

## Cu/ZnO<sub>x</sub> Colloids as Catalysts for Liquid Phase Methanol Synthesis

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The Cu/ZnO system is still of particular interest in reduction catalysis, because it is the leading industrial catalyst for the synthesis of methanol. However, many questions are still subject to controversial discussions, such as the nature of the active sites, the role of the various oxidation states of copper, the role of ZnO and the reaction mechanism. The industrial catalysts are very complex and are less suitable to study such fundamental properties. Copper colloids of defined size and shape therefore represent a well defined model system. An advantage of colloids is their solubility in various solvents owing to the ligand sphere around the particles. Furthermore, colloidal systems show a great potential as catalysts due to the large surface area of the particles. In a previous publication we studied the adsorption of CO on Cu colloids [1] using ATR-FTIR spectroscopy to clarify whether the ligand sphere influences the surface reactions and the adsorption properties. In the present work Cu and Cu/ZnO<sub>x</sub> colloids are applied in the liquid phase to clarify the role of the different components in methanol synthesis catalysts.

The synthesis of the Cu and the Cu/ZnO<sub>x</sub> colloids is described elsewhere [2]. For the catalytic test the preparation of the Cu/Zn colloids was slightly modified. The pyrolysis of [Cu(OCH(Me)CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>] in squalane at 473 K and the addition of ZnEt<sub>2</sub> after 2 min yielded Cu/ZnO<sub>x</sub> nanoparticles of 2–4 nm in diameter. It was not necessary to add stabilizer. Squalane was used as solvent according to the LPMeOH process because it is thermostable and chemically resistant to the reaction mixture under synthesis conditions. The catalytic tests were carried out continuously in a laboratory stainless steel reactor (CSTR) at 2.6 MPa. For comparison, a conventional ternary Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst powder was suspended in squalane. The activation of the solid catalyst was carried out in H<sub>2</sub> diluted with N<sub>2</sub>. The online analysis was performed by gas chromatography [3].

The formation of methanol over the Cu/ZnO<sub>x</sub> colloids started at 493 K. The activity and the stability were found to depend strongly on the Cu/ZnO<sub>x</sub> ratio. To elucidate the carbon source for the methanol formation a variation of the CO/CO<sub>2</sub> ratio in the feed gas was performed. An increase of the partial pressure of CO<sub>2</sub> in the feed gas resulted in slightly more methanol, and also more water was formed indicating that the water-gas shift reaction proceeded in the reverse direction. When adding more CO<sub>2</sub> the reverse water-gas shift reaction became faster than its hydrogenation. In contrast, the more CO was in the feed gas, the more methanol was produced, and the more water was converted due to the forward water-gas shift reaction. Thus, CO may be the primary carbon source for methanol using Cu/ZnO colloids [4].

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