfactory long-term stability and selectivity to CO under changing reaction conditions. In this work in situ X-ray diffraction and X-ray absorption spectroscopy in combination with mass spectrometry were used to monitor structural changes and catalytic activity of various Cu/ZrO₂ catalysts under methanol steam reforming (MSR) conditions, whereas a three-channel plug flow reactor was used to perform detailed catalytic characterizations.

The initial low MSR activity (MeOH:H₂O = 2:1) could be significantly improved by a short addition of oxygen to the feed. We could also observe that after extended times in the MSR feed and elevated temperatures (673 K, 2 vol-% H₂/He), the catalysts were still active or could be activated (via short O₂ addition) again, indicating an improved stability compared to conventional Cu/ZnO catalyst. To simulate the experimental spectra of the copper clusters under reaction conditions an additional Cu-O shell was necessary (XAS). The corresponding oxygen amount could be correlated to the increase of the activity. The measurement of methanol conversion as a function of contact time shows clearly that a macroporous CuO/ZrO₂ catalyst is more active than the commercial CuO/ZnO/Al₂O₃ catalyst. Moreover, less CO was formed over the CuO/ZrO₂ catalysts, especially significant at higher methanol conversion.