

CO₂ Hydrogenation with Cu/ZnO/Al₂O₃: A Benchmark Study

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The suitability of a commercial and industrially applied Cu-based catalyst for the synthesis of methanol by CO₂ hydrogenation was investigated. Unexpectedly, this system showed high stability and well-performance under conditions that may be relevant for chemical energy conversion using hydrogen and

energy from renewable technologies. This Cu-based catalyst demonstrated excellent suitability for dynamical process operation that may be essential for effective compensation of the volatility of renewable energy sources.

Introduction

Chemical energy conversion (CEC) is a central element in the design of sustainable energy systems.^[1] This element enables the coupling of all energy sectors with primary electricity, solves the storage challenge for long-term and bulk quantities of renewable energy and allows its trading on a global scale using the existing infrastructures for present fossil energy carriers.^[2] In the desired carbon-based cyclic economy, it is critical to achieve an efficient conversion of primary hydrogen gas into secondary energy carriers compatible with existing large-scale transport and storage infrastructures.^[3] One widely suggested key compound in such a carbon cycle is methanol as it is well-known and one of the most important bulk chemicals today and can be used as platform molecule in many energy and chemical production applications.^[4] In such an application scenario the process conditions may be different from the presently well-established methanol synthesis processes. The feed gas would be ideally pure CO₂, while the process operation can always ensure to avoid conditions where the feed becomes excessive in reducing CO, a condition that may damage the technical Cu/ZnO system. The feed may, however, be variable in the CO₂ content and CO₂/H₂ ratios to allow the fluctuating hydrogen output of a water electrolyser unit in response to fluctuating electricity from the renewable generation plants.^[5] The operating pressure may be lower than the conventional conditions of

around 50–80 bar in order to minimize compression cost and considering the large recycle ratios that are dictated by the equilibrium situation of the system. In terms of the choice of the catalyst, the ternary industrial Cu/ZnO/Al₂O₃ system is still the most promising candidate, considering its high activity compared to other catalytic systems in CO₂ hydrogenation to methanol.^[6] The first industrial plant for large-scale CO₂ hydrogenation to methanol was established by Carbon Recycling International in Iceland, where CO₂ from flue gas released by a geothermal power plant was captured and subsequently hydrogenated with hydrogen generated by electrolysis of water to produce methanol with a capacity of 4000 ton per year.^[7]

The present work explores the unique opportunities to use existing catalyst technologies to convert tail gases from a steel mill with green hydrogen to bulk chemicals including methanol as a CEC application. The project Carbon2Chem[®] explores the inter-industrial solutions for the challenges in realizing such a process as part of efforts to reduce CO₂ emissions from base technologies.^[8] A core concern is the large abundance of water formed with a feed gas rich in CO₂. As shown in previous studies, water may damage the delicate structure of the synergistic Cu–ZnO interaction.^[9] Similarly, variable operation conditions such as temperatures or pressures may also be detrimental. The fact that the CO₂/H₂ system generates at high performance substantial amounts of CO through the water gas shift equilibrium counteracts these concerns. It seems indeed important for high performance to continuously refresh the defective form of ZnO to profit from its synergy with Cu.^[10] This requires the presence of CO. Over-reduction of ZnO to brass^[11] that is also a working system albeit with lower activity^[12] than the Cu/ZnO_{1-x} form must also be avoided to maximize performance which is achieved by modulating the reducing potential of CO by water. The catalytic reduction of excessive CO₂ is thus not as unsuitable for MeOH synthesis as it seems at first glance.

The feed gas may contain unusual impurities such as oxygen from the combustion process generating CO₂, which could also deactivate the working catalysts.^[13] The presence of poisons like sulfur- or nitrogen-containing molecules must be excluded by suitable gas cleaning measures as in present industrial realizations. Another major concern is regarding the CO selectivity. The competitive reverse water gas shift reaction

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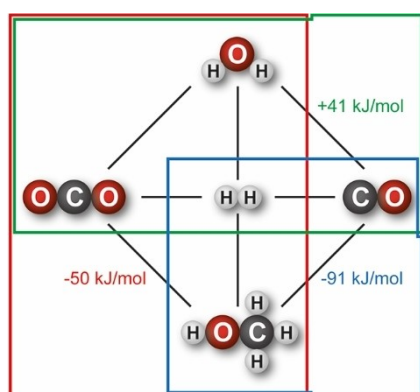
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(RWGS) and methanol synthesis reaction are in equilibria over Cu-based catalysts, as shown in Scheme 1.^[14]

A potential concept to increase the MeOH yield would be the use of a catalyst that cannot activate the RWGS reaction. Indium oxide was suggested as an impressive catalyst for such purpose.^[15] However, it can't exceed the limitations of the equilibria shown in Scheme 1. Even when the RWGS is kinetically inhibited, here far higher temperatures are required compared to the Cu/ZnO system. As the feed gas CO₂ and hydrogen constitutes a reaction network controlled by two equilibria under relevant operation conditions, the achievable MeOH yield is far less due to these limitations.

Under the desired conditions of high productivity of traditional MeOH synthesis,^[16] the above equilibria will effectively create CO and water besides MeOH. Usually, the production conditions are chosen such as to minimize the separating needs and, therefore, a feed gas composition is selected to achieve a maximum MeOH yield at the lowest reaction temperature by effectively eliminating excess water *via* the water-gas shift equilibrium. However, in the present application the maximal reduction of CO₂ is the primary target. As the equilibrium under technically relevant conditions of 30 bar pressure leads only to a limited conversion of CO₂, the unconverted feed has to be recycled and dilute the initial feed stream. The practical feed in a technical reactor will thus contain all components of Scheme 1 with different partial pressures compared to the conventional MeOH synthesis conditions. It seems plausible that a commercial catalyst may be suitable for this application as suggested by a preliminary study.^[17] In view of the urgency to develop world-scale sustainable energy systems keeping the carbon in the loop,^[18] it seems adequate to deepen such studies rather than to try to develop hypothetically more potential catalysts^[15] that may work at much lower temperatures and thus enable the more effective production of MeOH with less CO selectivity, lower recycle ratios and lower separating cost. These attributes become highly relevant when smaller units of decentralized system architectures are considered. It is less relevant to improve the CO selectivity issue on expense of



Scheme 1. The simplest realization of hydrogen and CO₂ under reaction conditions of methanol synthesis. The values in the scheme refer to $\Delta H_{298\text{ K}}$ for the reactions CO₂ + 3H₂ ⇌ CH₃OH + H₂O (−50 kJ/mol), CO + 2H₂ ⇌ CH₃OH (−91 kJ/mol), CO + H₂O ⇌ CO₂ + H₂ (RWGS, 41 kJ/mol).

catalyst productivity.^[19] Hence, the focus of the present work is to report productivity data on the expense of being able to correlate these results to the pertaining mechanistic discussion that can be only meaningful discussed in the kinetic regime and far away from equilibrium performance.

Results and Discussion

Catalyst characterizations and activation

In Table 1, some relevant data of the applied catalyst are given. The Cu surface area and BET surface area is 26.2 m²/g and 118.2 m²/g, respectively. The catalyst has a pore diameter of 9.3 nm and a pore volume of 0.32 cm³/g. It constitutes interconnected nanoparticles of reduced Cu metal nanoparticles and alumina-modified ZnO.^[17] The oxide component fulfills the dual function of a mineral spacer between the Cu particles and of providing an interface between Cu and ZnO, which is widely regarded as where the active sites for CO₂ hydrogenation are located.^[20] Recent literature provides more insightful discussion on the synergy of Cu and ZnO at the interface which facilitates methanol synthesis via formate intermediates.^[21] However, the nature of the active interface sites is still under debate and not solved until today.^[11,21,22]

The tests focused on establishing steady-state data under various stationary and dynamically varying feed conditions. In particular, the stability over timescales relevant for detecting structural deteriorations was addressed with a standard testing time window of 900–1000 h. A critical part of the catalyst testing is the final activation of the pre-catalyst in the reactor. In order to preserve the delicate nanostructure of the system reduction conditions with a very low chemical potential of hydrogen are chosen as described in the experimental part.

Stationary and dynamic experiments

In Table 2 the quantitative results of testing of the industrially applied catalyst under various conditions are shown. Reported are rates and weight time yields (WTY) allowing to judge on the productivity. MeOH synthesis has been carried out at 483 K and 523 K in for of various CO/CO₂ ratios. Furthermore, the obtained WTY_{MeOH} versus CO₂ concentration in the feed gas have been plotted in Figure S1 including the equilibrium values to prove that they are not influenced by the thermodynamic equilibrium. At 483 K the WTY_{MeOH} continuously increases from 0.05 kg_{MeOH}/

Table 1. Physicochemical properties and reaction rate of Cu/ZnO/Al₂O₃ catalysts.

Catalyst	S _{BET} [m ² /g] ^[a]	V _{pore} [cm ³ /g] ^[a]	d _{pore} [nm] ^[a]	S _{Cu} [m ² /g] ^[b]	S _{H₂} [m ² /g] ^[c]
Cu/ZnO/Al ₂ O ₃	118.2	0.32	9.3	26.2	21.1

[a] BET surface area, BJH pore volume and pore diameter determined by N₂ physisorption, [b] Cu surface area determined by N₂O reactive frontal chromatography, [c] Cu surface determined by H₂ chemisorption.

Table 2. MeOH production rates and MeOH WTYs for various feed gas compositions for a Cu/ZnO/Al₂O₃ catalysts at 60 bar.

T [K]	CO ₂ [vol.-%]	CO [vol.-%]	H ₂ [vol.-%]	N ₂ [vol.-%]	r _{MeOH} [mol/kg _{cat} /h]	WTY _{MeOH} [kg _{MeOH} /kg _{cat} /h]
483	0	17	73.5	9.5	1.56	0.05
483	0.5	16.5	73.5	9.5	3.43	0.11
483	3.5	13.5	73.5	9.5	4.99	0.16
483	5.0	12.0	73.5	9.5	5.31	0.17
483	10.0	7.0	73.5	9.5	6.55	0.21
483	17	0	73.5	9.5	11.24	0.36
523	0	17	73.5	9.5	9.05	0.29
523	0.5	16.5	73.5	9.5	69.29	2.22
523	3.5	13.5	73.5	9.5	83.65	2.68
523	5.0	12.0	73.5	9.5	76.47	2.45
523	10.0	7.0	73.5	9.5	55.87	1.79
523	17	0	73.5	9.5	38.08	1.22

Activation conditions: The fresh catalyst was reduced in-situ first at 448 K (1 K/min) for 15 h followed by a further reduction at 513 K (1 K/min) for 0.5 h under a total flow of 100 NmL/min/g_{cat} of a gas mixture of 2% H₂ in N₂ as described in the experimental section.

kg_{cat}/h to 0.36 kg_{MeOH}/kg_{cat}/h with increasing CO₂ concentration. However, at 523 K a maximum for the WTY_{MeOH} was observed with 2.68 kg_{MeOH}/kg_{cat}/h at a CO₂ concentration of 3.5%. These results prove the important role of the CO₂/CO ratio in methanol synthesis and corroborate the primarily methanol formation by the hydrogenation of CO₂ rather than of CO.^[14] At higher conversions achieved at higher temperatures the product inhibition by water becomes more severe with increasing CO₂ content in the feed gas,^[23] but still high MeOH yields are achievable. The introduction of higher amounts of H₂O into the feed gas might even lead to an irreversible change of the catalyst surface structure and the Cu/ZnO interface resulting in a severe deactivation.^[24] However, this was not observed under the conditions applied in the present study.

Figure 1 shows the excellent stability of the catalyst under typical stationary as well as dynamic operation conditions. In the first 1250 h, the feed gas is shifting between H₂:CO₂=3:1 to H₂:CO₂:N₂=1.5:1:1.5 every 15 min interrupted by determination of values at reference condition (H₂:CO₂=3:1) for comparison. Subsequently, more straining conditions were

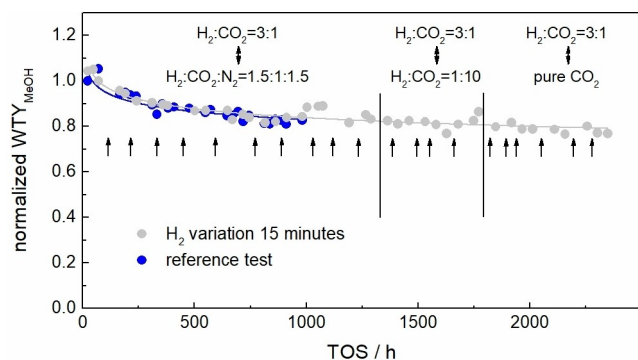


Figure 1. Stability of the catalyst under stationary conditions (blue) and during dynamical operation (grey) with several scenarios. Reaction conditions: 500 NmL/g_{cat}/min, 523 K, 30 bar.

applied for these variations by switching the H₂/CO₂ ratio to 1:10 and in the end to pure CO₂. The deactivation rate after the initial drop of activity in the early stage arising from restructuring of Cu nanostructures^[9] is with 9.5×10^{-8} /h quite tolerable for practical operation and the rate does not deteriorate by the fluctuating H₂/CO₂ ratio.

In Figure 2a the performance for a characteristic set of conditions as function of temperature is shown. From those data points that are not too close to equilibrium apparent activation energies for the MeOH (36 kJ/mol) and for the CO formation (86 kJ/mol) were derived. These data agree well (MeOH 43 kJ/mol, CO 84 kJ/mol) with previous findings derived under similar conditions with, however, an experimental rather than a commercial catalyst sample.^[17]

Figure 2 b reveals that the technical Cu/ZnO system does not output the CO concentration as expected from the RWGS equilibrium for pure CO₂ hydrogenation. It remains elusive if this effect working in favour for a technical MeOH synthesis is due to a kinetic hindrance of the equilibration (few active sites or active sites poisoned by either CO or hydrogenation products (formate, methoxy) that are different from those of the MeOH synthesis) or due to the concomitant action of the RWGS

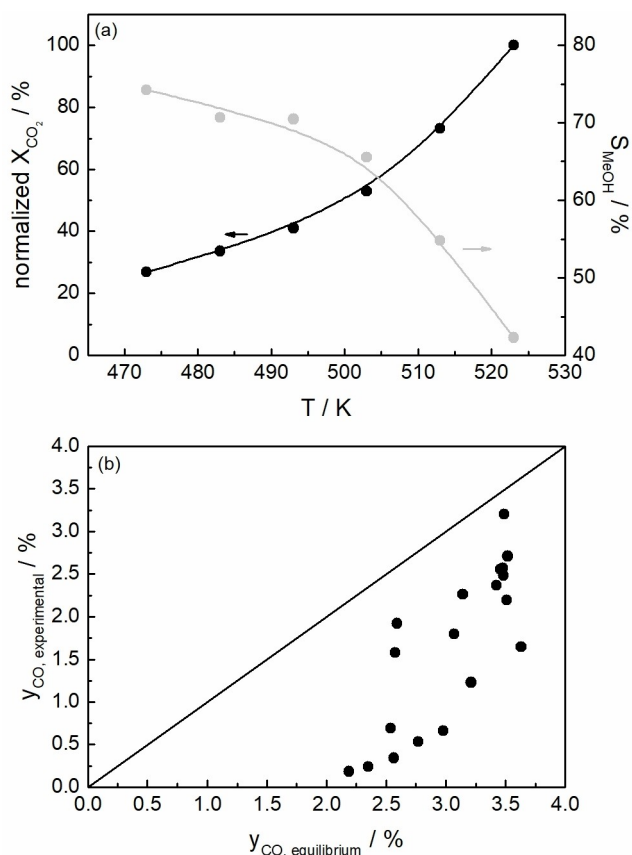


Figure 2. a) Conversion of CO₂ and MeOH selectivity after 1000 h TOS at the following reaction conditions: 500 NmL/g_{cat}/min, H₂:CO₂=3:1, 473–523 K, 30 bar. b) Parity plot for experimentally obtained vs. equilibrium CO concentrations under various operation conditions. Equilibrium values for the RWGS were calculated with CHEMCAD considering the experimentally determined MeOH formation.

reaction forming additional CO₂ reacting further to MeOH.^[14] From previous studies it can be excluded that the parallel reaction of CO to MeOH plays a relevant role in the reaction network.^[14,25] The combined action of CO and water may modify the active catalyst form compared to standard feed compositions by enhancing the interface area between the two phases and so reduce the RWGS activity by reducing the site density of bare Cu being responsible for RWGS.^[26]

Triggered by the well-established studies on structural dynamics of the Cu/ZnO system^[27] that found a conceptual explanation in a corresponding dynamical microkinetic model^[28] it may be expected that the Cu/ZnO system can be operative without damage under fluctuating feed conditions. The structural origin of this unusual property of a heterogeneous catalyst is the creation of active sites at the perimeter of the synergistic components Cu metal and defective ZnO. The defect concentration of ZnO controlled by the chemical potential of the feed (and promoters X) defines the wetting behaviour to Cu, which affects the structure-sensitive MeOH synthesis. This interplay may be more complex by the action of traces of oxygen species^[20b] which will not be discussed further here. In the context of CEC this property of the Cu/ZnO system may be used to construct a “chemical battery”.

The fluctuations of renewable energy translate directly into fluctuations of hydrogen generated from it. Instead of integrating a suitably large storage facility for hydrogen one may consider operating part or the whole methanol reactor system under dynamical load and thus buffer the initial fluctuations of energy in the MeOH tank at the end of the process which is considerably more economic.

In order to explore this option a large number of dynamical experiments was carried out in an attempt to find the operation window for a chemical storage scenario. As strategy sequences of dynamical operation times were intermixed with steady-state operation over a total of 900–1000 h TOS each (Figure S2–6). The resulting performance was compared to the steady-state operated case in order to observe possible degradation effects. In Table 3 typical scenarios and the relative weight time yields are reported. A graphical representation of the data from Table 3 is given in Figure S2–6. As a result, none of the investigated dynamic conditions led to an increased deactivation rate for the industrial Cu-based catalyst. The remarkable stabilities of catalysts under various fluctuations are summar-

ized in Figure S6. Corresponding with the results of the catalytic measurements, the Cu-based catalyst after dynamic operation exhibits a very similar XRD pattern as the catalyst after reference test (Figure S7), indicating the phase composition of the catalyst was not significantly changed by these intermitting conditions.

In Figure 3 an example of a dynamical experiment is presented. This example uses a relative short interval with respect to possible hysteresis effects of a solid-state transformation. The dwell time of 15 min was chosen to mimic the possible load change of the water electrolyser controlled by the electric grid as a fraction of green energy available in the German electricity supply system.

In Figure 3a, a section of responses following the hydrogen switches with a concentration from 37.5% to 75% is shown. The pulse shapes are corrupted by condensation effects of the products in the reactor system. In Figure 3b a similar experiment was carried out with the same catalyst but in a reactor equipped with suitable heating devices for time-resolved detection. The response of the catalyst is instantaneous to the change in the chemical potential within the experimental time resolution of 30 s. In Figure 3c the compilation of pulse periods (one set of experiments for 20 h per arrow) and of steady-state operation is compared to a continuous run using a fresh catalyst sample. The identity of the two traces documents the absence of any detectable structural or chemical damage of the catalyst based on the WTY_{MeOH}.

According to Table 3 and Figure 3, it is evident that the system operates under all chosen variations of the chemical potential of the feed without any signs of degradation. This unexpected property of a catalytic system is in line with the dynamical nature of the active sites. The observations are thus not circumstantial but well supported by a deep functional understanding.^[22b] An operation scheme of MeOH synthesis as chemical battery is thus a realistic alternative to hydrogen storage tanks in a CEC plant operating on fluctuating primary electricity.

Conclusion

In summary, the present experiments reveal the suitability of the Cu/ZnO/Al₂O₃ system in technical realizations for the CO₂

Table 3. Selectivity and WTY for MeOH under dynamic reaction conditions for CO₂ conversion over an industrial Cu/ZnO/Al₂O₃ catalyst.

Scenario ^[a]	P [bar]	T [K]	CO ₂ [vol.-%]	H ₂ [vol.-%]	Flow rate [NmL/g _{cat} /min]	S _{MeOH} [%] ^[a,b]	normalized WTY _{MeOH} ^[b]
Reference test	30	523	25	75	500	40	0.85
Temperature variation*	30	523	25	75	500	37	0.87
	30	483	25	75	500	54	0.49
Flow rate variation	30	523	25	75	500	42	0.86
	30	523	25	75	1000	44	1.32
Pressure variation	30	523	25	75	500	43	0.78
	50	523	25	75	500	50	1.14
H ₂ conc. variation	30	523	25	75	500	44	0.78
	30	523	62.5	37.5	500	28	0.32

[a] MeOH and CO are the only two products. Therefore, S_{CO} = 100 - S_{MeOH}. [b] Values at around 900 h TOS; *after 600 h TOS.

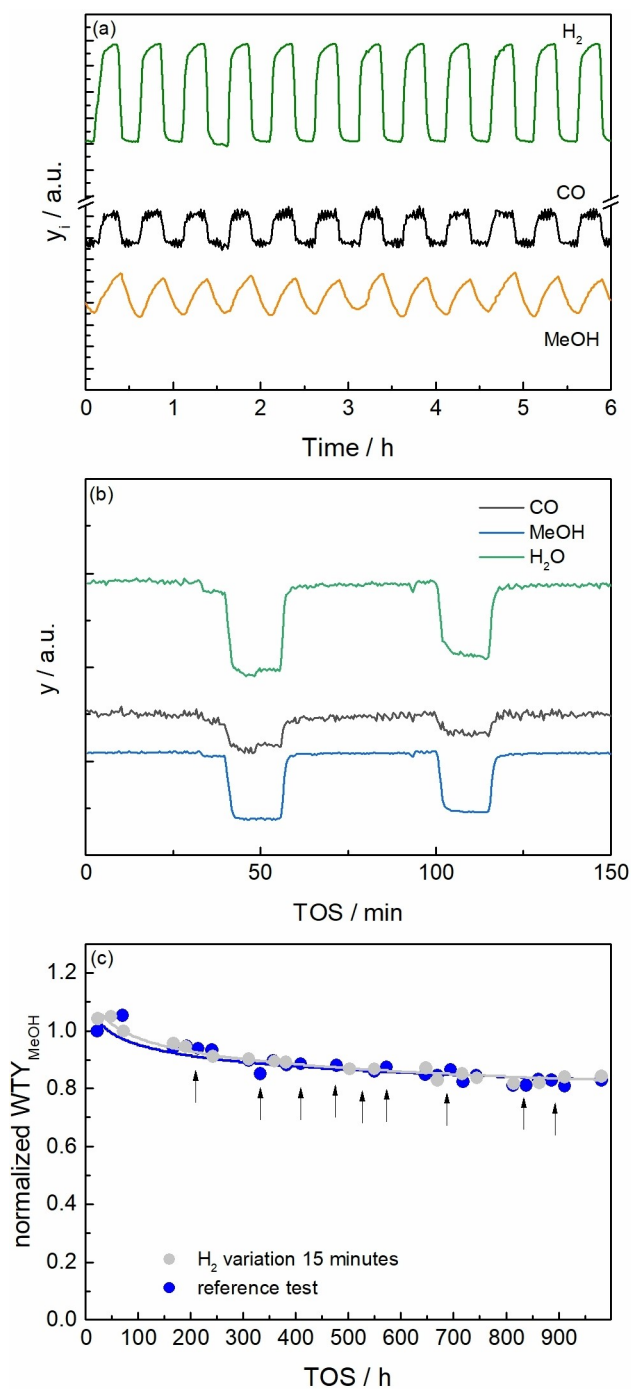


Figure 3. Example of a dynamical operation of MeOH synthesis acting as chemical battery. (a) The effect of H₂ switches every 15 min for MeOH production measured by IR (b) similar to a, but with suitable heating devices (c) Normalized WTY_{MeOH} for H₂ variation every 15 min for 900 h at reaction conditions: 500 Nml/g_{cat}/min, H₂:CO₂ = 3:1 and H₂:CO₂:N₂ = 1.5:1:1.5, 523 K, 30 bar.

conversion to MeOH. Especially, the dynamic experiments show that the highly stable Cu/ZnO/Al₂O₃ catalyst enables the concept of methanol synthesis as a chemical battery to compensate fluctuations of the H₂ supply, which commonly accompany the generation of green H₂ using renewable energy.

Considering the cost and safety issues, methanol is significantly more attractive than H₂ as a short-term storage of energy, especially for large-scale applications. The system performance is limited by lower thermodynamic equilibrium conversions compared to the conventional syngas feeds.^[6] The stability of the catalyst is not problematic under the applied conditions despite the enhanced load with water compared to conventional MeOH synthesis. In a practical realization of a MeOH plant the necessary recycle of the feed gas enforced by the low equilibrium conversion (25% at 30 bar) will automatically lead to an average feed gas that contains both, CO and CO₂, shifting the working point of the catalyst closer to that of a conventional process.^[6] The task to realize a CEC MeOH plant becomes thus an optimization challenge of where to remove excess water and how to realize recycle and the necessary removal of tail gas rather than a task for catalyst material science. A challenging research opportunity for catalysis science lies in reducing the operation temperature of the process into regimes where the process could operate as slurry in its liquid products. Then the equilibrium conversions would be attractively higher, the recycle problem as well as the total process energy would be reduced. It is questionable that a reaction concept based upon the Cu/ZnO system may solve such a challenge. The observation that at the limiting lower reaction temperature of about 483 K the catalyst interface is made up of a combined layer of water and of organic intermediates strongly points to the fact that product inhibition marks the lower limit of the reaction temperature.^[29] A way forward to overcome this limitation could be a catalyst material designed with the idea of a modified Fischer-Tropsch reaction as working concept. Then selective hydrogenation of CO generated by preceding RWGS either within the same reaction network or as a pre-process may be the source of MeOH. If this alternative process could be highly selective towards alcohols and not to alkanes then completely new avenues of CEC would be opened. Reports on Mo-based systems that work from CO/CO₂ as feed indicate that such a possibility may serve as alternative to the Cu/ZnO system.^[30] It would be highly desirable to evolve the operation scheme away from conventional Cu/ZnO conditions into low-temperature and high-pressure parameter combinations where liquid phase synthesis may be possible to explore novel schemes of MeOH synthesis as a breakthrough against the now well-established Cu/ZnO system. Suitable catalyst formulations could even react the excess CO with olefin byproducts to higher alcohols and generate a mixture of compounds that may serve as a low-pollution synthetic fuel. Such a multi-functional process converting CO₂ and hydrogen in one step to a transportation fuel with minimal local emissions may be an attractive path forward.

Experimental Section

Catalysts and chemicals

A commercial Cu/ZnO/Al₂O₃ catalyst provided to the Carbon2-Chem® project by Clariant Produkte (Deutschland) GmbH was used in the present study.

Catalyst activation and testing

The catalytic testing in CO₂ hydrogenation is performed in a flow setup equipped with a fixed-bed reactor. The setup is described in detail in [17]. 1 g of the Cu/ZnO/Al₂O₃ catalyst in a sieve fraction of 250–355 μm is placed between two quartz wool plugs in the middle of the isothermal zone, while the rest of the reactor is filled with SiC to minimize the dead zones in the setup. For each experiment a fresh catalyst sample is used and activated prior to the catalytic tests. The catalyst is reduced in-situ first at 448 K (1 K/min) for 15 h followed by a further reduction at 513 K (1 K/min) for 0.5 h applying a flow of 100 NmL/min/g_{cat} with a gas mixture of 2% H₂ in N₂. Afterwards, a total syngas flow of 500 NmL/min/g_{cat} with a H₂:CO₂ ratio of 3:1 was adjusted and the pressure increased to 30 bar. The catalyst was stabilized for one week at 523 K after the beginning of the MeOH synthesis and prior to the variations of the experimental conditions. For comparison, one measurement was performed where these conditions were kept for 1000 h to be able to judge on the impact of intermitting conditions on the deactivation rate. For the dynamic experiments, the time-on-stream measurements were performed up to 1000 h with frequent switches between defined reaction parameters. The parameters considered for these variations are mainly temperature, pressure, residence time as well as the partial pressure of H₂. The applied parameters in the conducted measurements are given in Table 3. After switching the reaction conditions, the system was equilibrated for 4 h to ensure steady-state. As the products MeOH and water are condensed at 278 K, a time of around 20 h was required to collect a suitable amount of product for reproducible quantification and analysis. After determination of the performance of the catalyst at the changed reaction conditions the parameters were changed back for comparison to the reference test at constant conditions. In the ongoing measurement, the parameters were changed alternating between the two given conditions (in the figures switches are marked with arrows). For the experiment with fast switches the liquid products were not condensed. Here, the gas composition was followed by an IR detector.

Catalyst characterization

Before desorption and RFC experiments, the catalyst is reduced with a flow of 10 NmL/min of 2% H₂ in He (very high pure, ≥ 99.9999%). The temperature is first increased to 448 K with a rate of 1 K/min and then hold for 12 h. After that, the temperature raised to 513 K with a rate of 1 K/min and hold for 1 h. Then the catalyst was flushed with He for 1 h and cooled to room temperature. The detailed experimental procedure for the H₂ TPD as well as for the N₂O RFC measurements is described in [31].

Nitrogen physisorption measurements were performed at 77 K using a BELSORP-mini apparatus (BEL Japan, Inc.). In order to remove adsorbed water, the sample (250–355 μm sieve fraction) was pretreated at 473 K for 2 h under vacuum. The specific surface area was derived from the adsorption isotherm using the BET method. The pore size and pore volume were obtained by applying the BJH method. X-ray diffractograms of the powdered samples were recorded using a Bruker D8 DISCOVER diffractometer with Cu Kα radiation (λ = 1.5418 Å, 40 kV, and 40 mA). The powders were

deposited on a Si zero background sample holder, and investigated in the range from 5 to 80° 2θ with a step size of 0.02° 2θ and a counting time of 5.0 s per step. The obtained XRD patterns were analyzed with the DIFFRAC.EVA software by Bruker. All samples were exposed to air briefly before the measurement.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ hydrogenation · Energy conversion · Heterogeneous catalysis · Chemical battery · Cu/ZnO/Al₂O₃

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