Real Condition High Throughput Screening of $Cu/ZnO/Al_2O_3$ Catalysts for Methanol Synthesis

C. Baltes, S. Vukojević, F. Schüth

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

Abstract

Ternary $Cu/ZnO/Al_2O_3$ catalysts were systematically prepared via the co-precipitation route under strict control of parameters such as pH, precipitation temperature and calcination temperature. All catalysts were tested with respect to their methanol activity in a 49-fold multitubular high-throughput experimentation setup under conditions similar to the commercial methanol production route, using a syngas mixture of CO, CO_2 and H_2.

Statistically representative catalysts were chosen for more detailed structure and morphology analysis in order to study correlations between the catalyst "preparation history" and the methanol productivity.

The highest catalyst performance was observed for catalysts obtained in the pH range from 6 to 8 at 70 °C. XRD measurements allowed the "grouping" of catalysts based on their composition. It was found that a group of best-performance catalysts exhibited the characteristic XRD pattern of non-calcined Cu/Zn hydroxycarbonate residues, leading to the assumption that carbonate species in the final catalyst structure may enhance its productivity. Further investigations of these hydroxycarbonate containing catalysts gave more detailed insights into the dynamic aging process and its influence on the catalytic performance. Highest methanol activitiy was observed for catalysts aged between 20 and 60 minutes after an initial phase formation time. The optimum calcination temperature was found to be in the range from 250 to 300 °C. Under these conditions the resulting Cu/Zn/Al hydroxycarbonates remained stable.

Additionally, the syngas feed composition was varied under reaction conditions and correlated to catalytic activities. Highest methanol productivity over $Cu/ZnO/Al_2O_3$ catalysts was observed for the following gas concentrations; H_2: 50 – 60 %, CO: 30 – 40 % and CO_2: 5-10 % at 4.5 MPa and 245 °C.

Introduction

$Cu/ZnO/Al_2O_3$ catalysts are predominantly used in the industrial low-pressure methanol synthesis process starting from synthesis gas, a mixture of H_2, CO and CO_2.

So far, the best catalytic performance has been achieved over $Cu/ZnO/Al_2O_3$ catalysts prepared by the co-precipitation method using nitrates of Cu, Zn and Al and alkali hydroxycarbonates or alkali carbonates as basic precipitating agents. The resulting hydroxycarbonates are converted to metal oxides by subsequent calcination at ca. 300-500 °C. The final active catalyst is obtained by reduction of CuO to metallic Cu under diluted H_2 flow prior to feeding the synthesis gas mixture.[1,2,3] The role of metallic copper in the reaction mechanism has been discussed in literature highly controversial in the past 20 years. Today, it is widely accepted that metallic copper clusters are the active sites for the methanol synthesis reaction over Cu/ZnO based catalysts.[4,5] The main function attributed to the ZnO is the increasing of the Cu dispersion in the calcined sample thus providing a high number of active sites exposed to the reaction gases.[1] Studies on the phases in the precipitate of Cu/Zn hydroxycarbonates in combination with aging effects revealed that some precipitate phases seem to favour the dispersion of copper. For instance in aurichalcite $(Cu, Zn)_5(CO_3)_2(OH)_6$, Cu is atomically dispersed in a zinc hydroxycarbonate matrix, whereas in zincian-malachite $(Cu, Zn)_2(OH)_2CO_3$, Cu is atomically substituted by Zn in the typical malachite structure. Subsequent calcination leads to the formation of small CuO crystallites which are believed to be the ideal intermediates for obtaining the final reduced catalyst. Also dissolution of small amounts of Cu^{2+} ions in the ZnO framework is discussed as contribution to the high degree of copper dispersion[6]. The addition of M^{+3} ions, e. g. Al has been reported to increase the BET surface area and copper dispersion while inhibiting the sintering of Cu particles under on-stream conditions.[2,7,8] The nature and arrangement of carbonate residues in the calcined ternary $Cu/ZnO/Al_2O_3$ catalyst structure and their contribution to catalyst performance has so far not been studied in detail.

It is known from studies on Cu/ZnO hydroxycarbonate systems that the presence of residual carbonate in the calcined sample plays an important role, supposedly due to subsequent formation of a copper suboxide species and thus increasing the chemical activity of the catalysts.[9] One motivation for the ongoing research regarding the chemical and structural intensity of these precursors is the presumed conjunction with the activity of the final catalyst. The characteristics of the final catalyst are created in a multi-step procedure where each preparation step contributes separately to the catalyst properties. So far, there exist only few comparative studies on the effects of various synthesis procedures concerning the catalyst activity. Additionally, these studies often lack detailed information on reaction parameters and reveal contradictory statements.[10,11,8] Most studies of co-precipitated systems deal with the zinc-copper catalyst, assuming that effective investigation of the industrial catalyst system can only be successfully done upon a firm knowledge of the binary system.

As disputed as the nature of the active site is, as much controversy existed over the reaction mechanisms. While it was originally assumed that CO was the immediate precursor species for methanol formation,[12] there is by now strong evidence that the hydrogenation step starts from CO_2,[13,14,15,16,17] which is generated by the water gas shift reaction from CO. The CO_2 is then progressively hydrogenated to result in the formation of methanol, via adsorbed formate and methoxy species on the copper surface, with the rate determining step probably being the hydrogenation of the formate to methoxy species.

In the past 10 years, high throughput experimentation (HTE) has proven to be a reliable technology for the evaluation and development of solid catalysts.[18,19,20] Despite initial scepticism about the predictive power of catalytic data obtained by HTE, there is now a growing acceptance of HTE techniques within catalysis research. The main companies providing HTE services are *Avantium*, *hte AG* or *Symyx*, which nowadays maintain strategic collaborations with chemical and petrochemical companies. Also major chemical companies and academic groups have developed their own methods and tools, making HTE technology a basic tool in catalysis research.[21]

Methanol synthesis is an interesting example reaction for applying high throughput techniques, since it is a very time-consuming reaction. This is due to the need for high pressure conditions for satisfactorily high conversions and the carefully conducted activation and reduction process of the catalysts. Taking into account the industrial reduction and reactor start-up period, catalyst testing by conventional means may take few days. Our HTE parallel reaction setup allows us to operate as close as possible to single channel conventional catalyst testing while saving time by an initial *collective* catalyst pre-treatment.[22] The conditions applied during the activation and reaction period are very close to the industrial standard.

The objective of this study is the systematic investigation of structure/activity relationships of the ternary Cu/Zn/Al methanol synthesis catalyst by high throughput methods. The main focus is the study of different preparation parameters during the precursor formation process and their influence on the methanol productivity. A high number of catalysts are to be tested for their methanol activity by high throughput screening and interesting samples are to be analyzed in more detailed studies. In particular, selected catalysts and precursor materials are to be investigated with regard to phase and morphology changes which are induced by aging effects and calcination procedures.

Results and Discussion

1. Catalyst Screening

Two identical sets of catalysts (each containing 35 catalysts) were prepared by the co-precipitation method in the pH range 4.5 – 10 and precipitation temperature range 30 -70 ℃. All catalysts underwent controlled aging for 1 h in the mother liquor and were calcined under air atmosphere for 4h at 300 ℃. Amounts of 50 mg of each catalyst were used for the activity screening. The catalyst productivities of each set could be satisfactorily reproduced. The preparation-productivity relationship is presented in figure 1. The catalytic performance depends strongly on the precipitation conditions: Best productivities, even exceeding those of the commercial catalyst by 30 %, were obtained at neutral or even slightly acidic pH, namely pH 6 – 7. Materials with the best catalytic performance were obtained by precipitation at temperatures of about 70 ℃.

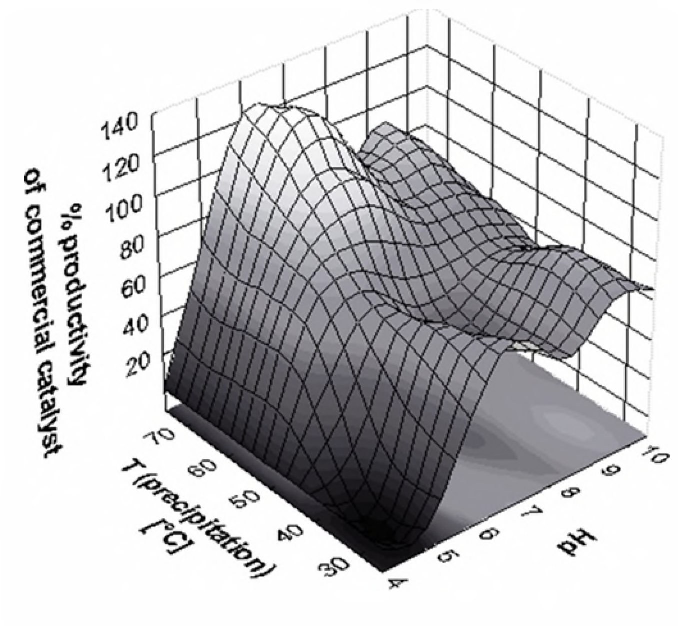

Figure 1: Precipitation conditions correlated to catalyst productivity

Generally, precipitation at temperatures higher than 50 ℃ leads to a strong increase in the catalysts' methanol productivity. Surprisingly, the productivity rises rapidly if pH is slightly increased from 4.5 to 5; this development can be observed especially at high precipitation temperatures. 20 catalysts of the first set, spread over the whole precipitation parameter range, were investigated by EDX analysis. The Cu/Zn/Al metal ratio for the precipitated as well as for the calcined catalysts corresponded to the metal ratio that was set for the starting precursor solutions. The compositon of the final catalyst appears to be independent of the preparation conditions, which is already known from studies of binary Cu/ZnO systems.

The Cu/Zn/Al metal ratio was found to be 60/30/10 mol % with deviations typically below 5 mol%. These results were in very good accordance with the composition intended for the final catalyst. All catalysts from the firstly prepared set were examined by XRD measurements. If an interesting XRD pattern was found for a catalyst, the catalyst was reproduced following the identical procedure and analyzed under the same conditions in order to validate the results.

Figure 2 depicts the two-dimensional preparation/activity plot, assigning square-shaped fields to the prepared and examined catalysts from the full range of preparation conditions. Generally, the catalysts can be grouped into three clusters with regard to their XRD signature. Some representative catalysts from each cluster are encoded by numbers. Their XRD patterns are given in figure 3. Catalysts produced at acidic conditions (pH 4.5 and 5 at 30 and 40 ℃) reveal in their XRD patterns defined reflections that can be assigned to big crystallites of CuO. Additionally, characteristic reflections for ZnO could be found. Al_2O_3 as a separate phase was not observed. These catalysts, which are marked as white-lined cluster in figure 2, exhibited very low catalytic performance in the range between 0 and 5 % compared to the benchmark methanol catalyst. Cat_6 is a representative sample for that cluster of catalysts. A second cluster comprises catalysts Cat_1-Cat_4, precipitated at 70 ℃ and at a pH range between 6 and 9, and Cat_5, obtained at 60 ℃ and pH 7. All catalysts from that cluster are framed by full black lines (cluster 1, figure 2). As depicted in figure 3, catalysts from cluster 1 exhibited XRD patterns typical for copper or copper/zinc hydroxycarbonates. The phases identified were malachite and zincian-malachite (rosasite, $(Cu, Zn)_2(OH)_2CO_3$).

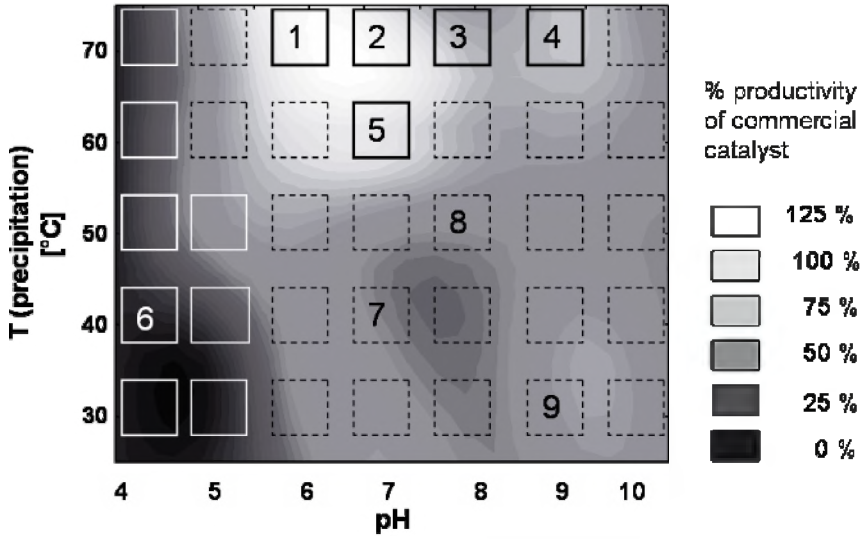

Figure 1: Productivity/preparation mapping of the tested catalyst set, clustering of catalysts based on their XRD signature: cluster 1 (full black line) including catalysts Cat$_1$-Cat$_5$, Cat$_6$ given as examples for cluster 2 (white line), cluster 3 (dashed black lines) represented by catalyst samples Cat$_7$-Cat$_9$

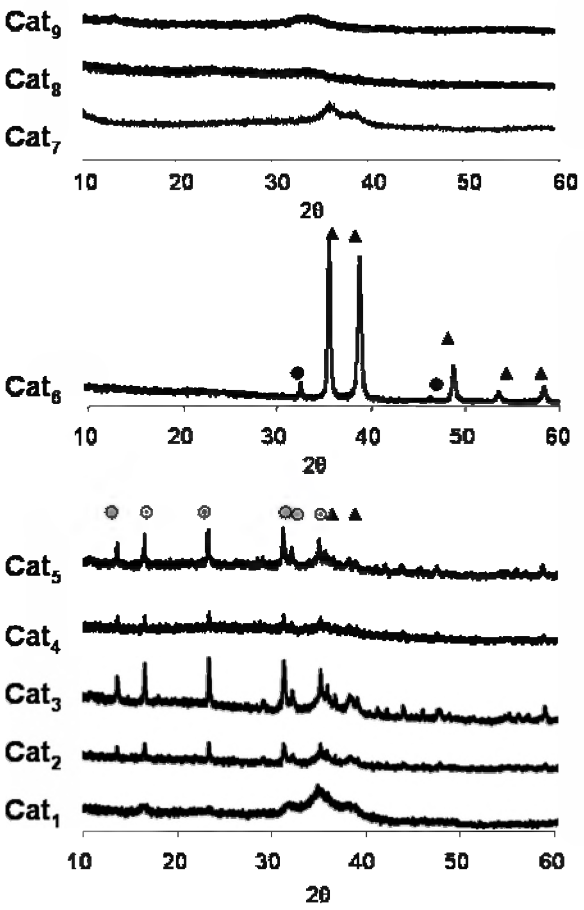

Figure 3: ***XRD patterns of few selected calcined catalysts (•: ZnO; ▲: CuO; •: Cu/Zn-malachite, (Cu,Zn)2(OH)2CO3)***

The main reflections and intensities correspond to the pure and mixed malachite type. These hydroxycarbonate phases are probably residues originating from the precipitated precursor material which had not been fully decomposed during calcination. These findings correspond to literature reports describing rosasite and malachite as favoured precipitation phases for a Cu amount higher than 50 mol%.[7]

As illustrated in figure 2, there is a clear correlation between samples containing hydroxycarbonate residues after calcination (cluster 1) and high methanol activity. Most of the catalysts which have reached 100 % or more of the benchmark catalyst productivity contained non-decomposed residues of the malachite phase.

The presence of this phase after calcination seems to enhance the catalytic properties of the Cu/ZnO/Al$_2$O$_3$ mixed-oxide material. The residual carbonates may be responsible for the formation of highly active sites. As reported by many authors, the calcination of mixed Cu/Zn hydroxycarbonate or hydrotalcite-like phases leads to formation of smaller CuO and ZnO crystals than those derived from single phases like "pure" malachite. On the other hand, the nature and arrangement of the CO$_3^{2-}$ units remaining in the mixed oxide have not been examined in detail in the literature so far.[23] Catalyst samples Cat$_1$-Cat$_5$ also exhibited the characteristic reflections for CuO in the XRD profiles. The XRD signals were very broad, indicating an ill-defined crystalline phase, probably overlapping with broad ZnO reflections.

For catalysts obtained at other precipitation conditions either broad peaks for CuO were found in the XRD profiles or the samples were completely X-ray amorphous. Some representative XRD patterns assigned for Cat_7, Cat_8 and Cat_9 are depicted in figure 3.

The broad reflections and the low signal intensity are a strong indication that a substantial fraction of the samples precipitated at neutral and basic conditions at temperatures between 30 and 60 ℃ was X-ray amorphous.

2. TEM studies

TEM photographs from figure 4 are illustrating the changes in catalyst morphology during the preparation procedure. Cat_2 (figure 2) was chosen for a more detailed study, since it exhibited the highest catalytic activity.

The 1h aged catalyst precursor mainly comprised large clusters of needles as can be seen in figure 4*a*. Besides that, agglomerates of snowflake-shaped small crystals and platelets were found as minor components. These findings are consistent with the results of Whittle and coworkers[24] who studied the precursor morphology development under aging conditions. They reported about the formation of the needle-like structures after aging of 1 h starting from irregularly-shaped grains.

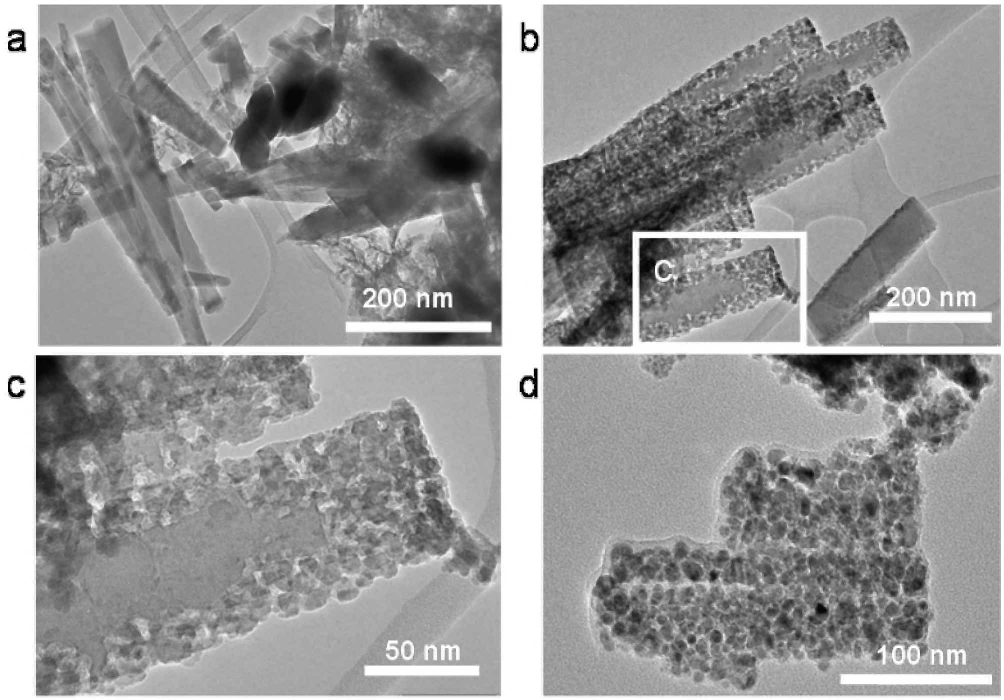

Figure 4: Catalyst morphology in dependence on the preparation conditions (a: catalyst precursor after aging of 1h, b: catalyst after 4 h calcination at 300 ℃, c: enlarged picture of the crystallite in picture b, d: catalyst after reduction prior to reaction)

The needle-shaped crystallites undergo a structural change during the calcination period at 300 ℃: Figure 4b shows the formation of small particles at the edges of the needle shaped crystallites, which is probably due to successive fragmentation of the precursor phase. The particle size was found to be around 10 nm. The composition of the particles was analyzed by EDX measurements, resulting in a Cu/Zn ratio of 4:1. A tiny but constant amount of Al (2 atom%) was also determined. The area highlighted by a white frame in figure 4b is enlarged in figure 4c, providing a more detailed view on the particle-bulk interface.

Figure 4d gives insight into the catalyst's morphology after reduction under H_2 atmosphere following the typical benchmark catalysts reduction procedure. The reduction was performed in a fixed-bed reactor and the sample then transferred under inert gas atmosphere to an argon filled glove-box. The sample was placed onto a lacey carbon coated Ni grid and transported by an air-protected transfer holder to the TEM instrument. The fragmentation observed for the reduced sample seems to be an ongoing process, which could be explained either by the thermal treatment of the sample (250 °C for 5h), the reducing conditions or combined effects.

From figure 4c it is clear that fragmentation and the formation of particles take place without changing the needle shape of the crystallites. Similar results were found for the reduced sample; however the degree of fragmentation was higher than in other samples (figure 4d). The particle size did not change during the reduction procedure.

Results from EDX analysis revealed that the oxygen amount was below the expected amount for oxidized Cu species. This was leading to the assumption that the particles mainly comprised reduced or zero-valent Cu. The composition of particles did not change during the reduction treatment. The copper particles appeared to be closely connected to the ZnO particles creating a high degree of interfacial contact. This kind of particle interaction enhanced drastically the catalytic performance of the studied samples. These observations are in good accordance with results found by Schlögl et al. who also studied the strong Cu/Zn interaction and its correlation with the catalytic activity.[25]

3. Reaction conditions

The influence of the syngas composition on the catalytic activity was studied using the high-throughput setup. The CO/CO_2 ratio in the syngas mixture is still a matter of discussion due to its importance for mechanistic studies and catalyst morphology effects. Our goal was finding the best operation conditions for the synthesized $Cu/ZnO/Al_2O_3$ catalysts. The tests were carried out for few selected catalysts at 4.5 and 3.5 MPa reaction pressure and at 245 °C reaction temperature. The feed gas flow was changed automatically every 2 hours, allowing the system to reach stable gas flow conditions before collecting catalytic data. The corresponding measurements for each gas composition are graphically shown in figure 5. Cat_2 was chosen for the case study. The data points in figure 5 were measured within the composition area given by a $H_2/(CO+CO_2)$ ratio from 1:3 up to 4:1. In general, for all $H_2/(CO+CO_2)$ ratios which were chosen, a detectable catalyst productivity was observed. Methanol was formed from only H_2/CO as well as from H_2/CO_2. It was found that the presence of CO is more crucial for the methanol formation than the presence of only CO_2. Nevertheless, CO_2 as an "additive" in the syngas feed was enhancing the catalytic activity. The data points were fitted by a special cubic operation, creating a full-area plot. According to the plot, the best reaction conditions for the $Cu/ZnO/Al_2O_3$ catalysts made by co-precipitation method were found for a feed gas composition in the range 50 – 70 % for H_2,, 25 – 40 % for CO and 5-20 % for CO_2.

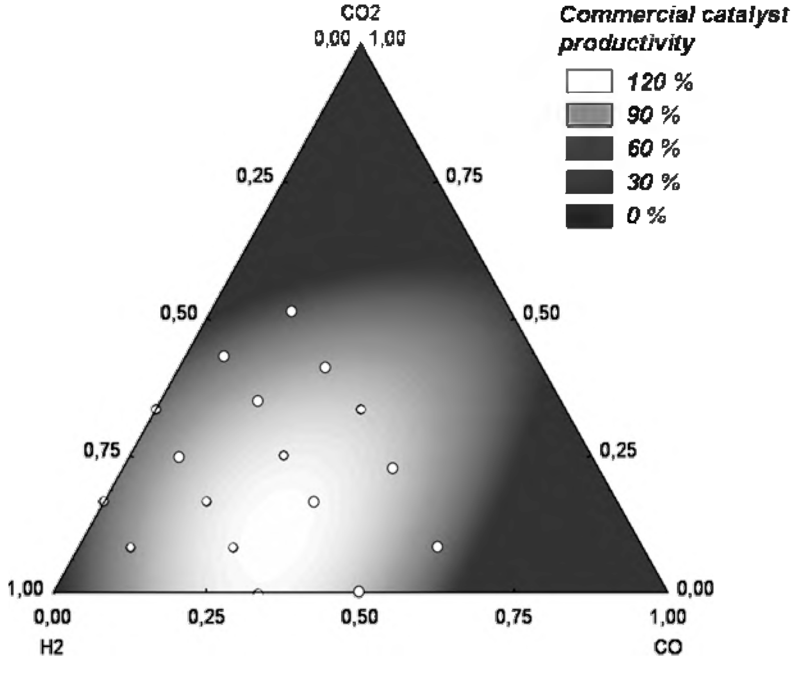

Figure 5: Productivity of a $Cu/Zn/Al_2O_3$ catalyst and its dependence on the syngas feed composition at 245 °C and 45 bar; white dots are representing measured data points

Furthermore, the methanol productivity maximum in the ternary gas feed plot was close to the H_2/CO mixture, slightly shifted towards low CO_2 feed fractions.

4. Experimental

Ternary $CuO/ZnO/Al_2O_3$ catalysts were prepared by co-precipitation analogous to the co-precipitation procedure described by Kiener et al.[22] A solution of metal nitrates ($Cu(NO_3)_2$ (0.6 mol/L), $Zn(NO_3)_2$ (0.3 mol/L), $Al(NO_3)_3$ (0,1 mol/L)) and a solution of Na_2CO_3 (1 mol/L) as precipitant were pumped (constant flow rate: 5 ml/min) into a stirred and heated glass reactor with a starting volume of 200 ml demineralised water. During the precipitation process pH, temperature and aging time were controlled. While the metal nitrate solution was pumped continuously, the sodium carbonate solution was added in order to keep a constant pH (+/- 0.1 unit), controlled by a WTW 296 pH meter. The pH was kept constant also during the aging process by controlled addition of metal nitrate or sodium carbonate solution. After aging for 1 h, the precipitates were filtered and washed three times with each 150 mL of demineralised water and subsequently dried over night at 80 ℃. After grinding, an amount of 200 – 500 mg of the dried precursors was calcined at 300 ℃ under air for 3 h (heating ramp: 2 ℃/min).

Catalytic measurements were performed in a high-throughput 49-parallel channel reactor described elsewhere.[22] The samples (ca. 50 mg diluted with 200 mg quartz per well) were placed in a sample holder consisting of a stainless steel cartridge closed at the bottom by a stainless-steel sinter metal frit. Prior to the catalytic measurements the catalysts were reduced with a 5% H_2/N_2 mixture at 245 ℃ following the procedure for the commercial benchmark catalyst ICI Katalco 51-8. Before measuring the catalytic activity, all samples were equilibrated for 3 h (reaction pressure 4.5 MPa, reaction temperature 245 ℃, analytic flow 20 ml/min). For the standard conditions, the reaction gas consisted of 70 vol% H_2, 24 vol% CO, and 6 vol% CO_2. A double GC system (HP GC 6890) was used for online gas analysis. Within 6 minutes a full analysis of low molecular mass carbon compounds was completed. Methanol productivities for all measured samples were compared to the productivity of the industrial benchmark catalyst ICI Katalco 51-8 (P_{ICI}=40 mol MeOH/ (kg cat h) at 245 ℃ and 4.5 MPa).

5. Summary and Conclusions

The correlations presented here indicate that crystallinity and phase composition of the resulting precipitate have a strong influence on the microstructural properties of the final copper catalyst. Furthermore it was found that thermal treatment and aging processes governed the catalytic properties.

The highest methanol productivity was observed for catalysts which exhibited the following "preparation history":

- 70 ℃ precipitation temperature, pH 6-8,
- aging time between 20 and 60 minutes,
- calcination at 300℃

The metal composition in the final catalyst was set by the composition of the metal source solutions. By doing so, it was possible to obtain catalysts with the preferred metal ratio of Cu/Zn/Al 60/30/10.

The most active catalysts contained malachite-type residues from the initial hydroxycarbonate precipitate. The presence of hydroxycarbonate phases distinctly enhanced the catalytic properties of the final $CuO/ZnO/Al_2O_3$ catalysts. Residual hydroxycarbonates presumably facilitate the formation of highly active sites, which is also known from studies on Cu/Zn hydroxycarbonates.[26] During the reduction of the catalyst the Cu/Zn malachite residues in the calcined catalyst structure presumably favors the formation of CuO crystallites and Cu nano particles which are smaller than particles derived from pure Cu phases such as CuO. Furthermore, we believe that the interfacial contact between Cu^0 and ZnO, which is known to be the key factor governing the catalytic activity, becomes more "intimate" after calcination and probably also after the reduction process. Both, the mixed Cu/Zn oxides and afterwards the Cu/ZnO phase were derived from Zn/Cu malachite. The structure of this phase allowes both metals to develop greater interaction than in pure phases. The high catalytic activity was observed if that kind of interaction state was preserved until the final activated catalyst stage. Furthermore we found that the presence of carbonate residues presumably delays the fragmentation of the material before the reduction of the copper species begins, resulting in formation of smaller and more interacting particles. This was also confirmed by TEM investigations: TEM-pictographs revealed that copper particles of 10 nm size were closely connected to a ZnO matrix. We believe that the residual hydroxycarbonates also facilitate the catalyst activation procedure allowing a much "gentler" reduction process. The ongoing decomposition of the carbonates leads to a release of CO_2, which could modify the reductive power of the gases during the activation process.

The hydroxycarbonate precursor was presumably partially calcined during the catalyst reduction period. Productivities measured for the non-calcined samples were close to the productivities measured for pre-calcined catalysts. We believe that a partially performed calcination was positively affecting the catalytic performance, giving rise to the assumption that the best results were obtained if CO_3^{2-} species were interdispersed within a pre-formed CuO/ZnO matrix. Calcination temperatures higher than 300 ℃ resulted in formation of pure CuO phases. The "mild" carbonate decomposition as a one-step reaction which facilitates the reduction process was inhibited at higher calcination temperatures.

The best reaction conditions for the co-precipitation-derived $Cu/ZnO/Al_2O_3$ catalysts were found at a syngas mixture of H_2: 50 – 60 %, CO: 30 – 40 % and CO_2: 5-10 %. The CO_2 in the reaction gas feed was found to act as an "additive" enhancing the catalytic performance. CO_2 can act as carbon source for the methanol molecules and can be additionally generated by the watergas shift reaction.[27] On the other hand it can function as a Cu-surface activating agent. In general, methanol productivity benefits from synergetic effects when CO/CO_2 mixtures are used for the hydrogenation.

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