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Cu-based ex-hydrotalcite catalyst synthesis - structural characterization and investigation of influencing parameters

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Introduction

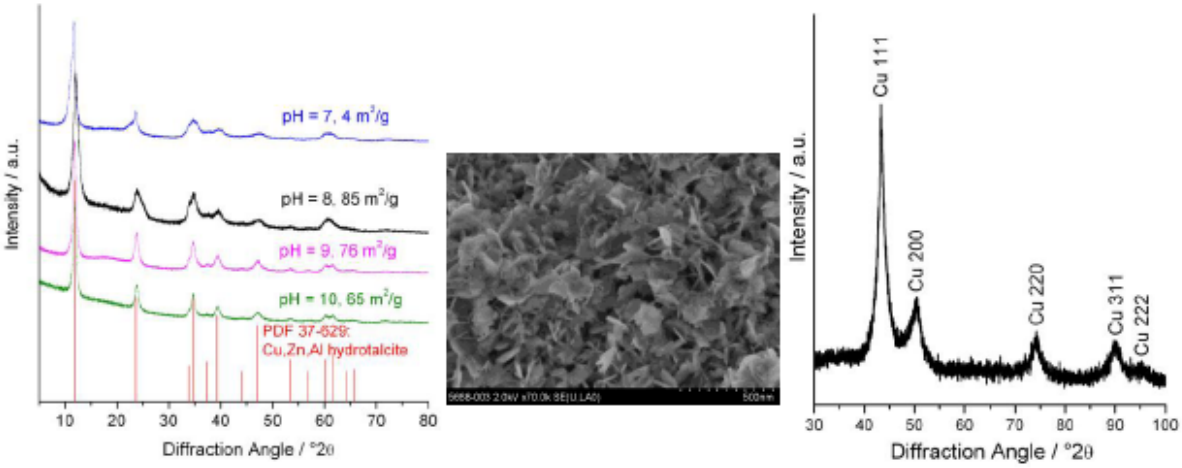
The well known $Cu/ZnO/Al_2O_3$ catalysts, mostly used in methanol chemistry, are synthesized by co-precipitation, followed by calcination and reduction. The product of the established co-precipitation is a mixture of different hydroxy carbonates, typically including the ternary Cu,Zn,Al hydrotalcite-like (htl) compounds with the general composition: $(Cu_{1-x}Zn_x)_{1-y}Al_y(OH_2)(CO_3)_{y/2} \cdot 2H_2O$ [1]. As phasepure Cu,Zn,Al hydrotalcites have a perfect distribution of all three metal components and a homogeneous microstructure they are interesting for deeper investigations. Besides, their structural investigation is less difficult compared to the phase mixture with binary components.
Preliminary results have shown that up to 50 mol-% Cu can be incorporated into the htl material. The most homogeneous microstructure was observed for a Zn:Al ratio close to 1:2 yielding a $Cu/ZnAl_2O_4$-type catalyst. Therefore, we used the nominal composition Cu:Zn:Al = 50 : 17 : 33. In our contribution we will present the structural characterization of this catalyst and its precursors as well as the investigation of some influencing synthesis parameters like pH and ageing.

Experimental

Cu,Zn,Al htl precursors were precipitated from a $Cu^{2+}/Zn^{2+}/Al^{3+}$ nitrate solution (total metal concentration: 0.43M) with an aqueous solution of NaOH (0.3M) and $NaCO_3$ (0.045M) as the precipitating agent. The reaction was carried out at a constant pH at room temperature. After an ageing time of one hour the blue powder was isolated by filtration, washing and drying at 110 °C for 17h. Upon calcination in air at 330 °C for 3h the precursor was converted into the mixed oxides. Finally, the Cu-based catalyst was obtained by reduction of the calcined sample in 5% H_2/Helium.
The resulted samples were characterized by (in situ-) XRD, BET, IR, SEM, TG-MS (for the precursors), TPR and TEM (for the calcined samples).

Results and discussion

The products of the described co-precipitation have a hydrotalcite-like structure (Fig. 1a). No other crystalline phases can be detected. As expected the particles appear in a platelet-like morphology which is maintained during calcination (Fig. 1b).
The 003 reflex of the sample obtained at pH 7 is shifted slightly to lower angles which indicates an increase of the interlayer distance. The surface areas are determined with the BET method and the results are given in figure 1a. They are in a quite good agreement with SEM investigations (Table1), which show for pH 7 and pH 10 in the biggest particle size and for pH 8 the smallest one. The most homogeneous particle size distribution was obtained at pH 10 and the most inhomogeneous one at pH 7.



a) b) c)

Figure 1: a) XRD pattern of htl precursor materials in dependence of the synthesis pH value; b) SEM image of the sample after calcination; c) XRD pattern of the Cu particles obtained after calcination and reduction of the precursor obtained at pH 8

After calcination and reduction Cu nano-particles are formed in the material. Their size is estimated on basis of the half-width of the Cu 111 reflection to approximately 4.8 nm, being a promising size for catalytic applications. Contrary to the industrial $Cu/ZnO/Al_2O_3$ catalyst, the oxide phase of the $Cu/ZnAl_2O_4$ samples was found to be completely X-ray amorphous (Fig. 1c).

Table 1: particle size and particle size distribution of the htl precursors obtained at different pH values measured by SEM (respective 50 particles)

pH	mean	min	max	max/min
7	104,16 nm	50,26 nm	161,93 nm	3.22
8	86,63 nm	48,29 nm	134,00 nm	2.77
9	96,55 nm	62,50 nm	171,52 nm	2.74
10	113,44 nm	74,08 nm	187,28 nm	2.53

Conclusions

Phasepure Cu,Zn,Al hydrotalcite was obtained with a high Cu content by a co-precipitation route. The best synthesis pH value was pH 8 yielding Cu based catalysts with a high surface area and small Cu particles.

Acknowledgements

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References

[1] F. Cavani, F. Trifiró, A. Vaccari, *Catal. Today* **11** (1991) 173.