Tuning of Stearate-Based Cu Colloids for Methanol Synthesis and ATR-FTIR Investigation of Strong Metal-Support Interactions

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Introduction

Copper colloids seem to be a promising alternative catalyst for the synthesis of methanol in the liquid phase because of their large surface area and high ratio of surface atoms [1-3]. Tuning possibilities of stearate-based Cu colloids are presented, which are prepared in the reactor used for methanol synthesis and the effects are analyzed, which affect the activation and deactivation of the Cu/Zn stearate colloids. *In situ* attenuated total reflection (ATR) infrared spectroscopy was used to study the metal-support interactions of Cu/Zn stearate colloids under methanol synthesis conditions. Adsorption studies with probe molecules (CO, CO_2) and in synthesis gas were performed. Composition and morphology of the colloids were characterized by SAED, TEM, XAFS, XPS and XRD.

Materials and Methods

The Cu/Zn stearate colloidal system is prepared by mixing copper stearate and zinc stearate with 200 ml of squalane ($C_{30}H_{62}$) in a continuously stirred tank reactor (CSTR) [4,5]. The copper stearate is reduced *in situ* in a H_2-containing atmosphere up to 493 K. During this process the Zn stearate-stabilized Cu colloids are formed which were tested for methanol productivity (493 K, 2.6 MPa; 72 % H_2, 10 % CO, 4 % CO_2, 14 % N_2). For the ATR measurements the Cu/Zn stearate colloidal system is prepared by mixing copper stearate and zinc stearate with 20 ml of hexadecane ($C_{16}H_{34}$) in a homemade steel vessel and reducing the mixture *in situ* in H_2 at 473 K for 16 h. During the measurements the colloidal solution is continuously pumped through the system. Adsorption studies were performed using CO, CO_2 and H_2 up to 1.0 MPa and 473 K. For other characterization methods the colloids were separated from squalane and dried to obtain a powder.

Results and Discussion

The productivity of the Cu/Zn stearate colloids is influenced by the conditions applied during pre-treatment and reduction procedure as shown in Figure 1 (H_2 partial pressure, a-d). A higher distribution of Cu and Zn stearate can be achieved by temperature pre-treatment (T*: heating up to 493 K in inert gas) before reduction, significantly increasing the methanol productivity (e-f). Further factors, such as the amount of water, the heating rate, the reduction time and the reaction start-up conditions also influence the productivity and stability of the colloids. High amounts of water, produced by methanol synthesis from CO_2 and the water-gas-shift reaction, seem to lower the stability of the colloids, resulting in a strong deactivation over time. Activity measurements in CO_2-poor synthesis gas reveal only a negligible deactivation of the colloids. Figure 2 shows spectra of the CO adsorption on the Cu/Zn stearate colloids at 473 K and 1.0 MPa. The bands at 2030 and 1979 cm^{-1} can be assigned to CO adsorbed on Cu with ZnO_x adatoms, originating from the reduction of Zn stearate under severe reducing conditions at high temperatures. These observations agree with the surface Cu-Zn alloying due to strong reducing conditions in methanol synthesis powder catalysts and confirm the presence of strong metal support interactions (SMSI) under methanol synthesis conditions in Cu/Zn catalysts [6].

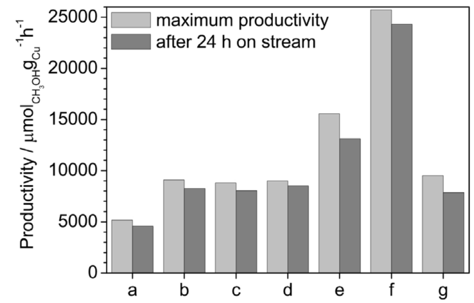

Figure 1. Productivity of the Cu/Zn stearate colloids (50/50) after different reducing conditions (493 K, 16 h): (a) 5 % H_2, 5 bar, (b) 100 % H_2, 5 bar, (c) 100 % H_2, 26 bar, (d) in synthesis gas, (e) T*, 100 % H_2, 5 bar, (f) T*, 100 % H_2, 5 bar, feed gas: 66 % H_2, 33 % CO, 1 % CO_2; (g) commercial catalyst (for comparison) ($Cu/ZnO/Al_2O_3$).

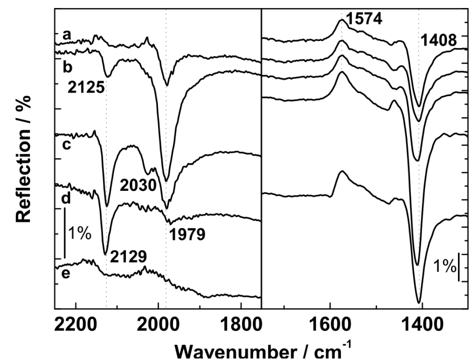

Figure 2. ATR spectra of the CO adsorption on Cu/Zn stearate particles at 10 bar, 473 K after (a) 5 min, (b) 30 min, (c) 40 min, (d) 75 min in CO (100 %), (e) 10 min in Ar.

Significance

The catalyst preparation was performed directly inside the CSTR, simply by mixing cheap, air stable, and easy to handle metal stearates. Since there is no need for a separate preparation, the process is easy to scale up for an industrial application. Furthermore, the variability of the system offers the possibility to tailor the colloid systems for different conditions.

References

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