Supporting information

Influence of gas impurities on the hydrogenation of CO$_2$ to methanol using Indium-based catalysts

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S1. Typical reaction procedure for methanol synthesis

Table S1. Typical reaction procedure for CO_2 hydrogenation to methanol using In_2O_3/ZrO_2 catalysts at a total pressure of 53.8 ± 0.5 bar. Reaction gas was premixed in a ratio of $CO_2/H_2 = 1/3$.

Step	Time / min	$T_{reactor}$ / °C	$\dot{V}_{H_2/CO_2}$ / Nml min^{-1}	$\dot{V}_{H_2}$ / Nml min^{-1}	$\dot{V}_{He}$ / Nml min^{-1}
1 (Preforming)	30	200	0	0	610
2 (Reaction)	180	225	565.5	0	0
3 (Reaction)	240	250	565.5	0	0
4 (Reaction)	180	275	565.5	0	0
5 (Reaction)	180	250	565.5	0	0
6 (Reaction)	180	225	565.5	0	0
7 (Cool down)	180	20	0	0	700

Table S2. Typical reaction procedure for CO_2 hydrogenation to methanol using a commercial $Cu/ZnO/Al_2O_3$ catalyst at a total pressure of 53.8 ± 0.5 bar. Reaction gas was premixed in a ratio of $CO_2/H_2 = 1/3$.

Step	Time / min	$T_{reactor}$ / °C	$\dot{V}_{H_2/CO_2}$ / Nml min^{-1}	$\dot{V}_{H_2}$ / Nml min^{-1}	$\dot{V}_{He}$ / Nml min^{-1}
1 (Preforming)	60	100	0	100	0
2 (Preforming)	30	150	0	100	0
3 (Preforming)	30	200	0	100	0
4 (Reaction)	180	200	565.5	0	0
5 (Reaction)	180	225	565.5	0	0
6 (Reaction)	240	250	565.5	0	0
7 (Reaction)	180	225	565.5	0	0
8 (Reaction)	180	200	565.5	0	0
9 (Cool down)	180	20	0	0	700

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S2. Calculations

Calculation of process parameters

The calculation of process parameters to evaluate the catalytic performance was done as follows. Using the adjusted standard volume flow ($\dot{V}_N$) and the known composition of the feed gas ($y_{i,in}$) enabled the calculation of the molar flow of component *i* entering the reactor, under consideration of the ideal gas law:

$$\dot{n}_{i,in} = \frac{p_N \cdot y_{i,in} \cdot \dot{V}_N}{R \cdot T_N}$$

(Eq.-S1)

Thereby, p_N and T_N are standard pressure and temperature. Giving regard to the carbon balance of the reaction system, the total molar flow at the reactor outlet can be determined, using the molar fractions of CO_2, CO and methanol, known from online-GC analysis:

$$\dot{n}_{ges,out} = \frac{\dot{n}_{CO_2, in}}{y_{CO_2,out} + y_{CO,out} + y_{MeOH,out}}$$

(Eq.-S2)

Thereafter, the molar flow of the component *i*, leaving the reactor was calculated as follows:

$$\dot{n}_{i,out} = \dot{n}_{ges,out} \cdot y_{i,out}$$

(Eq.-S3)

Based on the determined molar flows, the methanol productivity was calculated in relation to the mass of the active component ($m_{catalyst} \cdot w_{active}$) in the catalyst, which was namely indium or copper:

$$P_{active} = \frac{\dot{n}_{MeOH.out} \cdot M_{MeOH}}{m_{catalyst} \cdot w_{active}}$$

(Eq.-S4)

Thereby M_{MeOH} is the molar mass of the product methanol. Selectivity to methanol was determined as a function of converted amount of carbon dioxide:

$$S_{MeOH} = \frac{\dot{n}_{MeOH,out} - \dot{n}_{MeOH,in}}{\dot{n}_{CO_2, in} - \dot{n}_{CO_2,out}}$$

(Eq.-S5)

S3. Catalyst batches used for parameter variation study

Table S3. Indium loading of the catalyst batches used for the investigations, determined by ICP-OES prior to catalyst poisoning and methanol synthesis.

Catalyst batch	In-loading[a] / wt.%	Composition of poisoning gas
B1 (SO_2-study)	10.3	505 ± 10 ppm SO_2 in N_2
B2 (H_2S-study)	10.3	610 ± 10 ppm H_2S in N_2
B3 (NO_2-study)	10.8	531 ± 11 ppm NO_2 in N_2
B4 (NH_3-study)	10.4	509 ± 10 ppm NH_3 in N_2
B5 (C_xH_y-study)	10.2	CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6 (each 5.0 ± 0.1 vol.%) in H_2

Table S4. BET-surface area, total pore volume and intermediate pore diameter of the catalyst batches prior to poisoning.

Catalyst batch	a_{BET} / m^2 g^{-1}	$v_{p,tot}$ / cm^3 g^{-1}	$\bar{d}_p$ / nm
B1 (SO_2-study)	46	0.21	18.2
B2 (H_2S-study)	45	0.22	19.6
B3 (NO_2-study)	45	0.21	18.7
B4 (NH_3-study)	45	0.21	18.9
B5 (C_xH_y-study)	45	0.21	18.7

S4. Temperature influence on poisoning of In$_2$O$_3$/ZrO$_2$-catalyst with SO$_2$
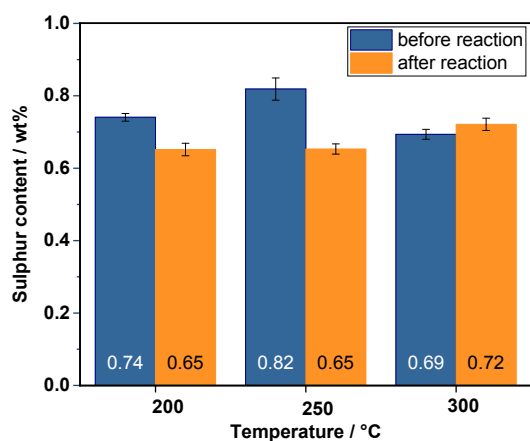
Fig. S1. Influence on temperature in SO_2-poisoning on the weight based sulphur content of the In_2O_3/ZrO_2 catalyst.

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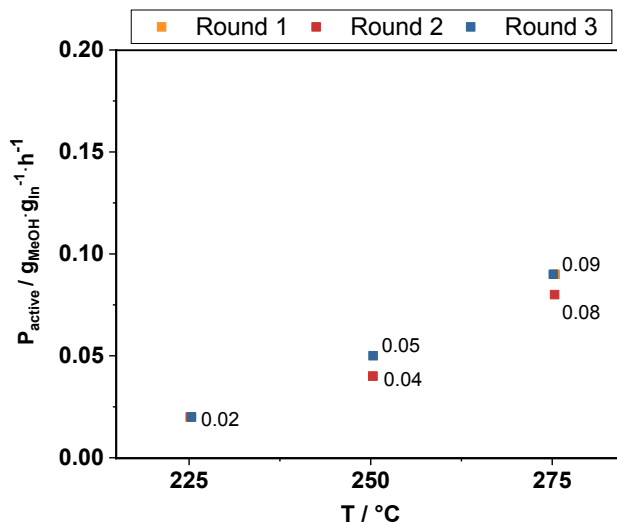## S5. Recycling of SO_2-poisoned In_2O_3/ZrO_2 catalyst

Fig. S2. Influence of In_2O_3/ZrO_2 catalyst poisoning with H_2S on methanol productivity. Catalyst was recycled three times to examine the reversibility of SO_2-poisoning. Reaction conditions: $CO_2/H_2 = 1/3$; GHSV = 1952 h^{-1}; $p_{total} = 53.8 \pm 0.5$ bar; TOS = 960 min; $h_{bed} = 6.4 \pm 0.1$ cm; $m_{cat} = 5.0 \pm 0.1$ g; $m_{Raschig} = 5.0 \pm 0.1$ g; Catalyst batch B1 (see Tables S3-S4).

S6. Procedure and results for wet chemical detection of sulphates

Being able to identify weather the formed sulphates on the catalyst surface after SO_2-poisoning were preferably bound to zirconium- or indium-species, a wet chemical detection method was applied as follows: 50 mg of solid sample (e.g. SO_2-poisoned catalyst) was stirred for 1 h with 10 ml of boiling water in a 20 ml glass vial. Afterwards, the suspension was filtered to remove the solid residue and the liquid solution collected in a 100 ml measuring cylinder. The solid residue in the filter was washed with boiling water to fill up the measuring cylinder to its nominal volume. Afterwards, the liquid sample was examined using ICP-OES according the method described in the main manuscript. As both, $In_2(SO_4)_3$ and $Zr(SO_4)_2$ have almost equal soluble in water (539 g L^{-1} and 525 g L^{-1} at 20°C, respectively), the relative amount of zirconium and indium, present in the catalyst-extract, gives information about the cationic binding partner of the sulphates on the catalyst.

Table S5. Molar balance of sulphur and indium before and after wet chemical extraction; Proportions of the elements found in liquid and solid phase after the experiment, respectively.

Sample	Molar balance n_{after} n_{before}^{-1} / %		Proportion in solution / %		Proportion in solid residue / %	
	In	S	In	S	In	S
untreated In$_2$O$_3$/ZrO$_2$	111.7	n/a	1.0	n/a	99.0	n/a
In$_2$O$_3$/ZrO$_2$ 18 h-SO$_2$	100.0	103.0	5.3	50.1	94.7	49.9

S7. Results of nitrogen sorption analysis of the H$_2$S-poisoned In$_2$O$_3$/ZrO$_2$ catalyst

Table S6. Total surface area, total pore volume and intermediate pore diameter of untreated and 18 h-H$_2$S poisoned In$_2$O$_3$/ZrO$_2$ catalyst

Sample	a_{BET} / m^2 g^{-1}	$v_{p,tot}$ / cm^3 g^{-1}	$\bar{d}_p$ / nm
untreated, before reaction	45	0.22	19.6
untreated, after reaction	48	0.23	19.8
18h-H$_2$S, before reaction	45	0.22	19.6
18h-H$_2$S, after reaction	46	0.22	18.6

S8. Microscopic pictures of In$_2$O$_3$/ZrO$_2$ catalysts

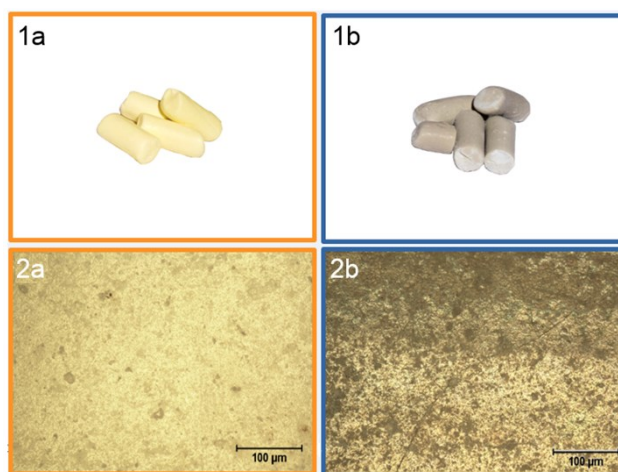**Fig. S3**. Photos (1) and light microscopy images (2) of an untreated In$_2$O$_3$/ZrO$_2$ catalyst before (a) and after methanol synthesis (b).
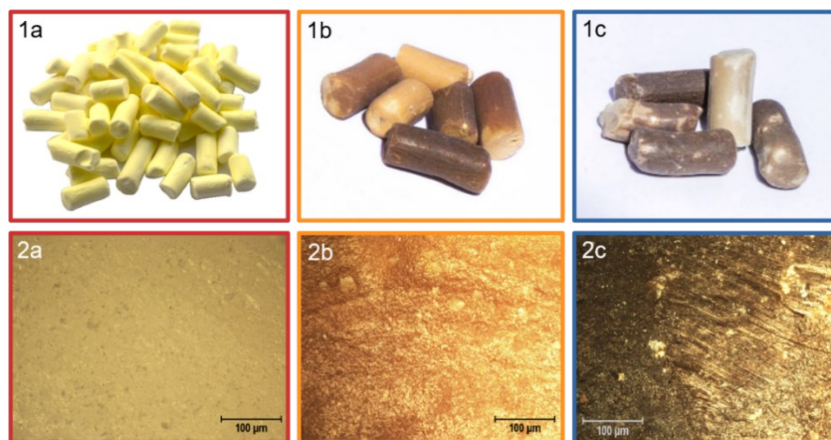
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Fig. S4. Photos (1) and light microscopy pictures (2) of an In_2O_3/ZrO_2 catalyst untreated (a), after H_2S-poisoning for 18 hours (b) and after methanol synthesis (c).

S9. XPS data

Sample Preparation and Out-gassing

A few mg of finely ground powdered samples (SO_2 series: "untreated", "18h-SO_2 before reaction" and "18h-SO_2 after reaction"; H_2S series: "untreated", "18h-H_2S before reaction" and "18h-H_2S after reaction") were pressed onto carbon pads, which in turn were supported on an aluminium plate. Samples in pellet form (SO_2 series: "18h-SO_2" and "18h-SO_2, after reaction"; H_2S series: "18h-H_2S" and "18h-H_2S, after reaction") were cut in the middle using a scalpel as shown in Fig. S9a. One of the resulting halves was supported on a carbon pad, which in turn was placed on an aluminium plate, as shown in Fig. S9b. The cut faced the X-ray gun and measurements were performed at two locations, namely "Center" and "Outer Shell". The blue ellipsoids indicate the irradiation spots (100 µm) and are roughly to scale.
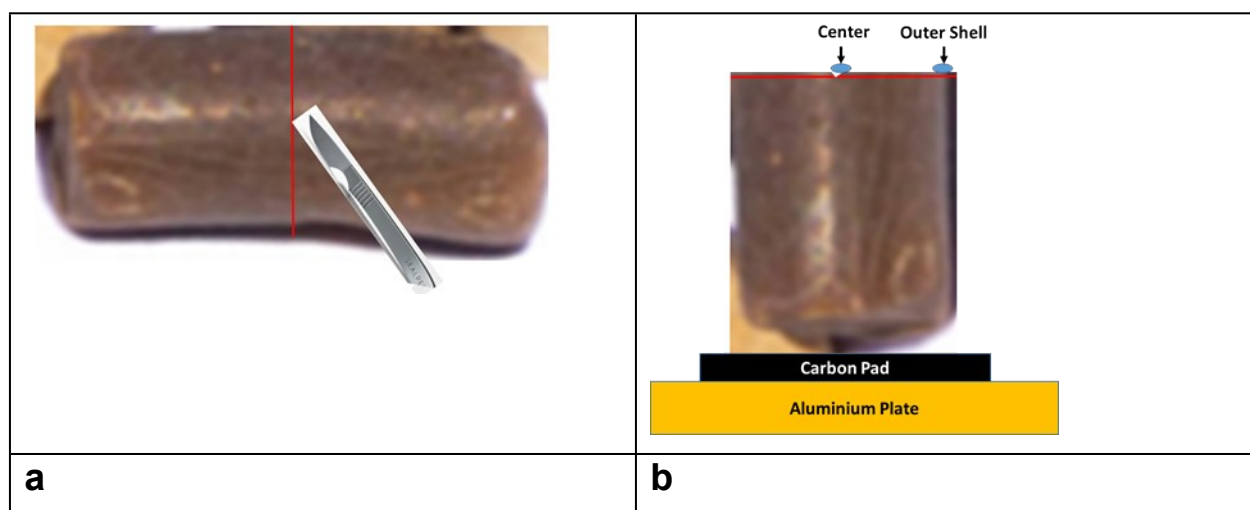

Fig. S5: Representation of pellet preparation for XPS measurements. (a): cutting of pellet. (b): mounting of pellet halve and location of "Center" and "Outer Shell" measurement locations.

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Sample out-gassing was performed for at room temperature in the pre-chamber of the Thermo Scientific instrument, which was also used for the actual measurements. The out-gassing was deemed to be completed once the pressure of the pre-chamber was reduced to below $8 \cdot 10^{-7}$ mbar (took around 1 h), where after the samples were transferred to the analysis chamber. Measurements were only commenced if the pressure did not rise to over $2 \cdot 10^{-7}$ mbar, otherwise additional outgassing was applied to the samples.

Data Acquisition

The samples were exposed to Al K_α radiation (1484.6 eV) at room temperature. A spot size of 100 µm was used. Sample charging effects were reduced using a flood gun. A "survey spectrum" (-9.92 to 1350.08 eV) using two scans was measured for each sample. The survey spectra were used to rule out the presence of unexpected impurities and to determine the 1s orbital peak position of adventitious carbon. The S2p (50 scans), Zr3d (20 scans) and In3d (20 scans) orbitals were measured separately and used for the relative concentration calculations, see equation Eq.-S6.

Data Manipulation

Data manipulation was performed with the Thermo Avantage 4.87 software. A "smart" background correction was applied to all spectra and charging effects corrected by setting the C1s signal of adventitious carbon to 284.8 eV. The area under the curve of the background corrected spectra (denoted "$A_{Orbital}$") was used for the relative concentration (S to Zr+In) calculations, see equation Eq.-S6.

$$\frac{S}{Zr + In} = \frac{\dfrac{A_{S2p}}{SF_{S2p}}}{\dfrac{A_{Zr3d}}{SF_{Zr3d}} + \dfrac{A_{In3d}}{SF_{In3d}}}$$

(Eq.-S6)

The sensitivity factors (denoted "$SF_{Orbital}$") were used as provided by the software.
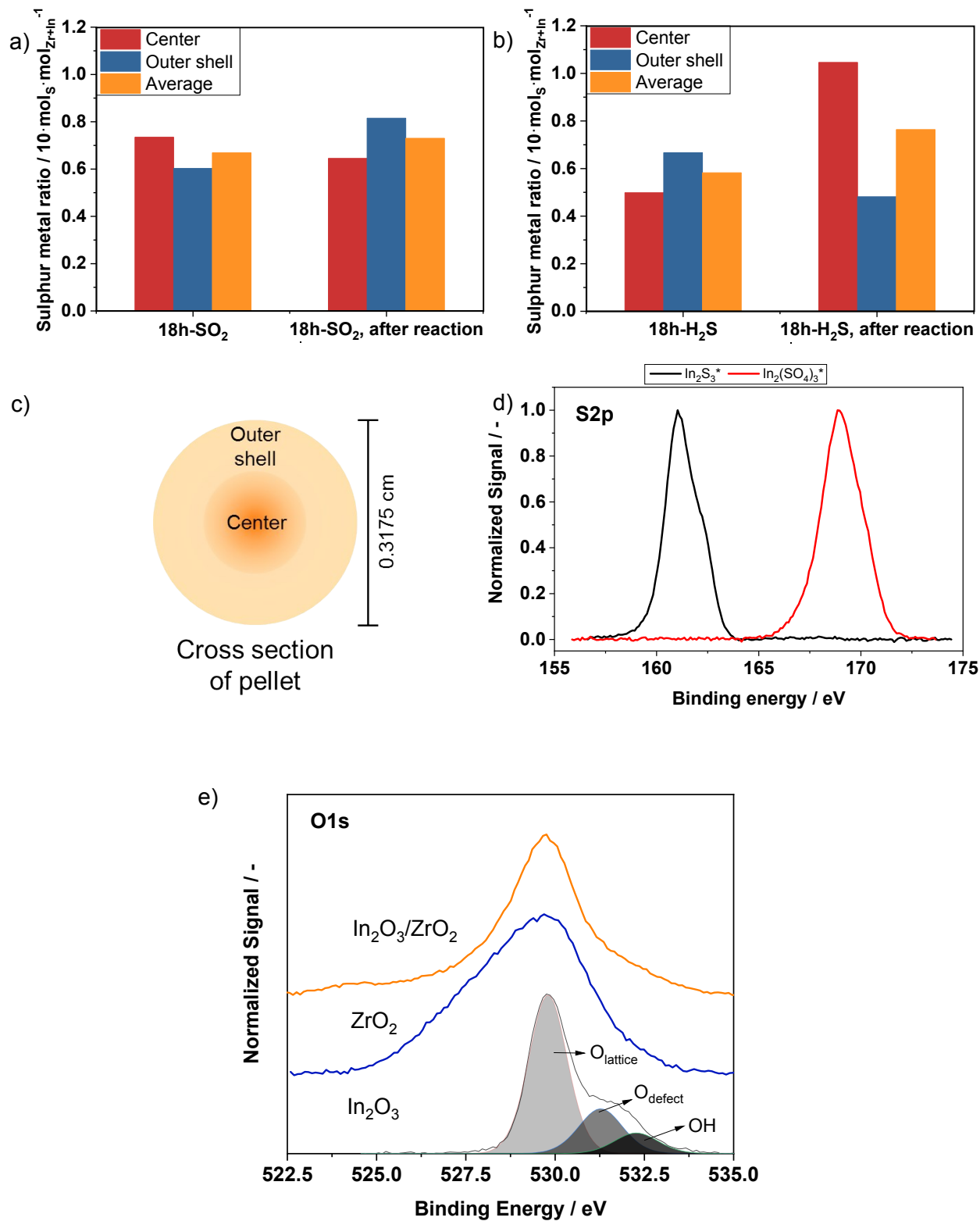
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Fig. S6. Sulphur metal ratio in the center and the outer shell of the catalyst pellet (c) after 18 h of (a) SO_2- and (b) H_2S-poisoning, determined by In3d-, Zr3d- and S2p-XPS measurements. (d) XPS -Investigation S2p-orbitals of commercial In_2S_3 and $In_2(SO_3)_4$ after air-exposure at room-temperature. (e) XPS O1s spectra of In_2O_3, ZrO_2 and fresh In_2O_3/ZrO_2.

The concentration of oxygen atoms next to a defect (O_{defect}) is often taken as a gauge for oxygen vacancies and can be determined by deconvolution of the O1s XPS spectra as reported by Martin et al. [12]. For unsupported In_2O_3 an O_{defect} share of 22.0 % was measured in the present study, which is close to the values reported in [12]. Deconvolution of both ZrO_2 and fresh In_2O_3/ZrO_2 was deemed unpractical due to the symmetric nature of the O1s spectra, see Fig. S6. The absence of O_{defect} in In_2O_3/ZrO_2 can be explained by the fact that about 85% of the measured oxygen atoms originate from ZrO_2 which does not exhibit such sites. Also Chen et al [18] reported nearly symmetrical O1s spectra for In_2O_3 supported on ZrO_2.
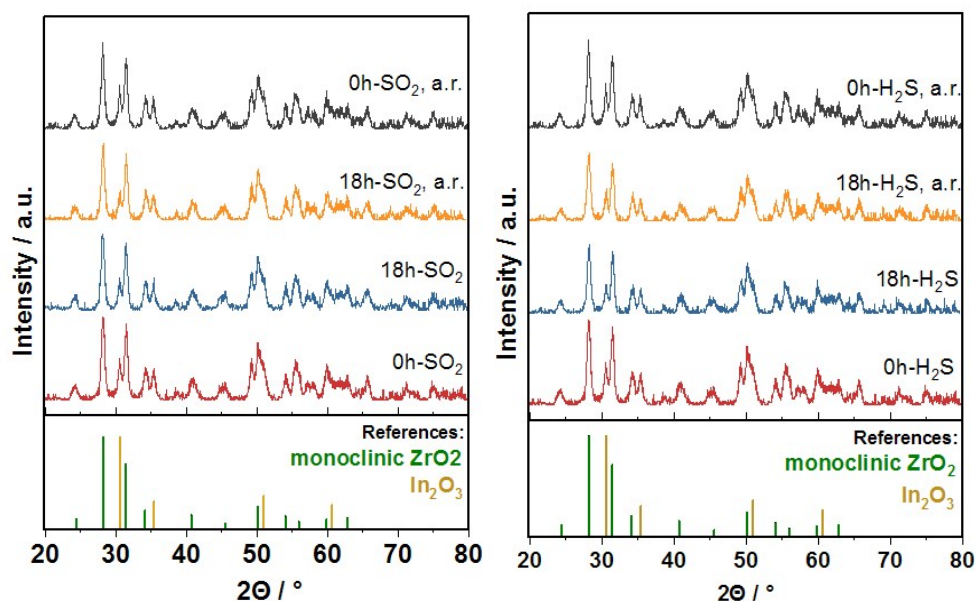
S10.   XRD data

Fig. S7. XRD patterns of untreated, as well as SO_2- and H_2S-poisoned (18 h) In_2O_3/ZrO_2 catalysts before and after methanol synthesis reaction (a.r.). Reference spectra for ZrO_2 and In_2O_3 are given taken from [1].

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S11. Deactivation of commercial Cu/ZnO/Al$_2$O$_3$ catalyst by sulphur gas impurities
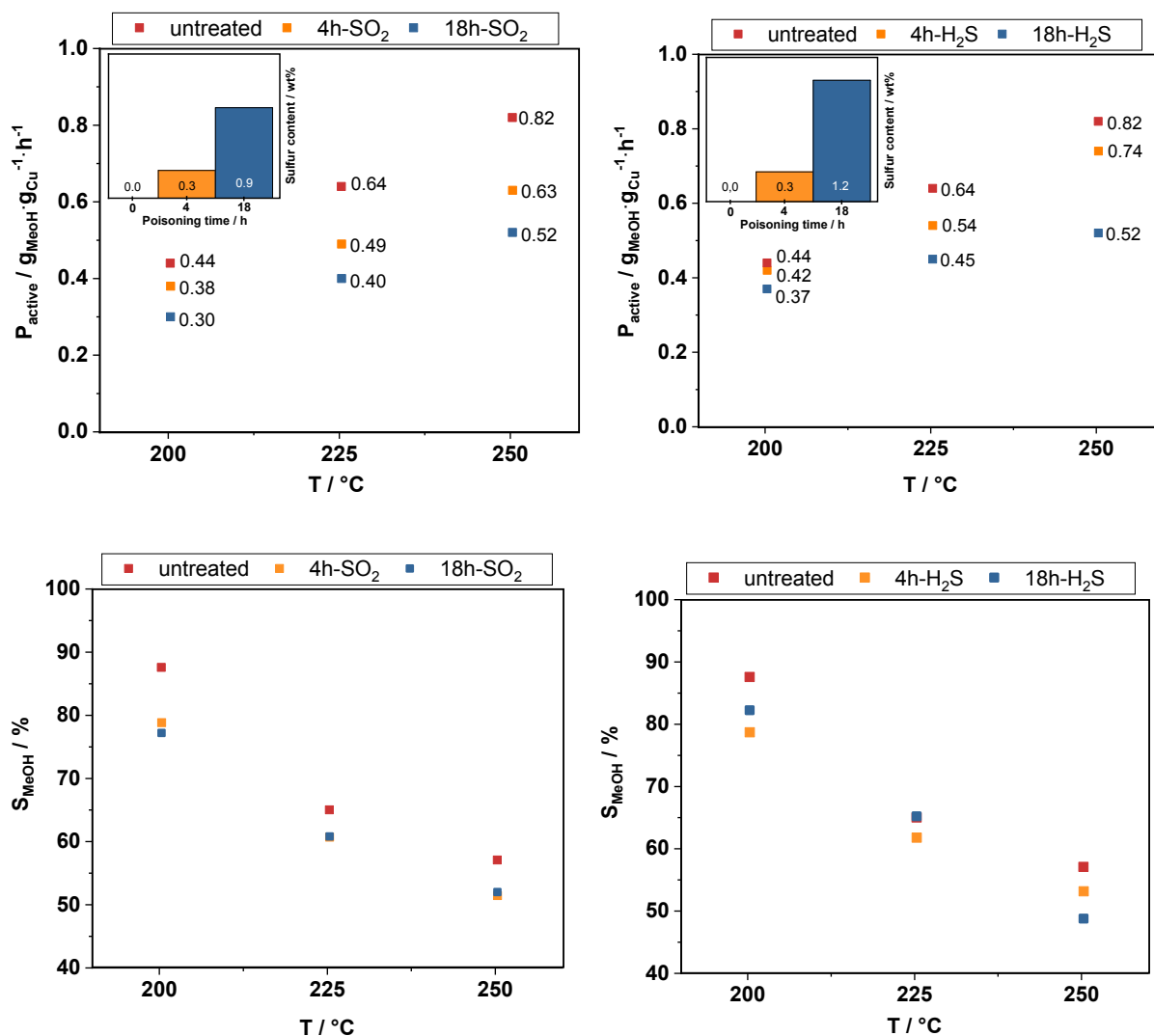

Fig. S8. Influence of commercial Cu/ZnO/Al$_2$O$_3$ (Alfa Aeser) catalyst poisoning with SO$_2$ (left) and H$_2$S (right) on methanol productivity (top) and selectivity (bottom). Reaction conditions: CO$_2$/H$_2$ = 1/3; GHSV = 1952 h^{-1}; p_{total} = 53.8 ± 0.5 bar; TOS = 960 min; h_{bed} = 6.4 ± 0.1 cm; m_{cat} = 2.5 ± 0.1 g; $m_{Raschig}$ = 7.5 ± 0.1 g; w_{Cu} = 63.5 wt.%.
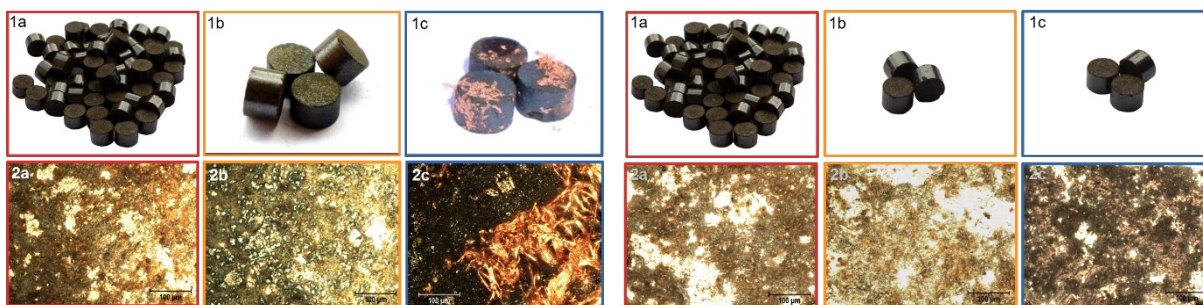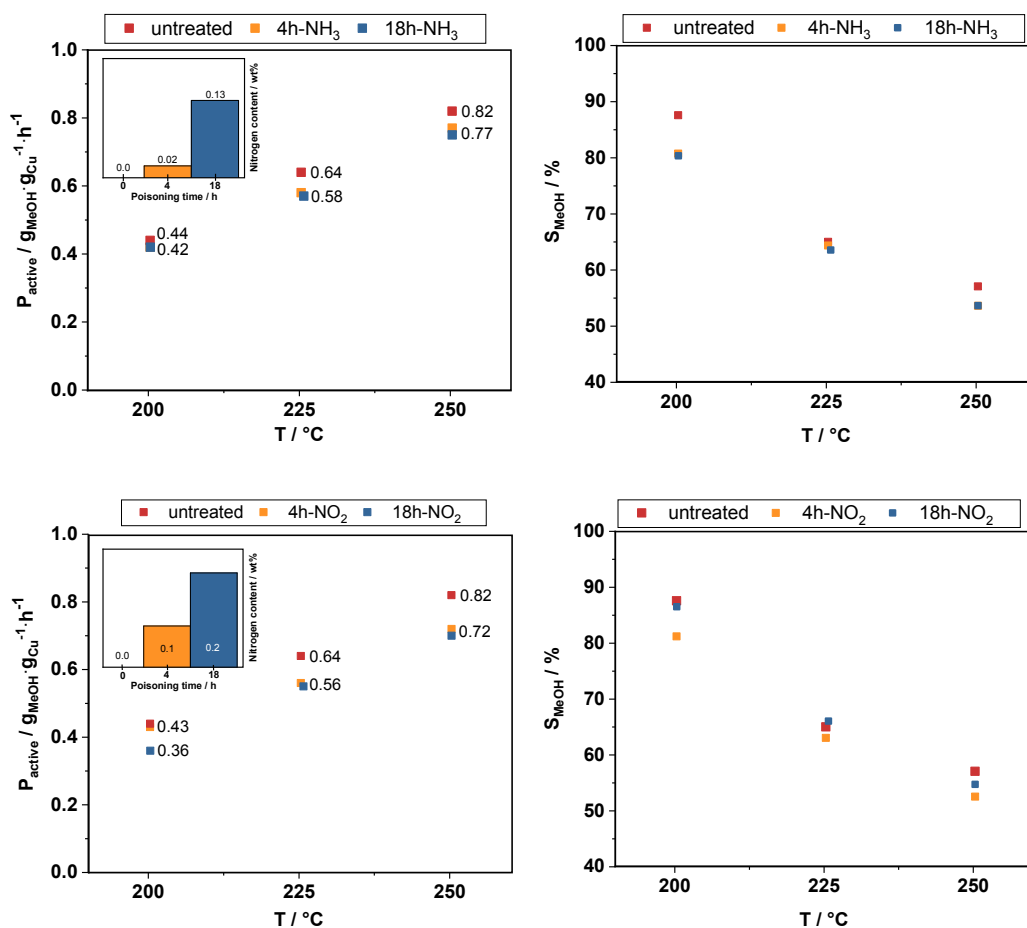
Fig. S9. Photos and light microscopy pictures of non-poisoned catalysts, poisoned catalysts and poisoned catalysts after reaction. Poisoning of $Cu/ZnO/Al_2O_3$ performed with H_2S (left) and SO_2 (right).

S12.   Deactivation of commercial Cu-catalyst by nitrogen gas impurities
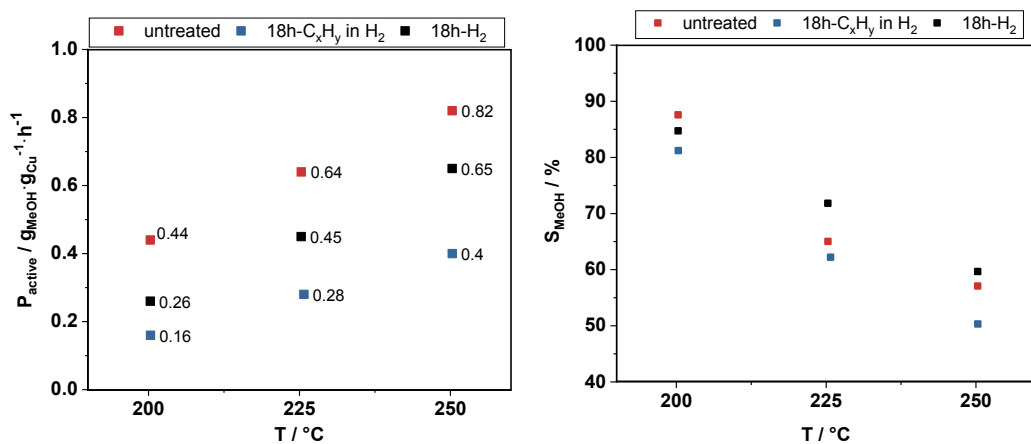
Fig. S10. Influence of commercial Cu/ZnO/Al$_2$O$_3$ (Alfa Aeser) catalyst poisoning with NH$_3$ (top), NO$_2$ (middle) and a mixture of hydrocarbons in hydrogen (bottom) on methanol productivity (left) and selectivity (right). Reaction conditions: CO$_2$/H$_2$ = 1/3; GHSV = 1952 h^{-1}; p$_{total}$ = 53.8 ± 0.5 bar; TOS = 960 min; h$_{bed}$ = 6.4 ± 0.1 cm; m$_{cat}$ = 2.5 ± 0.1 g; m$_{Raschig}$ = 7.5 ± 0.1 g; w$_{Cu}$ = 63.5 wt.%.

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