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Ternary and quaternary Cr or Ga-containing ex-LDH catalysts—Influence of the additional oxides onto the microstructure and activity of $Cu/ZnAl_2O_4$ catalysts

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ABSTRACT

The stepwise substitution of Al by Cr and Ga leads to quaternary LDH precursors for Cu/ZnM_2O_4 (M = Al, Ga, Cr) catalysts. With the substitution of Al by Cr the interaction of the Cu phase with the oxide matrix is gradually weakened, which is caused by the participation of the chromium oxide phase in the redox processes during catalyst preparation. Such reactive Cr oxide matrix is less efficient than the inert Al oxide matrix in stabilizing the special microstructure of Cu/ZnM_2O_4 catalysts. These weakened interactions led to a lowering of the Cu particle embedment, coinciding with a pronounced Cu crystallite growth during reduction. Both effects partially compensate each other and a maximum in Cu surface area is observed for intermediate Cr contents. In the Ga-substituted catalysts, two distinct Cu species were found for high Ga contents. This is attributed to the presence of partially crystalline spinel and the resulting different strength of interface interaction of the CuO phase with the crystalline and the amorphous oxide. After reduction Cu catalysts with similar average Cu particle sizes as well as Cu surface areas were obtained. In both sample series, the catalytic activity in methanol synthesis does not scale with the Cu surface area and the experiments show that a strong interaction to the oxide is necessary to gain stability and activity of the Cu phase. Al substitution thus confirms that interface interactions between Cu and the oxide seem to beneficially affect the activity of the Cu particles and the optimal catalyst requires a compromise of exposed surface and interface.

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1. Introduction

Besides ammonia and sulfuric acid, methanol belongs to the most important, industrially produced basic chemicals. It is considered as a potential substitute for traditional fuels, e.g. for the storage and generation of hydrogen for fuel cell applications [1,2]. Recently, around one-third of methanol is used in production of energy products [3]. For methanol production effective catalysts are necessary, which were investigated intensively over the last decades [3,4]. Nowadays, all catalysts used for the low-pressure methanol synthesis consist of copper and zinc oxide, and often alumina as stabilizing component [5,6]. Mostly empirical optimization has led to a preparation route for the widely used $Cu/ZnO/Al_2O_3$ catalysts based on co-precipitation, followed by calcination and reduction [7,8]. Cu,Zn,Al-hydrotalcite-like compounds (or layered double hydroxide–LDH) are a typical component of the precursor mixture of different hydroxycarbonates of the co-precipitation step in this synthesis [9,10]. Recently, Cu-based catalysts obtained from LDH precursors were investigated in CO_2 hydrogenation [11,12] as well as low temperature shift reactions [13] and methanol oxidation [14]. In a previous study [15] we presented a Cu-based catalyst with a high intrinsic activity in methanol synthesis obtained from Cu,Zn,Al LDH precursors. The hydrotalcite-like structure enables, furthermore, the insertion of a broad variety of cations, within a certain ionic size range and M(II)/M(III) ratio [16]. Thus, these materials can be seen as a precursor system representing a powerful basis to study the effect of different promoter species on the redox- and catalytic properties of the Cu/ZnO/X catalyst with the same Cu content and the same preparation history. Several multicomponent catalysts were described in literature, comprehensive overviews are given in [3,4].

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Among first catalysts applied for methanol synthesis was ZnO/Cr_2O_3 [17,18], which was replaced by the $Cu/ZnO/Al_2O_3$ catalyst in the 1960s. Besides, Chromium oxide was used in ternary Cu based catalysts in industry in the early 1970s, e.g. BASF (German Patent 2,116,949) [19]. In 1996 Saito et al. presented multi-component Cu/ZnO based catalysts using Cr_2O_3 as well as Ga_2O_3 as ternary component [20]. Furthermore, Ga_2O_3 was reported as catalyst promotor by Fujitani et al. [21] and Toyir et al. [22]. In addition, studies presented in literature [23–26] have already shown that it is possible to obtain LDH compounds with Cr and Ga as trivalent cation. Binary pure and well crystallized Cu,Cr LDH was prepared by Jiao et al. [25] with a molar ratio of 2:1. Venugopal et al. described ternary $Cu/Zn/Cr_2O_3$ catalysts with a constant Cu content of 50 mol% [23] as well as quaternary Cu,Zn,Al,Ga catalysts [26], which were used for dimethyl ether synthesis. Additionally, Nunan et al. [24] presented Cs-doped Cu,Zn,X (X = Cr, Ga) catalysts obtained from LDH. For X = Cr the catalyst was characterized by very poor crystallinity and small crystallites. On the other hand, the Cu,Zn,Ga catalyst showed similar properties like an analogous Cu,Zn,Al catalyst. Anyway, it has to be mentioned, that nowadays chromium has mostly academic interests, e.g. in CO oxidation studies [27] and is no longer used in industry due to its toxicity.

Al in its oxidic form is thought to be a multifunctional promoter, which is working as a separator as well as an important species on the interface to Cu [28,29]. Herein we present a systematic study, where Al is substituted stepwise by Cr and Ga to gain understanding of the functionality of Al within the LDH-system as well as the resulting catalysts and to introduce new properties into the system. The general composition was always Cu:Zn:(Al + M) = 50:17:33, in which Al was substituted in 5% steps. The Cu,Zn,Al LDH is the common origin of both the Cr- and Ga-sample series and was described in detail in our previous study [15].

2. Material and methods

The Cu,Zn,(Al),M-LDH precursors (M = Cr, Ga) were precipitated from a mixed $Cu^{2+}/Zn^{2+}/Al^{3+} + M^{3+}$ nitrate solution with an aqueous solution of NaOH (0.3 M) and Na_2CO_3 (0.045 M) as the precipitating agent (total metal concentration: 0.43 M with Cu:Zn:(Al + M) = 50:17:33). The reaction was carried out at a constant pH value (pH = 8 ± 0.7) at 25 °C–pH and temperature were controlled by the automated lab reactor system (Labmax from Mettler Toledo). After an ageing time of one hour the blue powder was isolated by filtration, washing and drying at 100 °C for 13 h. Afterwards the sample was calcined in air at 330 °C for 3 h (heating rate 2 K/min). Finally, the Cu based catalyst was obtained by reduction of the calcined sample in 5% H_2/Argon and a heating rate of 6 K/min. The reduction temperature was adjusted for each catalyst to 15 °C above T_{max} of the TPR profiles.

The precursor sample without Cr or Ga is labeled as CZA, accordingly the calcined sample is labeled as CZA-calc and the reduced one as CZA-red. The Cr or Ga containing samples (Al was substituted stepwise by Cr or Ga) are labeled as Cr*X* and Cr*X*-calc as well as Ga*X* and Ga*X*-calc, respectively, where *X* is the amount of Cr or Ga in at%.

Methanol synthesis employing the calcined samples was carried out in a fixed bed micro reactor with an inner diameter of 2 mm filled with 180 mg of the sieve fraction (100–200 μm. Prior to the activity measurements, the samples were activated by reduction in H_2. The samples were first treated for 12 h in a mixture of 5% H_2 in He at 200 °C using a heating rate of 0.3 K/min and then for 4 h in pure H_2 at 250 °C. Methanol synthesis was performed at total pressure of 60 bar. The synthesis gas was composed of 72% H_2, 10% CO, 4% CO_2 and balanced by He. Total flow was kept at 60 mL/min by mass flow controllers. Methanol synthesis activity was measured under steady state conditions after 65 h at 250 °C and 60 bar by on-line GC analysis (Varian MicroGC 4900) equipped with a TCD using a PPU column, a CO_x column, and a molsieve 5 Å column for separating polar products, such as water, methanol, CO_2 and CO. After a formation period of ca. 12 h, there is no major deactivation detectable in our experiments. Furthermore, no side products have been detected under these conditions, as the used syngas mixture contained CO_2 and CO the selectivity towards methanol is 100%. The methanol weight time yields (WTY) were calculated using the methanol concentration in the outlet gas and the uncertainty was estimated to 0.03 $g_{MeOH}\, g_{Cat}{}^{-1}\, h^{-1}$ on basis of reproduction experiments. The uncertainties of the relative WTYs (related to CZA-calc) as well as the intrinsic activities were calculated applying the rules for propagation of errors (Gauss).

All details for catalyst characterization as well as used materials can be found in the supplemenatary data information (SI, see Appendix A).

3. Results and discussion

3.1. Microstructure of Cr and Ga containing LDH precursor and calcined samples

For a detailed investigation of the effect of Cr and Ga on the Cu based catalysts, seven Cr containing and seven Ga containing samples were prepared and compared to the Cu,Zn,Al sample. The overall composition was Cu: Zn:(Al + M) = 50:17:33 (M = Cr, Ga), where Al was substituted in 5% steps. The XRF results in Table 1 (calcined samples measured) show that the composition is in good agreement with the nominal one used for preparing the starting solutions, especially regarding the herein interesting Cr and Ga contents. Unfortunately, in Cr20 the Cu content shows a quite high deviance from the nominal value. Furthermore, Cr33 still contains 1.6 at% Al possibly due to cross-contamination. But this small amount of Al is considered as only a minor influence on the catalyst behavior.

The structural investigation by XRD, presented in Fig. 1 indicates a hydrotalcite structure for all samples, showing a significant change of the pattern for Cr contents ≥15 at% and an increasing crystallinity with increasing Ga content. By incorporation of Cr or Ga into the hydrotalcite lattice an increased M–M distance is expected, as the ionic radius of Cr^{3+} (0.615 Å) and Ga^{3+} (0.62 Å) are larger than the one of Al^{3+} (0.535 Å) [30].

The analysis of the peak position of the (110) reflection of LDH, presented in Fig. 2, shows an increased *d*-spacing for increasing Ga content. As this lattice plane is perpendicular to the brucite-like layers, this result proves an incorporation of Ga into the LDH structure.

In agreement with observations described in literature [23,31] the crystallinity is decreasing with increasing Cr content. Therefore, a quantitative determination of the peak shift is not possible for the Cr series, but one can assume by visual comparison that the (1 1 0) reflection is shifted to lower angles or a larger *d*-spacing. Furthermore, as no other crystalline phase is observed the incorporation of Cr into the LDH structure is very likely, especially as Cr33 still shows the hydrotalcite structure.

The average lateral particle size of the LDH platelets, which was determined from SEM images (see SI Fig. S1 for exemplary images), is 60–69 nm for small Cr contents (≤10 at%) and decreasing to ≈40 nm for higher Cr contents (see Table 2). This observation explains the apparently lower crystallinity manifested in the broader reflections (XRD) for higher Cr contents. As presented in Table 2, the BET surface area for the Cr containing samples is significantly higher than for CZA and a maximum is found for Cr15.

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