



Continuous precipitation of Cu/ZnO/Al₂O₃ catalysts for methanol synthesis in microstructured reactors with alternative precipitating agents

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ABSTRACT

Ternary Cu/ZnO/Al₂O₃ catalyst systems were systematically prepared by innovative synthesis routes in microstructured synthesis setups, allowing to study different types of micromixers. The coprecipitation in the slit plate and valve-assisted mixers was operated continuously under exact control of pH, temperature, concentration and ageing time. Due to the enhanced surface to volume ratio in microstructured reactors, a precise temperature control and efficient mixing of the reactants are enabled. The precipitation was performed with sodium, ammonium and potassium carbonate as well as sodium hydroxide. To evaluate the potential of the novel synthesis routes, reference samples in a conventional batch process were prepared. The catalysts were synthesized according to the *constant pH method* with a molar ratio of 60:30:10 for copper, zinc and aluminum. The synthesis routes applied have a significant influence on the structures of hydroxycarbonate precursors and on the catalytic activity in methanol synthesis. XRD patterns of hydroxycarbonate precursors from the synthesis in micromixers, especially using ammonium carbonate as precipitating agent, display high crystallinity and sharp reflections of malachite and rosasite. Cu/ZnO/Al₂O₃ catalysts prepared in continuously operated micromixers in general show higher specific copper surface areas than catalysts prepared in conventional batch processes. The highest methanol productivity of all prepared catalyst systems was observed with the catalyst precipitated in the slit plate mixer with ammonium carbonate.

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1. Introduction

The ternary Cu/ZnO/Al₂O₃ catalyst system is industrially employed in low-pressure methanol synthesis from a CO/CO₂/H₂-containing synthesis gas. The adding of Al₂O₃ to the previously used binary Cu/ZnO system leads to a remarkable increase in catalyst activity and, in particular, stability. Al₂O₃ is believed to inhibit thermal sintering of copper particles [1–3]. Crystal phase structures of the ternary hydroxycarbonate precursors such as malachite, rosasite and aurichalcite strongly affect the activity of the calcined catalyst [4–8]. The complex ternary catalyst system is believed to be subject to a so called ‘chemical memory’. That means that calcined precursors which show similar structures have different activities in methanol synthesis, depending on the crystal phase structures of the preceding hydroxycarbonate precursors [9–12]. Thus, precipitation parameters are crucial for the activity of the later catalyst. Conventionally, catalyst synthesis is performed by batch precipitation with aqueous solutions of metal nitrates and sodium

carbonate. Formed hydroxycarbonate precursors are subsequently calcined at 573–773 K and mixed metal oxides are produced. Mild reduction of CuO to Cu⁰ in diluted H₂ prior to reaction, results in the active catalyst species. In industrial batch catalyst production, it is challenging to control the synthesis parameters during precipitation, however a considerable number of studies proved the crucial influence of pH value [13,14], temperature [13,15], ageing conditions [10,16] and additionally temperature and concentration gradients [10] on precursor structures and thus later on the catalytic activity. Depending on each synthesis parameter, the resulting hydroxycarbonate precursors show varying properties, particularly in crystal size and structure and hence in optical, electronic and particularly catalytic properties. Therefore, the exact control of process parameters during the synthesis of catalysts is decisive for the catalytic activity and stability.

With respect to the control of process parameters, microreaction engineering offers significant advantages. Thus, huge developments and clear progress have been made over the last few years. Because of their outstanding characteristics in heat and mass transfer and high degree of automation, microstructured reactors provide a promising alternative to common batch synthesis routes. Micromixers are already widely used in pharmacy, biotechnology and production of fine chemicals [17–19]. Especially their

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superior heat transfer properties are applied in highly exothermic reactions, such as the fluoridation of organic compounds using elemental fluorine [20], to give a prominent example. Besides gas phase and liquid phase reactions, first attempts in the application of micromixers in synthesis of solid particles have been made. Schur et al. [21] performed principle experiments on the binary Cu/ZnO system. They showed that catalysts, synthesized in continuously operated micromixers, can even provide superior properties compared to batch synthesis routes. In solid particle synthesis, low temperature and concentration gradients are determining for catalyst structure and thus for catalytic activity. Recently, Kaluza and Muhler [22,23] showed that a continuous precipitation method using a micromixer is a powerful tool to investigate precipitation reactions, also in combination with the subsequent steps such as ageing and spray drying [24].

Besides the Cu/ZnO system, only few solid phase syntheses have been performed in microstructured continuously operated systems with respect to catalyst manufacturing and formulation. Commercially available micromixers, for example from *Ehrfeld Microtechnik BTS*, use a multi lamination principle, which is based on the splitting of the reactants into thin liquid layers, which are successively recombined in layers. Splitting into layers is achieved by fine slits in the central microstructure. An aperture plate realizes the downstream in the mixer comb and is attached vertically to the slit plate in the central microstructure. For solid particle synthesis an additional back pressure valve, located before the mixing zone, prevents back streaming of the reactants and thus a blockage of the microstructures.

Process parameters such as temperature or pH value as well as the choice of the precipitation agent itself can have an enormous influence on structural and catalytic properties of the final catalyst. Commercially, sodium carbonate is used to precipitate the metal nitrates, however residual sodium is known to poison the catalyst and to enhance sintering of the metallic particles in methanol synthesis. It is proposed that a high sodium content leads to a lowering of the metal-support interaction of copper and ZnO [25,26], thus promoting deactivation. Moreover, sodium in hydroxycarbonate precursors causes more pronounced growth of ZnO particles during calcination and reduction, decreasing the catalytically active copper surface [27]. Studies using alternative precipitation agents such as ammonium carbonate, potassium carbonate or sodium hydroxide can provide deeper insight into deactivation processes and activity–structure relationship.

The purpose of this study is to evaluate the feasibility of microstructured continuously operated synthesis routes for the precipitation of ternary Cu/ZnO/Al₂O₃ precursors and to compare their activity in methanol synthesis to both an industrial reference catalyst and batch synthesis routes. Varying the precipitation agent provides information on catalyst poisoning and especially on the formation of materials with high surface areas of the active component. Application of various synthesis conditions with varying pH values and ageing periods gives insight into the processes during solid particle synthesis in micromixers.

2. Experimental

2.1. Sample preparation

Ternary Cu/ZnO/Al₂O₃ catalyst systems were prepared in microstructured mixers by coprecipitation of a solution of metal nitrates and an alkaline solution analogous to the coprecipitation method described by various research groups [10,13,14]. The precipitation was performed with sodium, ammonium and potassium carbonate as well as sodium hydroxide. 300 mL of a solution of copper, zinc and aluminum nitrates (0.15 mol/L) with a molar ratio of

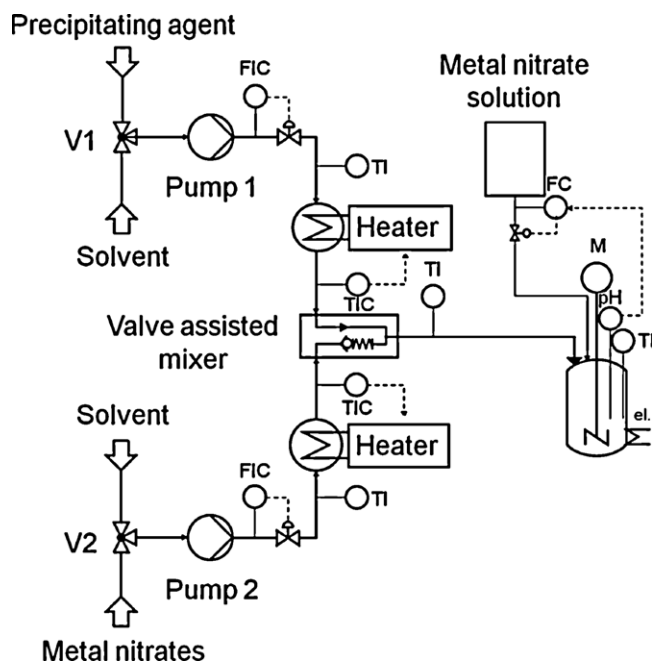


Fig. 1. Schematic drawing of piping and instrumentation of the precipitation set-up with the valve-assisted mixer.

60:30:10 for Cu:Zn:Al and 300 mL of a precipitating agent solution (0.18 mol/L) were pumped (HPLC pump, Smartline Pump 100, Fa. Knauer) into the microstructured reaction setups (Fig. 1) with a constant flow rate of 35 mL/min. The solutions were preheated at 338 K, whereas ammonium carbonate was kept at 303 K to prevent thermal decomposition. Before entering the mixing chamber, further heating to 338 K took place in two heating modules, followed by the precipitation reaction in the micromixers. The produced precipitates were collected in a stirred and heated glass tank reactor with a starting volume of 400 mL demineralized water. The process in either the slit plate mixer or the valve-assisted mixer was operated continuously under exact control of pH value (pH 6 and pH 7), temperature (338 K), concentration and ageing time (0 h, 1 h, 2 h). During the precipitation and the ageing process the solution of metal nitrates was added drop wise to the slurry to maintain a constant pH (± 0.05 unit), controlled by an automatic titrator (DMS-Titrino 716, Metrohm AG, dosing volume is about 10 mL). The total amount of the solution added for pH maintenance was below 1% compared to the amount of solution fed to the micromixer. After ageing, the precipitates were recovered by filtration under vacuum and washed three times with 400 mL ultra pure water each and then dried in air at 383 K for 20 h. The calcination of the milled hydroxycarbonate precursors was performed at 623 K for 4 h (heated up at a rate of 5 K/min) under synthetic air (20% O₂/80% N₂) with a flow rate of 100 mL/min. Moreover, ternary Cu/ZnO/Al₂O₃ catalysts were prepared in a conventional batch process as reported elsewhere [10,13] under the same reaction conditions and used as reference material.

2.2. Characterization

The catalyst samples were characterized by inductively coupled plasma optical emission spectrometry (ICP-OES), elemental analysis, X-ray diffraction (XRD), nitrogen physisorption measurements, transmission electron microscopy (TEM) and thermal analysis (TG/DTG). The metal contents of the calcined precursors were determined by ICP-OES, carried out on a SpectroFlame type FTMOA81A (Spectro Analytical Instruments). Trace element analysis of sodium and potassium in the calcined precursors was

performed on a Varian AA280FS Fast Sequential Atomic Absorption Spectrometer. The elemental analysis of carbon, hydrogen and nitrogen in the calcined precursors was performed on a vario EL CHNOS element analyzer. XRD patterns of the hydroxycarbonate precursors and the calcined precursors were performed on a Phillips XiPERT (type 3040/60 MPD Pro DY 1467) diffractometer with Cu K α radiation (1.54056 Å) operating at 45 kV and 40 mA. The XRD patterns were recorded in the range of 3.9–71.0° (2 θ). Nitrogen physisorption measurements were realized in a NOVA 4000e Surface Area & Pore Size Analyzer (Quantachrome Instruments). Before analysis, all samples were activated under vacuum at 523 K for 2 h. The 10 points nitrogen adsorption measurements were recorded at 78 K. The BET surface area was calculated from the adsorption data in the relative pressure interval from 0.05 to 0.3. TEM images were taken with a JEOL JEM 100CX transmission electron microscope operated at 100 kV, equipped with a tungsten cathode. The samples were dispersed ultrasonically in ethanol and then deposited onto a continuous carbon film supported on a copper mesh grid. The images were processed with ImageJ image processing software to obtain the particle size distribution of the samples. In general, 100 particles per sample were counted. Thermogravimetric analyses (TG/DTG) were carried out in a STA 409C Netzsch thermobalance coupled to a Pfeiffer Vacuum OmniStar GSD 301 O quadrupole mass spectrometer for quantitative data monitoring. Measurements were performed with approximately 60 mg of the samples in open Al₂O₃ crucibles in argon flow (50 mL/min) with a heating rate of 5 K/min from 298 to 1073 K.

2.3. Specific copper surface area and catalytic measurements

The specific copper surface area and the catalytic activity measurements were carried out in a single-pass fixed-bed reactor hosted in a flow setup equivalent to that described in references [28,29]. The following gases and mixtures (purities) were used: He (99.9999%), H₂ (99.9999%), CO (99.999%), CO₂ (99.997%), H₂/He (2.2% H₂, 99.9999%), CO₂/He (6% CO₂ 99.9995%), MeOH/He (2941 ppm MeOH), N₂O/He (1% N₂O, 99.999%) and a mixture of 59.5% H₂, 8% CO₂, 6% CO and 1.5% Ar in residual He used as feed gas/synthesis gas for methanol synthesis. The analysis of the product gas mixture was performed by a calibrated quadrupole mass spectrometer (Pfeiffer Vacuum OmniStar GSD 301 O). 200 mg of the 250–355 μ m sieve fraction of the samples were filled into the reactor and secured with quartz wool. The tubular reactor is a glass lined U-tube (GLT) with an inner diameter of 4 mm, which results in a bed height of the catalyst of about 24 mm. The catalyst samples were reduced in two steps under mild conditions to prevent the copper particles from sintering [30–32]. In the first step the samples were treated with a flow of 10 N mL/min of a H₂/He mixture at 448 K for 15 h, applying a heating rate of 1 K/min. To ensure full reduction, the catalyst is treated in a pure flow of H₂ for 100 min at 513 K. The reduction of the catalyst is followed by purging the samples with He for 30 min to remove any impurities.

The specific copper surface area of the Cu/ZnO/Al₂O₃ catalyst was measured, using reactive frontal chromatography with nitrous oxide (N₂O RFC). In general, the N₂O RFC measurement was performed corresponding to the method introduced by Chinchén et al. [33] under slightly more moderate reaction conditions [34]. At the end of the N₂O RFC the gas flow is switched to He for 30 min in order to flush the catalyst bed. Then, the catalyst was heated to 483 K with a heating rate of 1 K/min in a flow of 78 N mL/min synthesis gas. In a typical run, methanol synthesis measurements were performed under steady-state conditions at 0.5 MPa and 1 MPa for 6 h. The Cu surface area was measured for freshly reduced and used samples.

An industrial benchmark catalyst, which is produced batchwise, was used as reference material. The catalytic activity and the copper surface area of all measured samples were compared to this

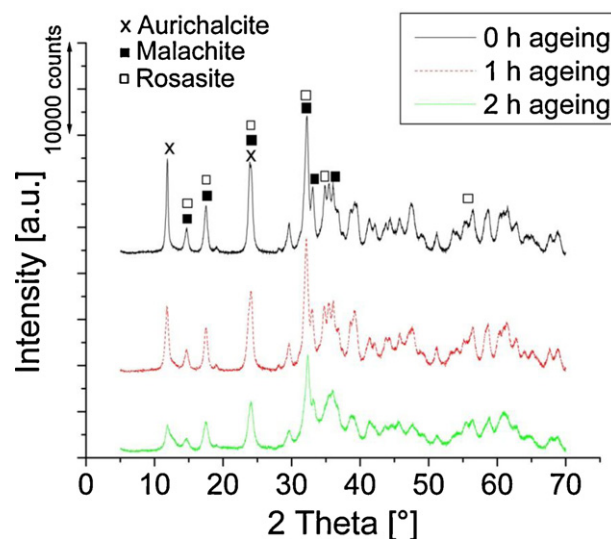


Fig. 2. XRD patterns of hydroxycarbonate precursors prepared with K₂CO₃ with the slit plate mixer at pH value of 6.

catalyst. The benchmark catalyst achieved a specific copper surface area $S_{Cu} = 22.4 \text{ m}^2/\text{g}_{cat}$ before and $S_{Cu} = 21.6 \text{ m}^2/\text{g}_{cat}$ after standard test conditions. The methanol productivity of the benchmark catalyst at 483 K was determined to $P_{MeOH} = 5.5 \text{ mmol}_{MeOH}/(\text{g}_{cat} \text{ s})$ at 0.5 MPa and $P_{MeOH} = 12.5 \text{ mmol}_{MeOH}/(\text{g}_{cat} \text{ s})$ at 1 MPa.

3. Results and discussion

3.1. Characterization of hydroxycarbonate precursors

The phase composition of the precursors was qualitatively investigated by powder diffraction. XRD patterns of hydroxycarbonate precursors prepared in the synthesis route using a slit plate mixer with K₂CO₃ as precipitating agent are illustrated in Fig. 2. Ageing duration leads to negligible crystalline improvements in precursors. Reflections representing malachite (Cu₂(OH)₂CO₃) or rosasite ((Cu;Zn)₂(OH)₂CO₃) in the non-aged precursor are even sharper than those in aged precursors. In the production of non-aged precursors, water could not be fully quenched from the system and the following drying step at 383 K may have promoted further ageing of the wet precursors at even higher temperatures. On the other hand, precursors aged for 1 or 2 h show similar diffractograms. This evidence is supported by the results of Bems et al. [10] who also found that the crystal growth ended after 30 min ageing. Moreover, the aurichalcite phase ((Cu;Zn)₅(OH)₆(CO₃)₂), represented by reflections at 2 $\theta = 13^\circ$ and 24° , is less observed in precursors aged for at least 1 h, while the malachite and rosasite bands retain most of their intensity. This finding is in accordance with the studies of Waller et al. [35], who proposed the dissolution of aurichalcite during ageing in mother liquor.

Fig. 3 displays the XRD patterns of hydroxycarbonate precursors prepared with Na₂CO₃ in various synthesis routes performed. Precursors generated with micromixers exhibit bolder copper zinc hydroxycarbonate phases, especially aurichalcite, malachite and rosasite along with a less amorphous structure. These effects are observed particularly in precursors prepared with the slit plate mixer based on its split and recombine principle, enabling a high degree of micromixing. These trends are observed in all precursors prepared with the micromixers, regardless of the precipitating agent applied. Small aurichalcite reflections at characteristic angles 2 $\theta = 13^\circ$ and 24° are observed in precursors prepared with the slit plate mixer with Na₂CO₃ and (NH₄)₂CO₃ as precipitating agents. Since the restructuring processes, including the dissolution of

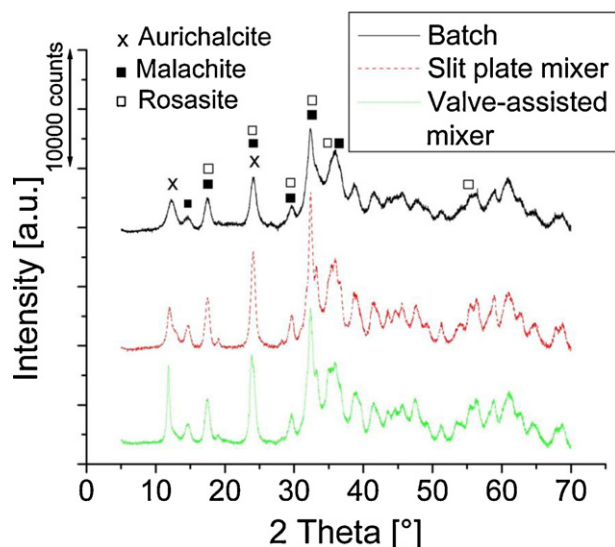


Fig. 3. XRD patterns of hydroxycarbonate precursors prepared with Na_2CO_3 at a pH value of 6, aged for 2 h.

aurichalcite phases, take place mainly during the ageing process, slightly lower aurichalcite bands in all precursors precipitated with the slit plate mixer cannot be directly correlated with the micromixing effects during the coprecipitation in the mixer, but rather with ageing processes in the mother liquor.

The effect of the precipitating agent applied regarding crystallinity and exposing of phases in hydroxycarbonate precursors is illustrated in Figs. 4 and 5. Synthesis with $(\text{NH}_4)_2\text{CO}_3$ generates precursors with high crystallinity and distinctive reflections (Fig. 4). Furthermore, the sample prepared with $(\text{NH}_4)_2\text{CO}_3$ displays intense reflections of both highly active phases malachite and rosasite as well as slight reflections of the less active aurichalcite phase. The precipitation with Na_2CO_3 results in precursors displaying reflections of aurichalcite at $2\theta = 13^\circ$ and 24° more intensely compared to reflections of malachite at $2\theta = 32^\circ$ and rosasite at $2\theta = 34\text{--}38^\circ$ and 55° . In general, $(\text{NH}_4)_2\text{CO}_3$ produces catalysts with the least amorphous structures and high malachite and rosasite contents (Fig. 5). On the other hand, both K_2CO_3 and Na_2CO_3 generate catalysts with similar crystallinity, independent of the synthesis route applied in precipitation reaction. However, K_2CO_3

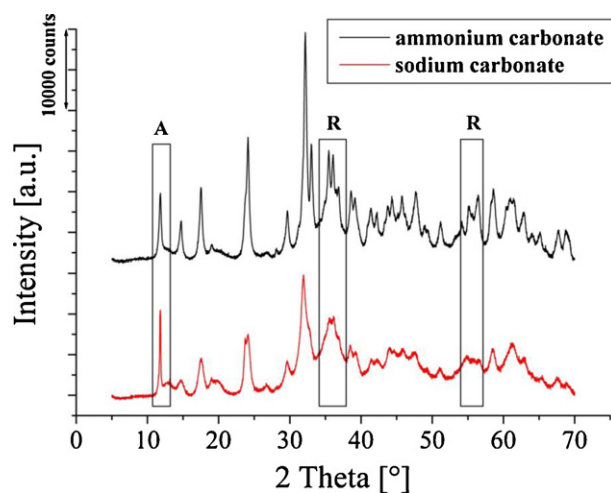


Fig. 4. XRD patterns of hydroxycarbonate precursors prepared in a batch process at pH value of 7, aged for 2 h. Comparison of results using precipitating agents Na_2CO_3 and $(\text{NH}_4)_2\text{CO}_3$ is shown.

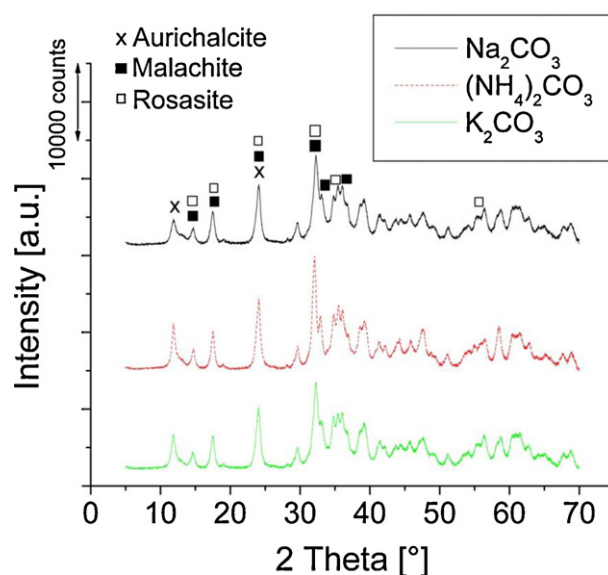


Fig. 5. XRD patterns of hydroxycarbonate precursors prepared in a slit plate mixer at a pH value of 6, aged for 2 h. Comparison of precipitation with different carbonate species is shown.

displays slightly more pronounced aurichalcite bands, particularly the band at $2\theta = 13^\circ$. Moreover, the malachite and rosasite bands for these two precipitating agents K_2CO_3 and Na_2CO_3 show a strong resemblance. Similar to Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ samples, non-aged precursors prepared with K_2CO_3 exhibit a less amorphous structure. Non-aged precursors are still susceptible to ageing since water cannot be fully extracted during the filtration process. The aurichalcite bands are also observed weaker in all catalysts aged for 2 h regardless of the precipitating agents used. This evidence confirms the dissolution of aurichalcite as already discussed in the previous section.

The pH value in precipitation reaction and ageing has an important impact on the structure of the hydroxycarbonate precursors. XRD patterns for precursors prepared with $(\text{NH}_4)_2\text{CO}_3$ in as precipitating agents using a valve-assisted mixer are illustrated in Fig. 6. Higher pH values ensure a high degree of crystallinity along with sharper, bolder malachite and rosasite bands. The

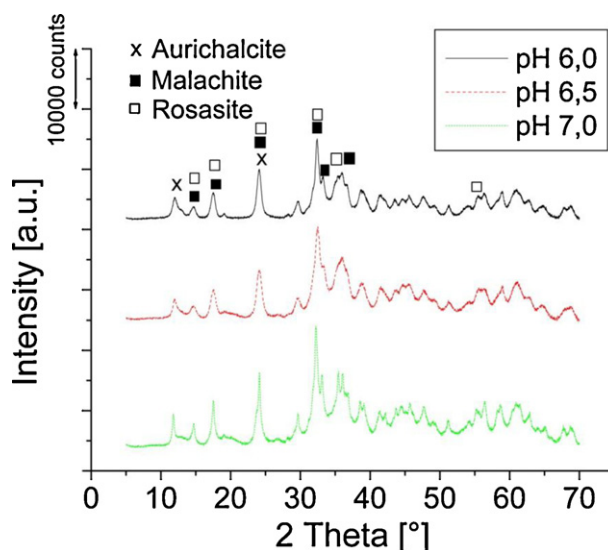
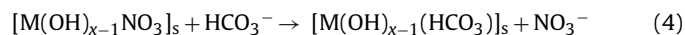
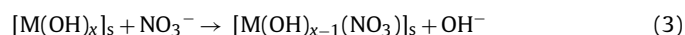
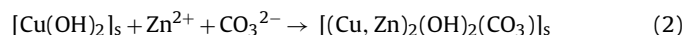


Fig. 6. XRD patterns of hydroxycarbonate precursors prepared in a valve-assisted mixer with $(\text{NH}_4)_2\text{CO}_3$, aged for 2 h. Influence of pH value in precipitation is shown.

pH value of precipitation affects all precursors prepared with Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, K_2CO_3 and NaOH regardless of the synthesis route applied. A basic pH value amplifies the crystallinity of the hydroxycarbonate precursors, especially of those prepared with micromixers. Wassermann et al. [36] and Li und Inui [15] studied the effect of the pH value onto the $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ system in batch synthesis and correlated the precipitation pH value with the phase composition of the precursors. When carbonate salts are added to an aqueous solution of metal nitrates $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ under pH control, the solid formation starts with the initial precipitation of amorphous copper hydroxide (Eq. (1)). The copper hydroxide then reacts with zinc and carbonate ions, forming a mixed amorphous hydroxycarbonate precursor (Eq. (2)). Concurrently, the more slowly solidifying zinc forms a hydroxyl-rich material together with the residual copper ions.



The concentration of H^+ ions in the mother liquor increases with the decrease of the pH value applied during precipitation and ageing process, whereby the concentration of carbonate ions is directly affected. Due to the shift of equilibrium, the concentration of carbonate ions is reduced by protonation to hydrogen carbonate (Eq. (5)) followed by further protonation to carbonic acid and decomposition to CO_2 and H_2O .



Therefore, the reorganization of the precipitate (Eq. (3) and Eq. (4)) is hindered at acid pH values. The reorganization of the solid eventually leads to the formation of zincian malachite and aurichalcite from either georgeite or the amorphous hydroxyl-rich material. As a result, high concentration of carbonate ions at a basic pH value facilitates the formation of more zincian malachite, rosasite and aurichalcite, resulting in less amorphous products.

In thermogravimetric analysis the thermal decomposition reaction of hydroxycarbonate precursors elapses in three main steps analogous to the results presented by Melian-Cabrera et al. [37]. The first step shows the release of crystallization water present in the hydroxycarbonate structure as well as weakly adsorbed CO_2 at a temperature around 400–420 K followed by the elimination of structural hydroxyl groups with the release of H_2O and decomposition of rosasite, malachite, aurichalcite and other carbonate containing phases, forming CO_2 at about 620 K. Finally, the decomposition of high-temperature carbonates occurs in the range of 700–900 K. High-temperature carbonates are attributed to amplify the interaction of active metal species and support material (Cu-ZnO) [10]. As a result, the sintering process of copper particles is reduced and thus more active catalysts are obtained. The decomposition of precursors prepared with Na_2CO_3 occurs in these three steps with the first mass loss of 2.5% associated with the release of crystallization water and weakly adsorbed CO_2 at a temperature of 416 K (Fig. 7). The second mass loss of 20% over a broad temperature range of about 523–623 K is mainly due to the decomposition of hydroxycarbonate structures and nitrates which are still left after the washing step, releasing mainly H_2O , CO , CO_2 and NO . The decomposition reaction of the so-called high-temperature carbonates is responsible for the third mass loss of 5% at 847 K, as indicated by CO and CO_2 detected in the mass spectrometer. Thermogravimetric analysis results of precursors prepared with $(\text{NH}_4)_2\text{CO}_3$ in a slit plate mixer (Fig. 7) display a similarity to the precursors prepared with Na_2CO_3 except a broader mass loss in temperature range of about 473–623 K. The first mass loss of 3%

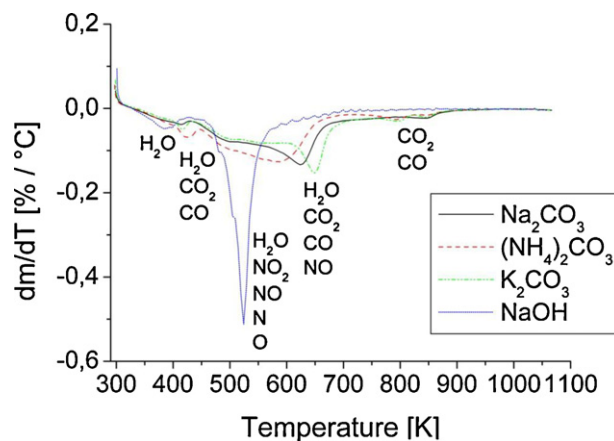


Fig. 7. Thermal analysis of hydroxycarbonate precursors prepared in a slit plate mixer at a pH value of 6, aged for 2 h. Comparison of precipitating agents is shown.

due to the release of H_2O and CO_2 is similar to that of Na_2CO_3 . The second mass loss of about 21% occurs as a continuous mass loss of H_2O , CO , CO_2 and NO between 473 and 623 K. The third and fourth mass losses at 792 and 843 K are caused primarily by high-temperature carbonates (HT-CO_3). Different from the single step mass loss of HT-CO_3 in precursors prepared with Na_2CO_3 , the double step mass loss indicates two different carbonates with two different decomposition temperatures present in the precursors. The results of thermogravimetric analysis of precursors prepared with the conventional precipitating agent Na_2CO_3 . The first mass loss of 2.5% is correlated with H_2O and CO_2 present in hydroxycarbonate precursors. The sharp mass loss of 20% at 649 K comprises of mainly the evolution of H_2O , CO , CO_2 and NO . The decomposition of HT-CO_3 occurs in two steps at 794 and 844 K. Similar to the $(\text{NH}_4)_2\text{CO}_3$ samples, the decomposition of precursors prepared with K_2CO_3 indicates two different carbonates present in the precursors. The thermal decomposition of precursors prepared with NaOH elapses in two main steps according to the different chemical system compared to precipitation with carbonate species. This evidence is in accordance with the results presented in Ref. [38]. In the temperature range of 383–413 K crystallization water is released from the sample. The decomposition of hydroxide compounds and gerhardite associated with the release of H_2O , NO , NO_2 and O_2 occur at 503–533 K. Both mass losses can be attributed with a sharp band at 384 K (2.4%) to the release of H_2O and at 524 K (22.4%) to the decomposition of hydroxides and gerhardite. Further temperature increase above 1073 K reveals another mass loss of the catalyst samples, which released mainly O_2 , CO and CO_2 from the system. The composition of the evolved gases points to the reducing reaction of copper (II) oxide (CuO) to copper (I) oxide (Cu_2O) or even elemental copper with formation of brass [39], as indicated by the reddish brown color of the sample after thermogravimetric analysis.

In general, the decomposition behavior of catalysts prepared with carbonate species as precipitating agents is similar. Due to the different chemical composition, the decomposition behavior of NaOH samples deviates according to expectations from the behavior of carbonate species. The precipitation reaction in the presented different synthesis routes results in precursors with a comparable decomposition behavior.

3.2. Characterization of calcined precursors

The metal contents of the ternary $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts prepared at different pH values were determined. Table 1, for example, summarizes the results for the samples prepared at pH 6. For the

Table 1
Metal contents of Cu/ZnO/Al₂O₃ catalysts prepared in synthesis route “slit plate mixer” at pH 6 depending on duration of ageing period.

Precipitating agent	Ageing duration	Cu [wt.%]	Zn [wt.%]	Al [wt.%]
Na ₂ CO ₃	0 h	63.3	24.7	12.0
	1 h	62.5	25.9	11.6
	2 h	62.6	25.9	11.5
(NH ₄) ₂ CO ₃	0 h	63.3	24.7	12.0
	1 h	62.6	25.9	11.5
	2 h	62.6	25.9	11.5
K ₂ CO ₃	0 h	65.0	24.0	11.0
	1 h	63.4	26.0	10.6
	2 h	63.5	25.8	10.7
NaOH	0 h	70.9	16.9	12.2
	1 h	70.4	18.0	11.6
	2 h	70.4	18.1	11.5

precipitation with carbonate species the copper contents were measured in the range of 62.5–64.0 mol%, while zinc and aluminum was detected in the range of at 24.5–26.0 mol% and 11–12 mol%, respectively. Hence, different synthesis routes do not affect the metal contents in the produced catalysts significantly. The molar ratio of Cu:Zn:Al has been determined to 63:25:12, clearly different from the deployed molar ratio in the synthesis process. Samples prepared at pH 7 (results are not shown here) attain the deployed ratio of 60:30:10 also very close. Precursors prepared with ammonium carbonate at pH 7 showed a slightly lower copper content than the other precursors. The molar ratio of 59 mol% copper in the (NH₄)₂CO₃ samples can be explained by a “leaching” effect, caused by the formation of copper ammine complexes during the precipitation reaction. At pH 7 the release of NH₃ from (NH₄)₂CO₃ cannot be suppressed. The characteristic blue complex compound is soluble in the mother liquor and thus removed from the system during the washing step.

The effect of the pH value during precipitation reaction on the final metal composition of precipitated catalysts is reported by many authors [15,36]. The extended reaction model by Baltes et al. [13] is further modified for the used precipitating agents (Eqs. (1)–(5)). The reduced incorporation of zinc into the precipitate can be correlated directly to the pH value and the precipitation process. By adding a carbonates-containing basic solution to an aqueous nitrate solution of copper, zinc and aluminum, the precipitation starts with the formation of amorphous copper hydroxide. The shaped copper precipitate reacts with Zn and carbonate ions to form mixed amorphous hydroxycarbonate precursors. Parallel slowly crystallizing Zn ions form a precipitate rich in hydroxides with residual copper. Using an acidic pH value in the precipitation process the equilibrium of carbonate ions is relocated to hydrogen carbonate and thus hinders the formation of a Zinc-rich precipitate. The effect of reduced incorporation of Zn into the precipitate is increasingly observed using sodium hydroxide as precipitating agent. As displayed in Table 1, the molar ratio of copper, zinc and aluminum in calcined precursors is determined to be 70:18:12 and therefore far-off the deployed ratios. That is due to the fact, that in precipitation with NaOH a completely different chemical system exists compared to the precipitation reaction with the carbonate species Na₂CO₃, (NH₄)₂CO₃ and K₂CO₃. In synthesis with NaOH only the hydroxides of copper, zinc and aluminum are obtained. Based on the absence of carbonate species, the incorporation of Zn ions with carbonate ions into the initially formed copper hydroxides is hindered. Another reason for the decreased precipitation of Zn is the higher solubility of zinc hydroxide in acidic solutions compared to hydroxides of copper and aluminum. The ratio of aluminum in the precipitate is constant, since the precipitation of aluminum hydroxide is independent of the concentration of

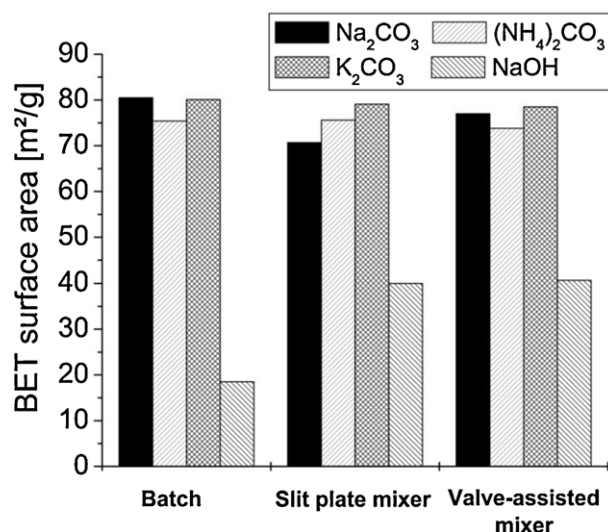


Fig. 8. BET surface areas of calcined precursors prepared at a pH value of 6 depending on synthesis route and precipitating agent applied.

carbonate ions. Regarding the molar ratios of copper, zinc and aluminum a minor influence on the ageing duration can be observed. Samples without ageing (0 h) display a slightly higher copper content and a slightly lower zinc content than catalysts after ageing for one or 2 h. These findings confirm the reaction model for the precipitation of hydroxycarbonate precursors explained earlier. The metal contents of the catalysts are barely affected by the applied synthesis route (*batch-process*, *slit plate mixer* and *valve-assisted mixer*) and the duration of ageing time. The choice of the precipitating agent and pH value in contrast exhibits a big influence on the reorganization of the precipitate and the incorporation of zinc in the primary precipitation product. A neutral pH value and the presence of carbonate ions in the mother liquor promote the precipitation of zinc.

The results of trace element analysis as well do not show any influence of the applied synthesis routes (*batch-process*, *slit plate mixer* and *valve-assisted mixer*), pH value or ageing time on residual contents of carbon, nitrogen and hydrogen in the calcined precursors. On an average the residual contents of carbon are in the range of 0.6–1.0 wt.%. Hydrogen and nitrogen residues are detected in the range of 0.3–0.5 wt.% and 0.1–0.3 wt.% or even below, respectively. The degree of removal of reagents and byproducts is substantially affected by the processes of washing and calcination rather than by the synthesis route. Using a longer ageing period however leads to a decreasing amount of residues of sodium and potassium in catalyst samples. During the ageing process in mother liquor the reorganization of the precipitate with ion exchange, dissolution and re-crystallization takes place. Enclosures out of place like sodium and potassium ions can be removed from the precipitate during this process. The separation of Na⁺ and K⁺ ions from the Cu/ZnO/Al₂O₃ catalyst is important since both alkali metals act as catalyst poison. Sodium and potassium cause an increasing sintering process of the specific copper surface area associated with a decrease of catalytic activity in methanol synthesis [10,41]. The critical limit of 0.15 wt.% for sodium was achieved in the majority of catalyst samples [42]. The driblet of residues is a good evidence for the sufficient removal of metal nitrates, carbonates and particularly sodium and potassium.

Fig. 8 summarizes the data of BET surface areas calculated from nitrogen adsorption measurements for the calcined precursors. Using ammonium and potassium carbonate-containing precipitating agents, BET surface areas of 71–81 m²/g_{cat} are obtained, which are equal to the surface areas achieved with conventional

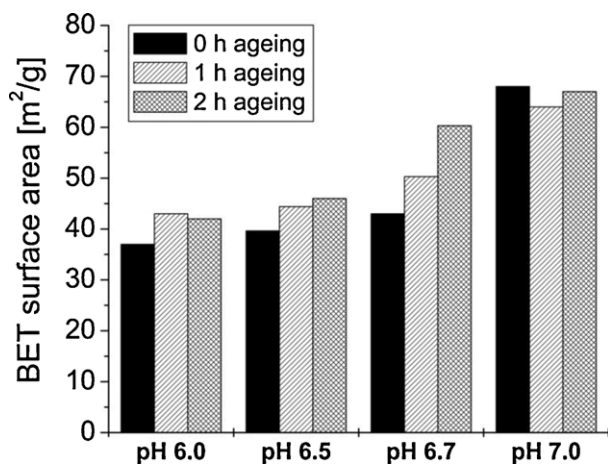


Fig. 9. BET surface areas of calcined precursors prepared in a valve-assisted mixer with NaOH at different pH values.

sodium carbonate precipitation within the accuracy of measurement. The ternary catalysts from the synthesis with carbonate species display an equal BET surface area independent from the synthesis route applied. Using sodium hydroxide as precipitating reagent leads to significantly smaller BET surface areas than in precipitation with carbonate species. Catalyst samples prepared in a conventional batch process display the lowest BET surface areas with $18 \text{ m}^2/\text{g}_{\text{cat}}$. The application of the synthesis routes using the micromixers achieves catalysts with BET surface areas in the range of $40\text{--}41 \text{ m}^2/\text{g}_{\text{cat}}$.

Independent from precipitating agent and precipitation method, a higher BET surface area at pH value of 7 can be observed than in the precipitation process at pH 6. Applying carbonate species in precipitation the increase of the surface area is with $2\text{--}4 \text{ m}^2/\text{g}_{\text{cat}}$ rather small compared to precipitation with sodium hydroxide with an increase of $16 \text{ m}^2/\text{g}_{\text{cat}}$. Fig. 9 exemplarily shows the detailed study of the effect of pH value on the BET surface area during synthesis of hydroxycarbonate precursors with sodium hydroxide in a micromixer. Syntheses were conducted at varying pH values of 6.0, 6.5, 6.7 and 7.0. The illustration clearly displays the increase of BET surface area with increasing pH values in catalyst synthesis. Starting from a surface area of $40 \text{ m}^2/\text{g}_{\text{cat}}$ at pH value 6.0 in precipitation, an increasing surface area is detected, leading to $66 \text{ m}^2/\text{g}_{\text{cat}}$ at pH 7.0. Analogous to an acid base titration, the maximum increase of BET surface area is observed in the step from a pH value of 6.7 to pH 7.0. The influence of the duration of ageing on the BET surface area is included in Fig. 9. As a general trend samples with higher surface area are obtained with ageing times up to for 2 h in the mother liquor. Moreover, it can be observed in all synthesis routes that an ageing time of 2 h enlarges the surface area of the Cu/ZnO/Al₂O₃ catalysts up to 40%.

The XRD patterns of the calcined catalysts prepared with sodium carbonate in all synthesis routes are shown in Fig. 10. The phase structures of the calcined samples are mainly composed of tenorite (CuO), zincite (ZnO) and other copper, zinc and aluminum oxide composites. The diffractograms of all calcined catalysts show similarities separate from the synthesis route applied. The characteristic band for CuO at $2\theta = 39^\circ$ displays the presence of tenorite with more distinctive bands for those catalysts prepared at higher pH values. The phase of zincite is observed by the characteristic bands at $2\theta = 32^\circ$ and 57° . Typical bands for alumina ($2\theta = 19^\circ, 45^\circ$) are not observed. That is probably due to the fact that alumina is incorporated into the other phases of Cu/ZnO/Al₂O₃ catalysts as amorphous phase [43]. The introduction of amorphous Al₂O₃ in the Cu/ZnO/Al₂O₃ catalyst systems leads to a higher surface area than in the binary Cu/ZnO system by up to 50%. Fig. 11 displays the XRD

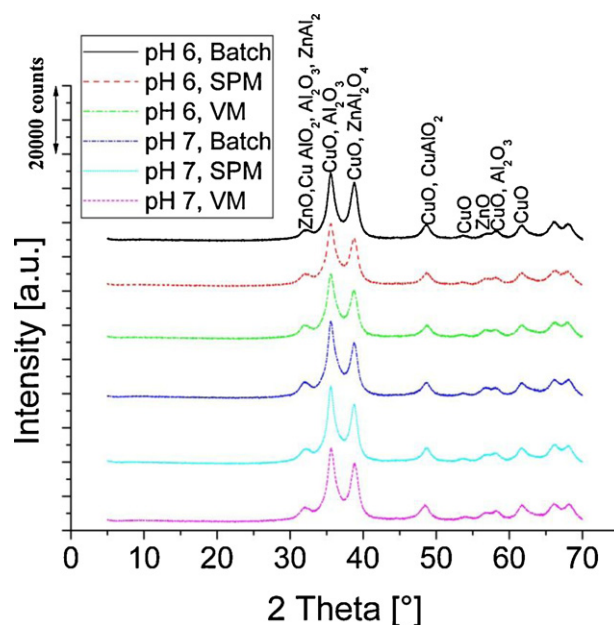


Fig. 10. XRD patterns of calcined precursors prepared with Na₂CO₃, aged for 2 h. Comparison of synthesis route and pH value applied.

patterns of catalyst samples prepared in the synthesis route using the slit plate mixer with Na₂CO₃, (NH₄)₂CO₃, K₂CO₃ and NaOH as precipitating agent. XRD patterns of catalyst samples prepared with carbonate species do not indicate any differences. NaOH samples show the same patterns like carbonate samples but display sharper and more distinctive bands with higher intensities. In total, XRD patterns of NaOH samples exhibit less amorphous structures than carbonate samples.

Calcination transforms the hydroxycarbonates present in the precursors into oxides while removing the nitrates and other volatile impurities. At a temperature of 623 K almost all nitrates, hydroxyl groups and carbonates present in the precursors were successfully removed, as illustrated by the results of elemental analysis. Another increase of the calcination temperature would reduce the amount of high-temperature carbonates in the catalyst and promote sintering processes of the copper surface area

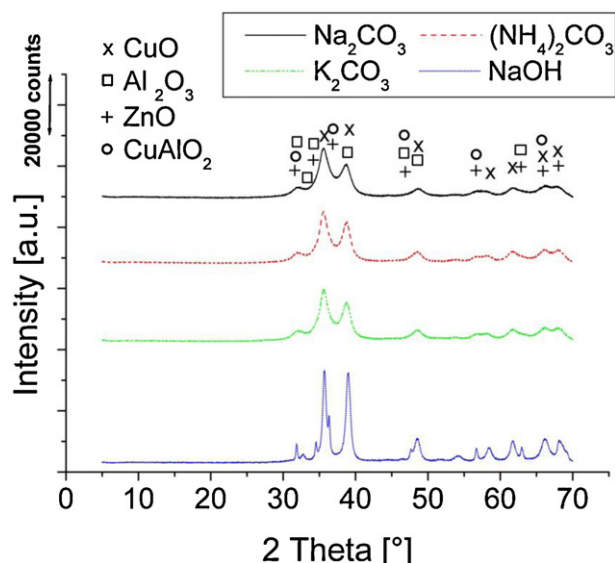


Fig. 11. XRD patterns of calcined precursors prepared in a slit plate mixer at a pH value of 6, aged for 2 h. Comparison of precipitating agent is shown.

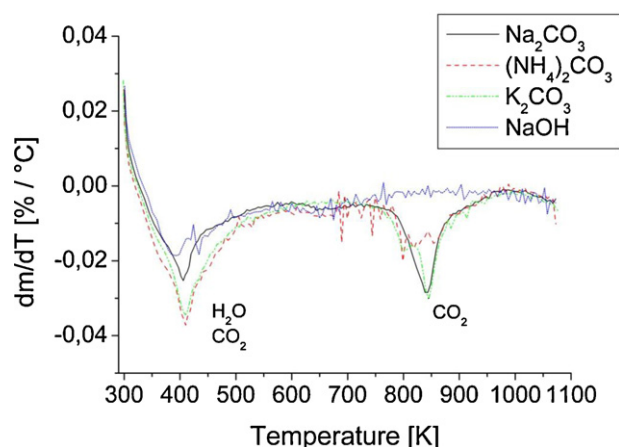


Fig. 12. Thermal analysis of calcined precursors prepared in a slit plate mixer at a pH value of 6, aged 2 h. Comparison of precipitating agents is shown.

and consequently lowering its catalytic activity. The calcined catalysts were analyzed in thermogravimetric experiments to verify the presence of high-temperature carbonates as well as to affirm a complete decomposition of nitrates during the calcination process. In general, calcined Cu/ZnO/Al₂O₃ catalysts decompose in two main steps (Fig. 12). The first mass loss occurring at 403–413 K is due to the release of the crystallization water as well as the weakly absorbed CO₂ present in the Cu/Zn hydroxycarbonates structure. This phenomenon can also be observed during the thermal decomposition process of hydroxycarbonate precursors. The second mass loss is associated with the decomposition of high-temperature carbonates. Fig. 12 shows the thermal decomposition of calcined precursors prepared in the synthesis route using the slit plate mixer with different reagents. In case of calcined catalysts prepared with Na₂CO₃, this occurs at 843 K with a mass loss of about 1.8%. Volatile components detected by mass spectrometry were mainly CO and CO₂. The presence of more HT-CO₃ in calcined catalysts is beneficial since it could delay the sintering process in the activated Cu/ZnO/Al₂O₃ catalyst. In catalysts prepared with (NH₄)₂CO₃, the decomposition reaction of HT-CO₃ took place at a slightly lower temperature (803 K) with a mass loss of about 1.6%. A slightly lower HT-CO₃ part was released from the system, although the residual carbon content of the catalyst sample is similar to the Na₂CO₃ sample. This effect is probably caused by a strong HT-CO₃ copper–zinc interaction. Thermal analysis of catalysts precipitated with K₂CO₃ matches that of Na₂CO₃. A slightly higher HT-CO₃ mass loss of about 2.2% was detected at a temperature of about 845 K. In calcined samples prepared with NaOH, no further mass loss except the one for water at 395 K can be observed at defined temperature bands. Therefore, the thermal decomposition of gerhardtite structures and hydroxides of copper, zinc and aluminum completely took place during the calcination process. In synthesis with NaOH no compounds comparable to the HT-CO₃ in precipitation with carbonate species can be obtained. Fig. 12 confirms the strong similarities in the thermal decomposition of the calcined precursors particularly of the carbonate species separate from the precipitating agent applied in synthesis. As described before in Section 3.1 a further temperature increase above 1073 K reveals another mass loss of catalyst samples, related to the reducing reaction of copper (II) oxide (CuO) to copper (I) oxide (Cu₂O) [39].

Analysis with transmission electron microscopy demonstrates no clear relationship between particle size and the synthesis route applied in the precipitation process with carbonate species. Both batch process and micromixers produce catalyst particles with similar morphology as shown in Fig. 13. The corresponding particle size distributions are drawn in Fig. 14. Synthesis in the batch process

Table 2

Specific copper surface area of Cu/ZnO/Al₂O₃ catalysts prepared at a pH value of 6, aged for 2 h – before and after methanol synthesis, Batch (batch process), SPM (slit plate mixer), VAM (valve-assisted mixer).

Precipitating agent	Batch [m ² /g _{cat}]		SPM [m ² /g _{cat}]		VAM [m ² /g _{cat}]	
	Before	After	Before	After	Before	After
	MeOH synthesis		MeOH synthesis		MeOH synthesis	
Na ₂ CO ₃	17.5	16.8	20.5	19.3	19.0	18.3
(NH ₄) ₂ CO ₃	16.8	15.5	17.2	16.4	18.6	17.8
K ₂ CO ₃	4.6	2.0	16.9	10.5	18.0	12.4
NaOH	4.9	2.6	4.6	3.8	7.9	2.5

generated catalysts with a mean particle size of about 7.6 nm while precipitation in the micromixers leads to mean particle sizes of 7.5 nm and 7.1 nm, respectively. All synthesis routes display similar particle size distribution for carbonate species. The results obtained from TEM analysis show that the morphology as well as the particle size of the catalysts do not correlate directly with the synthesis routes implemented. This can be regarded as a result of the ion exchange reactions during the ageing in the mother liquor. Within the series of precipitating reactions with carbonate agents no significant differences in morphology and particle size distribution can be observed. All samples contain round and oval particles with mean particle sizes of 7–9 nm. With using NaOH as precipitating agent, substantially bigger particles were obtained (Fig. 15). In the batchwise synthesis route particles with a mean size of 54 nm were produced, whereas in the micromixers slightly smaller particles with mean sizes of 42 nm (slit plate mixer) and 49 nm (valve-assisted mixer), respectively, were received. Hence, precipitation with NaOH results in particles increased by a factor of 6–7 compared to synthesis with carbonate species. A maximum particle size of about 19 nm is found in catalysts prepared with carbonate species, whereas a maximum of about 200 nm is observed in NaOH samples. Therefore particle size distributions in Cu/ZnO/Al₂O₃ catalysts precipitated with NaOH are significantly broader. The particle morphology of NaOH samples is very inconsistent (Fig. 13). Large shapeless particles together with small particles with round or oval shape can be observed.

In summary, the different synthesis routes applied in precipitation leads after calcination to similar Cu/ZnO/Al₂O₃ with respect to elemental and structural composition. Preparation in both types of micromixers generates particles with analogous properties compared to the conventional batch process. However, the choice of the precipitating agent and pH value in contrast exhibits a big influence on the reorganization of the precipitate and therefore on catalyst properties. Within synthesis with carbonate-containing precipitating agents no striking differences can be observed. In precipitation with sodium hydroxide remarkable differences in catalyst properties are observed due to the different chemical system.

3.3. Specific copper surface area and methanol synthesis

The specific copper surface areas of the prepared Cu/ZnO/Al₂O₃ catalysts were quantitatively measured with reactive frontal chromatography (RFC) using N₂O as described elsewhere [33,34]. The N₂O RFC measurement of the activated catalyst (Section 2.3) was performed in a standardized procedure. The results of N₂O RFC measurements are summarized in Table 2. The specific copper surface areas of the freshly reduced catalysts are always higher than those of spent catalysts. Cu/ZnO/Al₂O₃ catalysts prepared with Na₂CO₃ in micromixer achieve 91.5% and 84.8% compared to the industrial reference material (Section 2.3). Using Na₂CO₃ and (NH₄)₂CO₃ as precipitating agent generates catalysts with high copper surface areas, whereas synthesis with NaOH produces

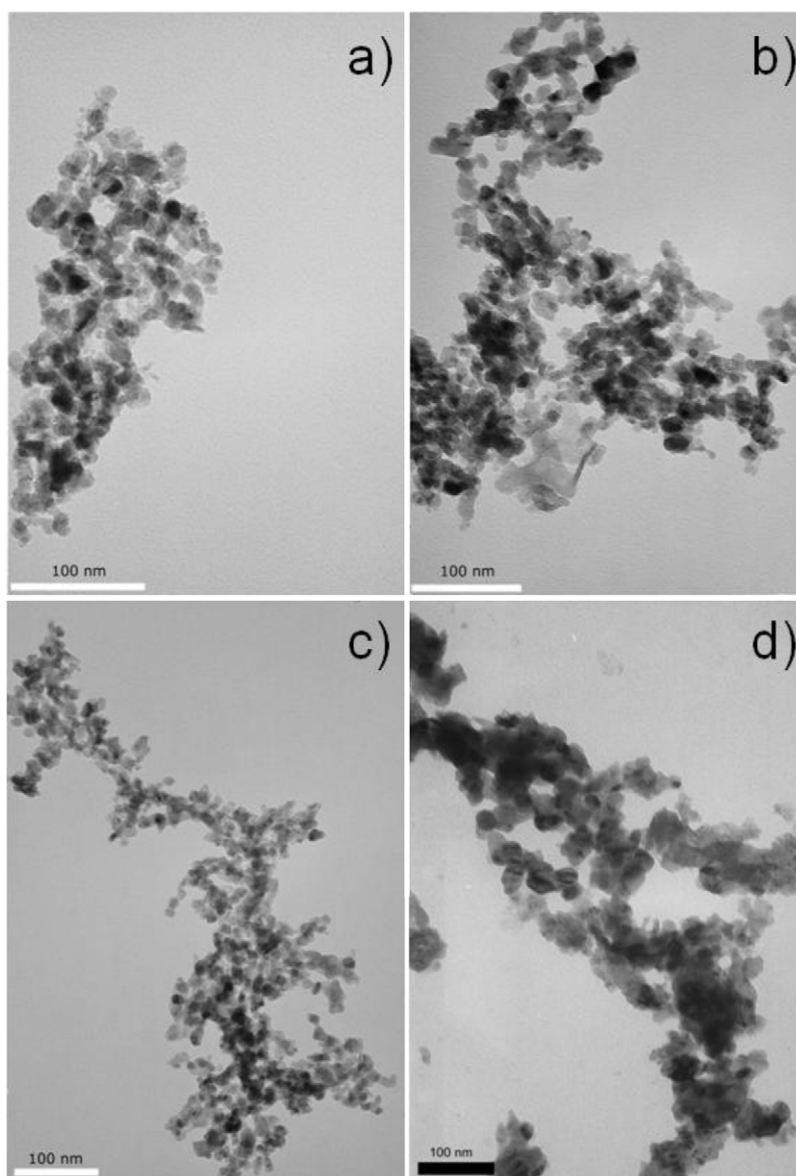


Fig. 13. TEM images of Cu/ZnO/Al₂O₃ catalysts prepared in (a) a batch process, (b) a slit plate mixer and (c) a valve-assisted mixer with Na₂CO₃ at pH 6, aged for 2 h. Image (d) shows a sample prepared with NaOH in a valve-assisted mixer at a pH value of 6, aged for 2 h.

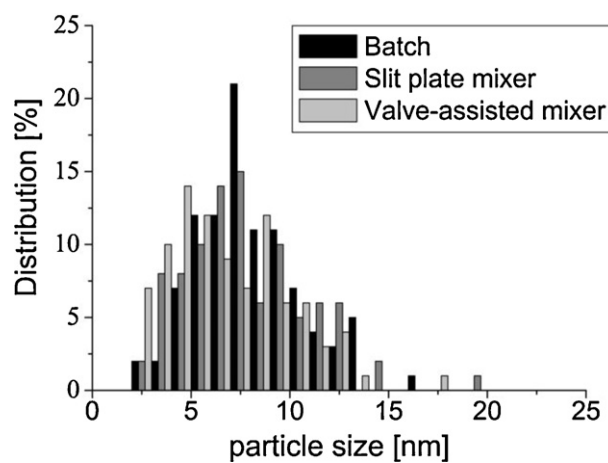


Fig. 14. Particle size distribution of catalysts prepared in a batch process, a slit plate mixer and a valve-assisted mixer with Na₂CO₃ at a pH value of 6, aged for 2 h.

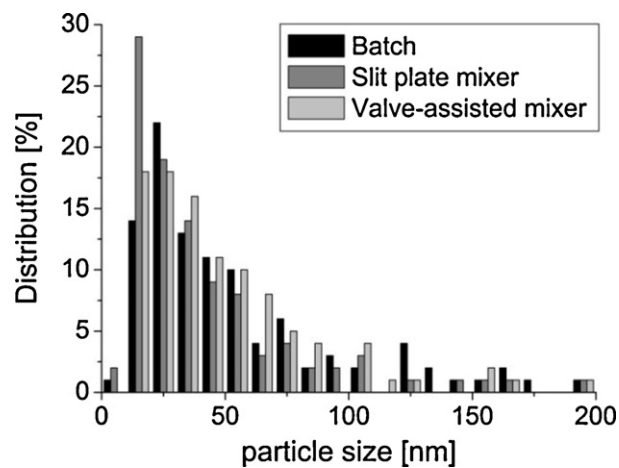


Fig. 15. Particle size distribution of catalysts prepared in a batch process, a slit plate mixer and a valve-assisted mixer with NaOH at pH 6, aged for 2 h.

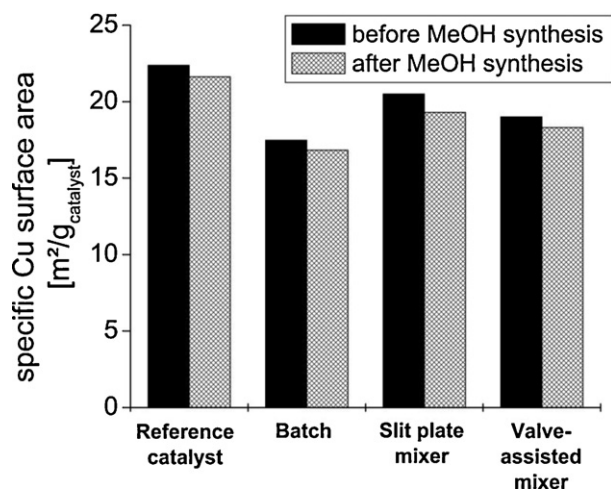


Fig. 16. Specific copper surface area of Cu/ZnO/Al₂O₃ catalysts prepared with Na₂CO₃ at a pH value of 6, aged for 2 h. Comparison of different synthesis routes is shown.

catalyst samples with low copper surface areas together with the highest decrease of copper surface during methanol synthesis with an average of 44%. Fig. 16 illustrates the copper surface areas achieved in precipitation with Na₂CO₃ in the different synthesis routes applied. Precipitation in the micromixers generates catalyst samples with specific copper surface areas of $S_{Cu} = 20.5 \text{ m}^2/\text{g}_{cat}$ and $S_{Cu} = 19.0 \text{ m}^2/\text{g}_{cat}$, whereby this value is significantly higher than in the batchwise precipitation process, yielding a value of $S_{Cu} = 17.5 \text{ m}^2/\text{g}_{cat}$. In general catalysts precipitated with Na₂CO₃ display the lowest decrease of copper surface area during methanol synthesis with an average decrease of 4.3%. The minimum of copper surface area lost during MeOH synthesis is shown by the catalyst prepared in the valve-assisted mixer. With only 3.7% of loss it gets very close to the industrial reference catalyst with 3.6% loss of copper surface area. Using K₂CO₃ and (NH₄)₂CO₃ as precipitating agents in the different synthesis routes displays similar trends than precipitation with Na₂CO₃. The copper surface areas obtained in the continuously operated micromixers are higher than in conventional batch synthesis. The catalyst sample prepared with K₂CO₃ in the batch process displays a copper surface area of $S_{Cu} = 4.6 \text{ m}^2/\text{g}_{cat}$, which is far below the values for the samples prepared in the micromixers. This result is associated with a high residual content of potassium ions of 0.2 wt.% in this catalyst sample, which may result from an insufficient washing step or a mistake in catalyst preparation. Although the role of K⁺ in catalysts is not yet fully understood, it is accepted, that residues of K⁺ promote sintering processes of copper crystals and therefore lead to a substantial decrease of copper surface area [41]. Separate from the synthesis route applied, catalysts prepared with NaOH show very small copper surface areas. Related to the industrial reference sample they merely achieve 20–35% of the specific copper surface areas.

Table 3

Maximum and minimum of specific copper surface area and relative decrease of copper surface area for catalysts prepared with carbonate species in different synthesis routes, Batch (batch process), SPM (slit plate mixer), VAM (valve-assisted mixer).

Precipitating agent	Specific Cu surface area		Rel. decrease of Cu surface area	
	Maximum	Minimum	Maximum	Minimum
Na ₂ CO ₃	SPM	Batch	SPM	VAM
(NH ₄) ₂ CO ₃	VAM	Batch	Batch	SPM
K ₂ CO ₃	VAM	Batch	Batch	VAM

Table 4

Methanol production rate over Cu/ZnO/Al₂O₃ catalysts prepared at pH value of 6, aged 2 h, Batch (batch process), SPM (slit plate mixer), VAM (valve-assisted mixer).

Precipitating agent	Batch		SPM		VAM	
	5 bar	10 bar	5 bar	10 bar	5 bar	10 bar
	[mmol _{MeOH} /g _{cat} s]		[mmol _{MeOH} /g _{cat} s]		[mmol _{MeOH} /g _{cat} s]	
Na ₂ CO ₃	4.0	9.2	4.2	9.9	3.9	9.0
(NH ₄) ₂ CO ₃	3.6	8.3	4.7	11.2	4.3	10.1
K ₂ CO ₃	0.7	1.4	3.7	8.8	3.7	9.4
NaOH	1.9	4.3	3.0	6.5	2.9	5.5

In Table 3 the influence of the different synthesis routes (batch process, slit plate mixer and valve-assisted mixer) on the specific copper surface area of Cu/ZnO/Al₂O₃ catalysts prepared with carbonate species is shown. From this overview the advantages of the novel, continuously operated precipitation routes in micromixers compared to the conventional batch process get obvious. The maximum of specific copper surface area is either obtained in the synthesis route using a slit plate mixer or valve-assisted mixer, whereas the minimum for copper surface area in synthesis with carbonate species is always obtained in the classical batch process. Likewise the minimum of copper surface area decrease during methanol synthesis is achieved throughout in catalyst samples prepared in micromixers.

The methanol productivity of the prepared ternary catalyst systems is reported in Table 4. The catalyst samples prepared in the continuously operated synthesis route using a slit plate mixer displays the highest methanol production rate of all produced samples. Cu/ZnO/Al₂O₃ catalysts prepared in micromixers with the alternative precipitating agents (NH₄)₂CO₃ and K₂CO₃ in general display higher or at least the same activity than samples prepared according to the classical batch process with Na₂CO₃. Samples precipitated with NaOH basically show very slight catalytic activity in methanol synthesis and achieve about 44–55% of the catalytic performance of the reference material. The minimum of catalytic activity is displayed for the samples obtained by K₂CO₃ in a batch process. This is in accordance with the small specific copper surface area of the catalyst sample (Table 2), which is related to the high residual content of potassium in the sample as described before. Fig. 17 illustrates the achieved methanol productivity for the catalysts prepared with (NH₄)₂CO₃ in the different synthesis routes. The catalytic activity correlates with the

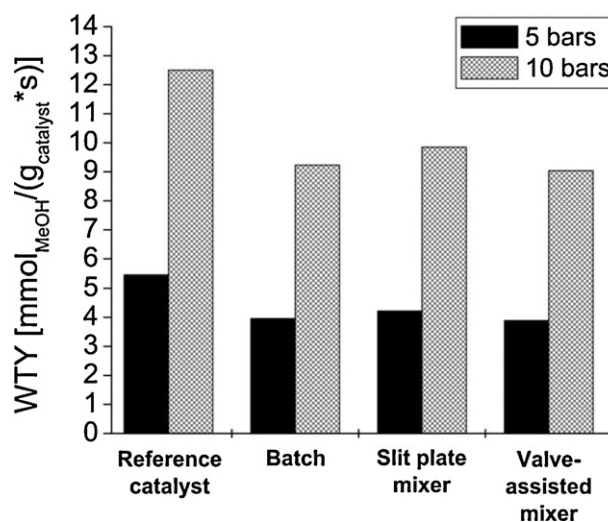


Fig. 17. Methanol productivity of Cu/ZnO/Al₂O₃ catalysts prepared with (NH₄)₂CO₃ at pH 6, aged for 2 h. Comparison of different synthesis routes is shown.

Table 5

Maximum and minimum methanol production rate over Cu/ZnO/Al₂O₃ catalysts in terms of synthesis route applied.

Precipitating agent	MeOH production rate	
	Maximum	Minimum
Na ₂ CO ₃	SPM	VAM
(NH ₄) ₂ CO ₃	SPM	Batch
K ₂ CO ₃	VAM	Batch
NaOH	SPM	Batch

Table 6

Maximum and minimum methanol production rate over Cu/ZnO/Al₂O₃ catalysts in terms of precipitating agent applied.

Synthesis route	MeOH production rate	
	Maximum	Minimum
Batch	Na ₂ CO ₃	K ₂ CO ₃
SPM	(NH ₄) ₂ CO ₃	NaOH
VAM	(NH ₄) ₂ CO ₃	NaOH

trend of specific copper surface areas (Table 2). Catalysts precipitated in micromixers clearly display higher methanol production rates than the batch sample. The Cu/ZnO/Al₂O₃ sample prepared with (NH₄)₂CO₃ in a slit plate mixer reaches the industrial reference catalyst by 86% at 0.5 MPa respectively 89% at 1 MPa. The catalytic activity of catalysts prepared with K₂CO₃ and NaOH in the three synthesis routes shows qualitatively the same trend like (NH₄)₂CO₃ samples. The methanol productivity of the catalysts from synthesis in micromixers is significantly higher than of those prepared in classical batch precipitation. Table 5 gives a summary of the maximum and minimum methanol productivity of catalysts prepared with Na₂CO₃, (NH₄)₂CO₃, K₂CO₃ and NaOH in terms of the synthesis route applied. Separate from the precipitating agent applied, the maximum of catalytic activity in methanol synthesis is found with a catalyst prepared in the innovative, continuously operated micromixers. The minimum of catalytic activity in synthesis with (NH₄)₂CO₃, K₂CO₃ and NaOH is found in the conventional batch precipitation. Only in synthesis with Na₂CO₃ the minimum is obtained in micromixer synthesis, whereby it has to be pointed out, that the methanol productivity of Na₂CO₃ samples is within a close range. The results displayed in Table 5 affirm the potential of the novel microstructured setups with continuous operational mode to provide an alternative solution to the preparation of Cu/ZnO/Al₂O₃ catalyst systems in conventional batch synthesis. Table 6 indicates the possibility to produce highly active catalysts for methanol synthesis using the alternative precipitating agent (NH₄)₂CO₃. Especially in continuously operated micromixer synthesis (NH₄)₂CO₃ samples display the maximum of methanol productivity. In synthesis with Na₂CO₃ and K₂CO₃ catalysts with good catalytic activities are obtained likewise. The low catalytic activity of the K₂CO₃ sample in batch process is evaluated as aberration due to the content of potassium in the sample. The other K₂CO₃ samples indeed show methanol productivity comparable to the Na₂CO₃ samples. Finally, it can be noticed that the application of NaOH as precipitating agent is not suitable for the production of highly active Cu/ZnO/Al₂O₃ catalyst systems for methanol synthesis.

4. Conclusions

In this study ternary Cu/ZnO/Al₂O₃ catalyst systems were prepared systematically in innovative synthesis routes using microstructured synthesis setups with micromixers as a main component. The precipitation in a slit plate mixer and valve-assisted mixer was operated continuously under exact control

of the pH value, temperature, concentration and ageing time. Reaction conditions were kept constant over the complete reaction time. The catalysts were prepared according to the *constant pH method* by coprecipitation of aqueous metal nitrate solutions of copper, zinc and aluminum with aqueous solutions of sodium, ammonium and potassium carbonate as well as sodium hydroxide. After precipitation and ageing the precipitate was transferred to conventional post processing. The characterization of the Cu/ZnO/Al₂O₃ catalysts illustrates that a completely different chemical system exists in precipitation reaction with carbonate species than in precipitation with sodium hydroxide. In synthesis with carbonate species a complex system of hydroxycarbonates is obtained in addition to hydroxide compounds of copper, zinc and aluminum.

The metal contents of the catalysts are barely affected by the synthesis route applied and the duration of the ageing process. However, the choice of precipitating agent and pH value exhibits a distinct influence upon the reorganization of the precipitate. A neutral pH value and the presence of carbonate ions facilitate the incorporation of zinc, leading to the deployed metal ratios in the catalyst. The operation of synthesis in micromixers amplifies the specific Cu surface area of samples prepared with NaOH by a factor of 2, whereas in synthesis with carbonate species no substantial influence of the synthesis routes applied can be observed. XRD patterns of hydroxycarbonate precursors from synthesis in a slit plate mixer and a valve-assisted mixer, especially with the alternative precipitating agent (NH₄)₂CO₃, display high crystallinity and sharp reflections of malachite and roasite. These phases are thought to be responsible for the high catalytic activity in methanol synthesis [4–8]. The effect of fast and intense mixing as well as a high degree of micromixing is responsible for this observation. Synthesis in the conventional batch process produces samples with lower crystallinity and higher intensity of the less active phase aurichalcite. For catalysts prepared with NaOH only reflections of the crystal phases of gerhardtite and hydroxide compounds of copper, zinc and aluminum are obtained.

The results of the N₂O RFC measurements for catalysts prepared in continuously operated micromixers in general show higher specific copper surface areas than catalysts prepared by conventional batch precipitation. Furthermore, the samples obtained from the micromixers exhibit a less pronounced decrease of copper surface area during methanol synthesis and therefore present a higher stability of the achieved copper surface area. Employing Na₂CO₃ and (NH₄)₂CO₃ as precipitating agents results in catalysts with high specific copper surface areas, whereas precipitation with K₂CO₃ and NaOH provides samples with lower copper surface area, leading also to a pronounced decrease in copper surface area during methanol synthesis. The maximum of methanol productivity of all prepared Cu/ZnO/Al₂O₃ catalysts is observed with samples synthesized in the continuously operated microstructured synthesis setup regardless of the precipitating agent applied. Particularly catalysts based on the (NH₄)₂CO₃ route display a high catalytic activity, which is comparable to the performance of an industrial reference catalyst. Therefore, the precipitating agent (NH₄)₂CO₃ has the potential to replace the conventionally used Na₂CO₃ as a sodium free alternative.

In summary, the continuous coprecipitation using micromixers generates ternary Cu/ZnO/Al₂O₃ catalyst systems with equivalent or even superior physicochemical properties compared to the conventional batch processing. Especially the composition of crystal phases, the specific copper surface area and the catalytic activity in methanol synthesis of catalyst samples prepared in micromixers displayed industrially important capabilities. Hence, the continuously operation in precipitation of methanol synthesis catalysts possesses the potential to replace the conventional synthesis in batch reactors.

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