



Ab initio study of CO₂ hydrogenation mechanisms on inverse ZnO/Cu catalysts [☆]



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ABSTRACT

Methanol formation from CO₂ and molecular hydrogen on ZnO/Cu catalysts is studied by gradient corrected density functional theory. The catalytically active region is modeled as a minimum size inverse catalyst represented by Zn_xO_y(H) clusters of different size and a ZnO nano-ribbon on an extended Cu (111) surface. These systems are chosen as a representative of thermodynamically stable catalyst structures under typical reaction conditions. Comparison to a high level wave function method reveals that density functional theory systematically underestimates reaction barriers, but nevertheless conserves their energetic ordering. In contrast to other metal-supported oxides like ceria and zirconia, the reaction proceeds through the formation of formate on ZnO_x/Cu, thus avoiding the CO intermediate. The difference between the oxides is attributed to variance in the initial activation of CO₂. The energetics of the formate reaction pathway is insensitive to the exact environment of undercoordinated Zn active sites, which points to a general mechanism for Cu-Zn based catalysts.

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1. Introduction

Mankind is facing considerable challenges in their quest to secure sufficient energy supply for the future and to solve the global warming problem [1]. Future energy sources have to be renewables. Most of all wind and solar energy already cover an unexpectedly large part of our energy production and are likely to dominate the energy market in near future. However, renewable energies are often produced when they are not needed while their production is low at times of large demand. Therefore, large scale effective energy storage is needed. Electric energy can be used to split water resulting in H₂ as energy carrier. Since molecular hydrogen is delicate to handle, it should be processed further. The synthesis of the base chemical methanol (currently produced from

[☆] Supplementary Material (SM) available: [Details of the computational methodology, the global minima search and comparison to (DLPNO-)CCSD(T) calculations. Methodology for the inclusion of thermodynamics. Evaluation of the crucial steps using different models. Structure of the nano-ribbons. Wannier orbitals analysis of CO₂. Energetics and structures of the full reaction network.]

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fossil resources) from the greenhouse gas CO₂ and H₂ is a promising strategy to store renewable energy and produce a chemical feedstock (CO₂ + 3H₂ → CH₃OH + H₂O) [2,3]. Contrary to H₂, methanol is liquid at room temperature and thus it can easily be stored, transported and further processed e.g. to oxymethylenedimethylethers (a novel class of fuels that promises rich applications [4]). Furthermore, conversion of CO₂ to methanol is of great environmental relevance as a strategy for reducing the concentration of this anthropogenic green house gas in the atmosphere [5,6].

The catalyst used for synthesizing methanol from synthesis gas (syngas) containing CO and CO₂ on industrial scale corresponds to composites of Cu/ZnO/Al₂O₃ [7–9] and the role and interplay of the different components under reaction conditions are under active debate. Some studies claim that the active phase corresponds to the CuZn alloy formed under reaction conditions upon the partial reduction of the ZnO phase [10,9,11]. In contrast, industrial catalysts were reported to contain a ZnO_x-overlayer on metallic Cu-nanoparticles [7] and recent experimental results show evidence of an improved catalytic activity [12,13] of ZnO_x particles on Cu (111) as compared to the conventional metal-on-oxide configuration [14–16]. These results strongly suggest that the active sites in methanol synthesis catalysts correspond to the ZnO phase or to the ZnO-Cu interface [8,12,7,17,18,13]. In addition to their often supe-

rior activity, inverse catalysts have become a valuable tool for investigating reaction mechanisms and the role of the oxide and the metal-oxide interface [19–22]. Similarly, recent density functional theory studies of supported oxide-clusters-models brought new insights to the catalytic activity of PtCo/TiO₂ and PtCo/ZrO₂-catalysts regarding CO₂-hydrogenation [23]. The CeO_x/Cu(111)-system was reported to show an even superior performance as compared to ZnO_x/Cu(111), with the reaction mechanism consisting of a reverse water–gas shift (RWGS, CO₂+H₂ → CO + H₂O) followed by the CO hydrogenation (CO + 2H₂ → CH₃OH) [19]. A similar reaction path was recently proposed on Cu supported ZrO₂ and on TiO₂ [24]. In contrast, the majority of theoretical and experimental investigations indicate that the hydrogenation of CO₂ does not proceed through a CO-intermediate using Cu/ZnO catalysts [8,25,18,26,27,13]. Although the ZnO_x/Cu(111) was already suggested and explored in early experiments [12,28], only very recently a copper supported Zn₆(OH)₇ structure was considered as possible catalyst [13]. Our work further rationalizes the importance of such structures, explores their global minima structure, and shows the broad independence of the results from the explicit size and composition of the reduced ZnO/Cu inverse catalyst.

2. Computational setup

We have explored the complex reaction network for methanol synthesis catalyzed by Cu-supported zinc oxide by means of ab initio modeling. Because of the heavy computational burden of the high level quantum chemistry, we use the smallest possible supported zinc oxide unit that still describes the relevant reactions. Methods based on density functional theory (DFT) are used for large scale electronic structure calculations of nanostructures supported by extended surfaces. The accuracy of these calculations is verified by comparing the DFT energetics of gas-phase reactions and a subset of catalytic processes with the Coupled Cluster method (CCSD(T)), the gold standard of quantum chemistry, that is considered to give accurate agreement with experiment [29–32] if numerical settings are converged [33,34].

The main part of the calculations use the projector augmented wave method as implemented in GPAW [35,36] where the wave functions are represented on real space grids with grid spacing $h \approx 0.18 \text{ \AA}$. The exchange correlation energy is modeled in the generalized gradient approximation as proposed by Perdew, Burke and Ernzerhof (PBE) [37]. We contrast these results using the BEEF-vdW-functional [38], which is better suited for van der Waals contributions. A detailed description of the methods applied and parameters chosen can be found in [Supplementary Material \(SM\)](#).

3. Discussion

As the first step, we have searched for global minima of the Zn_X-O_Y/Cu(111)-system using a recently implemented genetic algorithm [39,40] in the size range $X = 3 - 9$ and selected Y . The Zn_XO_Y units were modeled on a continuous Cu(111) slab to take into account the metallic nature of the copper support. This study revealed that the typical ZnO/Cu-interface can be conveniently approximated by a Zn₃O-unit, i.e. a reduced form of ZnO, c.f. [Fig. 1](#). Interestingly, the Zn₃O-unit is part of the bulk ZnO wurtzite structure and this structural motif can also be found in ZnO overlayers in industrial Cu/ZnO catalysts under certain conditions [7].

Larger Zn_XO_Y units show similar motifs and additional oxygen atoms do not improve stability (see [Supplementary Material for details](#)). According to our ab initio thermodynamics analysis, zinc-oxide is strongly reduced at typical reaction conditions [8], such that Zn₃O and Zn₇O₃ from [Fig. 1](#) are thermodynamically stable

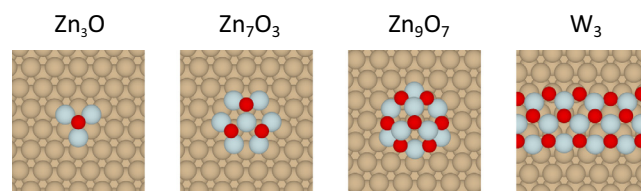


Fig. 1. Global minima structures of Zn₃O, Zn₇O₃, Zn₉O₇ and a zigzag edge ZnO nanoribbon (W₃) supported on Cu(111). Zn: light blue, O: red, Cu: brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

forms. This results in a stabilized Zn₃O unit on the extended Cu(111) surface as a minimal model for ZnO/Cu catalysts. A more detailed description of the full thermodynamic analysis performed in preparation and will be published elsewhere.

In the next step, reaction pathways and transition barriers for methanol formation catalyzed by Zn₃O/Cu(111) are determined. However, before studying the entire reaction network the applicability of DFT was verified.

The PBE functional is able to predict the relevant gas-phase energetics in good agreement to CCSD(T), DLPNO-CCSD(T) [42–49] (see SM for the details) and experiment as is shown in [Table 1](#), where BEEF-vdW performs much worse [50,51]. The only exception is RWGS with a deviation of 0.45eV with respect to experiment. This error can be attributed to a destabilization of gas-phase CO by the PBE functional [52]. Accordingly, CO adsorption on Cu(111) is known to be overestimated within the generalised gradient approximation (GGA) by 0.32–0.41 eV [53]. The erroneous gas-phase CO energetics in GGAs is therefore not to be expected to affect the energetic ordering of supported species discussed below and a correction [51] is not needed.

DFT within the generalized gradient approximation is also known to underestimate reaction barriers [54,55] (database tests for catalysis showed mean signed errors of PBE up to –0.59 eV [56]), however. In order to approve the accuracy and applicability of our DFT approach in the present systems we have performed single point high level DLPNO-CCSD(T) quantum chemistry calculations for selected key reactions. DLPNO-CCSD(T) is computationally very demanding such that the reactions have to be described on a copper cluster model of finite size.

We have chosen the Cu₄Zn₃O cluster as structural model (see lower panels of [Fig. 2 a](#)). The four Cu-atoms were fixed using the experimental lattice constant 3.61 Å of bulk Cu to imitate the Cu(111)-surface [57], while the supported Zn₃O and the adsorbates were relaxed using PBE. The values reported for BEEF-vdW and for DLPNO-CCSD(T) were obtained from subsequent single-point calculations.

Four key reaction steps have been chosen as benchmark. A: initial transition of CO₂ from a linear to a bent configuration, B: hydrogenation of oxygen in a carboxyl intermediate, C: second hydrogenation of an HCO intermediate and D: hydrogenation of the carbon atom in the carboxyl group. The energetics was determined for the Zn₃OCu₄ cluster model as well as for the Zn₃O/Cu(111) extended surface model for all four test reactions. The differences between the energies of the initial state E_{IS} and the final state E_{FS} compare reasonably well between all computational approaches on the cluster model, i.e. these energy differences are fairly well described by DFT.

The most important quantities are the barriers determined by their corresponding transition state energy E_{TS} . These were determined by the nudged elastic band method [58] combined with a climbing image condition [59]. [Fig. 2](#) shows both forward ($E_{TS} - E_{IS}$) and backward barriers ($E_{TS} - E_{FS}$) for the chosen reactions. The predicted barrier heights from PBE and BEEF-vdW are

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