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Continuous precipitation of $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis in microstructured reactors with alternative precipitating agents

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ABSTRACT

Ternary $Cu/ZnO/Al_2O_3$ catalyst systems were systematically prepared by innovative synthesis routes in microstructured synthesis setups, allowing to study different types of micromixers. The coprecipitation in the slit plate and valve-assisted mixers was operated continuously under exact control of pH, temperature, concentration and ageing time. Due to the enhanced surface to volume ratio in microstructured reactors, a precise temperature control and efficient mixing of the reactants are enabled. The precipitation was performed with sodium, ammonium and potassium carbonate as well as sodium hydroxide. To evaluate the potential of the novel synthesis routes, reference samples in a conventional batch process were prepared. The catalysts were synthesized according to the *constant pH method* with a molar ratio of 60:30:10 for copper, zinc and aluminum. The synthesis routes applied have a significant influence on the structures of hydroxycarbonate precursors and on the catalytic activity in methanol synthesis. XRD patterns of hydroxycarbonate precursors from the synthesis in micromixers, especially using ammonium carbonate as precipitating agent, display high crystallinity and sharp reflections of malachite and rosasite. $Cu/ZnO/Al_2O_3$ catalysts prepared in continuously operated micromixers in general show higher specific copper surface areas than catalysts prepared in conventional batch processes. The highest methanol productivity of all prepared catalyst systems was observed with the catalyst precipitated in the slit plate mixer with ammonium carbonate.

1. Introduction

The ternary $Cu/ZnO/Al_2O_3$ catalyst system is industrially employed in low-pressure methanol synthesis from a $CO/CO_2/H_2$-containing synthesis gas. The adding of Al_2O_3 to the previously used binary Cu/ZnO system leads to a remarkable increase in catalyst activity and, in particular, stability. Al_2O_3 is believed to inhibit thermal sintering of copper particles [1–3]. Crystal phase structures of the ternary hydroxycarbonate precursors such as malachite, rosasite and aurichalcite strongly affect the activity of the calcined catalyst [4–8]. The complex ternary catalyst system is believed to be subject to a so called ‘chemical memory’. That means that calcined precursors which show similar structures have different activities in methanol synthesis, depending on the crystal phase structures of the preceding hydroxycarbonate precursors [9–12]. Thus, precipitation parameters are crucial for the activity of the later catalyst. Conventionally, catalyst synthesis is performed by batch precipitation with aqueous solutions of metal nitrates and sodium carbonate. Formed hydroxycarbonate precursors are subsequently calcined at 573–773 K and mixed metal oxides are produced. Mild reduction of CuO to Cu^0 in diluted H_2 prior to reaction, results in the active catalyst species. In industrial batch catalyst production, it is challenging to control the synthesis parameters during precipitation, however a considerable number of studies proved the crucial influence of pH value [13,14], temperature [13,15], ageing conditions [10,16] and additionally temperature and concentration gradients [10] on precursor structures and thus later on the catalytic activity. Depending on each synthesis parameter, the resulting hydroxycarbonate precursors show varying properties, particularly in crystal size and structure and hence in optical, electronic and particularly catalytic properties. Therefore, the exact control of process parameters during the synthesis of catalysts is decisive for the catalytic activity and stability.

With respect to the control of process parameters, microreaction engineering offers significant advantages. Thus, huge developments and clear progress have been made over the last few years. Because of their outstanding characteristics in heat and mass transfer and high degree of automation, microstructured reactors provide a promising alternative to common batch synthesis routes. Micromixers are already widely used in pharmacy, biotechnology and production of fine chemicals [17–19]. Especially their

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