# Cu,Zn,Al Layered Double Hydroxides as Precursors for Copper Catalysts in Methanol Steam Reforming – pH-controlled Synthesis by Microemulsion Technique

### - Supplementary Information -

A microemulsion is characterized by thermodynamic stability, transparency or weak opalescence and a low viscosity. The composition of the mixture is specified by the weight proportion of the oil in the mixture water and oil  $\alpha$  (Eq. (1)) and by the weight fraction of the surfactant in the ternary mixture  $\gamma$  (Eq. (2)).

$$\alpha = \frac{m_{oil}}{m_{water} + m_{oil}} \tag{1}$$

$$\gamma = \frac{m_{surfactant}}{m_{water} + m_{oil} + m_{surfactant}} \tag{2}$$

W/O-microemulsions, which consist of small water droplets dispersed within an oil phase, are generally used for the synthesis of nanoparticles. In such a mixture new particles are formed by the fast exchange between the kinetic instable micelles<sup>1</sup>. Applying the microemulsion technique for the precipitation of nanoparticles can be done either by mixing two microemulsions – one containing the metal salts and one containing the precipitating agent. The second possibility is to work with just one microemulsion containing the metal salts or the precipitating agent and add the second reactant directly to this one.

#### Phase behaviour of the reactants

Before applying a microemulsion synthesis it is necessary to investigate the phase behaviour of all components. Herein, only was investigated the oil-rich part of the phase prism (w/o-microemulsions). In this part of the Marlipal O13/40 system an optically clear and isotropic w/o-microemulsion region is present<sup>2</sup>. Based on the former Cu,Zn,Al hydrotalcite synthesis<sup>3</sup> a total metal concentration of 0.43 M was chosen while the base concentration has to be reduced to 0.3M NaOH and 0.045 M Na<sub>2</sub>CO<sub>3</sub>. (For higher concentrations of the bases either no microemulsion was observed or it was stable only in a small temperature range.) In Figure S1 the one-phase domain (hatched area) for two surfactant ratios of both reactants is shown as a function of temperature T and oil weight fraction  $\alpha$ . As the higher surfactant ratio ( $\gamma = 0.25$ ) shows the bigger overlap of the microemulsion regions of both solutions, this ratio was chosen for the synthesis. Furthermore, to work



**Figure S1** Oil-rich part of the phase prism of the quaternary system water/salt/cyclohexane/Marlipal O13/40: a)  $\gamma = 0.225$ , b)  $\gamma = 0.25$ ; c(M) = 0.43 M, c(Na<sub>2</sub>CO<sub>3</sub>) = 0.3 M, c(NaOH) = 0.045 M; the hatched area is suitable carrying out the precipitation within the microemulsion droplets.

with a water content as high as possible and to make sure that the microemulsion is stable during reaction, the oil weight fraction should be approximately  $\alpha = 0.9$  (8% H<sub>2</sub>O) and the reaction has to be carried out at 30°C (see ellipses and arrows in Fig. S1).



Figure S2 size distribution of the water droplets of the template microemulsion measured by DLS.

The droplet size of different microemulsions was investigated by the Dynamic Light Scattering (DLS). As illustrated in Figure S2 the applied microemulsion is a mono dispersed system with an average size of the water droplets of approximately

salt	γ	$\rm H_2O$ ratio /%	α	droplet size /nm
no	0.25	6	0.92	15
	0.25	8	0.89	21
	0.25	10	0.87	30
	0.225	8	0.9	20
	0.225	10	0.87	22
	0.225	12	0.85	39
metal	0.25	8	0.89	22
	0.225	8	0.9	22
base	0.25	8	0.89	25
	0.225	10	0.87	31

**Table S1** Droplet size determined by DLS in dependence of  $\gamma$  and  $\alpha$ .

20nm (see Tab. S1). With higher water content (smaller  $\alpha$ ) the droplet size is increasing, whereas the surfactant ratio has no influence on the droplet size.

## **Course of reaction**



Figure S3 Protocol of microemulsion synthesis (Labmax).

The course of reaction of a Cu,Zn,Al hydrotalcite synthesis by using the microemulsion technique is shown in Figure S3. As the metal salt solution was added continuously the basic microemulsion was added simultaneously to control the pH. During reaction the composition of the ME changes due to a higher water content to approximately  $\alpha = 0.86$  and  $\gamma = 0.24$  which also leads to a smaller range of stability – on the limits regarding the metal salt solution. Accordingly, the observed

pH drop (see Fig. S3) at the end of the dosing could be explained by reaching the stability limit of the microemulsion of the product.

### Nitrogen physisorption isotherms

The adsorption behavior of the samples was investigated by  $N_2$  physisorption. According to IUPAC (International Union of Pure and Applied Chemistry), the isotherm of both LDH samples is a type IV isotherm (Fig. S4), which is typical for mesoporous materials. The calcination had no influence on the nitrogen adsorption-desorption isotherm for the coprecipitated sample, whereas the isotherm of ME-calc is slightly changed. This obersavation is in agreement with the decrease of the BET surface area upon calcination.



**Figure S4** Nitrogen adsorption-desorption isotherm measured at -196 °C: (a) microemulsion samples, (b) coprecipitated samples.

The analysis of the pore size distribution with the BJH method using the desorption branch (Fig. S5) revealed that ME-calc has a higher average pore diameter than ME-LDH. This observation shows that calcination of ME-LDH led to an agglomeration of the platelets as the pore size is to understand as the average distance between the platelets.



Figure S5 Pore size distribution determined from  $\mathrm{N}_2$  isotherms with BJH method.

## TEM

Whereas the Cu particles have a similar size of below 8 nm for both samples, the secondary particles (aggregates of Cu nanoparticles and oxide matrix) appear less bulky for ME-red (see Fig. S6).



Figure S6 TEM images of reduced samples: (a) ME-red and (b) co-red.

#### **Determination of interface ratio**

With the knowledge of the Cu content it is possible to calculate the theoretical Cu surface area from averaged Cu particle sizes. As the Cu particles are more or less spherical the volume (V) as well as the surface area  $(A_O)$  of one particle can easily be calculated from its averaged diameter:  $V = 1/6\Pi d^3$ ,  $A_O = \Pi \cdot d^2$ . Thus, the surface area of one particle and the amount (z) of particles per gram catalyst add up to the theoretical (maximal) Cu surface area:

Cu SA<sub>theo</sub> = 
$$A_O(\text{particle}) + z(\text{particle})g_{\text{cat}}^{-1}$$
 (3)  
=  $\pi d^2 \cdot \frac{wt \% \text{Cu}}{m(\text{particle})}$ ,

where the mass of one Cu particle is calculated from its volume and the density of Cu  $(8.92 \text{ g/cm}^3)$ :

$$m(\text{particle}) = \rho \cdot V(\text{particle}).$$
 (4)

The ratio of surface area exposed to gas (5) as well as the interface ratio (IFR, 6) are resulting by comparison of the maximal (theoretical) Cu surface area with the one measured by  $N_2O$ -RFC.

$$Cu SA_{expo} = \frac{Cu SA_{meas}}{Cu SA_{theo}}$$
(5)

$$IFR = 1 - Cu SA_{expo}$$
(6)

# Sample identification - FHI intern

Table S2 Samples of microemulsion synthesis and co-precipitated one for comparison.

Label	FHI samplenumber
ME-LDH	6020, 6852
ME-calc	6054, 6853
co-LDH	6391
co-calc	6522

## References

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- [2] F. Rauscher, P. Veit, K. Sundmacher, Coll. Surf. A, 2005, 254, 183-191.
- [3] M. Behrens, I. Kasatkin, G. Weinberg, S. Kühl, Chem. Mater., 2010, 22, 386–397.