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Negative Charging of Au Nanoparticles during Methanol Synthesis from CO₂/H₂ on a Au/ZnO Catalyst: Insights from *Operando* Infrared and Near-ambient Pressure XPS and XAS

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Abstract: Kinetic measurements in combination with time resolved operando infrared (DRIFTS), in situ near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and X-ray absorption near edge spectroscopy (XANES) measurements at the O K-edge together with high resolution electron microscopy were applied to evaluate the electronic and structural properties of Au/ZnO under industrial and idealized methanol synthesis conditions. CO adsorption during the reaction revealed the presence of negatively charged Au nanoparticles / Au sites under reaction conditions, which are formed during the initial phase of the reaction. Near ambient pressure XPS and XANES demonstrate the build-up of O-vacancies during the reaction, which goes along with a substantial increase in the methanol formation rate. The results are discussed in comparison with previous findings for Cu/ZnO and Au/ZnO catalysts.

Supported Au catalysts have attracted considerable interest due to their high activity at rather mild conditions in a number of reactions, $^{[1]}$ including the hydrogenation of CO2 to methanol. $^{[2:3]}$ For the latter reaction, supported gold catalysts, in particular Au/ZnO, were found to be at least as active as commercial Cu/ZnO catalysts. $^{[4]}$ In addition, they showed a higher selectivity for methanol formation relative to the competing reverse water gas shift (RWGS) reaction at pressures up to 50 bar. $^{[3:4]}$ To better understand the origin of the high activity and selectivity of these catalysts, a detailed knowledge of their electronic and geometric structure under reaction conditions is required.

First of all this requires reliable information on the oxidation state of the active Au species and of the oxide support during reaction. We had recently shown for Au/TiO₂ catalysts in the CO oxidation reaction^[5;6] that the number of surface oxygen vacancies on the TiO₂ support depends sensitively on the composition

of the gas phase, specifically on the CO : O_2 ratio. $^{[7]}$ In the same way one might expect that a reductive reaction atmosphere, as encountered for a CO_2 / H_2 methanol synthesis mixture, will lead to a partial reduction of the ZnO support in the Au/ZnO catalysts. Similar reduction effects have been debated controversially for Cu/ZnO catalysts. $^{[8-12]}$ Some of those authors had suggested that the Cu crystallites are overgrown by a metastable layer of partially reduced ZnO $_x$ during reaction. $^{[10;13]}$ It can also be envisaged that the electronic properties of the metal nanoparticles (NPs) are modified by such changes in the ZnO support. Therefore, scrutinizing the electronic properties of the Au NPs and of the ZnO support and their mutual interactions under reaction conditions is a prerequisite for the detailed understanding of their catalytic performance.

In this work, we employed kinetic measurements as well as time resolved operando diffuse reflectance FTIR spectroscopy (DRIFTS) in the pressure range of up to industrial methanol synthesis conditions (up to 50 bar, 240°C), together with in situ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and X-ray absorption near edge spectroscopy (XANES) to i) probe the changes in the electronic state of Au during methanol synthesis and to ii) inspect how the changes in the (defect) structure of ZnO can induce or be related to changes in the electronic state of the Au NPs. In addition, we make use of information on the Au particle size, obtained from transmission electron microscopy (TEM), and of results on the atomic Au:Zn surface ratios derived from quasi in situ laboratory XPS measurements. Based on these data we will discuss changes in the electronic / geometric structure of the Au/ZnO catalyst during time on stream and their effect on the activity for methanol formation. The trends mapped out for Au/ZnO are expected to provide insight also for the more complex Cu/ZnO system.

First, we monitored possible changes in the electronic state of the Au NPs during reaction, following the vibrational properties of CO adsorbed on the Au/ZnO catalyst by *operando* DRIFTS measurements at 240°C and pressures from 1 to 50 bar. Here, we make use of the ongoing CO formation during methanol synthesis via the competing RWGS reaction. Representative spectra, recorded under steady-state conditions at different pressures, are displayed in Figure 1a. Under these conditions, there is essentially no CO adsorption detectable at 1 bar. A $\rm CO_{ad}$ related band centered at 2078 cm $^{-1}$ appears at 5 bar and increases in intensity with increasing pressure. Starting at 20 bar, a broad band evolves, ranging from 2050 – 2130 cm $^{-1}$, and at 40 - 50 bar, distinct maxima appear at 2109 cm $^{-1}$ as well as at 2018, 2068, and 2094 cm $^{-1}$, respectively. Bands in these ranges are characteristic for CO adsorption on small metallic Au NPs (Au 0 ,

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2100 - 2130 cm $^{-1}),$ and on negatively charged Au NPs/sites (Au $^{\delta-}$ -CO: 2020-2100 cm $^{-1}). ^{[14;15]}$

Independent of the pressure, there are no bands characteristic for CO adsorption on cationic species such as Zn^{2+} (typically at 2170-2190 cm⁻¹ [^{16]}) or oxidized $Au^{\delta+}$ species (Au_2O_3 : 2156 cm⁻¹ [^{17]}). Significant CO adsorption on uncharged, metallic NPs or sites can only be detected at pressures \geq 20 bar, while the $Au^{\delta-}$ -CO species was observed at significantly lower pressures. Considering that there is little change in the CO formation rate (via the RWGS) at pressures between 20 and 50 bar (see Figure S1, Supporting Information (SI)), the increase in CO_{ad} band intensity and thus in CO_{ad} coverage with increasing total pressure is not due to changes in the CO formation rates, but mainly caused by an increase in CO adsorption strength or an increase in active Au surface area. It also fits well with the trend in the methanol formation rate (Figure 1b).

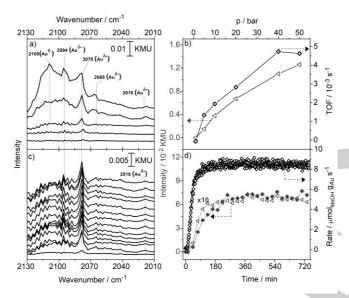


Figure 1. (a) Operando DRIFTS spectra in CO₂/H₂ (1:3) recorded under steady-state conditions at 240°C and pressures from 5 to 50 bar (bottom to top: 5, 10, 20, 40 and 50 bar, intensities in Kubelka-Munk (KMU) units, see experimental part in SI)). (b) Time sequence of spectra recorded at 20 bar under otherwise similar reaction conditions (bottom to top: after 15, 30, 45, 75, 105, 135,165, 195, 255, 375, 495, 615, 715, 735 min). (c) Steady-state methanol formation rate in TOFs (right scale) and steady-state Au-CO band intensity (peak height at 2078 cm⁻¹,in KMUs, left scale) as a function of reaction gas pressure. (d) Time evolution of the Au mass normalized methanol formation rate (♦), the Au-CO band peak intensity at 2078 cm⁻¹ (◄, intensity multiplied by 10) and of the OH stretch vibration in adsorbed methanol at 3567 cm⁻¹ at 20 bar (♠, data from spectra like those in b) and Figure S6). Reaction rates in micro-reactor and DRIFTS cell are compared in Figure S2, SI.

In a similar way we followed the build-up of the $CO_{ad}@Au^{\delta-}$ species with time at a constant pressure of 20 bar (CO_2 : $H_2=1:3$) by recording time resolved DRIFTS spectra (see Figure 1c). The evolution of the CO_{ad} band intensity around 2078 cm⁻¹ (peak height), which is representative for CO adsorption on negatively charged $Au^{\delta-}$ species, is plotted in Figure 1d, together with the Au mass-normalized methanol formation rate. Qualitatively, this shows a rather good agreement between the time evolution of the methanol formation rate and the CO_{ad} band intensity and thus, in a first order approximation, with the CO_{ad} coverage on these sites.

During the initial phase of the reaction, both the methanol formation rate and the coverage of the $CO_{ad}@Au\delta^{-}$ species increase steadily, while at longer times they both remain stable. These observations are in good agreement with previous findings of negligible catalyst deactivation. [3:4] Interestingly, this activation period takes about 50 - 70 min for the methanol formation rate, while the CO_{ad} band intensity increases for up to ~150 min. These activation periods are reversible, upon subsequent re-calcination (10% O_2/Ar , 400°C) we found a similar activation behavior (see Figure S3 - SI).

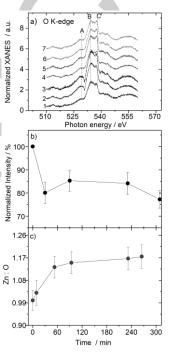


Figure 2 (a) Normalized XANES spectra of the oxygen K-edge recorded in 0.3 mbar Ar at 400°C (spectrum 1), in 0.3 mbar O_2/Ar (1:1) at 400°C (spectrum 2) and at 240°C (spectrum 3), and during methanol synthesis in CO_2 : H_2 (1:3, 0.3 mbar) recorded at different times on stream (13, 90, 230 and 309 min; spectra 4 -7). (b) Normalized intensity of the features B, C in the XANES spectra (intensity ratio of reaction spectra (4-7) with respect to spectrum (3)), integrated over the peak area from 530.5 to 540 eV. (c) Atomic Zn: O surface ratio during reaction based on the Zn 2p and the O 1s peak intensities (spectra in SI, Figure S7)

Comparing similar measurements at different pressures, it turned out that the duration of the activation period in the methanol formation rate decreases with increasing pressure, from about 100 min at 5 bar to 50 min at 50 bar (Figure S4b, SI), while the build-up of CO_{ad}@ Auδ- species takes 100 – 150 min, independent of the total pressure (Figure S4a, SI). Note that the slow increase in CO_{ad} coverage with time cannot be related to changes in the CO formation rate, since the trends in both features are opposite (initial increase in CO_{ad} intensity, initial decrease in CO_{ad} formation rate, see Figure S5, SI). Thus, these activation periods must result from modifications of the adsorption properties of the Au NPs during time on stream, either directly by charging of the Au NPs or by an increase of the active Au surface area due to surface de-encapsulation. This is accompanied by an increase in the methanol formation rate. While qualitatively closely related, a quantitative comparison shows differences in how these

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modifications affect the CO adsorption and the methanol formation rate.

Finally, to ensure that the initial activation period is characteristic for Au/ZnO and changes therein, we examined the initial stages of the MeOH formation reaction on 3 related catalysts of different composition (5 bar, 240°C, see Figure S8 and Table S1 - SI). For a Au/Al $_2$ O $_3$ catalyst, we found a much lower activity and essentially no activation period, Au/CeO $_2$ with a more reducible support showed the highest activity and a relatively fast activation (13 min), while an activation period of $\sim\!\!30$ min was observed for a commercial Cu/ZnO catalyst. Hence, the extended activation period is characteristic for the Au/ZnO catalyst and points to a pronounced influence of the support reducibility on both activity and activation behavior.

In total, these results clearly indicate that the interaction of the calcined Au/ZnO catalyst with the methanol synthesis gas mixture results in the formation of negatively charged Au sites / NPs, which may affect different reaction steps such as H_2 activation or the dissociation of a C-O bond. This goes along with an increase in the methanol formation rate and in CO adsorption. Based on the IR results, these trends apply over a wide pressure range.

To directly probe the electronic properties of ZnO during methanol synthesis, we first explored changes in the near edge region of the oxygen K-edge upon exposure to different gas mixtures and temperatures, using pressures in the mbar range. A series of XANES spectra is presented in Figure 2a. The features B and C in the spectra are characteristic for the excitation of O1s electrons into the unoccupied O 2p states, and their intensity is about proportional to the density of unoccupied states (UDOS).[18] Comparing the first spectrum (spectrum 1, Figure 2a), which was recorded during exposure to an Ar atmosphere (0.3 mbar) at 400°C, with the spectra taken in O₂/Ar (1:1) at 400°C and at 240°C (spectra 2 and 3, Figure 2a), we find significant differences in the normalized intensities of these features. The much higher intensity of the features B and C in spectra 2 and 3 compared to spectrum 1 can be explained by the replenishment of O vacancies in the ZnO lattice during exposure to O2/Ar, which had been created before by heating in Ar. Filling the oxygen vacancies results in an increased UDOS above E_F. Integration of the intensity in the range between 530.4 eV and 540.0 eV (features B, C) during methanol synthesis at 240°C (spectra 4 – 7 in Figure 2a) shows a decrease of the intensity of these features by roughly 18 ± 5 % relative to the spectrum recorded after oxidation of the catalyst at 400°C (spectrum 3 in Figure 2a, intensity ratio in Figure 2b). Furthermore, the pre-edge feature A at around 528 - 530 eV, which was not present in the first spectrum, evolved once O₂/Ar was admitted. This feature had been attributed earlier to an excitation from the O 1s state into unoccupied, hybridized O 2p and Zn 4s/Zn 3d states,[19] which is less efficient in the presence of oxygen vacancies. Overall, the XANES data indicate considerable oxygen vacancy formation upon annealing in Ar atmosphere, and their replenishment upon exposure to 0.3 mbar O₂/Ar. This is supported also by the changes in the DRIFTS spectra, which show a drastically lower reflected intensity after heating in Ar to 400°C (1 bar) as compared to a fully oxidized sample (Figure S9, SI). The lower IR intensity of the partly reduced sample was explained by an increase in the charge carrier density upon oxygen vacancy formation.[20]

During subsequent exposure to a methanol synthesis atmosphere the intensity of the features B and C decreased significantly already after 2 min on stream, and the pre-edge feature A almost vanished. Both changes point to the re-formation of Ovacancies in the ZnO support, in good agreement with the drastic increase in IR absorption observed in the DRIFTS spectra (Figure S10, SI). With longer time on stream, the general shape of the XANES spectra did not change any more.

For further information on the creation and relative concentration of O-vacancies we followed the intensities of the Zn 2p and O1s XP signals, which were recorded after calcination and at different times during reaction in a 1:3 mixture of CO₂ and H₂, also at 0.3 mbar. Here we used the integrated intensities of the Zn $2p_{3/2}$ peak at 1022.3 ± 0.1 eV and of the lower binding energy (BE) contribution of the O 1s peak at 530.3 ± 0.1 eV (see the peak deconvolution in Figure S7, SI). The latter peak contribution is characteristic for the O2- ions of the wurtzite structure of ZnO (for the other peaks see caption of Figure S7. SI).[21;22] From the intensities of the respective Zn 2p and O1s signals we obtained an atomic Zn: O ratio of slightly above the stoichiometric value of 1 for the calcined sample (for details see the SI, section 4), Using this intensity ratio for normalization, the Zn: O atomic ratio then increases gradually during reaction from 1 to a value of ~1.17 after 268 min of reaction (Figure 2c). The depletion of O in the ZnO support surface reflects the creation of O-vacancies. The resulting intensity ratio roughly corresponds to an O-vacancy concentration of ~13.2 % in the surface region, which is much more than the amount of lattice oxygen at Au-ZnO perimeter sites (0.044 x 1015 O_{atom} cm⁻²). Even when considering the error range, this clearly supports our claim of significant O-vacancy formation during the reaction. This value is compatible also with the (lower) amount of removable surface oxygen determined recently by TAP reactor measurements upon CO₂/H₂ pulsing on the same Au/ZnO catalyst. [23] Slight differences in the time scales in the XANES and NAP-XPS measurements may result from differences in the surface sensitivities of the electrons used for detection (see Tables S2 and S3, SI). Overall, the changes in the XANES and NAP-XPS data, which were recorded in the mbar regime, fit well with the distinct increase of the methanol formation activity and the increasing formation of the CO_{ads}@Auδ- species, which were detected in high pressure kinetic and DRIFTS measurements. The changes in the support (O-vacancy formation) are induced already at pressures in the mbar regime and persist also at the realistic higher reaction pressures. Most likely, the concentration of O-vacancies is governed by a competition of vacancy formation (by reaction with H_2 , CO) and vacancy replenishment (by reaction with CO₂, H₂O), and hence by the ratio between CO₂ and H₂ partial pressures.

A significant change in the reactivity upon formation of surface oxygen defects was reported earlier by Yoon et al., who showed that small Au₈ clusters deposited on O-vacancies on MgO(001) are very active for CO oxidation, while on a defect free MgO substrate they are inactive.^[14] In addition, these authors also observed a distinct red-shift of the CO vibrational band from 2109 to 2055 cm⁻¹, which they interpreted as due to the formation of negatively charged Au clusters. Those results clearly demonstrate the influence the formation of these Au⁸⁻ sites can exert on the reactivity of Au catalysts.

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Next, we characterized the electronic properties of the Au/ZnO catalyst, in particular of the Au NPs, both after oxidative pretreatment (O400: 1 h in 10% O₂/Ar at 400°C, 1 atm) and after an additional reaction step for 1000 min at 5 bar in a CO₂/H₂ (1:3) mixture, using laboratory based quasi-in situ XPS measurements, without exposure of the sample to air between pretreatment / reaction and XPS measurements (see Figures S11, S12 - SI). The binding energies (BEs) of the Au 4 f_{7/2} state after pretreatment and subsequent methanol synthesis were essentially identical, with 83.8 and 83.7 eV, respectively, close to the typical BE of metallic Au.[24] Furthermore, analysis of the atomic surface concentrations of Zn and Au indicated a slight increase of the Zn: Au intensity ratio during reaction, from 78 after O400 pretreatment to 84 after reaction, which points to a slight increase of the Zn surface concentration during the reaction. At the same time, the Zn: O intensity ratio increased from 0.8 (after O400) to 0.89 after reaction. These results obtained after reaction at 5 bar are in good agreement with those obtained at 0.3 mbar using NAP-XPS. Apparently, the formation of surface O-vacancies is accompanied by a slight structural rearrangement during time on stream, e.g., due to subtle changes in the Au particle shape such as a flattening of the Au NPs, induced by O-vacancy formation. Alternatively, this may be caused by de-encapsulation of the Au NPs, as it had been suggested by Liu et al. for reduction of a pre-oxidized Au/ZnO catalyst in H_2 (see below). [25] Comparison of the quasi-in situ XP spectra showed that the C1s intensity is unchanged (Figure S12 - SI). Hence, the change in the Zn : O or Zn : Au ratio is not related to the buildup of carbon containing species.

In addition, we characterized the particle size distribution of the Au NPs after pretreatment and after subsequent reaction at 5 bar by HR-TEM. The TEM images revealed a homogeneous distribution of the Au NPs on the ZnO surface both before and after the reaction, while the particle sizes did not change much (Figure 3). After the reaction, the Au particle size distribution is slightly broader than before reaction, in particular the fraction of particles with sizes below 2.0 nm (Figure 3), but there is no evidence for significant changes in the Au NP size.

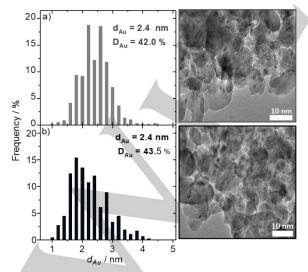


Figure 3 TEM micrographs of the Au/ZnO catalyst and Au particle size distribution after O400 pretreatment (a) and after subsequent reaction at 240°C / 5 bar for 1000 min in a CO_2/H_2 (1:3) gas mixture (b).

It is interesting to compare these results with related findings for Cu/ZnO catalysts, where several groups reported a partial overgrowth of the Cu NPs by a reduced ZnO_x layer upon exposure to a methanol reaction mixture. ^[10] This would be consistent with the increasing Zn surface concentration observed by XPS in our experiments. It would be, however, in direct contrast to the activation in the initial stage of the reaction and the constant CO_{ad} coverage after the initial activation period (Figure 1d). If there were a slow overgrowth of the Au NPs by a ZnO_x layer, we would expect that the CO_{ad} coverage decreases with time and possibly also the MeOH formation rate. On the other hand, Nakamura, Chorkendorff and coworkers had concluded that under reaction conditions metallic Zn is formed and incorporated into the Cu surface, forming the active phase responsible for the promoted synthesis of methanol. ^[8;12;26]

Returning to Au/ZnO catalysts, Liu et al reported that an oxidative pre-treatment of Au/ZnO results in an electron transfer from Au NPs to the ZnO (positive charging of the Au NPs) and claimed a (partial) encapsulation of the Au NPs by a ZnO layer, while reduction in H₂ leads to charge transfer from ZnO_x to Au, de-encapsulation of the Au NPs and formation of AuZn alloys. [25] After reduction in H₂, these authors observed also the formation of CO_{ad} bands at 2048 cm⁻¹, representative for CO_{ad} on negatively charged Au sites. In the present work, where the reaction gas mixture is strongly reductive, we suggest a similar scenario. The formation of O-vacancies goes along with the formation of negatively charged Au NPs / Au sites, reflecting pronounced electronic metal-support interactions, as well as a drastic increase of CO adsorption and of the activity for methanol formation during the initial activation period. The changes in CO adsorption behavior may either be directly caused by the electronic modification of the Au NPs, or by a partial de-encapsulation of the Au NPs as a result of O-vacancy formation. Finally, we postulate that similar to findings for reduction by CO,[5] the surface reduction of the ZnO support by the H₂/CO₂ reaction gas is enhanced by the Au NPs, taking place at the perimeter sites of the Au-ZnO interface.

In summary, we have investigated changes in the electronic and geometric structure of Au/ZnO catalyst under up to industrial synthesis conditions as a first step towards a more comprehensive mechanistic understanding of the methanol synthesis by hydrogenation of CO₂ over Au/ZnO catalysts. Employing operando DRIFTS as well as in situ XANES and NAP-XPS and quasi in situ XPS together with kinetic measurements, we find a rapid formation of O-vacancies in the ZnO surface region in the initial stages of the reaction (first 1-2 h). This goes along with the formation of negatively charged Auδ- sites, as evidenced by the formation of Auδ-CO species with vibrational frequencies well below 2100 cm⁻¹, and a pronounced increase in CO adsorption and in the methanol formation activity during the initial activation period. The results underline the importance of a partial reduction of the ZnO support under reaction conditions for its activity for methanol formation, which is considered to play an important role also for Cu/ZnO catalysts.

Experimental Section

The experimental details are described in the Supporting Information.

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Keywords: Methanol synthesis, Au charging, Au/ZnO catalyst, operando FTIR, near ambient pressure (NAP) XPS, XANES

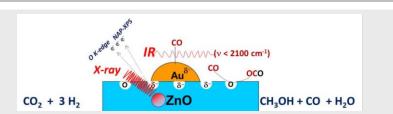
- [1.] G. C. Bond, C. Louis, D. T. Thompson, Catalysis by Gold, Imperial Press, London 2007, pp. 1-366.
- [2.] H. Sakurai, M. Haruta, Synergism in Methanol Synthesis from Carbon Dioxide over Gold Catalysts Supported on Metal Oxides, Catal. Today 1996, 29 361-365.
- [3.] Y. Hartadi, D. Widmann, R.J. Behm, CO₂ Hydrogenation to Methanol on Supported Au Catalysts under Moderate Reaction Conditions: Support and Particle Size Effects, ChemSusChem 2015, 8 456-465.
- [4.] Y. Hartadi, D. Widmann, R.J. Behm, Methanol Formation by CO₂ Hydrogenation on Au/ZnO Catalysts - Effect of Total Pressure and Influence of CO on the Reaction Characteristics, J. Catal. 2016, 333 238-250.
- [5.] D. Widmann, R.J. Behm, Active Oxygen on a Au/TiO₂ Catalyst -Formation, Stability and CO Oxidation Activity, Angew. Chem. Int. Ed. 2011, 50 10241-10245.
- [6.] A.Y. Klyushin, M.T. Greiner, X. Huang, T. Lunkenbein, X. Li, O. Timpe, M. Friedrich, M. Hävecker, A. Knop-Gericke, R. Schlögl, Is Nanostructuring Sufficient To Get Catalytically Active Au?, ACS Catal. 2016, 6 3372-3380.
- [7.] D. Widmann, R.J. Behm, Dynamic Surface Composition in a Mars van Krevelen Type Reaction: CO Oxidation on Au/TiO₂, J. Catal. 2018, 357 263-273
- [8.] T. Fujitani, I. Nakamura, T. Uchijima, J. Nakamura, The Kinetics and Mechanism of Methanol Synthesis by Hydrogenation of CO₂ over a Zndeposited Cu (111) Surface, Surf. Sci. 1997, 383 285-298.
- [9.] J.D. Grunwaldt, A.M. Molenbroek, N.Y. Tøpse, H. Tøpse, B.S. Clausen, In Situ Investigations of Structural Changes in Cu/ZnO Catalysts, J. Catal. 2000. 194 452-460.
- [10.] T. Lunkenbein, J. Schumann, M. Behrens, R. Schlögl, M.G. Willinger, Formation of a ZnO Overlayer in Industrial Cu/ZnO/Al₂O₃ Catalysts Induced by Strong Metal-Support Interactions, Angew. Chem. 2015, 127 4627-4631.
- [11.] S. Kattel, P.J. Ramírez, J.G. Chen, J.A. Rodriguez, P. Liu, Active Sites for CO₂ Hydrogenation to Methanol on Cu/ZnO Catalysts, Science 2017, 355 1296-1299.
- [12.] J. Nakamura, T. Fujitani, S. Kuld, S. Helveg, I. Chorkendorff, J. Sehested, Comment on "Active sites for CO₂ Hydrogenation to Methanol on Cu/ZnO Catalysts", Science 2017, 357 eaan8074.
- [13.] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R.W. Fischer, J.K. Nørskov, R. Schlögl, The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts, Science 2012, 336 893-897.
- [14.] B. Yoon, H. Häkkinen, U. Landman, A.S. Wörz, M. Antonietti, S. Abbet, K. Judai, U. Heiz, Charging Effects on Bonding and Catalyzed Oxidation of CO on Au₈ Clusters on MgO, Science 2005, 307 403-407.
- [15.] M. Sterrer, M. Yulikov, E. Fischbach, M. Heyde, H.P. Rust, G. Pacchioni, T. Risse, H.J. Freund, *Interaction of Gold Clusters with Color Centers on MgO(001) Films*, Angew. Chem. Int. Ed. **2006**, 45 2630-2632.
- [16.] M. Buchholz, X. Yu, C. Yang, S. Heißler, A. Nefedov, Y. Wang, C. Wöll, IR-spectroscopy of CO Adsorption on Mixed-terminated ZnO Surfaces, Surf. Sci. 2016, 652 247-252.
- [17.] A.M. Abdel-Mageed, G. Kucèrová, J. Bansmann, R.J. Behm, Active Au Species during the Low-temperature Water Gas Shift Reaction on

- Au/CeO₂: A Time-resolved Operando XAS and DRIFTS Study, ACS Catal. **2017**, 17 6471-6484.
- [18.] M. Wang, F. Ren, J. Zhou, G. Cai, L. Cai, Y. Hu, D. Wang, Y. Liu, L. Guo, S. Shen, N doping to ZnO nanorods for photoelectrochemical water splitting under visible light: engineered impurity distribution and terraced band structure, Sci. Rep. 2015, 5 1-13.
- [19.] J.H. Guo, A. Gupta, P. Sharma, K.V. Rao, M.A. Marcus, C.L. Dong, J.M.O. Guillen, S.M. Butorin, M. Mattesini, P.A. Glans, X-ray Spectroscopic Study of the Charge State and Local Ordering of Roomtemperature Ferromagnetic Mn-doped ZnO, J. Phys. Condensed Matter 2007, 19 172202.
- [20.] S. Matsushita, T. Nakata, Infrared Absorption of Zinc Oxide and of Adsorbed CO₂. II, J. Chem. Phys. 1962, 36 665-669.
- [21.] M. Chen, X. Wang, Y.H. Yu, Z.L. Pei, X.D. Bai, C. Sun, R.F. Huang, L.S. Wen, X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy Studies of Al-doped ZnO films, Appl. Surf. Sci. 2000, 158 134-140.
- [22.] P.T. Hsieh, Y.C. Chen, K.S. Kao, C.M. Wang, Luminescence mechanism of ZnO thin film investigated by XPS measurement, Appl. Phys. A 2008, 90.317-321.
- [23.] K. Wiese, A.M. Abdel-Mageed, A.Y. Klyushin, R.J. Behm, Dynamic changes of Au/ZnO catalysts during methanol synthesis: A model study by temporal analysis of products and Zn L.III near edge X-ray absorption spectroscopy. Topics Catal., DOI: 10.1016/j.cattod.2018.11.074.
- [24.] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, (Ed.: J. Chastain) Perkin Elmer Corp., Eden Prairie/USA 1992.
- [25.] X. Liu, M.H. Liu, Y.C. Luo, C.-Y. Mou, S.D. Lin, H. Cheng, J.M. Chen, J.F. Lee, T.S. Lin, Strong Metal-Support Interactions between Gold Nanoparticles and ZnO Nanorods in CO Oxidation, J. Am. Chem. Soc. 2012, 134 10251-10258.
- [26.] S. Kuld, C. Conradsen, P.G. Moses, I. Chorkendorff, J. Sehested, Quantification of Zinc Atoms in a Surface Alloy on Copper in an Industrial-Type Methanol Synthesis Catalyst, Angew. Chem. Int. Ed. 2014, 53 5941-5946.

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Methanol synthesis activity goes along with the formation of O-vacancies during the initial activation period, which as consequence results in a negative charging of Au nanoparticles during reaction.

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