Influence of Contaminants in Steel Mill Exhaust Gases on Cu/ZnO/Al$_2$O$_3$ Catalysts Applied in Methanol Synthesis

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Supporting Information available online

The influence of impurities in steel mill exhaust gases on ternary Cu/ZnO/Al$_2$O$_3$ catalysts was studied for conventional methanol synthesis, which is one of the central reactions within the cross-industrial approach of Carbon2Chem®. A series of hydrocarbons was identified as inert spectators for methanol synthesis. Several catalyst poisons like N-containing compounds or O$_2$ show reversible characteristics at low pressure. However, by increasing the partial pressure of O$_2$, poisoning becomes irreversible, indicating different poisoning mechanisms concerning the reversibility of deactivation.

1 Introduction

The global temperature increase caused by the cumulative CO$_2$ emissions in recent years implies an urgent demand to reduce the greenhouse gas released from industry in order to achieve the long-term temperature stabilization goal [1]. In the light of the Paris agreement, the German federal government will continue to lay down the further reduction steps up to the year 2050 to become carbon neutral [2, 3]. Accordingly, many efforts have been devoted from both academia and industry to eliminate the greenhouse gas [4, 5]. Among those, methanol synthesis appears to be one of the most promising processes to transform carbon dioxide to a widely used platform molecule [6], which already plays a critical role in the refinery factories as an important intermediate to produce bulk chemicals and transportation fuels [7]. Thus, methanol produced from CO$_2$ could be readily integrated into the current value chain of the petroleum industry [8].

Up to date, the almost exclusively applied heterogeneous catalyst for methanol production from synthesis gas mixtures (CO$_2$, CO, H$_2$) is the ternary Cu/ZnO/Al$_2$O$_3$ catalyst, which was first developed and patented by Imperial Chemical Industries Ltd (ICI) in the 1960s [9, 10]. During about 60 years of efforts to improve this catalyst, a carbon efficiency of 83 % and methanol selectivity >99.8 % have been achieved with energy efficiencies of 70–75 % [11, 12]. Therefore, this well-known technology provides a good starting point for the application of industrial off-gases as raw material for the production of bulk chemicals. Considering the fact that the CO$_2$ footprint related to steel mills across the world accounts for 5–7 % of the global CO$_2$ emission [13, 14], the catalytic conversion of these exhaust gases would contribute significantly to the goal of climate neutrality. The state-of-art steel mills generate several gas streams that differ in composition with respect to the reactants CO, CO$_2$ and H$_2$ [14, 15]. These potential sources of raw gases can be distinguished by their total amounts and availabilities. Numerous case studies showed that steel-work exhaust gases can be utilized with economic and environmental benefits due to the systemic use of renewable energy for

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generating H_2 [15, 16]. However, current industrial $Cu/ZnO/Al_2O_3$ catalysts are optimized for the conversion of highly purified feedstocks obtained by, e.g., steam reforming of methane [6]. Thus, poisoning-induced deactivation is a rare problem for conventional methanol synthesis. As a high number of potential impurities at ppm or ppb levels are present in the exhaust gases from steel mills [8, 18], new challenges have to be overcome applying these gases as feedstock. As the H_2 content in these gases is usually low, additional H_2 is required, which should ideally originate from sustainable sources such as water electrolysis to retain a positive carbon footprint.

According to previous studies [19], the major potential issues derived from the usually heteroatom-containing impurities include their reversible or irreversible adsorption on the surface of the catalyst. This could block the active sites for methanol production or modify the catalyst surface morphology resulting in a lower catalytic activity and/or a lower methanol selectivity [20]. The most studied case for the conventional methanol synthesis from syngas is sulfur poisoning, mainly by H_2S, COS, SO_2 and thiols [6], which form adsorption equilibria between those S-containing species depending on the reaction conditions. In previous studies it has been shown that the ZnO component in $Cu/ZnO/Al_2O_3$ catalysts can act as a self-guard part protecting the active sites from sulfur poisoning to a certain extent [6, 19]. However, when the mass fraction of sulfur exceeds several weight percent of the catalysts, severe deactivation will take place [21, 22].

Other known irreversible poisons are halides, heavy metal carbonyls, P-containing compounds and AsH_3. In addition, small amounts of O_2 are also problematic for metallic catalysts [6]. Therefore, the removal of O_2 from the gas stream is mandatory. An established technique to remove O_2 from a gas mixture, in this case from coke oven gas, is pressure swing adsorption [23, 24]. Leaving minor residuals of O_2 in the remaining gas, for a complete removal of O_2 an additional deoxygenation step is required [12]. To the best of our knowledge, regarding the impacts of other impurities in off-gases from steel mills, such as hydrocarbons, aromatics, polycyclic aromatics, O- and N-containing compounds on $Cu/ZnO/Al_2O_3$ catalysts, there is no significant and systematical information reported in literature for gas-phase methanol synthesis [23, 25]. This information is essential to determine the applicability of using steel mill exhaust gases as feedstock for methanol synthesis and, furthermore, to transfer this technology to other industries releasing substantial amounts of CO_2, like cement production, power plants and chemical industry [26, 27].

In this study, various setups are applied within the Carbon2Chem[®] framework in methanol synthesis from the steel mill exhaust gases to explore the effect of poisoning on the performance of the industrial $Cu/ZnO/Al_2O_3$ catalyst. Initially, reproducibility tests were carried out in order to ensure a meaningful comparison of the results obtained with the different experimental setups. Afterwards, the influence of possible contaminants was investigated by dosing these substances into the feed gas mixture while operating methanol synthesis. Based on the gathered information and detailed analyses regarding trace compounds in the steel mill exhaust gases the required gas cleaning for their application in methanol synthesis can be determined.

2 Experimental

An overview on the setups used in this work is given in Tab. 1. The corresponding flow charts and the further experimental procedure for the investigations on the impact of impurities on the industrial $Cu/ZnO/Al_2O_3$ catalyst are described in detail in the Supporting Information (SI). Further information on the catalyst used in this study can be found in a previous publication [28]. To ensure the comparability of the results obtained with different setups applied in the Carbon2Chem[®] project, a standardized benchmark test was performed. Here, 0.2–1.0 g of catalyst mass (sieve fraction of 250–355 µm) were mounted as fixed bed in the isothermal zone of the tubular stainless-steel reactors of the corresponding setup. As pretreatment, the catalyst was gently reduced by increasing the temperature from room temperature to 448 K with $1 \, K \, min^{-1}$ in $0.50 \, NL \, g_{cat}^{-1} \, min^{-1}$ diluted H_2 (5.0) (2 % in inert gas (5.0)) according to the procedure described in [29]. This first temperature plateau was held for 15 h, and then the reduction temperature was further increased to 513 K with the same heating rate and held for 30 min. This type of activation procedure was performed before every experiment shown in this work. After activation, the catalyst was cooled to room temperature to introduce the syngas mixture consisting of 73.5 % H_2 (5.0), 13.5 % CO (4.7), 3.5 % CO_2 (4.8), and 9.5 % of inert gas (5.0) with a flow rate of $0.50 \, NL \, g_{cat}^{-1} min^{-1}$. The reaction temperature and pressure were set at 523 K and 50 bar, respectively, and kept for around 100 h time on stream (TOS).

Table 1. Catalyst loadings and detectors of various setups.

Reactor	Catalyst loading [g]	Detector
CEC 1	0.5	online GC
CEC 2	1.0	offline GC-MS
RUB 1	0.3	FTIR and micro GC
RUB 2	0.2	FTIR and micro GC

The detailed description of the further investigations on the impact of impurities in the feed gas are provided in the SI.

3 Results and Discussions

3.1 Benchmark Tests on Different Setups

In order to ensure the reproducibility and comparability of the investigations on methanol synthesis within the Carbon2Chem® project framework, all flow setups were tested using standardized benchmark conditions. Here, the reaction conditions were chosen to be comparable to industrial methanol synthesis conditions including a similar stoichiometric number S of the makeup gas. The reaction pressure and temperature as well as total flow rate were selected to exclude thermodynamic equilibrium conditions. Moreover, the set points were easily assessable for all setups. Four reactor setups were used in this study (Tab. 1). The general flow scheme of every setup as well as the corresponding analysis procedures are provided in the SI.

The degrees of conversion of CO_x (X_{COx}) including both CO_2 and CO as well as the WTY_{MeOH} over as long as 100 h achieved in all setups are shown in Fig. 1. The results are normalized to the initial values of CEC 1. The relative difference in X_{COx} is around ± 5 %. According to Fig. 1a, X_{COx}
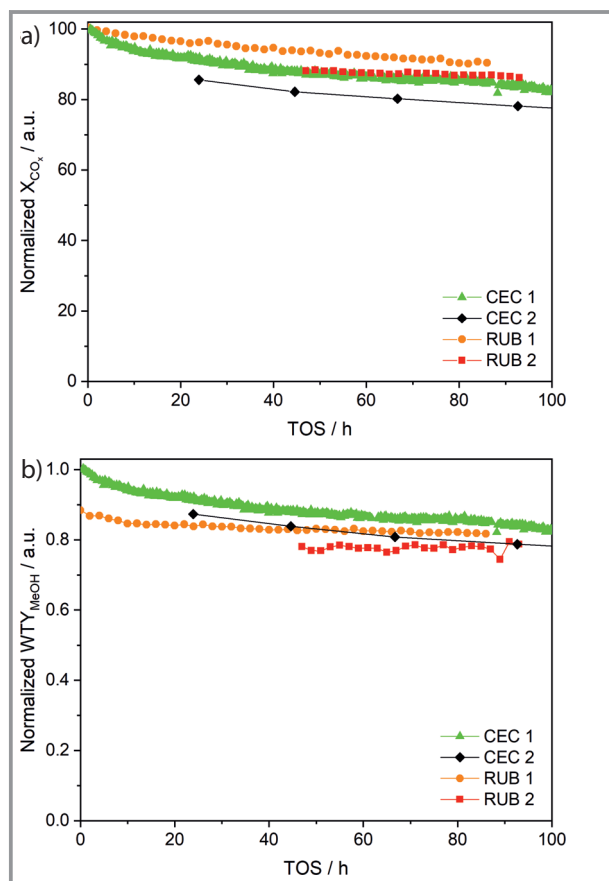

Figure 1. Results of the standardized benchmark test for methanol synthesis over an industrial Cu/ZnO/Al$_2$O$_3$ catalyst in the applied setups at 523 K and 50 bar. a) Normalized degree of conversion of CO_x (X_{COx}), b) normalized weight time yield of methanol (WTY_{MeOH}).

for all setups over 100 h TOS gradually decreases following a similar trend. This drop in activity is common for Cu-based catalysts in methanol synthesis due to thermal sintering. As shown in previous studies, one third to one half of the activity can be lost over the course of the first 1000 h on stream [6, 20, 25].

As shown in Fig. 1b, the WTY_{MeOH} for all four setups shows a very comparable trend and decreases gradually over the course of 100 h TOS, similar to the observations for X_{COx}. Accordingly, this drop in WTY_{MeOH} can also be assigned to the sintering-related catalyst deactivation in agreement with literature [6, 20, 25]. Also, for the WTY_{MeOH}, the relative difference is around ± 5 %.

The observed deviation of around ± 5 % for X_{COx} and WTY_{MeOH} could be caused by the following factors: (a) temperature uncertainties of the different temperature control systems, (b) pressure uncertainties of pressure gauges, (c) gas flow rate uncertainties of mass flow controllers (MFCs) as well as the related uncertainties in feed gas composition, (d) uncertainties by the used analytics.

According to the standard IEC 60584-1 [30], the error of a grade K-type thermocouple applied is ± 2.2 K, which means the potential temperature differences for the various setups could be as high as 4.4 K. The influence of this possible temperature deviation on the reaction rate can be estimated by using the Arrhenius equation $k = A\exp\left(-\dfrac{E_A}{RT}\right)$, whereas k, A, E_A, R, and T are the rate constant, the pre-exponential factor, the activation energy, the ideal gas constant and the temperature, respectively. Since the pre-exponential factor A in this equation is approximately constant for such a small temperature change, the critical factor for the reaction rate difference is depending on changes in $\exp\left(-\dfrac{E_A}{RT}\right)$. Considering an activation energy for methanol synthesis under the applied conditions of 72 kJ mol^{-1} [31], rate constants of $5.98 \times 10^{-8}\,A$ (520.95 K) as well as $6.88 \times 10^{-8}\,A$ (525.35 K) can be estimated. The ratio of both rate constants ($k_{520.95\,K}/k_{525.35\,K}$) results in a value of 115 %, and temperature uncertainties of 4.4 K could already lead to 15 % (± 7.5 %) difference in reaction rate. As both X_{COx} and WTY_{MeOH} are directly proportional to the reaction rate, this should be one of the major factors for the observed differences in X_{COx} and WTY_{MeOH}.

For pressure gauges [32] the uncertainty is between 0.5–2.5 %. In addition, for methanol synthesis, the reaction orders for CO_2, CO, and H_2 are 0.55, 0, and 1.25, respectively [31]. Because of this, the pressure uncertainties can be estimated by a power-law rate equation: $r_{MeOH} = k\,[CO]^0[CO_2]^{0.55}[H_2]^{1.22}$, in which r_{MeOH}, k, [CO], [CO$_2$] and [H$_2$] are the formation rate of methanol under the desired reaction conditions, the rate constant, the partial pressures of CO, CO$_2$ and H$_2$, respectively. Therefore, an uncertainty of ± 2.5 % of the pressure may lead to a deviation of ± 4.5 % on X_{COx} and WTY_{MeOH}. Additionally, for each MFC applied for in situ mixing, the feed gas can have

an uncertainty of around 0.6 % [33], resulting in an ignorable deviation smaller than 1.1 % for X_{CO_x} and WTY_{MeOH}.

Another important factor is the used analytics for recording of the product stream composition (SI). For CEC 2, the condensable products MeOH and H_2O are first collected in a cold trap at 278 K, which are afterwards transferred and analyzed by an offline GC-MS. Here, an error of around 5 % for different injections of the same liquid sample is determined. In the other three setups online GC analysis is applied. Generally, online GC analysis can provide results with smaller errors of around 1–2 % than offline GC analysis. Additionally, while condensing the products for analysis, a small amount of methanol and water remain in the product gas stream at 278 K, which could lower the obtained X_{CO_x} and WTY_{MeOH} for CEC 2 by around 1 %. To ensure a well-working setup and analytical device for the setups equipped with online analytics, the inlet feed gas was analyzed prior to the measurement and used to determine the carbon balance for each measurement during methanol synthesis. Here, the carbon balance was determined to 100 ± 2 % proving the high reliability of obtained results in every setup.

In summary, the determined deviation of ±5 % (10 %) indicates a very good comparability of the different setups with each other for the standardized benchmark test within the Carbon2Chem® framework. Therefore, these setups were used in the following to study the influence of contaminants on methanol synthesis with a meaningful comparability.

3.2 Influence of Common Impurities in Tail Gas from Steel Mill

The large variety of impurities in off-gases from steel mills and the lack of detailed poisoning studies in literature for $Cu/ZnO/Al_2O_3$ catalysts leads to a lack of knowledge about the effect of the most impurity classes on the catalytic activity, selectivity, and stability. To address this issue, a screening test was developed consisting of the continuous dosing of selected compounds over the methanol catalyst to clarify the corresponding effects. This test was performed at atmospheric pressure and with relatively high impurity concentrations to obtain the desired results for numerous compounds in a short period. Here, detailed investigations with classical irreversible poisons like halides, heavy metals as well as S- and P-containing compounds were neglected, since their negative effect on the performance of Cu-based catalyst is known from previous studies [6, 8, 34, 35]. The fast deactivation in the presence of H_2S is exemplarily shown in the SI (Fig. S1).

The selected compound classes for the screening test were hydrocarbons, aromatics, N- and O-containing compounds, which are common in exhaust gases of steel production. Fig. 2 shows the results of the continuous dosing of different hydrocarbons, aromatics and NH_3 into the syngas feed during methanol synthesis. The other dosed impurities can be found in the SI (Figs. S2–S4). In case of hydrocarbons and aromatics, the catalytic activity of the industrial catalyst is not affected, since no significant decrease of conversion can be observed. Therefore, all types of hydrocarbons can be classified as inert spectators under methanol synthesis conditions and the coking of the catalyst surface can be excluded, since Cu-based catalysts are not prominent candidates for cracking of C–C bonds due to the low surface acidity [6]. In contrast, the addition of N-containing compounds (Fig. 2b, S3) directly leads to a significant decrease of conversion. During this deactivation process, the catalyst reaches a new steady state in the presence of the impurity.
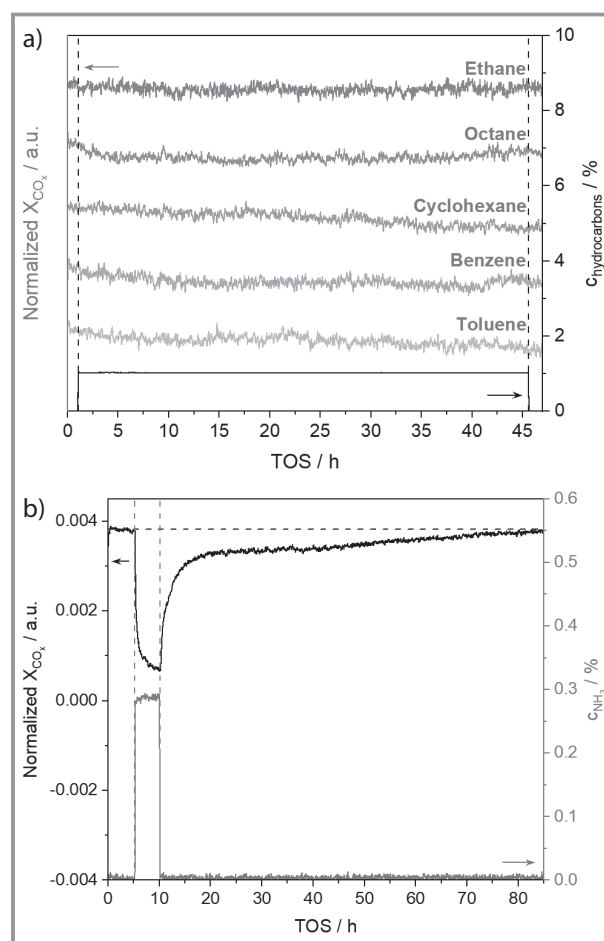

Figure 2. a) Continuous dosing of various hydrocarbons over an industrial $Cu/ZnO/Al_2O_3$ catalyst under methanol synthesis conditions at 483 K and 1 bar. Switching from clean syngas to syngas including the hydrocarbons and back is indicated with vertical dashed lines (black). The curves in gray describe the normalized X_{CO_x} values in the presence of the corresponding hydrocarbon and the black curve the hydrocarbon concentration of 1 % in the product gas stream. b) Dosing of 0.3 % NH_3 over the industrial $Cu/ZnO/Al_2O_3$ catalyst under methanol synthesis conditions at 483 K and 1 bar. Switching from clean syngas to syngas including NH_3 and back is indicated with vertical dashed lines (gray). The black curve describes the normalized X_{CO_x} values and the gray curve the NH_3 concentration in the product gas stream.

The switching-off and the resulting removal of the N-containing compounds from the syngas feed regenerates the catalytic activity until the initial degree of conversion is regained. The observed deactivation behavior and self-regeneration of the catalyst surface are strong indications for reversible poisoning. From the measurements with the hydrocarbons it can be concluded that only the N atom as functional group can interact with the surface by a Lewis or Brønsted acid-base mechanism to suppress the methanol formation. Furthermore, O_2 (Fig. 3a) also acts as reversible poison. Here, the hydrogenation to H_2O can be detected.

For the validation of the screening test under industrially relevant conditions, some experiments were repeated under high-pressure conditions (Fig. 3b, S2, S4). Increasing the pressure does not change the effect of hydrocarbons (inert spectators) and N-containing compounds (reversible poisons) on the catalytic activity. Thus, the screening test performed at 1 bar is also valid for high-pressure conditions. However, higher pressures increase the period of time
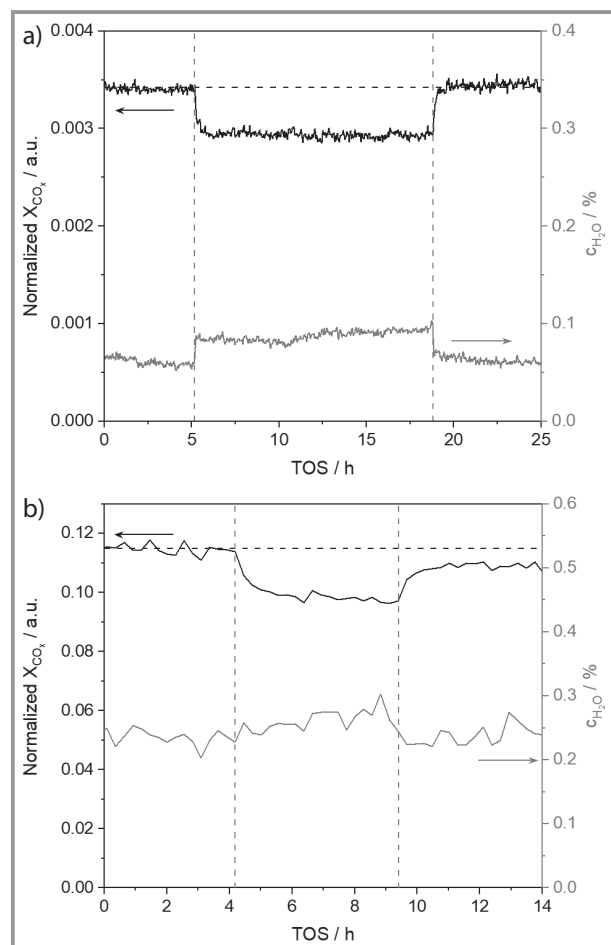
until steady state after the injection of the impurities is achieved. In addition, the poisoning mechanism of O_2 is changed from reversible to irreversible by significantly increasing the partial pressure of the impurity. Here, an irreversible destruction of the catalyst surface cannot be excluded, since the initial conversion degree is not regained (Fig. 3b).

In Fig. 4, the effect of O_2 on the catalytic activity is analyzed in detail with respect to O_2 mole fraction, temperature and exposure time at 30 and 50 bar. For a rough estimation of the maximum tolerable O_2 concentration, the measurements shown in Fig. 3 were extended from 473 K to 523 K at 30 bar as well as 50 bar (Fig. 4, S5). While adding 0.01 % and 0.02 % O_2 no clear influence on the methanol productivity was observed. During O_2 exposure, the methanol production rate is lowered by 0.5 % (0.01 % O_2) and 1.8 % (0.02 % O_2) independent of the temperature. Furthermore, the overall drop of activity was insignificantly small with
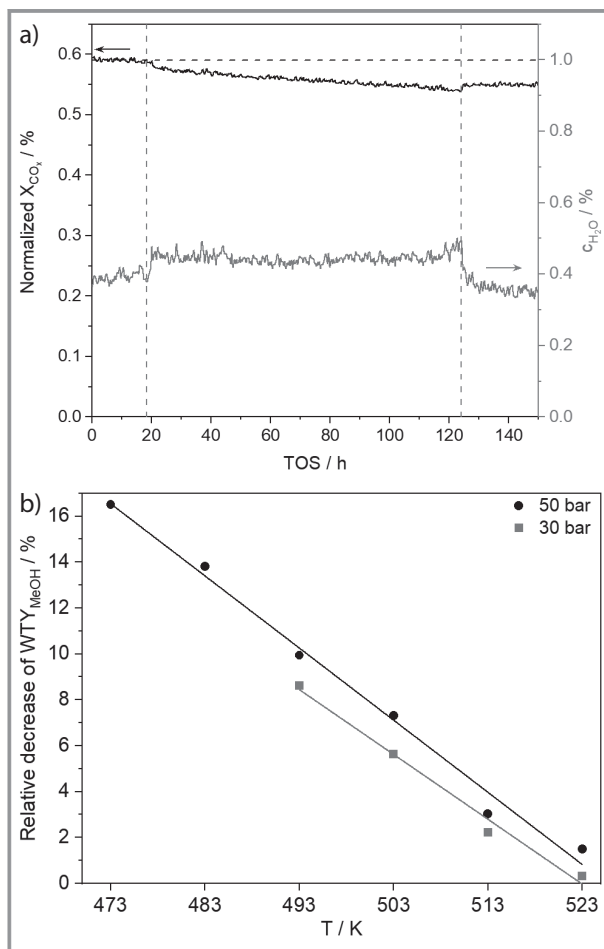
Figure 3. Continuous dosing of a) 0.05 % O_2 at 483 K and 1 bar and of b) 0.06 % O_2 at 483 K and 50 bar over an industrial Cu/ZnO/Al$_2$O$_3$ catalyst under methanol synthesis conditions. Switching from clean syngas to syngas including O_2 and back is indicated with vertical dashed lines (gray). Normalized X_{CO_x} values (black) and H$_2$O concentrations (gray).

Figure 4. a) Continuous dosing of 0.06 % O_2 over an industrial Cu/ZnO/Al$_2$O$_3$ catalyst under methanol synthesis conditions at 523 K and 50 bar for 108 h. Switching from clean syngas to syngas including O_2 and back is indicated with vertical dashed lines (gray). Normalized X_{CO_x} values (black) and H$_2$O concentrations (gray). b) Relative decrease of WTY_{MeOH} while adding 0.06 % O_2 into the feed gas in a temperature range of 473 K to 523 K and pressures of 30 bar (gray) and 50 bar (black).

0.1 % in total for both concentrations. However, the addition of 0.06 % O_2 to the feed gas stream led to an irreversible deactivation of the catalyst, where the overall loss of initial activity is in a range of 0.5 % to 4.4 % (30 bar) and up to 6 % (50 bar) distributed over the whole temperature range from 473 K to 523 K.

Additionally, the relative decrease of the WTY_{MeOH} during the dosing of O_2 is decreasing with increasing temperature (Fig. 4b), as here the total conversion is also increasing lowering the relative effect of O_2 poisoning. This effect is slightly higher at a higher pressure of 50 bar due to the higher total amount of O_2 under these conditions. The constant deactivation during O_2 dosing is shown more clearly in Fig. 4a, where the catalyst was exposed to O_2 for more than 4 days. During the exposure time deactivation was constantly occurring resulting in a lowered conversion of around 7 % compared with the initial activity. As shown above, at low O_2 partial pressures its poisoning effect is reversible, which may be due to a faster hydrogenation to H_2O than the oxidation of the reduced catalysts phases. However, at O_2 concentrations of 0.06 % as well as higher total pressures O_2 poisoning becomes irreversible indicating the partial oxidation of the metallic phases present in the catalyst. A significant inhibition effect by H_2O, which is produced by the hydrogenation of O_2, can be neglected, since the oxidation potential of O_2 is higher compared to H_2O. In addition, the added amount of O_2 and so of the corresponding H_2O after its hydrogenation is lower than the constant H_2O concentration from methanol synthesis (e.g., Fig. 3b), and Studt et al. [36] showed that H_2O concentrations produced in the differential kinetic region of methanol synthesis do not lead to a severe deactivation of the catalyst surface. However, further long-term investigations at several conditions are required to determine the poisoning effect of O_2 in more detail allowing quantifying its

impact on the catalyst lifetime as a function of the O_2 partial pressure during methanol synthesis.

Tab. 2 summarizes the experimental conditions of all investigated impurities and their effects on the catalytic activity including a conclusion whether it is necessary to remove them from the exhaust gases to protect the catalyst. This overview can be applied within the Carbon2Chem® project to determine the required gas cleaning for using exhaust gases from steel mills as feedstock for methanol synthesis. In combination with the detailed information on trace compounds in these gases an economically efficient purification process can be developed [37]. Within this scope, high O_2 concentrations and other irreversible poisons like H_2S must be removed from the exhaust gases beforehand. Additionally, also reversible poisons like NH_3 have to be removed due to formation of the by-product trimethylamine, which would affect the commercial value of the produced methanol [38, 39]. All types of hydrocarbons can remain in the exhaust gases, since no effect on the catalytic activity, selectivity, and stability of the standard $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst was observed.

4   Conclusion

Within the Carbon2Chem® project several tasks are addressed to determine the feasibility of using steel mill exhaust gases as feedstock for methanol synthesis. To ensure the comparability of the results obtained with the several test setups applied, a standardized benchmark test was carried out with all setups. The determined low deviation of ± 5 % for this test, which was found to originate from usual system uncertainties, indicates a very good comparability for all setups applied in this study. Therefore, these were used to carry out industrially relevant poisoning

Table 2. Summary of all measurements performed with the different impurities on an industrial $Cu/ZnO/Al_2O_3$ catalyst.

Impurity classes	Compounds	$c_{impurity}$ [%]	$T_{reaction}$ [K]	$p_{reaction}$ [bar]	t_{dosing} [h]	Poisoning	Removal
Hydrocarbons	ethane	1	483	1	45	–	no
	octane	1	483	1	45	–	no
	cyclohexane	1	483	1	45	–	no
Aromatics	benzene	1/0.03	483	1/60	45/77	–	no
	toluene	1	483	1	45	–	no
N-containing compounds	NH_3	0.3/0.05	483	1/60	5/165	reversible	yes
	cyclohexylamine	0.01	483	1	6	reversible	no
	pyridine	0.01	483	1	9	reversible	no
	acetonitrile	0.01	483	1	6	reversible	no
O-containing compound	O_2	0.05/0.06	483	1/50	14/108	reversible/irreversible	no/yes
S-containing compound	H_2S	0.005	483	60	1000	irreversible	yes

studies in methanol synthesis. The present work showed the different poisoning behavior of various types of impurities potentially present in exhaust gases of steel production on an industrial Cu/ZnO/Al$_2$O$_3$ catalyst for methanol synthesis. This screening test shows the reversible poisoning character of N- and O-containing compounds at atmospheric pressure. By increasing the pressure to 30 or 50 bar, O$_2$ showed an irreversible poisoning character. In contrast, all examined hydrocarbons are inert spectators for methanol formation. With this poisoning study, the Carbon2Chem® project is getting a step closer to the design of a suitable purification process for an application of these exhaust gases. Thus, a CO$_2$-neutral industrial production of steel and methanol is considered to be in reach.

Supporting Information

Supporting Information for this article can be found under DOI: 10.1002/cite.202000045. This section includes additional references to primary literature relevant for this research [40].

Symbols used

A	[–]	pre-exponential factor
E_A	[kJ mol^{-1}]	activation energy
k	[s^{-1}]	rate constant
r_{MeOH}	[mol min^{-1}]	methanol formation rate
R	[J mol^{-1}K^{-1}]	gas constant
S	[–]	stoichiometric number
T	[K]	temperature
TOS	[h]	time on stream
WTY_{MeOH}	[g g$_{cat}$$^{-1}$h^{-1}]	weight time yield
X	[%]	conversion
[CO$_2$]	[bar]	partial pressure of CO$_2$
[CO]	[bar]	partial pressure of CO
[H$_2$]	[bar]	partial pressure of H$_2$

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