

Methanol Synthesis from Steel Mill Exhaust Gases: Challenges for the Industrial Cu/ZnO/Al₂O₃ Catalyst

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One of the major goals of current research on energy conversion is the mitigation of CO₂ emission. A beneficial scenario for CO₂ utilization is the catalytic conversion of industrial waste or process gases into valuable products. Within the cross-industry approach of Carbon2Chem[®] the synthesis of methanol from steel mill exhaust gases is a promising way to close the carbon cycle based on additional sustainably produced H₂. New catalyst requirements have to be met due to fluctuating feed gas composition and availability as well as gas separation and purification issues.

Keywords: Carbon2Chem[®], CO₂ recycling, Methanol synthesis, Poisoning, Steel mill exhaust gases

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1 Introduction

Nowadays, the low efficiency of established energy systems, the scarcity of carbon-based energy resources as well as the worldwide rising energy consumption require alternatives for energy conversion and substitution of fossil fuels. Additionally, the strict regulation of CO₂ emission by the Kyoto agreement promotes defossilization. Hence, much effort is put on the development of strategies for utilizing CO₂ as an alternative carbon source due to its continuous and significant rise in the atmosphere and its resulting impact on global warming [1, 2]. One promising route is the conversion of industrial CO₂ sources into important platform chemicals such as methanol that can directly be integrated into the existing production chains of the manufacturing industry.

Methanol is one of the most important base chemicals worldwide, especially as C1 building block for industrial chemicals. The majority of methanol is produced by converting synthesis gas, a mixture of CO, CO₂, and H₂, usually derived from reforming of natural gas. The use of methanol has grown in the last decades to around 90 Mt in 2017 [3, 4], resulting in methanol synthesis being one of the most extensively researched topics. The global methanol demand by end-use are the production of formaldehyde (27%), olefins (18%), acetic acid (9%), and methyl *tert*-butyl ether/*tert*-amyl methyl ether (MTBE/TAME) (8%) [5]. Furthermore, more than 16% of methanol consumed is used as solvent or fuel additive [6, 7]. Due to its high octane number and low amount of undesired products during emission,

methanol was investigated as a clean transportation fuel for applications such as methanol/gasoline and methanol/diesel blends utilized in internal combustion engines/turbines [8].

Additionally, the methanol economy concept, earlier proposed by Olah [9], proposes carbon capture and recycling (CCR) from all kinds of anthropogenic or natural sources and subsequent formation of methanol using renewable energy resources, resulting in a carbon-neutral process. Methanol is proposed as a sustainable and universally available regenerative carbon platform, which can be used as transportation fuel, as liquid hydrogen carrier for energy storage, and as raw material for the formation of more complex chemicals [10–13]. Therefore, by the use of biomass-derived CO₂ or recycled CO₂ from industrial plants such as coal-fired power plants or steel mill plants, methanol synthesis can contribute to CO₂ mitigation of greenhouse gas

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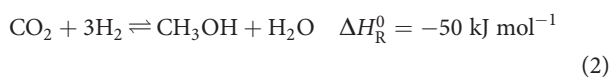
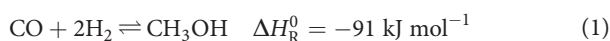
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concentrations in the atmosphere [14]. Thus, topics like emission-to-liquid or power-to-fuel [15,16], where CO₂ emissions can be utilized using renewable energy, are investigated intensively and several pilot plants have already been built [17–19]. The high energy demand of converting the thermodynamically very stable molecule CO₂ is the most challenging task. Moreover, although the industrial steady-state methanol synthesis process has already been extensively investigated during the last 50 years, its optimization to suit alternative process routes, fluctuating feed compositions as well as the increased energy demand is still challenging.

The first application of methanol synthesis in industry was achieved by BASF SE using a Zn/Cr₂O₃ catalyst for the conversion of a gas mixture containing CO, CO₂, and H₂ at high temperatures of 300 to 400 °C and pressures up to 300 bar in 1925 [20]. The catalyst showed high resistance against sulfuric and chlorine impurities occurring in the synthesis gas and was used during the following decades [21, 22], although the process parameters were energetically inefficient. With ongoing catalyst and process development, especially by improvement of gas purification techniques, an alternative catalyst system consisting of CuO (40–80%), ZnO (10–30%), and Al₂O₃ (5–10%) in the unreduced state [6], was introduced and patented by Imperial Chemical Industries (ICI) in 1966. Its high activity allowed to operate the process at reduced temperatures of 200 to 300 °C and lower pressures of 50 to 100 bar [6, 23–25]. Furthermore, due to the milder reaction conditions, the formation of light hydrocarbons was suppressed resulting in an increased overall methanol selectivity [26].

2 Thermodynamics and Kinetics

The ternary Cu/ZnO/Al₂O₃ catalyst has been applied under similar reaction conditions since more than 50 years. Due to the industrial importance of methanol synthesis, numerous investigations were performed to understand the nature of active sites on metallic Cu surfaces, the role of ZnO and Al₂O₃ as well as the specific reaction mechanism, leading to some controversially discussed results. Contrary to prior investigations by Klier et al. [27] who postulated CO being the main carbon source in methanol synthesis, it is now generally accepted that methanol is essentially formed from CO₂ [28–33]. By applying isotopic tracer techniques in combination with kinetic measurements, it was demonstrated that hydrogenation of CO₂ proceeds much faster than CO hydrogenation. The formation of methanol from synthesis gas is described according to the following equations [6]:



However, both reactions are coupled by the reverse water-gas shift (RWGS) reaction, which is also catalyzed by Cu:



The reactions in Eqs. (1) and (2) have a mild exothermic character. Increasing the temperature leads to a thermodynamic limitation of methanol formation shifting the reaction equilibrium towards reactant formation, while the RWGS rate (Eq. (3)) is increased. Additionally, the formation of methanol results in a volume contraction. Thus, to achieve high conversion of CO_x, low temperatures and high pressures (Le Châtelier's principle) are beneficial, requiring a highly active hydrogenation catalyst. Another thermodynamic limitation occurs by variation of the synthesis gas composition. For sufficiently high equilibrium conversion, the concentration of CO₂ and inert components in the make-up gas should be kept low [34]. Consequently, industrial applications for methanol production use a higher amount of CO compared with CO₂ in the feed gas, enhancing the equilibrium yield of methanol as shown in Fig. 1.

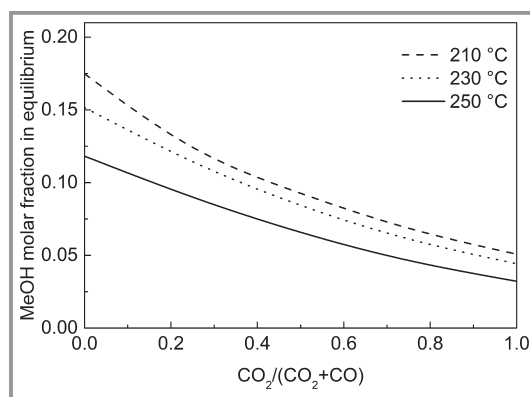


Figure 1. Equilibrium molar fraction of methanol with increasing CO₂/CO_x ratio (calculated using AspenPlus® software, adapted from [35]).

Due to the described thermodynamic limitations, only a small fraction of the synthesis gas is converted to methanol in a single pass ($Y_{\text{MeOH}} = 15–25\%$). Thus, for high overall degrees of conversion, the implementation of a recycle loop is necessary in combination with a purge gas stream to remove impurities that would otherwise accumulate over time. Additionally, the slow rate of methanol formation does not allow the reaction to be performed at lower temperature. Hence, to have a sufficient space-time yield, the process is carried out in the range of 200 to 300 °C. Methanol production is also affected by catalyst deactivation because of poisoning, thermal sintering, or carbon formation [36], with suitable catalysts remaining active up to 4 years [37]. Under typically applied process conditions, the water-gas shift (WGS) reaction can be assumed to be in equilibrium, leading to an improvement of methanol pro-

duction from synthesis gas due to the formation of additional CO₂ and H₂, which can be further converted into methanol [38]. Additionally, produced H₂O, which is known to inhibit active sites for methanol formation on the catalyst surface, is consumed by the WGS reaction [39, 40].

3 The Ternary Catalyst

Commonly used Cu/ZnO/Al₂O₃ catalysts are prepared by co-precipitation of a metal nitrate solution with sodium or ammonium carbonate, followed by calcination and reduction, leading to systems with slightly varying compositions [35, 41]. A linear relationship between the catalytic activity and the accessible Cu surface area for series of catalysts with similar preparation parameters is generally accepted [28]. Moreover, Rasmussen et al. [42] showed on a Cu(100) single crystal surface that unpromoted metallic Cu⁰ is able to catalyze methanol synthesis. Recently, Cu steps have been identified as active sites [43]. Additionally, the low amount of alumina acts as a structural promoter to prevent sintering of the Cu crystallites [44].

ZnO is regarded as a chemical promoter strongly influencing the overall catalytic activity. It enhances the dispersion of Cu particles and stabilizes the Cu crystals by suppressing agglomeration and, therefore, providing larger specific Cu surface areas [45]. Furthermore, surface defects resulting from ZnO promotion play an important role in methanol formation. The increasing activity was attributed to stronger bound intermediates on Cu stepped sites and the lower energy barrier between them [30, 43]. Additionally, strong metal-support interactions (SMSI) were found to originate from the partial reducibility of ZnO [46–48]. Due to this dynamic effect, Cu is partially covered with ZnO_x species, leading to a strong interaction between both compounds already under relatively mild conditions. Thus, experimental data and theory indicate a favorable effect of metallic Zn atoms at the surface of the Cu particles leading to highly active catalysts [45, 49–51]. Therefore, high dispersion of the active Cu component as well as an intimate contact between Cu, ZnO, and Al₂O₃ is crucial.

4 Methanol Synthesis Technologies

World-leading low-pressure processes for methanol synthesis are provided by Johnson Matthey (ex Syntex, ICI company), which have licensed over half of the world's methanol plants, and by Lurgi (a company of Air Liquide) [52–54]. Further processes via low-pressure technologies are offered by Topsoe, Mitsubishi Gas Chemical Company, and Halliburton [52, 55]. The processes are based on highly integrated technology concepts, comprising synthesis gas generation, gas purification, methanol synthesis, and product separation. Purification and composition of the synthesis gas are essential for methanol production, with respect

to operation and investment costs, which are more than 50 % when using natural gas as feedstock and more than 70 % when using coal [54]. In general, the reaction network of methanol synthesis leads to a favorable make-up gas composition described by the stoichiometric number SN, which should be slightly larger than 2.

$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \quad (4)$$

Commercial methanol plants based on synthesis gas operate at steady state using a broad variety of converter designs with methanol capacities up to 10 000 t d⁻¹ [54, 56]. One of the main tasks during these processes, which can be performed in either isothermal or adiabatic mode, is the removal of heat produced during the exothermic reaction to achieve high methanol yields [6, 57]. For further enhancement of the methanol yield, product separation through condensation steps and the application of recycle loops are required. Nowadays, a carbon efficiency of 83 % can be reached with a methanol selectivity of 99.8 % and energy efficiencies in the range of 70 to 75 % [54, 56]. All catalysts applied in these processes are based on the ternary Cu/ZnO/Al₂O₃ catalyst [58]. The optimization of the reactor concepts and the development of new production technologies is still part of ongoing research, in particular, aiming at minimizing the investment cost and improving energy efficiency [26].

5 CO₂ Utilization from Steel Mill Exhaust Gases

State-of-the-art steel mills as large and highly integrated sites generate different gas streams that are potential sources of CO₂, CO, and H₂. These streams differ in their composition and in their total amounts and availability. In addition, the gases are usually integrated in the internal heat and power supply of the steel mill. In addition to the current energetic utilization, steel mill gases provide the promising opportunity to be utilized as feedstock for bulk chemical production. Depending on the availability of sustainably produced H₂, the enormous CO₂ footprint of the steel mill can be reduced, which accounts for 5–7 % of anthropogenic CO₂ emission [59, 60]. However, the commercial Cu-based catalyst applied in industrial methanol synthesis is optimized for the conversion of CO-rich synthesis gas under steady-state conditions. A current challenge is to assess the applicability of commercial methanol synthesis catalysts in the conversion of synthesis gas derived from steel mill exhaust gases. For sufficient methanol productivity, these typically hydrogen-poor gases must be enriched with H₂ – ideally based on sustainable sources. The range of typical gas compositions is shown in Tab. 1. All gases contain some minor amounts of impurities, which may influence the stability and activity of the catalyst.

Table 1. Ranges of composition (in %) of steel mill off gases adapted from [14, 59, 61–65].

Compound	BFG	COG	BOFG
H ₂	3–4	55–66	4–5
CO	20–25	6–8	58–65
CH ₄	0	20–26	0
C ₂ H ₆	0	1–3	0
CO ₂	21–24	2–3	17–20
N ₂	48–55	2–10	14–18

Numerous case studies showed that utilization of steelwork exhaust gases can be applied with economic and environmental benefit [59–72]. In principle, two different scenarios of gas utilization are possible (Fig. 2). The first scenario refers to a utilization of H₂-rich coke oven gas (COG) in combination with CO-rich basic oxygen furnace gas (BOFG, converter gas). A mixture of both gas types, also with the possibility of previous H₂ separation from COG, as well as steam and dry reforming or partial oxidation from the CH₄-rich COG results in a synthesis gas mixture consisting of the main compounds with a stoichiometric number in the range of 1 to 3 similar to synthesis gas generated by steam reforming of natural gas [60–64]. Here, the major challenge is attributed to the presence of minor and trace compounds, which may detrimentally interact with the Cu/ZnO/Al₂O₃ catalyst.

The second way refers to using blast furnace gas (BFG). To significantly reduce the overall CO₂ emission of a steel mill, utilization and conversion of BFG is the key step as it provides the highest amount of CO₂ of all exhaust gases [68]. Due to its high amount of inert N₂ and its deficit in H₂ content, a direct conversion is less efficient [34]. Since

the availability of H₂-rich COG is limited, an enrichment of BFG with H₂ is mandatory. The generation of H₂ should be performed with regenerative energy sources to retain a positive carbon footprint. For the direct conversion of BFG, the high N₂ amount becomes a major issue. N₂ separation would be beneficial, but would come along with a high energy demand and high cost for an appropriate N₂ separation step. The other possibility is using BFG without N₂ separation, leading to a lower reaction rate, and hence, a reduced achievable degree of conversion making a recycling of nonconverted CO_x highly necessary. Nevertheless, for an efficient usage of BFG, the major requirement in this scenario is the applicability of the commercial Cu-based catalyst with respect to catalyst stability and performance in the hydrogenation of CO₂-rich or pure CO₂ gas streams.

6 Impact of Impurities in the Exhaust Gases on the Stability of the Catalyst

When mixing COG and BOFG to obtain a conventional synthesis gas for methanol synthesis, high amounts of various impurities have to be considered, which can act as catalyst poison leading to strong deactivation of the catalyst. In general, deactivation is defined as the loss of catalytic activity and/or selectivity over time and can be described by chemical or mechanical effects: poisoning (reversible or irreversible), thermal degradation (sintering), vapor compound formation accompanied by transport, vapor-solid and/or solid-solid reactions, fouling, and attrition/crushing [73]. For most catalysts, thermal sintering and poisoning are the main reasons for the loss of activity and reduction of lifetime. In case of conventional methanol synthesis over Cu/ZnO/Al₂O₃ catalysts, sintering can decrease the active Cu surface area and the ZnO support area impairing the Cu-ZnO interaction (SMSI). The mechanism is not com-

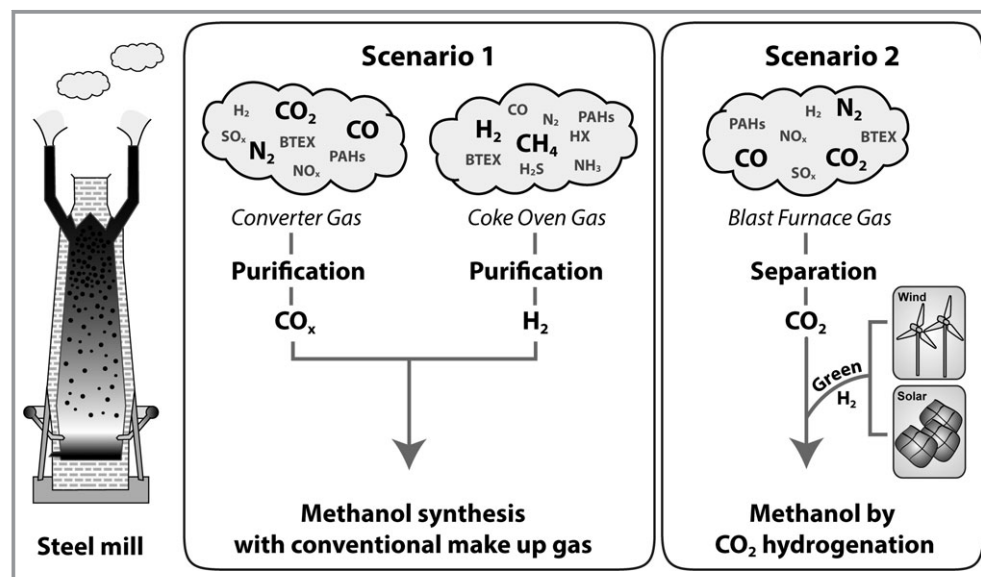


Figure 2. Possible utilization of steel mill exhaust gases to synthesize methanol. Purification and blending of COG and BOFG (scenario 1) or CO₂ separation of BFG in combination with sustainably produced H₂ (scenario 2). BTEX: benzene, toluene, ethylbenzene, xylenes. PAH: polycyclic aromatic hydrocarbons.

pletely clarified yet [44]. Relatively high operation temperatures and high degrees of conversion do not only lead to an enhanced mobility of the Cu particles, but also to a surface reconstruction and sintering of the ZnO support [74]. As a result, both phases separate from each other and the synergy is lost.

In contrast, poisoning is a rare problem for conventional methanol synthesis due to the high purification degree of synthesis gas from steam reforming. However, the usage of exhaust gases from steel production can result in new challenges due to the presence of a high number of different impurities in low concentrations (ppm or ppb region), which can act as catalyst poisons and are summarized in Tab. 2 [75].

Catalyst poisons interact with the active sites of the catalyst. This interaction results in deactivation by blocking of active sites or of the whole surface as well as by changing the surface morphology [73]. Poisons can deactivate a catalyst by irreversible or reversible mechanisms. Irreversible poisons interact specifically with the active sites by the formation of strong chemical bonds or by the reaction with catalytically active phases. The interaction between reversible poisons and the active sites is less pronounced, since the poison only weakly coordinates to the site, and the removal of the reversible poison from the process gas leads to the regeneration of the catalyst without applying additional regeneration procedures. For most of the impurities in Tab. 2 it is not known whether they interact as poisons, since only little information on catalyst poisoning is found in literature.

The best described compound with respect to its poisoning ability is H₂S. It is a common impurity in fossil fuel-derived synthesis gas and one of the strongest inhibitors in methanol synthesis over Cu/ZnO/Al₂O₃ catalysts [36, 76].

Table 2. Potential impurities of exhaust gases from steel production [75]. PCDD/F: polychlorinated dibenzodioxins and dibenzofuranes. PCB: polychlorinated biphenyl.

Compound class	Compound
Hydrocarbons	CH ₄ , C ₂ H ₄ , C ₂ H ₆ , cyclopentadiene, propane, propylene, butane, acetylene, pentene, heavy hydrocarbons
Aromatics	Phenol, benzene, toluene, xylene
Polycyclic aromatics	Naphthalene, phenanthrene, benzopyrene, fluoranthene
S-compounds	SO _x (SO ₂), H ₂ S, COS, CS ₂ , thiophene, mercaptan
N-compounds	NO _x (NO ₂ , NO), NH ₃ , HCN, tar bases (C _x H _y N), pyridine, (CN) ₂
O-compounds	O ₂ , H ₂ O, tar acids (C _x H _y OH)
Heavy metal compounds	Cr, Mn, Ni, Pb, Zn, Hg, As, Cd
Halides	HCl, HF, inorganic fluorides, PCDD/F, PCB
P-compounds	Trivalent phosphorus
Dust	FeO _x , alkali metals, alkali earth metals, metal oxides, CdO _x , elemental sulfur, elemental carbon, Hg

Based on thermodynamics, the adsorption of H₂S on Cu sites is highly favored due to the relatively low temperatures applied in methanol synthesis [36]. Therefore, the H₂S level should not exceed 0.1 ppm in the synthesis gas to realize a long lifetime of the catalyst [36]. However, H₂S interacts not only with the metallic Cu phase, but also with the ZnO support according to the following equations [36]:

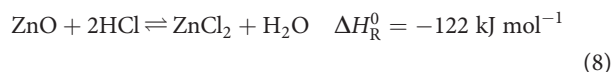


Here, the sphalerite form of ZnS is more stable than wurtzite [36]. The poisoning by H₂S is thermodynamically favored [36]. Furthermore, H₂S not only interacts with the catalyst surface, but also bulk sulfide phases (ZnS, CuS, Cu₂S, and CuSO₄) are formed [77]. These phases are inactive for methanol formation from synthesis gas [77]. In the case of industrial methanol synthesis, low concentrations of H₂S lead to a fast deactivation due to passivation of the outer surface of the catalyst pellet. Higher levels of H₂S result in an increasing thickness of an egg-shell arrangement of sulfide phases around the sulfur-free core [78]. In addition, redistribution and migration of the sulfide phases can take place. For example, the CuS phase tends to migrate over the surface due to the lower melting point compared to metallic Cu blocking the pore structure [77]. Consequently, the catalyst becomes inactive before the active phase is fully sulfided.

For methanol synthesis, the following affinity sequence towards H₂S adsorption was established: Al₂O₃ < ZnO < Cu₂O < Cu/ZnO < Cu [79]. At low sulfur coverages, atomic S interacts only with the metal centers. Increasing degrees of coverage lead to the formation of metal sulfide phases.

H₂S also reacts with metal oxide sites. Application of a perturbation theory and orbital mixing suggests that the reactivity to sulfur is enhanced with smaller band gaps allowing to rationalize the affinity sequence [79]. For the binary Cu/ZnO system, the introduction of ZnO leads to an electronic perturbation of the metallic Cu phase based on the SMSI effect. As a result, the sulfur affinity of the Cu sites decreases and, additionally, ZnO adsorbs H₂S to form ZnS and hereby protects the Cu sites. Therefore, industrial Cu/ZnO/Al₂O₃ catalysts with higher ZnO contents display a higher lifetime in methanol synthesis when H₂S is present in the synthesis gas [36].

In addition to H₂S, other impurities are known as irreversible poisons for the Cu/ZnO system like other sulfur compounds, metal carbonyls, trivalent phosphorus, and halides, which can also be present in the exhaust gases [36]. Examples of standard sulfur impurities are *tert*-butyl mercaptan (TBM), tetrahydro thiophene (THT), and dimethyl disulfide (DMS) [80–82]. However, H₂S is the most aggressive poison compared with other investigated sulfur components, since the breaking of a C–S bond needs more energy relative to H–S bonds to form metal sulfide species [80]. The poisoning mechanism by halides is comparable to the deactivation by sulfur compounds. One prominent candidate is HCl. The interaction of Cu/ZnO/Al₂O₃ catalysts with HCl also results in blocking of active sites as well as in reaction with the catalytic phases [36]:



The formation of the metal chlorides causes high surface mobility. Moreover, sintering is strongly accelerated due to the very low melting point of the chlorides.

So far, no regeneration procedures for poisoned methanol synthesis catalysts have been developed. Most of the regeneration strategies known for other catalysts require high temperatures far above normal synthesis temperatures. This would lead to higher thermal stress for Cu-based catalysts enhancing sintering and resulting in irreversible deactivation of the catalyst [36]. Therefore, alternative catalysts with higher poison resistance were developed to replace the Cu/ZnO/Al₂O₃ catalyst. With respect to sulfur poisoning, MoS₂-based catalysts, Pd sulfides on SiO₂, and Pd on CeO₂ are promising systems for methanol synthesis in the presence of H₂S [83–85].

Concerning the influence of hydrocarbons, aromatics, polycyclic aromatics, O-compounds, and N-compounds on the catalytic activity of the Cu/ZnO/Al₂O₃ catalyst, no significant information is found in literature. For liquid-phase methanol synthesis with a commercial Cu/ZnO/Al₂O₃ catalyst, the influence of sulfur compounds, halides, phosphine, metal carbonyls, and N-compounds (hydrogen cyanide, acetonitrile, and methylamine) was investigated [86–88]. Surprisingly, the presence of the N-compounds did not lead to a decrease of the catalytic activity, and it is assumed that these results are relevant for gas-phase methanol synthesis in a fixed-bed reactor. However, experimental validation of this statement and detailed studies on the influence of most of the impurities in Tab. 2 are mandatory to assess the necessary degree of purification of the exhaust gases for their application in methanol synthesis.

7 CO₂ Hydrogenation to Methanol

CO₂ from industrial sources can be recovered from the exhaust of industrial processes, e.g., from coal-fired power plants, cement factories, fermentation processes, water purification plants, and steel mill plants [89, 90]. However, the conversion of CO₂ is challenging due to its low reactivity and thermodynamic stability. Its utilization requires a huge amount of energy, optimal process parameters, and a highly active catalyst. Whereas conventional methanol synthesis is performed applying a feed gas containing only small amounts of CO₂ as well as high CO contents, the conversion of pure CO₂ into methanol has come into the focus of research. The effects of changing the reactant feed from a CO-rich synthesis gas to a CO₂-rich or pure CO₂ feed still require a deeper insight. Because the original catalyst based on copper, zinc and aluminum was optimized for a conventional synthesis gas composition, its suitability for application under these altered conditions has to be checked in more detail and/or additional catalysts have to be developed. Additionally, the beneficial WGS reaction for industrial synthesis gas conversion hardly proceeds in the absence of CO and, thus, only the RWGS reaction occurs and acts as a competitive reaction in CO₂ hydrogenation. The CO₂ and H₂ consumption by the RWGS will lower the methanol yield, and additional water formation may lead to a stronger deactivation of the catalyst [39, 91, 92]. By applying higher temperatures to increase the reaction rate of CO₂ hydrogenation, the RWGS is also favored as well as deactivation by sintering is enhanced. Therefore, the reaction conditions have to be optimized with respect to the two competitive reactions methanol synthesis and RWGS reaction. Despite these restrictions, the commercially available Cu-based catalyst is the most promising candidate for application in the near future, while alternative catalysts still have to be developed.

To suppress CO formation via the competing RWGS as well as to enhance the activity in CO₂ hydrogenation, several alternative promoters for the Cu-based catalyst such as Ga, Zr, and La were investigated in CO₂ hydrogenation to methanol. The beneficial effect of ZrO₂ addition to Cu-based catalyst for CO₂ hydrogenation to methanol has been demonstrated in several publications [93–101]. The effect of ZrO₂ is ascribed to highly dispersed and stable Cu nanoparticles resulting in an enhanced activity and remarkable stability in CO₂ hydrogenation [93, 94]. Furthermore, a high impact of zirconia phases as well as a correlation of the Cu-ZrO₂ interface with activity was described [99–101]. Gallium-promoted Cu-based catalysts also showed a high selectivity to methanol of around 99%, whereas the conversion to CO as well as the formation of hydrocarbons was very low [102, 103]. The decreased tendency to form CO was related to small particles of Ga₂O₃ on the Cu surface. Another possible catalyst for CO₂ hydrogenation is based on Pd on different supports such as Pd/ZnO [104] or Ga₂O₃-Pd/SiO₂ [105]. An additional promising catalyst for

CO₂ hydrogenation to methanol consists of ZrO₂-supported In₂O₃ which showed 100 % selectivity and only low deactivation over 1000 h on stream under industrially relevant conditions [106]. Comparing the performance of various catalysts, most alternative catalysts impress with their high selectivity to methanol, but have to be optimized with respect to conversion, whereas ternary Cu-based catalysts produce a significantly higher amount of methanol under well-chosen reaction conditions (Tab.3). Although many efforts were made to develop catalysts for optimized CO₂ hydrogenation to methanol, the industrially applied Cu-based catalyst still dominates CO₂ hydrogenation due to its outstanding performance [19, 89, 92–94, 115].

First practical applications in several pilot plants have already been established. A pilot plant for the production of 50 kg d⁻¹ methanol from a feed gas consisting of CO₂ and H₂ was built in Japan using a Cu/ZnO-based multicomponent catalyst at 200 to 300 °C and 3 to 7 MPa [116]. The first CO₂ recycling plant was built by Carbon Recycling International in Iceland, where CO₂ is converted to methanol using geothermal steam as a source for electricity and CO₂ [9, 117]. The required green H₂ is produced by water electrolysis using the excess volatile renewable electricity. This recycling plant is producing renewable fuel with a methanol capacity of 10 t a⁻¹.

8 Dynamics of Feed Concentration

The influence of intermitting process conditions on the catalyst is another challenge for future process development. Fluctuating gas compositions due to changes in plant production or accessible renewable energies are important factors for the implementation of these resources into novel methanol synthesis technologies. The field of research with respect to dynamic operation modes has barely been investigated. Preliminary modeling studies considered changing feed gas composition due to fluctuating supply of renewable H₂ in methanation of CO₂ with step responses as well as

periodic changes. They showed neither a significant improvement of the time average reaction rate compared with steady-state operation nor a decreasing rate [118, 119]. Grunwaldt and co-workers [120, 121] also investigated the effect of fast load changes on the catalyst morphology and its behavior. For a Ni-based catalyst, they demonstrated strong structural changes and a decreasing catalytic activity with increasing stress and strain under dynamic working conditions. Applying an atmosphere of lower reducing potential, the metallic Ni particles were oxidized. Furthermore, the changing concentrations can lead to severe inhomogeneous temperature gradients, which can favor cracking or sintering of the catalyst, requiring a superior cooling of the reactor [122].

Also for methanol synthesis from exhaust gases in combination with renewable H₂, detailed investigations under dynamic operation will be one key for assessing economic application. Cu/ZnO/Al₂O₃ catalysts are known to be influenced by pretreatment conditions leading to reversible structural changes, presumably by changing the morphology of the Cu particles [47, 123], whereby under severe conditions bulk alloy formation can lead to a decreasing catalytic activity. Unfortunately, publications considering fluctuating feed supply are scarce. So far, first investigations have shown that moderate variations of temperature and pressure do not seem to accelerate the deactivation of Cu-based catalysts in CO₂ hydrogenation [89]. Nevertheless, the influence of intermitting conditions during methanol synthesis has not yet been described in literature, and much effort is required to optimize conventional processes for a renewable energy network.

9 Conclusion

For the implementation of industrial methanol synthesis using steel mill exhaust gases, a sophisticated purification process is needed due to the high number of different impurities. The negative effect of S-containing compounds,

Table 3. Comparison of selected catalysts for methanol synthesis from CO₂ and H₂.

Catalysts	<i>T</i> [K]	<i>P</i> [MPa]	STY [g _{MeOH} h ⁻¹ g _{cat} ⁻¹]	<i>X</i> _{CO₂} [%]	<i>S</i> _{MeOH} [%]	CO ₂ /H ₂ ratio [-]	<i>F</i> / <i>W</i> [L kg ⁻¹ h ⁻¹]	SV [h ⁻¹]	Ref.
Cu/Zn/Ga/SiO ₂	543	2.0	0.349	5.6	99.5	3.0	18 000	–	[102, 103]
In ₂ O ₃ /ZrO ₂	573	5.0	0.295	5.2	99.8	4.0	20 000	16 000	[106]
Cu/ZnO/Al ₂ O ₃	573	5.0	0.122	2.1	10.9	4.0	20 000	16 000	[106]
Cu/ZnO/Al ₂ O ₃	523	3.0	0.750	18.2	33.0	3.5	–	30 000	[89]
Cu/ZnO/Al ₂ O ₃	523	5.0	0.721	21.4	52.3	3.0	18 000	–	[107–109]
Pd/Zn/ZrO ₂	523	3.0	0.035	6.3	99.6	3.0	1800	–	[110]
Ga/Pd/β-Ga ₂ O ₃	523	3.0	0.253	1.0	52.0	3.0	–	80 000	[105, 111]
Cu/Zn/ZrO ₂	493	8.0	0.179	21	68	3.0	–	3300	[112, 113]
CuO/ZnO/Al ₂ O ₃	493	1.3	0.218	35.2	64.7	3.0	–	3600	[114]

heavy metal compounds, halides, and P-compounds on the catalytic activity is known and, therefore, these components must be removed to avoid catalyst poisoning. For the majority of the other impurities, no information is found in literature, and it is unknown whether their removal from the synthesis gas is necessary. Here, further investigations are essential to determine whether the commercial methanol synthesis catalyst can be applied with respect to an adjusted gas purification or a new appropriately modified catalyst is required for an economically feasible process. As blast furnace gas is by far the largest steel mill exhaust gas stream, its utilization plays a crucial role in reducing the CO₂ emissions. In addition to the development of novel catalysts for an integrated methanol concept, optimized reaction conditions for commercially available catalysts have to be determined to achieve fast implementation in the near future. Furthermore, dynamic reaction conditions that may occur due to fluctuating gas compositions are challenging and have been studied until now mainly theoretically. Further experimental investigations concerning long-term catalyst stability and performance under these transient conditions are necessary. Although there are still many challenges, the concept of converting industrial waste or process gases into valuable products such as methanol is considered promising. Closing the carbon cycle with additional sustainably generated H₂ can contribute to significantly reduced CO₂ emissions.

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Symbols used

F/W	[L kg ⁻¹ h ⁻¹]	flow to weight ratio
ΔH_R^0	[kJ mol ⁻¹]	standard enthalpy of reaction
P	[Pa]	pressure
S	[%]	selectivity
SN	[-]	stoichiometric number
STY	[g h ⁻¹ g _{cat} ⁻¹]	space time yield
SV	[h ⁻¹]	space velocity
T	[K]	temperature
X	[%]	conversion

Abbreviations

BFG	blast furnace gas
BOFG	basic oxygen furnace gas
BTEX	benzene, toluene, ethylbenzene, xylenes
CCR	carbon capture and recycling
COG	coke oven gas
DMS	dimethyl disulfide

PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCDD/F	polychlorinated dibenzodioxins and dibenzofuranes
MTBE	methyl <i>tert</i> -butyl ether
RWGS	reverse water-gas shift
SMSI	strong metal-support interaction
TAME	<i>tert</i> -amyl methyl ether
TBM	<i>tert</i> -butyl mercaptan
THT	tetrahydro thiophene
WGS	water-gas shift

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