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High-throughput screening under demanding conditions: Cu/ZnO catalysts in high pressure methanol synthesis as an example

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Abstract

High-throughput experimentation is by now an established technology for the synthesis and evaluation of catalysts. However, so far most of the systems described in the literature for the study of gas-phase reactions have been restricted to less demanding reaction conditions, i.e., atmospheric pressure. We have developed a 49-channel parallel flow reactor for use under elevated pressures up to 5 MPa and used this system to screen methanol synthesis catalysts based on the Cu/ZnO system. The catalysts have been prepared by co-precipitation under various preparation conditions. Catalysts obtained from the same precursors, but showing vastly different performance, were then selected for a more detailed study. Differences in performance could be traced back to differences in phase composition and reduction behavior. This study demonstrates that high-throughput experimentation not only is a suitable tool to screen catalysts, giving little scientific insight—as it is often perceived—but can also be used as a first step to obtaining more fundamental insight by rapidly identifying those compositions which are most suitable for detailed study.

Keywords: High-throughput experimentation; Catalysis; Methanol synthesis; Combinatorial catalysis; Cu/ZnO; Catalyst synthesis; Parallel reactor; EXAFS

1. Introduction

Over the past five years, high-throughput experimentation (HTE) has become a valuable tool for the development of solid catalysts (reviewed in Refs. [1–5]). While initially there was severe skepticism with respect to the possibility of obtaining meaningful catalytic data by HTE approaches, very rapidly we have seen the technology becoming more and more accepted, and by now almost all major chemical company either have closed strategic collaborations with service providers, such as Symyx, hte AG, or Avantium, or have their own internal efforts. Also many academic groups have developed own tools and methods, and it can be predicted that within the next 5–10 years there will be almost no catalysis laboratory, which does not depend to some extent on components of HTE-technology, such as synthesis robots or parallel reactor technology. However, the field of high-throughput experimentation is still in a “volatile” stage; i.e., concepts are still being explored, different approaches are being evaluated, and not all components necessary are fully in place. In addition, the full reach of HTE in catalysis is not quite clear at this point, a feeling which condenses in the question: “Where is the science in HTE in catalysis?” This is a question which will, to some extent, be addressed in this contribution. As a preliminary answer, one can identify four different aspects with respect to the “science” in HTE: (i) There are interesting scientific aspects in the tool development for HTE, such as the various methods for mass spectrometric analysis of addressable arrays [6–10], thermal imaging [11,12], imaging FTIR-spectroscopy with focal plane array detectors [13], parallel laser-induced fluorescence [14], resonance-enhanced multiphoton ionization [15], parallel photoacoustic spectroscopy [16], or selective color detection schemes [17–19]. (ii) It is expected that the chance of achieving breakthrough discoveries is strongly enhanced by using HTE technologies. Such breakthrough discoveries would also typically present a major scientific achievement, since

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the gain in knowledge resulting from an unexpected discovery will be much higher than the gain from incremental improvements. (iii) The possibility of rapidly screening many different catalysts allows one to broadly evaluate the performance of differently prepared materials quickly and then focus on samples for more detailed study which are most interesting. This will help to generate more meaningful information on specific catalytic systems and will allow to extract trends much more clearly. (iv) The possibility of analyzing huge catalyst libraries under comparable conditions in a consistent manner will provide a basis for model development which as yet does not exist. This is something anybody will highly appreciate who has tried to compare and use literature data from different sources. The latter point specially is something which so far has not been fully acknowledged.

The present contribution will highlight especially the possibilities brought about by HTE catalysis to prescreen a wide set of parameters and then focus on interesting samples for detailed analysis (point (iii)) in a case study, where HTE evaluation of catalysts has been used to evaluate systematically part of the synthesis space for Cu/ZnO catalysts for methanol formation. Aluminum, which is present in the commercial catalyst, was deliberately not included in order to keep the system rather simple. Methanol synthesis has been investigated by a number of groups [20–25] and is an interesting example reaction, since the catalytic experiments are very time-consuming. This is due to the fact that the reaction has to be carried out under high pressure, since conversion is negligible at atmospheric pressure, and that the reduction and activation of the catalyst have to be done carefully and slowly. Industrial reduction and reactor start-up need between one and two days. Evaluation of one catalyst by conventional means will thus need around one week, which is prohibitive when large numbers of samples must be studied and synthesis fields should be explored carefully.

One obstacle in analyzing a reaction such as methanol synthesis with a parallel-flow reactor was the lack of suitable reactor technology. In the initial publications on HTE analysis of catalytic reactions, the design of the reactors was often driven by the format of the synthesized libraries and thus catalysts were tested under conditions that are far away from those normally employed in catalytic studies, such as flowing the reaction gases over the surfaces of minute amounts of catalyst deposited on a flat substrate. Our own developments followed a different path, in that we tried to stick as closely as possible to conventional catalyst testing and rather adapted our synthesis methods to be compatible with flow-through reactors as they are normally employed in catalysis research [26,27]. All reactors we use have some common features: The systems are equipped with a common gas inlet to minimize costs which would otherwise arise by multiple valves, mass flow controllers, and so on in the gas-handling system. The flow through each channel is in the simplest case not actively controlled, but passively determined by the pressure drop over each of the channels. Identical pressure drops over each channel and the prevention of backmixing are achieved via distributor elements in the inlet of the reactors and metal sinter frits in the catalyst cartridges as well as capillaries at the outlet of each reactor. Differences in flows between the channels caused by different pressure drops over the catalyst beds are thus minimized and typically lower than 5%. The exit gas from the parallel reactor channels is fed into a multiport valve or series of valves to distribute and switch the flows. One channel at a time is analyzed; the others are vented. Analysis is thus serial, with basically free choice of the analytical instrument. Comparability between different channels during measurement can be improved further by placing a defined restriction (i.e., a mass-flow controller or a high-precision needle valve) in the line to the GC. Heating of reactors is achieved by heating cartridges or heating conductors; in addition, the whole reactor including the inlet and outlet lines can be placed in an oven. These reactors have proven to be very robust and reliable and give data comparable to those from conventional single-channel systems [26,27]. Similar designs are also in use industrially at hte AG in Heidelberg. In constructing a high-pressure reactor suitable for the study of methanol synthesis catalysts, we adhered to the same design principles. However, additional features are necessary in order to allow operation under such demanding conditions. One should also keep in mind that parameters such as purge time for valves and tubes can become the time-limiting factor at high pressures, if the volumes of such parts are not kept sufficiently low. There is one report in the literature on a related reactor suitable to handle a pressure of 1 MPa with 12 parallel channels, which was also used to study methanol synthesis [28].

2. Experimental

2.1. Catalyst preparation

Binary Cu/ZnO catalysts were prepared by co-precipitation with different precipitants while pH, temperature, and aging process were controlled. $Cu(NO_3)_2$ and $Zn(NO_3)_2$, as well as the carbonates $NaHCO_3$ and Na_2CO_3, were dissolved at concentration 1.0 mol/L in Millipore water and filtered through a 0.45-μm cellulose acetate membrane filter to remove dust and other contaminants.

For co-precipitation, the solutions (metal solution: 0.3 mol/L $Zn(NO_3)_2$, 0.7 mol/L $Cu(NO_3)_2$; carbonate solution: 1.0 mol/L CO_3^{2-}) were pumped into a stirred and heated polypropylene vessel with a starting volume of 20 ml demineralized water at a temperature of 338 K. While carbonate solution was pumped continuously, metal solution was added according to the pH, controlled by a WTW 296 pH meter. Thus, during precipitation, the pH was kept within a range of ±0.1 units, except for small spikes when drops were added. pH was kept constant also during the aging process by controlled addition of additional metal nitrate solution. After aging for 3 h, precipitates were filtered and washed five times with 100 ml of Millipore water and subsequently dried at 363 K.

After grinding, 1.0 g of the precursor powder was calcined in an oven with a temperature ramp of 3 K/min and final temperatures of 523, 553, 573, 593, 613, 623, and 643 K for 10 h.

2.2. *Catalyst characterization*

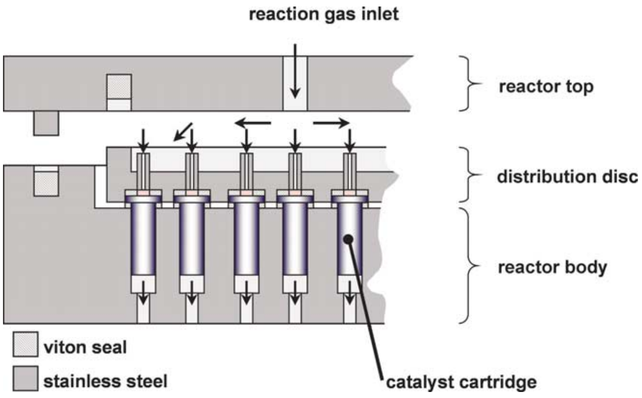
Catalyst precursors were investigated by mass spectrometry coupled with thermogravimetry using a thermobalance STA 449 C (Netzsch) with a heating rate of 5 K/min and an air flow of 60 ml/min. Mass spectra were taken with a ThermoStar 200 (Bazers) mass spectrometer.

X-ray diffraction experiments were done on flat prepared powder samples in reflection mode with a diffractometer STADI P (Stoe) with Cu-K_α radiation in 2θ–ω mode.

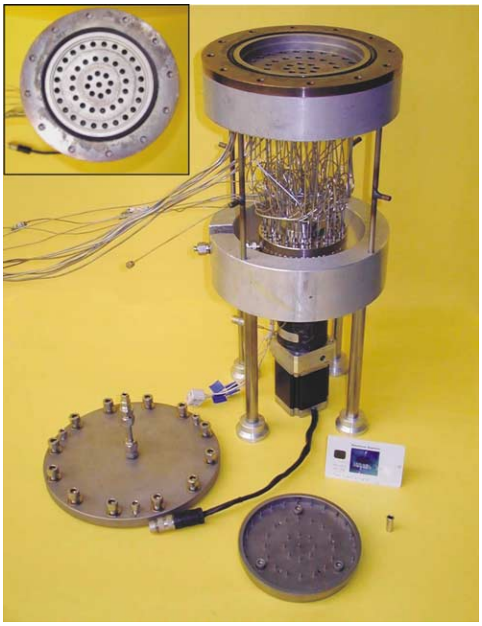
Copper surface area was determined by reactive frontal chromatography [29,30]. After reduction (1 vol% H_2 in He, room temperature to 518 K with ramp of 1 K/min, 12 h reduction time) the cooled catalyst was treated with 1 vol% N_2O in He at 300 K, assuming a mean surface atom density for copper of $1.47 \times 10^{19}\ \mathrm{m}^{-2}$ [31,32].

To understand the reduction behavior, selected catalysts were investigated in an in situ X-ray absorption spectroscopy study. The XAS experiments were performed at ESRF (Grenoble, France) using synchrotron radiation at beamline BM1B (Swiss–Norwegian Beam Line) in a reactor for pellet-shaped samples. Pellets with diameter of 13 mm and thickness of 1.5–2 mm were pressed from finely ground catalyst diluted with boron nitride powder. These pellets were fixed in a heatable stainless steel reaction chamber suitable for treatments in gas mixtures. X-ray transmittant windows in the reactor allow simultaneous structural analysis by X-ray absorption spectroscopy and gas analysis by mass spectroscopy. A detailed description of the reaction setup will be given elsewhere [33].

The XAS data were obtained in transmission geometry. The X-rays were monochromatized by using a Si (111) crystal as channel-cut monochromator, and a gold mirror was employed to reject harmonics. For XAS measurements at the Cu K-edge (8.980 keV) the incident and transmitted X-rays were recorded by use of ionization chambers. The chambers for measuring I_o and I_t, 17 and 31 cm in length, were filled with a mixture of argon and nitrogen. XAS spectra were recorded between 8700 and 9670 eV by step scanning the monochromator (3 min/scan). The raw data were background corrected and normalized using WINXAS 2.1 software [34].



(a)



(b)

Fig. 1. Schematic drawing of a cross section of the 49-parallel channel reactor (a) and photograph of the reactor (b) with open lid, distribution plate from side and top view (size comparison: credit card).

2.3. *Reactor*

The reactor (Fig. 1a) consists of a stainless steel body which is similar to the one described by Hoffmann et al. [27]. It consists of three concentric metal rings and an inner cylinder which are welded together. Each ring is heated separately by metal-mantled heating conductors (90 W/m, heating power adapted to the steel mass of each ring). Temperature is controlled via thermocouples placed in each circle. Each heating conductor is controlled independently by a PID controller. The catalyst (typically 50 to 300 mg per well) is placed in sample holders consisting of a stainless steel cartridge (ID 5 mm, height 18 mm) closed at the bottom by a 4-µm pore size stainless steel sinter metal frit. Thus, all 49 channels show the same gas resistance within a relative deviation of 0.8% in flow at atmospheric pressure. The cartridges are covered by a distribution disc and sealed with Viton O-rings against each other as well as against the reactor body. Small tubings (ID 0.1 mm, length 12 mm) in the distributor disc prevent backmixing even at high pressure (i.e., low linear flow velocity). This set-up is closed by a stainless steel top containing the gas inlet, as well. At the reactor outlet, each sample position is connected to a home-built 49-port valve by 1/16″ stainless steel tubings, ID 0.8 mm. This high-pressure valve system driven by a stepper motor connects one channel to the analytics line while all other 48 channels are collected to the exhaust gas line and vented. All tubings and the valve are heated to 420 K to prevent condensation. The fluid arrangement is able to work at least up to 5 MPa at temperatures of 540 K. The ceiling temperature is determined by the sealing materials used (Viton). It could be somewhat increased by using Kalrez seals or substantially increased by using graphite seals. In the latter case, however, the maximum pressure at which the system could be used would be substantially decreased (at hte AG, however, graphite-sealed reactors with a ceiling pressure of 10 MPa are in operation). The whole reactor set-up measures around 40 cm in height (Fig. 1b).

2.4. Reaction system

The reaction set-up is able to control reactions up to gas pressure 5.0 MPa in continuous flow reactions. Gases N_2 (99.99), CO (98.5% after passing a protection reactor at 463 K filled with γ-Al_2O_3), H_2 (99.999%), and 5% H_2/N_2 (test gas quality) are fed directly from gas cylinders at pressures of 6.5 MPa. For CO_2 (99.995), the cylinder and all tubings are heated to 338 K to keep the gas above the critical temperature at defined (p, T) conditions. Gas flows are controlled by Bronkhorst thermal mass flow controllers (MFC). After passing the reactor, gases reach the valve system, which separates one gas stream for analytics. Defined flow is regulated by passing a backpressure regulator (Dräger–Tescom) reducing from up to 5 MPa to 2.7×10^5 Pa and a needle valve (inlet pressure 2.7×10^5 Pa, outlet atmosphere) defining the analytics flow by gas burette. The pressure of the system is regulated by an electronic pressure controller in the line to the exhaust (Bronkhorst). Flows are adjusted so that the inlet flow is 49 times the flow directed to the analytical system.

For gas analysis, a double GC system (HP GC 6890) is used to provide rapid gas analysis. Carbon-containing compounds (CO, CO_2, CH_4, H_3COH, $HCOOCH_3$, $H_3CCOOCH_3$, H_3CCH_2OH) are detected with a methanizer FID in both GCs. As columns SuppelcoWAX 0.53 mm for oxo-product separation and Carboxen 1006 for $CO/CO_2/CH_4$ separation are used. Detection limits for the carbon compounds are below 0.005 vol%. Within 5.3 min a full analysis of all low molecular mass carbon compounds is completed. All lines to the analytical system and the exhaust are heated to prevent condensation of liquid products.

2.5. Reaction

Into each cartridge 80 mg of calcined powder catalyst precursor was filled. Reduction was performed with 5% H_2/N_2 at atmospheric pressure using a temperature ramp of 1 K/min up to 508 K at a flow of 180 nL/h for all 49 sample positions and kept there for 1 h. Then pressure was increased slowly within 2 h to 1.5 MPa and reduction gas replaced by pure hydrogen. After a further 2 h, pressure was increased to 4.5 MPa and reaction gases were switched on with flows of 5.2 nL/h CO_2, 42 nL/h CO, and 123 nL/h H_2, corresponding to a flow of 57 mL/min per cartridge, equivalent to WHSV of 43.000 L/(h kg). Before measuring, all 49 samples were equilibrated at specific conditions (temperature, flow, pressure) for 120 min and afterward measured subsequently.

3. Results and discussion

3.1. Commissioning of the reactor

Before different Cu/ZnO catalysts were analyzed, the performance of the 49-channel hig-pressure reactor was checked. Temperature homogeneity was analyzed using an IR camera mounted on top of the open reactor while the reactor was heated to the desired temperature. The temperature of the empty wells in the stainless steel reactor body was determined. It can be expected that homogeneity will be even better when the reactor is closed. Fig. 2 shows the thermal image of the reactor with temperatures within a 6-K range coded in black. Since almost no brighter color shows up, it can be concluded that the temperatures of all wells are within 6 K of the desired temperature. This or an even smaller range of temperature inhomogeneity was found over the whole temperature range up to 523 K. The fact that the average temperature recorded with the IR camera is lower that the set temperature is due to the fact that the reactor was open during this measurement.

Comparability of the results obtained in different wells was checked with a commercial catalyst. When the reactor was filled with identical catalyst in all wells except one blank (which showed zero methanol production), standard deviation for conversion to methanol between the different wells was typically below 10% rel. for the whole temperature range investigated. Reproducibility of results between different runs was high after complete removal of catalyst from the reactor and filling in new charges. Deviations were typically below 10%.

The results obtained with the 49-channel reactor were also checked against a single channel flow system operated in the Institut für Technische Chemie at the Ruhr-Universität Bochum [35] with a commercial methanol synthesis catalyst as reference. Due to the different setups as well as slight aberrations in the reduction process and gas composition which are crucial for reactor comparison in methanol synthesis processes [36–38], it was not possible to measure under exactly identical conditions. In the 49-channel reactor a rate of 1.7×10^{-4} mol min^{-1} g^{-1} was measured at 493 K and 2.5 MPa and a feed consisting of 73% H_2, 24% CO, and 3% CO_2, while the single-channel reactor at 493 K and

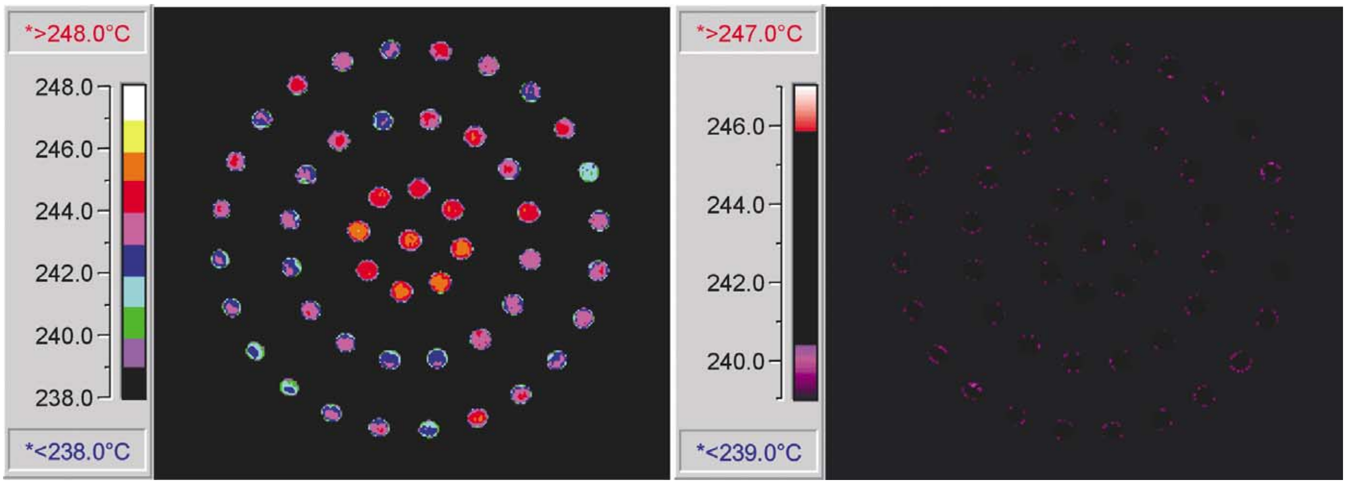


Fig. 2. Thermographic images of a top view into the empty wells of the open reactor. Temperature was set at 523 K in both pictures; a temperature range between 513.5 and 518.5 K was color-coded in black (right). One can see that all wells have temperatures within this range.

2 MPa gave a value of 9.5×10^{-5} mol min^{-1} g^{-1} with a feed composed of 13.5% N_2, 71% H_2, 10.5% CO, and 5% CO_2. This agreement seems to be satisfactory, considering the higher pressure in the parallel setup, the slightly different feed composition, and the different purity and CO/CO_2 ratios of gases used. In addition, also results from atmospheric pressure experiments from yet another flow system can be extrapolated with reasonable agreement to the high-pressure conditions in the parallel reactor, assuming a first order dependence of rate on total pressure, as has been done before in the literature [39] for a rough estimate, although other factors like different heat transfer conditions in the reactor could add to the discrepancy.

After it had been established that the reactor made it possible to record reproducible data that are reasonably consistent with single-channel reactor data and should easily allow comparison between different catalysts, the synthesis field of the Cu/ZnO catalysts was explored with respect to performance of the materials in methanol synthesis.

3.2. Parallel analysis of the catalytic performance of differently prepared Cu/ZnO catalysts

We have produced a series of 70 different catalysts by precipitation at different pH's, using different precipitation agents and calcination of the precipitate at different temperatures. Catalysts were evaluated at two temperature and three pressure levels. Table 1 gives an overview over the experiments conducted. In the following we will focus on a subset of these experiments. With $(NH_4)_2CO_3$, pH values > 8.2, as were possible with the other precipitation agents, could not be reached due to the formation of soluble complexes at this pH and the resulting lack of any precipitate. pH 9.2 could not be reached with ammonium carbonate in any case due to the buffer effect of this salt. The more detailed study including more careful analysis thus focused on catalysts precipitated at selected pH-values, precipitated with Na_2CO_3 or $NaHCO_3$ and calcined at different temperature levels. Precipitation and aging were carried out under tighter control than normally done for the synthesis of Cu/ZnO catalysts. In many cases, no pH control is reported; in other cases pH is controlled during the precipitation, but typically not during the aging. However, pH changes drastically during aging, depending on the starting pH. Fig. 3 shows, for four

Table 1
Overview of catalysts prepared and conditions studied

Cu/Zn ratio	1
Precipitation and aging temperature	338 ± 5 K under nitrogen
Precipitation pH	6.3, 7.2, 8.2, 9.2
Precipitation agent	Na_2CO_3, $NaHCO_3$, $(NH_4)_2CO_3$
Calcinations temperature	523, 553, 573, 593, 613, 623, 643 K
Gas feed	73% H_2, 24% CO, 3% CO_2
Reaction temperature	493 and 518 K
Pressure	2.5, 3.5, 4.5 MPa

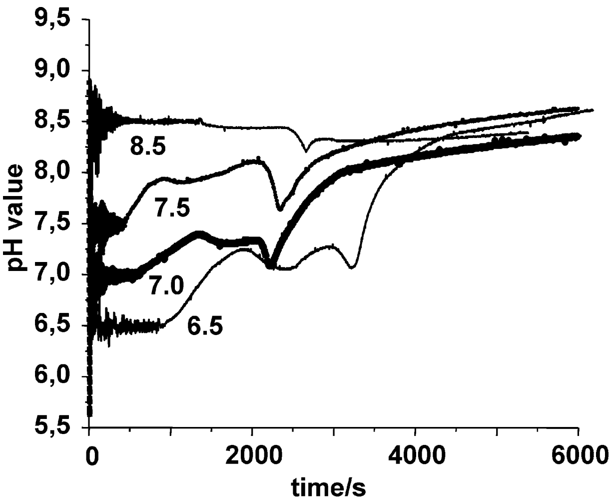


Fig. 3. Development of pH value during aging after precipitation has been carried out at different initial pH values. Initial pH is given in the figure; the oscillations in the first stages are due to the pH control.

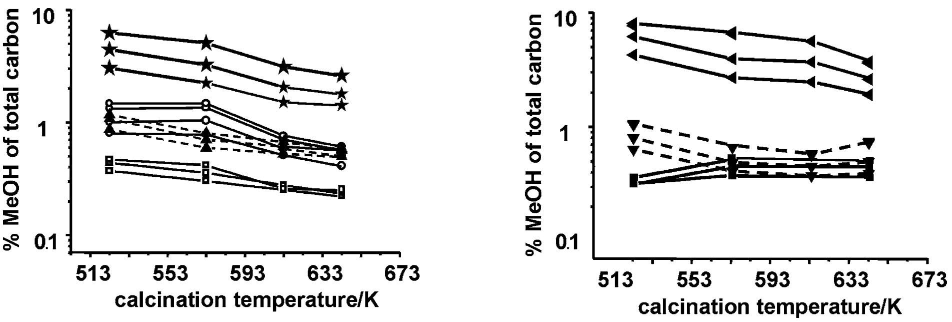


Fig. 4. Selected catalytic data obtained with the parallel reactor shown as extent of methanol in product gas related to total carbon content (i.e., sum of MeOH, CO, and CO_2). Left: Precursors precipitated with $NaHCO_3$. ★ precipitation pH 8.3, reaction temperature 518 K, ● pH 8.3, 493 K, ○ pH 7.3, 518 K, □ pH 7.3, 493 K. Right: Precursors precipitated with Na_2CO_3. ● pH 9.2, 518 K, ● pH 8.2, 518 K, ■ pH 6.3, 518 K. For each series highest conversion corresponds to 4.5 MPa, middle conversion 3.5 MPa, lowest conversion 2.5 MPa.

different starting pH values, how the pH of the system develops if it is not further controlled after the precipitation is complete. One can see that after precipitation is finished, the qualitative development of pH is the same for the curves corresponding to the lower precipitation pH. It increases, going through two not very pronounced maxima, until after a minimum, in which carbon dioxide is released and the color turns from blue to blue-green, the pH increases strongly to the final pH. However, even if the final pH is quite similar, the performance of catalysts precipitated at different starting pH in methanol synthesis is rather different, as is known from the literature [40].

Differences are even more pronounced if the pH is also kept constant during aging and not allowed to increase. Fig. 4 shows the catalytic data for several samples under different conditions (note the logarithmic scale to facilitate comparison). In all cases, catalysts were selective for methanol; no further oxo-products were detected. Several conclusions can be drawn from that figure:

(i) The higher the precipitation pH, the better the catalytic performance up to the maximum pH investigated (9.2);
(ii) The lower the calcination temperature of the precursor, the better the catalytic performance;
(iii) Under otherwise identical conditions, $NaHCO_3$ is somewhat superior to Na_2CO_3 as a precipitating agent.

However, it is not possible to reach a sufficiently high precipitation pH with $NaHCO_3$ for best-performing catalysts. In addition, the expected trends of increasing conversion with increasing temperature and increasing pressure can also be taken from the figure. Recording such a data set (here: 20 different samples from the library in this series, because samples were analyzed in duplicate and triplicate and reference catalysts or blanks were placed in several channels), including careful reduction of the samples, needs only approximately four days. This data set shows that there is a monotonic dependency of catalytic performance on synthesis parameters. In order to elucidate the reasons for the vastly differing catalytic performance, it is interesting to select in a final step extreme samples from the materials evaluated for further in-depth characterization. Chosen were the samples with precipitation pH 9.2 calcined at 523 K and 643 K and precipitation pH 6.3 calcined at 523 K.

3.3. Analysis of selected samples

A number of different phases have been identified in precipitates from copper/zinc/aluminum precursor solutions (a survey is found in Ref. [41] with further references), mostly mixed hydroxocarbonates. Similar compounds can also form in aluminum-free systems. In our case, the XRD patterns of the catalyst precursors precipitated at different pH are entirely different (Fig. 5). The sample precipitated at pH of 9.2 is not a pure phase but seems to be a mixture of hydroxycarbonates of copper and/or zinc. Due to the similarities of the diffraction patterns of different hydroxycarbonates and the broad reflections, clear assignment is difficult. Aurichalcite (JCPDS 17-743) can relatively reliably be identified, and some $(Cu_{0.3}Zn_{0.7})_5(CO_3)_2(OH)_6$ (JCPDS 38-152), $Zn_4CO_3(OH)_6H_2O$ (JCPDS 11-287), and malachite (JCPDS 41-1390) may be present. In addition, the broad background and the low reflection intensity are a strong indication that a substantial fraction of the sample precipitated at high pH is X-ray amorphous. The situation is totally different for the materials precipitated at pH 6.3. Crystallinity seems to be much higher, indicated by the high reflection intensity.

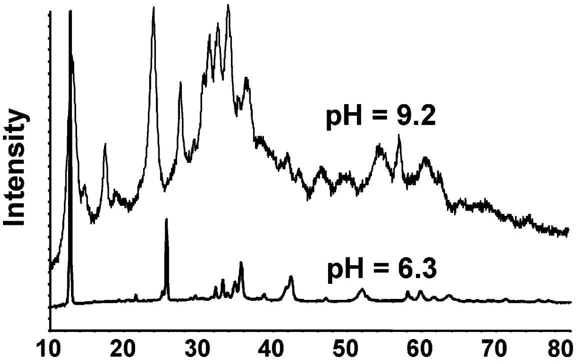


Fig. 5. XRD patterns of the precursors precipitated at pH 6.3 and 9.2 with Na_2CO_3 at constant pH during precipitation and aging. The pattern of the pH 9.2 sample is expanded by a factor of 10.

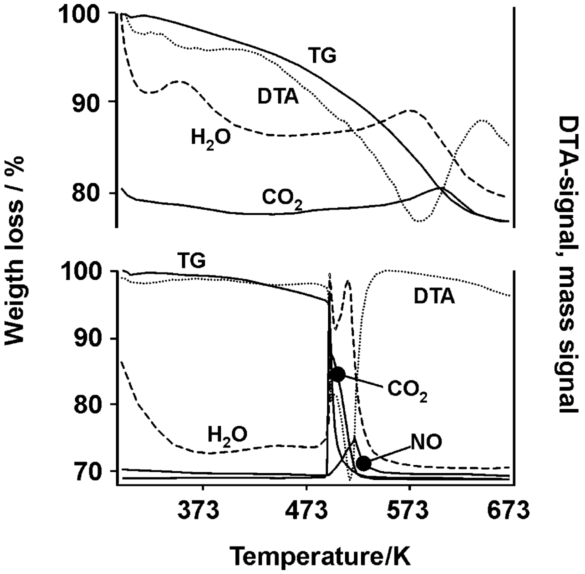


Fig. 6. TG/DTA/mass spectrometry data for the two different precursors. Top: pH 9.2; bottom-pH 6.3.

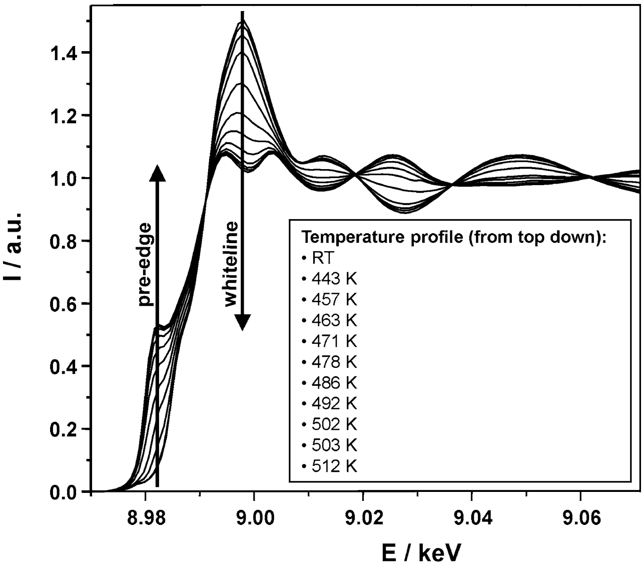


Fig. 7. In situ XAS spectra of the catalyst precipitated at pH 9.2 and calcined at 523 K during reduction with increasing temperature.

The pattern resembles that of copper hydroxyl nitrate (Gerhardtite), but neither the intensities nor the exact positions fully fit. Also, no other phase listed in the JCPDS database could fit the pattern satisfactorily. However, a material with a similar pattern, labeled as unidentified "phase X," has been described by Brahmi et al. [42], who precipitated the sample without pH control.

The thermal behavior of the samples was analyzed using TG/DTA coupled with mass spectrometry (Fig. 6). Again, the samples are markedly different. The sample precipitated at pH 6.3 loses carbonate already at a temperature of about 480 K in a sharp desorption peak and subsequently NO_x from nitrate decomposition at about temperature about 20 K higher, both together with loss of water. For Gerhardtite, a weight loss of approximately 34% would be expected, which corresponds reasonably well with the 31% observed, suggesting that related phases are formed under the conditions chosen here. Two DTA signals at about the same temperatures as here were also reported by Li and Inui and assigned to the decomposition of Gerhardtite [40]. In contrast to that, the sample precipitated at pH 9.2 does not contain nitrate species and loses CO_2 in two steps, one between approximately 473 and 523 K, the other with a peak at about 600 K. Expected weight losses for the different hydroxycarbonates are between 72 and 74%, which again reasonably well agrees with the weight loss of 76%. The TG data thus in both cases corroborate the tentative phase assignments from the XRD analysis. Obviously, at low pH, where the concentration of CO_3^{2-} is relatively low, nitrate can effectively compete for incorporation with carbonate into the solid, while at high pH, exclusively basic carbonates are formed.

It is well known that the precursor structure strongly determines the reducibility of the catalyst [43], which in turn is important in controlling the catalyst activity. In order to correlate the precursor structure and properties with the formation of the active catalysts, reduction experiments were carried out and followed by X-ray absorption spectroscopy, similar to previous studies [36,44]. Fig. 7 shows the X-ray absorption spectra of the sample prepared at pH 9.2 and pretreated at 523 K (diluted in BN) recorded in situ during ramping up the temperature with 1 K/min in a reduction gas stream consisting of 5% H_2 in helium. As can clearly be seen, pronounced changes occur in the pre-edge region as well as in the EXAFS range during reduction, indicating the change reported in the literature [45–47] from the oxidic Cu^{2+} environment (typical feature: whiteline at 9000 eV) to metallic copper (typical feature: shoulder at 8982 eV). In the mass spectrometer, hydrogen consumption was detected in all cases in parallel. A good indication for the progress of the reduction can be obtained from the XANES region. Fig. 8 shows plots of the intensity of the pre-edge peak and the white line with reduction temperature for the three samples discussed above. A distinct difference is again visible for the three catalysts: reduction sets in at about the same temperature for all three samples at 453 K. For the sample precipitated at pH 9.2 and calcined at 523 K reduction is complete at about 493 K; the one calcined at 643 K is fully reduced at about 543 K. For the one precipitated at pH 6.3 the reduction is completely shifted to higher temperatures and needs a temperature exceeding 600 K before reduction is complete. Similar results were obtained in TPR studies reported in Ref. [43] where CuO/ZnO obtained from a hydroxynitrate precursor was more difficult to reduce than the one obtained from the oxynitrate precursor. However, the reduction peaks of pure Gerhardtite was centered at about 517 K and less broad under the conditions employed in that study, suggesting that other copper phases also contribute to the sample precipitated at pH 6.3 in our investigation.

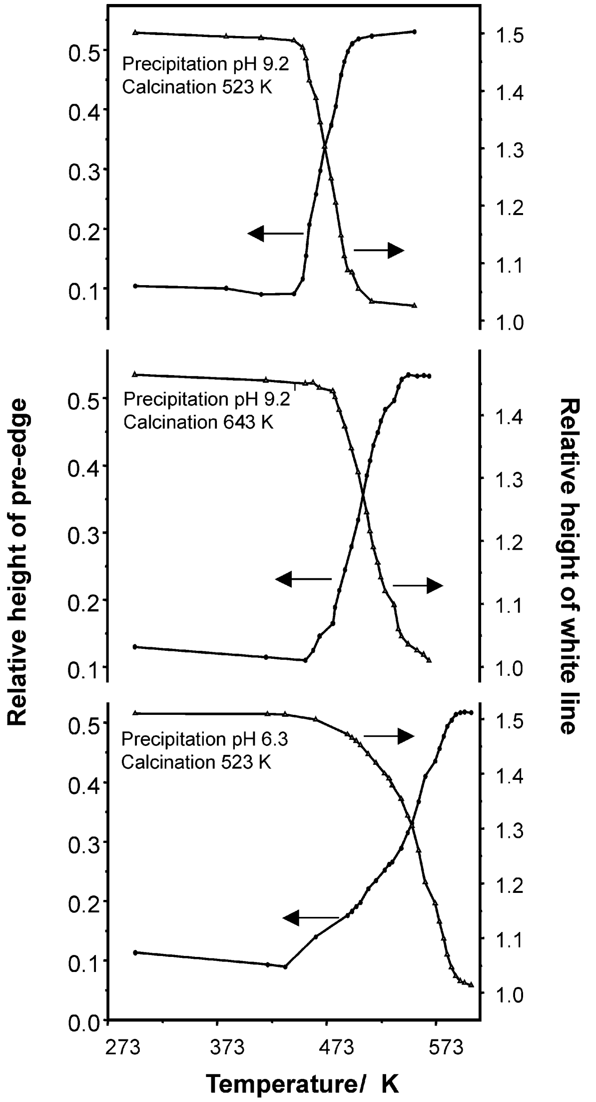


Fig. 8. Relative pre-edge intensities at 8982 eV and white line intensities at 9000 eV of the XAS spectra as a function of temperature during reduction for the samples given in the figures.

Also, in Ref. [45], it was found that the reduction of copper depends on the matrix. A more detailed analysis of the XANES region (Cu^{2+}, Cu^{+}, and Cu species) together with the mass spectrometric data and of the EXAFS region during the reduction process is under way and will be reported at a later stage. This points to an influence of particle size on reducibility, possibly together with other effects which also might contribute.

In order to obtain information on copper surface area, the samples were analyzed with N_2O frontal chromatography. The results are given in Table 2, together with normalized reaction rates calculated from the data reported in Fig. 4 for a temperature of 518 K. Note that the specific rates for the pH 6.3 sample are not very precise due to the low conversion for this sample. The results show that the catalyst precipitated at pH 6.3 has a substantially lower surface area, i.e., bigger copper particles, than the samples precipitated at pH 9.2, which would be expected from the more difficult reduction. The specific rates for these catalysts, obtained from such different precursors, do not seem to be identical, which points to additional influences determining the catalytic activity beyond the mere surface area effect. However, the rates for the low-activity catalyst were obtained at very low conversion and thus the analysis is not very reliable in this case, and more work is necessary to fully substantiate these findings. It has often been reported that the TOF of Cu/ZnO catalysts in methanol synthesis is more or less constant for different catalysts [39], with further references. If conditions of catalyst preparation vary substantially, as studied here, additional factors could influence catalytic activity, i.e., Cu–Zn alloying and strain [48,49]. Our observations are also in line with reports form Schlögl's group [44]: They have precipitated Cu/ZnO hydroxycarbonate precursors under pH control at pH 7 with systematically varying Cu/Zn ratio and carefully analyzed the resulting catalysts. It was found that the microstructure of the catalysts changed with composition, which strongly affected the catalytic performance in methanol synthesis. Strong deviations from a constant TOF were observed in this study. This was attributed to an influence of the precursor composition on the microstructure of the resulting catalyst, which could also be the case in our study.

4. Conclusion and outlook

In this contribution we have shown, using an illustrative example, how high-throughput experimentation not only can be used as a discovery technique, but could be integrated into more conventional catalysis research. We have described the most advanced generation of parallel reactor technology, capable of working under high pressure and con-

Table 2
Cu surface area determined by N_2O frontal chromatography together with normalized rates at high pressure and at 618 K (73% H_2, 24% CO, 3% CO_2). Rates for pH 6.3 catalyst in brackets due to large error margins at very low conversion.

Sample	Cu surface area (m^2/g)	Rate at 2.5 MPa ($mol\,min^{-1}\,m^{-2}$)	Rate at 3.5 MPa ($mol\,min^{-1}\,m^{-2}$)	Rate at 4.5 MPa ($mol\,min^{-1}\,m^{-2}$)
pH 9.2, 523 K	18.3	2.3×10^{-5}	3.4×10^{-5}	4.4×10^{-5}
pH 9.2, 643 K	11.1	1.7×10^{-5}	2.3×10^{-5}	3.1×10^{-5}
pH 6.3, 523 K	3.7	(8.3×10^{-6})	(8.2×10^{-6})	(9.5×10^{-6})

ditions which resemble those of conventional testing. In this study, however, the parallel reactor system was not used to screen vastly different samples in the discovery mode, but to systematically study the influence of preparation conditions for a well-investigated system, the Cu/ZnO methanol synthesis catalyst, on its catalytic performance. This screening then makes it possible to focus on the most relevant samples for an in-depth characterization with different analytical tools, here emphasized in a few examples by the use of TG/MS, XRD, N_2O frontal chromatography, and XAS. Such approaches could become more frequent with increasing availability of parallel reactor technology in many research laboratories, which will allow an increased pace in accumulating fundamental knowledge in catalysis. Catalyst synthesis and the analysis of catalyst synthesis fields are an often underestimated field of research, partly because it is extremely time-consuming to catalytically evaluate large numbers of samples by conventional procedures. Thus, often not those catalyst samples that would give the maximum amount of information, but catalysts prepared according to established and traditional procedures, are studied.

For the investigated system itself, this study—like several others from the recent past—suggests that the Cu/ZnO system, in spite of being known for several decades as a methanol synthesis catalyst, is far from being fully understood. As is known from the literature and again became obvious in this study, besides the gas composition during reduction and synthesis, the synthesis of the precursors can have a marked influence on the activity of the final catalyst. It is thus mandatory to describe in as much detail as possible the synthesis of the precursor. The fact that the pH of the system varies strongly during the aging of the precursor and the fact that depending on the history quite different catalysts are obtained necessitate further studies. Controlling pH not only during the precipitation but also during aging could allow better control of precursor properties and thus allow to reconcile apparent disagreements between published results.

Finally, we would like to address the future development of high-throughput experimentation in heterogeneous catalysis. As stated previously in this contribution, we feel that essentially any laboratory active in heterogeneous catalysis will to some extent rely on parallelized setups in the future to accelerate the work flow and to allow a more extensive prescreening of samples before the stage of detailed analysis is entered. The reactor technology to do this is basically available, even if not many systems are commercial as yet. By now, atmospheric pressure reactions can be handled in parallel reactors up to temperatures exceeding 900 K; reactions under pressure are possible up to the limits stated in this publication, i.e., 5 MPa and 523 K. We have a reactor under development which will reach pressures in the 10-MPa range at temperatures exceeding 1000 K. A useful degree of parallelization for such reactors is probably not much higher than around 50 parallel channels, since error probabilities of individual components multiply, and thus with too massive parallelization in such rather complex systems the susceptibility to system failures increases too strongly. Parallelization to this extent, however, already allows a dramatic increase in productivity in catalysis research.

These developments, at first sight, seem to be sufficient to suit all needs. However, there are still some problems for which suitable solutions are lacking and where more work concerning reactor technology is needed: (i) Most of the analysis is still done sequentially, which makes it difficult to pick up rapid deactivation processes for many samples simultaneously. (ii) The formation of high-boiling products or by products is a severe problem, as long as valves are needed in the exit of the reactor. Such valves are typically limited in temperature, and thus high-boiling products could block the valves and make parallel evaluation of such catalytic reactions impossible. (iii) Sample transfer under inert conditions is difficult in a massively parallelized setup. However, it is expected that such problems can be solved in the future. The developments we have seen so far seem to allow the statement that the basic hardware for HTE in heterogeneous catalysis is available or will be available in a relatively short time.

In addition, we were rather fortunate that performance depended in a monotonous fashion upon the parameters, which allowed us to choose only two extreme samples for detailed investigation. For more complex dependencies, however, this will not be sufficient, and more samples would have to be analyzed. Techniques for high-throughput characterization will then be necessary in order to gain deeper insight in the parameters governing the system behavior. This will be an important task for the community over the next several years.

One question has not been addressed at all so far. The most severe bottleneck in HTE in heterogeneous catalysis, however, is already at this stage—or will be in the near future: the lack of suitable informatics environments. Software support is needed for data storage, data retrieval, data mining, and library design, and we are only seeing the first attempts to solve part of these problems [50,51]. Developments in these fields are highly important, but will require close cooperation between catalysis researchers and software engineers, which is no simple task, since no common language exists. However, if success can be achieved in these fields, fundamental understanding of catalytic reactions could greatly benefit. If the generation of self-consistent large datasets using parallelized hardware is combined with the analysis of such datasets with powerful software, correlations might be discovered which have been elusive so far and which may lead to the development of superior catalysts not just by an increased number of experiments but by an increased number of experiments supported by a better understanding of the underlying correlations. The next 5 to 10 years will show how powerful the techniques described to some extent in this contribution really are.

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