

## Unraveling the surface properties of CuO/ZrO<sub>2</sub> systems with CO and CO<sub>2</sub> adsorption and TPR *in situ* FT-IR experiments

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For a climate-friendly future an economy based on hydrogen is claimed to be the most promising one. Methanol with its excellent properties for storage and distribution could be the ideal chemical hydrogen carrier and the carbon-neutral fuel of the future. [1] With the aid of an optimized methanol steam reforming (MSR) catalyst, hydrogen accompanied by CO<sub>2</sub> could be released and subsequently utilized in a proton exchange membrane fuel cell (PEMFC) for production of electrical energy. One of the most important factors in MSR is to tune the catalyst towards maximum CO<sub>2</sub> selectivity, because CO, originating from potential side reactions, poisons the PEMFC electrodes. Another crucial aspect refers to the long-term stability. [2] It was previously found by Purnama et. al. that under selected experimental conditions the Cu/tetragonal(t)-ZrO<sub>2</sub> interface is capable of catalyzing methanol steam reforming at higher CO<sub>2</sub> selectivity and long-term stability compared to the monoclinic ZrO<sub>2</sub> modification. [3]

We, thus, investigated CO and CO<sub>2</sub> adsorption on two representative CuO/t-ZrO<sub>2</sub> catalysts, which were prepared by impregnation and co-precipitation, to obtain the relevant surface acidity and basicity utilizing *in situ* FT-IR spectroscopy. Specific adsorptions, especially in the fingerprint area from 1600 – 1000 cm<sup>-1</sup>, are used to identify intermediates or spectators in the MSR reaction. Furthermore, TPre (temperature programmed reaction) experiments up to 723 K with CO under flowing conditions reveal that at 353 K CO<sub>2</sub> evolves and at 453 K CO reduces CuO to metallic Cu<sup>0</sup>. Specific carbonates, identified in the adsorption experiments, are then decomposed. At this point, also polydentate carbonates (closely-spaced Zr<sup>4+</sup> coordinatively unsaturated sites) and formates arise. These investigations could unravel crucial intermediates steering the reaction either towards MSR or potential side reactions.

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[1] G. A. Olah, *Angew. Chem. Int. Ed.* 44 (2005), Nr. 18, S. 2636–2639.

[2] M. Behrens, M. Armbrüster, *Catalysis for Alternative Energy Generation*, 2012, S. 175–235.

[3] H. Purnama et. al., *Catal. Lett.* 94 (2004), 1/2, S. 61–68.