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A Density Functional Study of the Methanol Synthesis at an Oxygen Vacancy on the Polar ZnO(000$\bar{1}$) Surface

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The elementary steps of the methanol synthesis reaction at oxygen vacancies on the polar ZnO(000$\bar{1}$) surface have been studied with density functional theory. We report results for reaction and activation energies for the most important elementary steps of the methanol synthesis reaction on this surface. At these oxygen vacancies the barriers for heterolytic cleavage of H_2 into protons, bound in surface OH groups, and hydrides, trapped in the vacancies, is low. The stabilized hydride facilitates the reduction of CO to formyl (stabilized in the vacancy) with a low barrier $\lesssim$100 kJ/mol. After a fast rearrangement to formaldehyde and hydroxymethylene species, a second reduction step leads probably to a surface-bound methoxide which at reducing conditions desorbs from the surface under regeneration of an oxygen vacancy. Beside formate, which appears as a side product, and formyl species, oxygen-bound hydroxymethylene might be another observable intermediate of the methanol synthesis reaction at oxygen vacancy sites on the ZnO(000$\bar{1}$) surface.

1. Introduction

Methanol is a key raw material in the production of a large variety of chemicals and materials, which is today produced on a large scale of several 10 million tons per year. As it has been suggested as alternative for fossil fuels in a possible future methanol economy,[1] its industrial importance is likely to even increase in the future. The heterogeneously catalyzed synthesis of methanol from CO or CO_2 and hydrogen has since decades been widely studied both experimentally and theoretically, but there are still many open questions concerning the active sites of the industrial Cu/ZnO/Al_2O_3 catalyst,[2,3] the role of the ZnO support, and the atomistic mechanism of the reaction. The investigation of the methanol synthesis reaction is a challenging task for both experimental and theoretical studies because of the complicated morphology of the catalyst, which depends in addition on the reaction conditions, and also because of the complexity of the reaction, which involves multiple elementary steps with yet not completely identified intermediates and possible competing side reactions.

The methanol synthesis is also an example for a strong metal-support interaction. The ZnO support can itself act as catalyst[4−13] for the synthesis of methanol from CO and H_2. Jones et al.[14] have recently reported finite cluster density functional theory (DFT) calculations for the intermediates and one transition state for a reaction mechanism proposed on the zinc-terminated ZnO(0001) surface. Recent kinetic studies[15,16] suggest, however, that the methanol synthesis reaction takes place at oxygen vacancies, presumably on the oxygen-terminated ZnO(000$\bar{1}$) surface. This would explain the observed inhibiting effect of CO_2, which can heal oxygen vacancy defects. A mechanism and some potential intermediates for the reaction at a F^{2+} center (or H_2O vacancy) on a hydroxylated oxygen-terminated ZnO(000$\bar{1}$) surface have been suggested in ref 15. For a similar vacancy, but on a hydrogen-free ZnO(000$\bar{1}$) surface stabilized by vacant oxygen interstitial surface sites (VOISS), French et al.[17,18] have investigated with a hybrid quantum mechanical/molecular mechanical approach the structure and energetics of possible intermediates of a proposed catalytic cycle for the synthesis of methanol starting from CO_2. Such a mechanism would, however, not explain the inhibiting effect[15] of CO_2 for the methanol synthesis if ZnO is used as catalyst (instead of Cu/ZnO or Cu/ZnO/Al_2O_3). Moreover, as discussed in a recent review by Wöll[19] latest experimental results show in agreement with theoretical calculations[20] that at the conditions of the methanol synthesis the oxygen-terminated ZnO(000$\bar{1}$) surface is not stabilized by the formation of VOISS but is instead hydroxylated; presumably at least 50% of the surface oxygen atoms are protonated if the surface is in equilibrium with H_2 gas.

The mechanism advocated by Kurtz et al.[15] can be summarized as successive hydrogen transfer to the carbon atom of CO, which is adsorbed at the vacancy. Thereby, the latter molecule is stepwise reduced to formyl, formaldehyde, and methoxide which—after capturing a proton from the surface—desorbs as methanol. There are, however, a number of unresolved questions concerning the precise elementary reaction steps of the hydrogen transfer and whether the activation barriers can be overcome at the conditions of the methanol synthesis reaction. An additional problem in the proposed mechanism is that CO is only weakly physisorbed at the F^{2+} center,[21] while the dissociative adsorption of methanol is strongly exothermic so that methoxide anions should block the active sites.

In the present paper we report the results of a comprehensive computational investigation of the elementary reaction steps for the methanol synthesis at an oxygen vacancy on the ZnO(000$\bar{1}$) surface with the aim to identify and characterize the intermediates and the transition states of this multistep reaction.

2. Computational Details

We used for the present work an embedded cluster approach, with the inner part (the "quantum cluster") described with DFT and the outer part represented by a point charge field to model the Madelung potential of the crystal at the site of the quantum cluster. As described in the introduction, we want to study the methanol synthesis reaction at an oxygen vacancy on the

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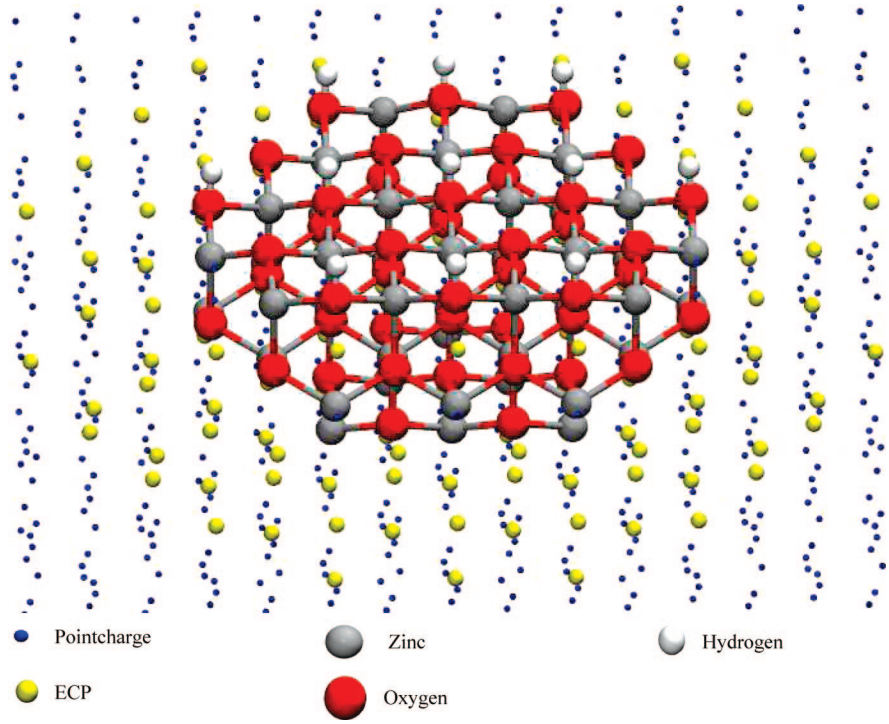


Figure 1. Embedded cluster model used for the present work. The fully quantum mechanically treated inner part of the cluster consists of 43 zinc, 44 oxygen, and 11 hydrogen atoms. It is embedded in a large point charge array which models the Madelung field generated by the surrounding ZnO bulk. In the vicinity of the quantum mechanically treated inner part the zinc ions are represented by 28 electron ECPs to model the interaction with the zinc core electrons.

ZnO(000$\bar{1}$) surface. As starting point for our model we took the (1 × 2) H covered surface, which according to the periodic DFT calculations by Meyer[20] is presumably the thermodynamically stable surface at the reducing hydrogen rich conditions of the methanol synthesis reaction. We first generated a large hexagonal point charge cluster with 20 O and Zn layers with a side length of ∼4.9 nm using the bulk structure of ZnO with the experimental values[22] for the lattice constants $a = 3.250$ Å and $c = 5.207$ Å and the internal coordinate $u = 0.3825$. For the point charges we used the nominal ionic charges of Zn^{2+} and O^{2-}, although smaller values might describe the ionicity of ZnO more realistically. In embedded cluster calculations the role of the point charges is to provide better boundary conditions at the border of the quantum cluster to enhance the convergence of the calculations with the cluster size. The choice of 2+ and 2− has by several authors been successfully applied for studying local bulk and surface properties of ZnO.[23,21] For the construction of the embedding point charge array we assumed for the hydroxide groups at the oxygen-terminated surface a bond length of 0.95 Å and the zinc-terminated surface was stabilized by adding negatively charged ions at a distance of 1.04 Å below each second Zn^{2+} ion. For these additional ions we used a charge of ±0.9414, which was chosen to balance the dipole moment of the cluster along the *c* axis. Because of this stabilization of the polar surfaces and the hexagonal symmetry this cluster has no dipole and only small quadrupole moments. We abstained therefore from an Evjen approximation to eliminate remaining higher electrostatic moments. At the center of the such generated point charge array we carved out a hemispherical cluster with 98 atoms (43 Zn, 44 O, and 11 H), which are replaced by the quantum cluster as shown in Figure 1. At the interface the cations which are within a distance of 4 Å of the quantum cluster are replaced by a 28 electron effective core potential for zinc[24] to provide a localizing embedding potential for the quantum cluster. With this setup we studied several conceivable intermediates and transition states of the methanol synthesis reaction at oxygen vacancy defects (F) in their closed-shell singlet ground states with formal oxidation states ranging from F^{2-} to F^{2+} (see below). Test calculations showed that with this size of the quantum clusters vibrational frequencies and adsorption energies at the center of the cluster are essentially converged. In particular, the energies for the formation of the vacancies changed with a 60% larger cluster by less than ±10 kJ/mol.

All quantum chemical calculations have been carried out with a development version of the TURBOMOLE program package.[25] DFT with the Perdue−Burke−Ernzerhof (PBE) functional[26] was employed as electronic structure method for the quantum cluster. The PBE functional has been shown in a previous study[27] to provide an accurate description of the ZnO structure. For our calculations we used the ridft module[28] of TURBOMOLE. The geometry optimizations for the reactants, products, and intermediates were carried out in the doubly polarized triple-ζ atomic orbital basis TZVPP,[29,30] which consists of 5s3p2d1f contracted basis functions for O and C and for H and Zn of, respectively, contracted 3s2p1d and 6s4p3d1f functions. For the optimization of the transition states and for the calculation of the zero-point vibrational energies we employed the polarized split-valence basis SVP[31] with contracted 3s2p1d at O and C, 2s1p at H, and 5s3p2d at Zn. Since the differences between the results in the TZVPP and the smaller SVP basis have been marginal for most investigated structures, we desisted from placing additional basis functions in the center of the vacancy, as this would increase basis set superposition errors. For the contribution of the rotational and translational degrees of freedom and the ΔPV contribution to the enthalpies we assumed 500 K as typical temperature for the methanol synthesis.[2,3,15,16] Free enthalpies were calculated for a pressure of 4.1 MPa and a gas mixture[15] with 73% H_2, 11% CO, 16% N_2, while the reaction product CH_3OH and possible intermediates and side products as H_2O, CO_2, and H_2CO were assumed

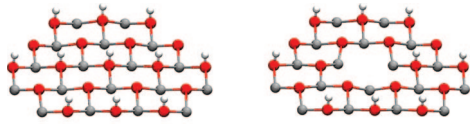


Figure 2. Left: The (1 × 2) H-covered oxygen-terminated ZnO(000$\bar{1}$) surface. In this structure every second row of oxygen atoms is protonated. Right: F^{2+} center (or H_2O vacancy) on the ZnO(000$\bar{1}$) surface. The vacancy has been created by removing an OH^- together with a proton from an adjacent hydroxy group.

to be in the gas phase only present in traces of 1 ppm. The electronic energies of the transition states were calculated in the TZVPP basis at the geometries optimized in the SVP basis. For the search of the transition paths we employed the growing string newton trajectory[32,33] (GS-NT) and nudged elastic band[34,35] methods followed by a trust-region image minimization[36] to locate the final transition structures. During the optimizations the outermost atoms at the interface, which have "dangling bonds" to atoms represented by point charges, were fixed at their bulk positions. In the inner part of the quantum cluster the positions of all atoms including hydrogen have been relaxed during the structure optimizations. For all reported transition structures a vibrational analysis was performed to check if they correspond to first order saddle points on the potential energy surface and to evaluate vibrational corrections for the activation energies. The optimized geometries and total energies are listed in the Supporting Information.

3. Results

As indicated in the introduction, there are several unresolved questions concerning the methanol synthesis from CO/H_2 on the ZnO (000$\bar{1}$) surface. Binding energies for the intermediates of the reaction have only been reported for a F^{2+} center. But at this vacancy the energy for the dissociative chemisorption of methanol as methoxide and a proton was calculated[15] to be −232 kJ/mol. Methoxide anions would thus be expected to block F^{2+} vacancies as active sites. The precise oxidation state of the vacancy and whether and how it might change in the course of the reaction is, however, not known since the precise mechanism for the hydrogen and/or electron transfer to the carbon atom is not yet clarified. If during the reaction electrons or H^- anions are transferred from the vacancy and the surrounding hydroxide groups, the vacancy has to assume variable oxidation and/or charge states and intermediates strongly bound at a F^{2+} center might only weakly interact with a F or F^{2-} center and vice versa. As we will elucidate in the following, this leads to a complex interplay between the vacancy and the reactants and intermediates. Our starting point was the above-described model for the (1 × 2) H covered ZnO(000$\bar{1}$) surface on which we introduced a F^{2+} center by removing a OH^- and a proton from the central surface hydroxide row, creating thereby a charge neutral V_{H_2O} vacancy (cf. Figure 2). Similarly, the F and F^{2-} centers are modeled by a charge neutral V_O and a hydrogenated oxygen vacancy H_2V_O, which can be thought of being produced by subsequent hydrogenation of V_{H_2O} with one and two H_2 molecules

$$\text{surface} \rightarrow V_{H_2O} + H_2O \quad \Delta H = +289\ \text{kJ/mol} \qquad (1)$$

$$V_{H_2O} + H_2 \rightarrow V_O \quad \Delta H = -212\ \text{kJ/mol} \qquad (2)$$

$$V_O + H_2 \rightarrow H_2V_O \quad \Delta H = +87\ \text{kJ/mol} \qquad (3)$$

Alternative reactions which create V_O vacancies are the reduction of the surface by CO or by H_2

$$\text{surface} + CO \rightarrow V_O + CO_2 \quad \Delta H = -21\ \text{kJ/mol} \qquad (4)$$

$$\text{surface} + H_2 \rightarrow V_O + H_2O \quad \Delta H = +77\ \text{kJ/mol} \qquad (5)$$

The energies for the formation of the vacancies depend on the precise positions of the hydroxide groups since the energies of the vacancies vary by ∼20−30 kJ/mol with displacements of the protons. The numbers given above are the results for the energetically lowest configurations, which are those with H atoms at the positions of the idealized (1 × 2) H covered surface as shown in Figure 2. At the reaction conditions described in section 2 we obtained for the free reaction enthalpies ΔG for the above reactions +209 (1), −174 (2), +104 (3), −5 (4), and +36 (5) kJ/mol. The entropy contributions slightly disfavor hydrogen adsorption because of the high temperature, but the effect does not change the overall picture. The thermodynamical most stable defects at the reaction conditions are V_O vacancies.

3.1. Adsorption of Carbon Monoxide. The physisorption of carbon monoxide at oxygen defects on the ZnO(000$\bar{1}$) surface has recently been studied in detail by Fink,[37] who found at the F^{2+}, F^+, and F^{2-} centers binding energies in the range of 0.23−0.36 eV (or 22−34 kJ/mol), while at the F center CO forms with the vacancy only a metastable complex. Apart from the latter case, CO is always bonded with the carbon atom directed toward the vacancy. This is in agreement with the results of our present calculations, where we also find that CO preferentially binds to the oxygen vacancies with the C atom directed to the surface, although the equilibrium geometries and binding energies vary somewhat with the distribution of the OH groups in the vicinity of the vacancy.

Carbon monoxide can alternatively be chemisorbed at the hydroxylated Zn(000$\bar{1}$) surface by inserting it formally into an OH group, which leads to surface stabilized formate anions as illustrated in Figure 3. The barriers for this reaction are, however, much lower (by more than 100 kJ/mol) when CO coordinates to a surface O^{2-} ion and the proton is then transferred from an adjacent OH group to the negatively charged C atom. Formate species on ZnO surfaces have been observed in several experimental studies (see, e.g., ref 38 and references therein) and are discussed[38,18,17] as intermediates in the methanol synthesis from CO_2/H_2 and the water−gas shift reactions. Next to an F center the barrier for the conversion of physisorbed CO to formate (structure 3d) is only ∼40 kJ/mol (GS-NT result in SVP basis). At this vacancy, the reaction is exothermic with a reaction energy of ∼−100 kJ/mol, and formate assumes a monodentate η^1 bound structure, which minimizes the repulsive interaction with the electron pair trapped in the vacancy. At an F^{2+} center the barrier for the reaction of physisorbed carbon monoxide with the hydroxylated surface to formate is considerably higher, ∼116 kJ/mol (GS-NT result in SVP basis), which is partly due to the larger physisorption energy for CO at the positively charged vacancy that has to be overcome to reach the transition state. With respect to carbon monoxide in the gas phase the activation energy is at this computational level for the reaction to formate also at the F^{2+} center only ∼40 kJ/mol. The formate anion has at this vacancy (structure 2d) a bidentate geometry with both oxygen atoms bonded to the surface and thereby partially filling the vacancy. Thus, the structure of the formate anions and the energy for the chemisorption depend at the oxygen vacancies strongly on the oxidation state of the latter. At the reducing conditions of the methanol synthesis reaction the monodentate formate at the F center will be the thermodynamically preferred species. However, at the high temperature (and the CO pressures) the methanol synthesis reaction is typically carried out, entropy contributions destabilize the format spezies.

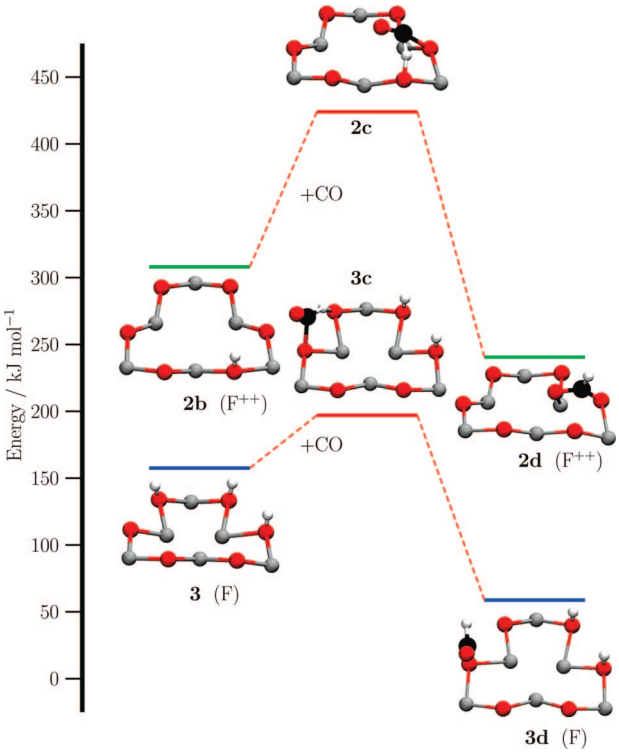


Figure 3. Transition states and energies for the chemisorption of CO as formate at oxygen vacancies on the ZnO(000$\bar{1}$) surface. Shown are only the atoms next to the vacancy, the positions of the remaining atoms are approximately the same as in Figure 1. Here and in the following figures light and dark gray lines indicate intermediate structure at, respectively, F^{2+} and F centers while dashed black lines are used for intermediates at F^{2-} centers. (Green is used for F^{2+}, blue for F, and magenta for F^{2-} centers).

3.2. Adsorption of Hydrogen at Oxygen Vacancies. A key question for the understanding of the methanol synthesis reaction is how hydrogen is made available and activated for the reduction of the carbon atom. In most studies it is assumed that after adsorption of CO either H_2 is split heterolytically into H^-, which is transferred to the carbon atom, and a proton, which binds to a nearby surface oxygen anion, or that the hydrogen atoms are transferred from the hydroxylated surface to intermediates in the vacancy. But only very little information is yet available in the literature about the activation energies for these processes. It is well-known[14,15,17] that hydrogen molecules are adsorbed dissociatively on ZnO surfaces and in particular at oxygen vacancies on the ZnO surfaces under formation of hydroxide and Zn−H groups. We calculated for this process the barriers at F and F^{2+} centers (see Figure 4). At the F center (structure 3 in Figure 4) we found for the heterolytic dissociation of a hydrogen molecule in the GS-NT calculation a barrier ∼130 kJ/mol. In the product (structure 5) one H atom binds to two Zn atoms with distances of 1.67 and 1.79 Å, while the distance to the third Zn atom is with 2.40 Å, considerably longer. The reduction of the F center in this configuration to F^{2-} is endothermic by ∼87 kJ/mol (cf. eq 3), which is somewhat smaller than the 147 kJ/mol found by Fink[37] for a smaller embedded cluster model. This difference is probably partially caused by the dependence of the HOMO−LUMO gap of ZnO on the size of the modeled system and the density functional. The smaller this gap is the less energy is needed to reduce the vacancy further and place additional electrons in the (at the F center) unoccupied one-electron states (see ref 37 for a detailed discussion). However, with a 60% larger embedded quantum cluster, where 85 instead of 52 atoms were geometry optimized, the reaction energy for the reduction of an F center to a F^{2-} center changed only by 2 kJ/mol so that we are confidend that the present results for the hydroxylated ZnO(000$\bar{1}$) surface are converged within the accuracy of DFT/PBE. Another point which effects the stability of strongly reduced F^{2-} vacancies is the number and the positions of the hydroxide groups adjacent to the vacancy: French et al.[17,18] reported for a model of the F center on a hydrogen free ZnO(000$\bar{1}$) surface even an exothermic reaction energy of −79 kJ/mol for the adsorption of H_2.

As can be anticipated, the activation energy for the dissociative adsorption of H_2 is at the F^{2+} center (structure 2) lower—we obtained in our calculations 32 kJ/mol—and the reaction is at this vacancy strongly exothermic with an reaction energy of ∼−199 kJ/mol, which is in good agreement with the −195 kJ/mol reported by French et al.[17] for their model of the F^{2+} center on a hydrogen-free ZnO(000$\bar{1}$) surface. In the product (structure 4) the hydride has essentially replaced the hydroxide which was removed to introduce the V_{H_2O} vacancy. This structure is assigned to the type II hydrides observed in IR measurements.[17,39] Subsequent reduction by heterolytic dissociation of a second H_2 leads to F^{2-} centers with both type I and type II hydrides,[17] as, e.g., structure 4c in Figure 4, which, according to our calculations, is about 20 kJ/mol lower in energy than the F^{2-} centers with only a type II hydride obtained from the reduction of the V_O vacancy. For the homolytic dissociation of H_2 at the F^{2+} center under formation of two hydroxide groups (and stabilization of the electron pair in the vacancy), we obtain with −212 kJ/mol a similar reaction energy as for the heterolytic dissociation, but a barrier >200 kJ/mol, so that we may exclude this process at the conditions of the methanol synthesis. Thus, according to our results the thermodynamically most stable vacancy is the F center with a type II hydride, but under the reducing conditions of the methanol synthesis with large CO and H_2 partial pressures F^{2-} centers will probably also be formed.

3.3. Reduction to Formyl. In a first reduction step CO is reduced by simultaneous transfer of an electron pair and a proton to a formyl species, which is stabilized in the vacancy by bonds to Zn atoms. We investigated three different pathways for this reaction step. The educts and products and the transitions states for the three reactions are summarized in Figure 5. The reduction of CO at an F center (structure 6) and at the F center with a type II hydride (structure 4) to formyl stabilized by the resulting F^{2+} center, and as a third possibility, the reduction at a F^{2-} center—also with a hydride located in the vacancy—to formyl bonded to a Zn atom in the F center (structure 8). At the F center the activation energies are similar for the transfer of a hydrogen atom from the center of the vacancy (96 kJ/mol) and from an OH group next to the F center (119 kJ/mol). Both reactions are endothermic with reaction energies of 39 and 79 kJ/mol, respectively. Most of the difference between the reaction energies can be attributed to the different position of one H atom in the products (structures 7 and 9) of the two investigated paths: already for the empty F^{2+} vacancy the configuration with the OH groups in the same position as in structure 7 is about 30 kJ/mol lower in energy than the configuration corresponding to structure 9. The reduction of CO by the hydride in the F^{2-} vacancy requires—due to the more reduced oxidation state of the vacancy—only an activation energy of 10 kJ/mol. The product of this reaction—formyl bonded to a Zn atom in the F center—is energetically more favorable than formyl at an F^{2+} center. Together with the energetically unfavorable educt this leads to an exothermic reaction with an enthalpy of −72 kJ/mol. The lower energy of the formyl species at the F center

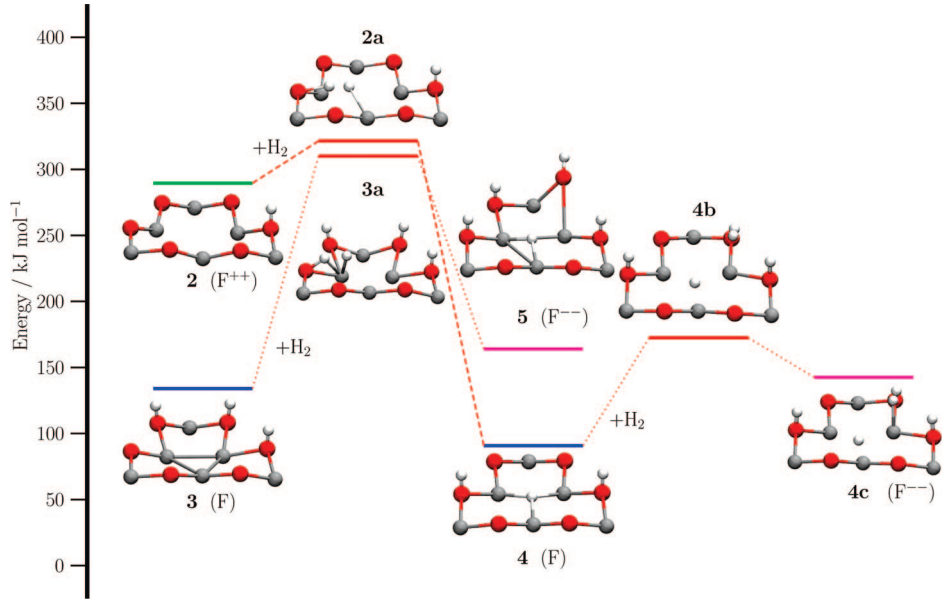


Figure 4. Transition states and activation and reaction enthalpies for the heterolytic hydrogenation of the F^{2+} (V_{H_2O}, structure 2) and F (V_O, structure 3) centers to, respectively, F (V_O, structure 4) and F^{2-} (H_2V_O, structure 5) centers with hydride anions in the centers of the vacancies. (For the color code of the horizontal lines see caption of Figure 3.)

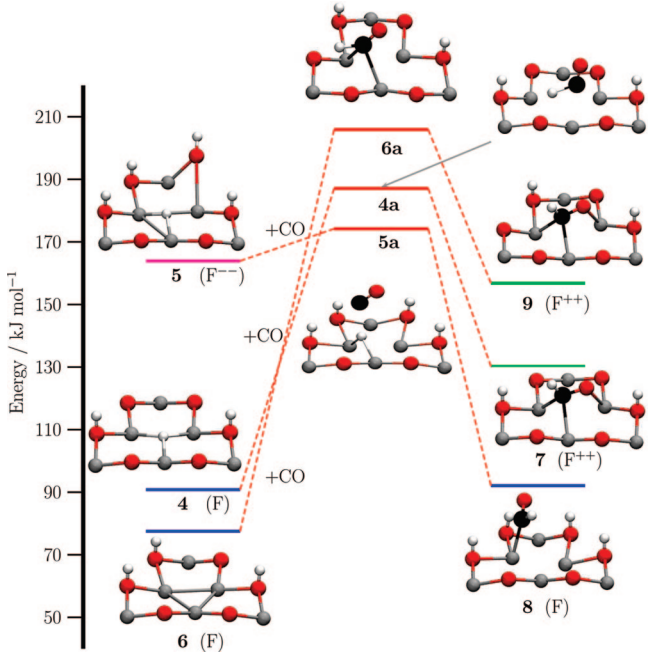


Figure 5. Transition states and activation and reaction enthalpies for the reductive adsorption of CO as surface (or vacancy) stabilized formyl species at F (structures 4 and 6) and F^{2-} (structure 5) centers. (For the color code of the horizontal lines see caption of Figure 3.)

(compared to its energy at the F^{2+} center) is caused by the binding energy of the additional H atoms at an F center. Only at the F^{2+} center is the formyl species lower in energy than the vacancy (and CO and H_2 in the gas phase), while structure 8 is higher in energy than the V_O defect (structure 6).

The reason for this is that at the F^{2+} center the formyl moiety can bind with the carbon and the oxygen atom to zinc atoms in the vacancy (structures 9 and 7 in Figure 5). In fact, the carbon atom forms in addition to a bond of 2.08 Å another weak contact of 2.36 Å to the third zinc atom in the vacancy. These species can thus be understood as OCH^- anion compensating the missing OH anion, which has been removed to create the F^{2+} center. At the F center the formyl species (structure 8) is only stabilized by a zinc−carbon bond and a hydrogen bridge interaction between the oxygen atom and an OH group of the surface. A bond of the formyl oxygen to zinc atoms of the defect is inhibited by the two additional electrons bonded in the F center.

We also investigated whether the formate species at an F center can be reduced to a formaldehyde species by transfer of H^- from a surface OH group. The reaction path found for this conversion in a GS-NT calculation has, however, a rather high barrier >250 kJ/mol. It seems thus that the formation of formate at oxygen vacancies on the ZnO(000$\bar{1}$) surface is a (reversible) side reaction which does not proceed further to methanol. Formate is thus only a spectator, and CO is reduced on the ZnO(000$\bar{1}$) surface via transient formyl species.

3.4. Formyl and Formaldehyde Species at Oxygen Vacancies. At vacancies on the hydroxylated ZnO(000$\bar{1}$) surface the formyl anion can be protonated by the surrounding OH groups, but for some of these conversions the barriers are relatively high. Because of the exposition of both Lewis acid (Zn^{2+}) and base (O^{2-}) sites at the V_{H_2O} vacancy the transfer of a proton to the carbon atom of the formyl anion leads at this center directly to a bidentate chemisorbed formaldehyde species (structure 11 in Figure 6), which fills partially the vacancy and is strongly bound by ionic interactions with the surface. The reaction is therefore exothermic by ∼−45 kJ/mol but has a relatively high barrier of ∼100 kJ/mol. At the F center the transfer of a proton to the carbon atom leads initially to physisorbed formaldehyde (structure 10 in Figure 6). At this vacancy the barrier for the proton transfer is with 28 kJ/mol much smaller. Formaldehyde is, however, also at the F center not a stable intermediate. It can in subsequent steps easily be reduced to a zinc-bonded hydroxymethylene species (vide infra), where the carbon atom is already in the same oxidation state as in methanol, or coordinate (barrierless) to the hydroxylated ZnO(000$\bar{1}$) surface under formation of a hydroxymethylene species bonded to an oxygen atom of the surface (cf. Figure 6). This structure resembles the formaldehyde hydrate in aqueous solution. In difference to the F^{2+} the F center does not support a bidentate coordination of formaldehyde. This chemisorption is with $\Delta H \approx -80$ kJ/mol strongly exothermic, but at typical reaction temperatures of about ∼500 K entropic contributions destabilize the hydroxymethylene

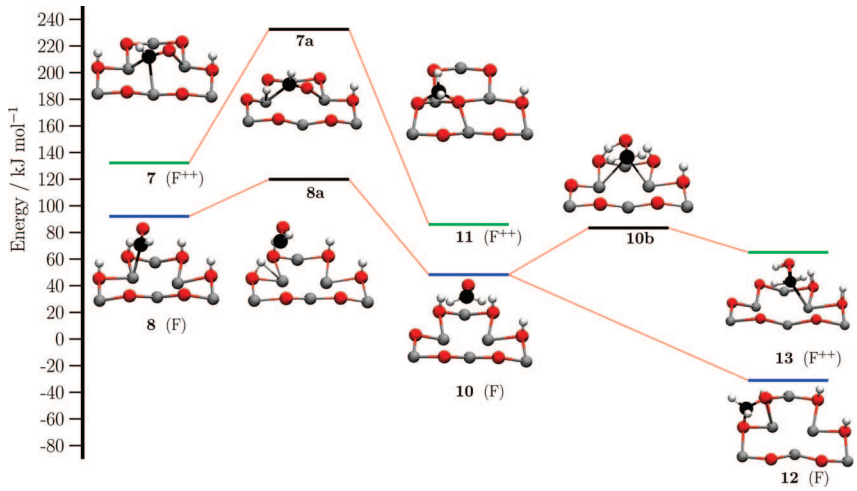


Figure 6. Transition states and activation and reaction enthalpies for some selected rearrangements of formyl to formaldehyde and hydroxymethylene species at the F^{2+} (structures 7, 7a, 11, 13) and F (structures 8, 8a, 10, 10a, 12) centers. (For the color code of the horizontal lines see caption of Figure 3.)

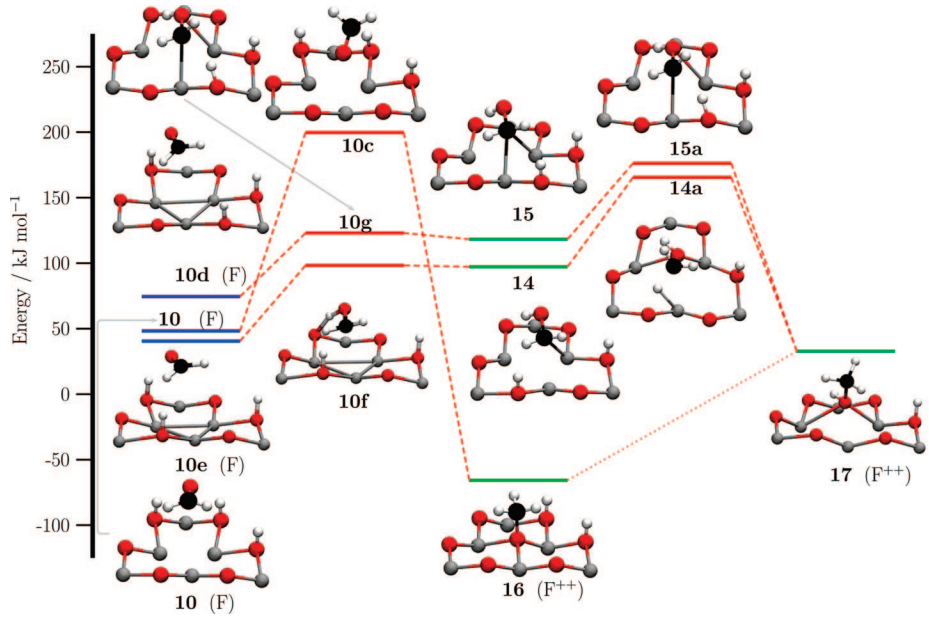


Figure 7. Some selected reaction paths for the conversion of formaldehyde and hydroxymethylene species to a methoxy anion stabilized in the oxygen vacancy. (For the color code of the horizontal lines see caption of Figure 3.)

species ($\Delta G \approx 3$ kJ/mol) in favor of formaldehyde, which can desorb and diffuse to nearby vacancies. The O-bound hydroxymethylene and the bidentate chemisorbed formaldehyde are probably also spectator species for the methanol synthesis reaction on ZnO(000$\bar{1}$). The further reduction proceeds directly through formaldehyde, possibly through transient zinc-bound hydroxymethylene species.

3.5. Reduction to Methanol or Hydroxymethyl. For the species investigated with carbon in oxidation state 0 at the F center, we found only for physisorbed formaldehyde a reaction path to the methoxy anion with a realistic activation energy. The reduction of formaldehyde to a methoxy anion by a simultaneous transfer of an electron pair from the vacancy and a proton from a nearby OH group has a relatively high barrier of 151 kJ/mol (Figure 7). To reach the transition structure the carbonyl oxygen atom must approach the electron pair localized in the F center, so that the latter can enter the antibonding π^* orbital of the carbonyl group and break the CO π bond before the new H−C bond can be formed.

Alternatively, formaldehyde can at the F center be reduced under formation of a carbon zinc bond to Zn-CH_2OH species (structures 13 and 14), which are stabilized by hydrogen bridges to the surrounding O and OH groups and polar interactions between the OH oxygen and zinc cations of the O^{2-} vacancy. As mentioned in the previous subsection, e.g., for the conversion of structure 10 to Zn-CH_2OH (structure 13), the activation enthalpy is only 35 kJ/mol (Figure 6), and the reaction is only slightly endothermic (17 kJ/mol). The formation of the isomeric structure 14, which is only a very flat minimum on the potential energy surface, requires a slightly larger activation enthalpy of 55 kJ/mol. But for this structure we could locate a transition path with a barrier of only 72 kJ/mol for the conversion to methanol. The transition state 15a for the alternative pathway via intermediates 10d and 15 differs from the transition state 14a only in the positions of the H atoms at the border of the vacancy. Also this reaction path goes through a flat region of the potential energy surface with a shallow minimum for a Zn-CH_2OH-like structure.

We thus conclude that under the conditions of the methanol synthesis reaction (high temperature and reducing atmosphere) formaldehyde is at the F centers on the Zn(000$\bar{1}$) surface in a dynamic equilibrium with hydroxymethyl species bonded to zinc

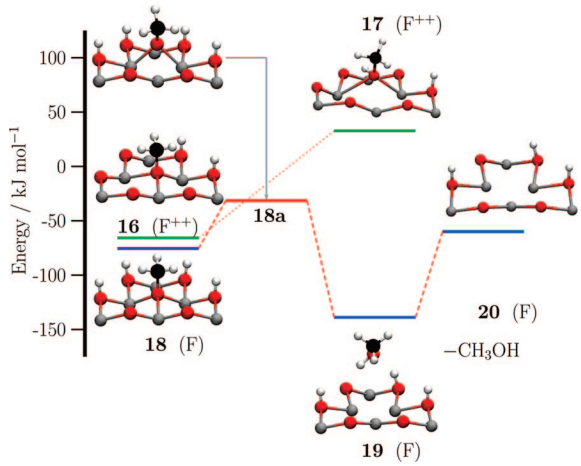


Figure 8. Reaction profile for the desorption of methanol from F^{2+} and F centers. (For the color code of the horizontal lines see caption of Figure 3.)

atoms at the oxygen vacancy. In these species the carbon atom is already reduced and can uptake a proton from a nearby OH group and rearrange to methanol.

As mentioned above, formaldehyde can at the Zn(000$\bar{1}$) surface be chemisorbed O-CH_2OH species. The barrier for the chemisorption is at F centers with ~40 kJ/mol quite low so that the O-CH_2OH species is probably a sink for formaldehyde and Zn-CH_2OH. We could, however, not locate a reaction path for the direct reduction of O-CH_2OH to methoxy or methanol at the F center with a reasonable reaction barrier. (The lowest lying path located with GS-NT calculations has a barrier >300 kJ/mol.) First if the defect is further reduced by heterolytic adsorption of an H_2 molecule to an F^{2-} center with a hydride anion bound in the vacancy, a realistic reaction path to methanol becomes accessible. But still the barrier for this reaction is with ~170 kJ/mol comparatively high, since the chemisorbed formaldehyde must first dissociate from the surface before the H^- can be transferred from the vacancy to the carbon atom.

The most important pathways for the reduction to methanol are thus those via Zn-CH_2OH structures, either as intermediate species or transition states. The barrier heights for the two investigated pathways from formaldehyde via transition states 14a and 15a to methanol, which differ slightly in the positions of the OH groups in the vicinity of the vacancy, are 125 and 102 kJ/mol.

3.6. Desorption of Methanol from the Surface. As depicted in Figure 8, at the F^{2+} center, i.e., a V_{H_2O} vacancy, methanol dissociates heterolytically into a methoxy anion which fills the vacancy and a proton which binds to an adjacent oxygen anion of the surface (structure 16). This reaction is with an enthalpy of −220 kJ/mol strongly exothermic and at the PBE/DFT level with the SVP basis barrierless. We can thus probably exclude that under the conditions of the methanol synthesis methanol desorbs from F^{2+} centers. Rather the vacancy will first be reduced to an F center, e.g., by adsorption of a H_2 molecule at a neighboring defect, the scavenging of an adjacent oxygen atom by CO (under formation of CO_2), or migration of electrons from other defects at the surface or from the bulk. At F centers on the hydroxylated surface, methoxy anions are metastable and can detach from the surface under formation of methanol. The barrier for the desorption is with 44 kJ/mol small compared to those of previous steps in the methanol synthesis. For structure 18 shown in Figure 8 the conversion of the surface stabilized methoxy anion into physisorbed methanol is exothermic by 64 kJ/mol. The binding enthalpy of physisorbed methanol is at the F center 81 kJ/mol. But at typical reaction conditions (high temperature, low concentration of CH_3OH in the gas mixture) the desorption is exergonic ($\Delta G \approx -48$ kJ/mol for 500 K and 1 ppm CH_3OH at 4.1 MPa). As noted in the previous section, methanol can alternatively be formed directly (without methoxy intermediate) from formaldehyde at F^{2-} centers.

4. Summary and Conclusions

Our calculations show that for the methanol synthesis reaction at an oxygen vacancy on the ZnO(000$\bar{1}$) surface there is probably not just one path with a few well-defined intermediates but rather a whole network of elementary reactions which connect a large zoo of possible intermediate or transient structures. We have evaluated for a number of prototypical reactions the activation energies. The most important ones have been reported and discussed in the previous sections. On the basis of these results we can exclude some of the considered elementary reactions and assign at least a plausible representative reaction path, which is summarized in Figure 9.

Taking into account the small barrier and the large exothermic reaction energy of the heterolytic hydrogenation of the F^{2+} center, it seems very likely that at the hydrogen-rich reducing conditions of the methanol synthesis reaction oxygen vacancies are reduced and have a hydride trapped in the center. In this state the vacancies can reduce CO to a formyl species, which

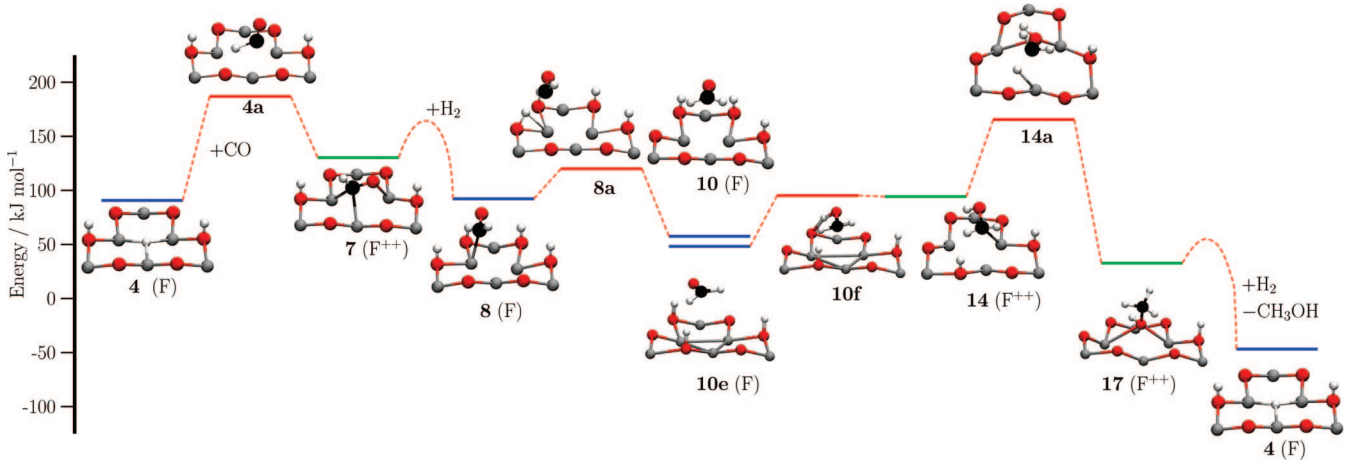


Figure 9. Summary of a possible reaction path for a catalytic cycle starting from an (empty) V_O vacancy (F defect). (Dashed arcs indicate elementary steps which have not been investigated in the present study. For the color code of the horizontal lines see caption of Figure 3.)

is stabilized by Zn−C and probably also O−Zn bonds to the zinc ions of the vacancy and eventually are protonated to formaldehyde or oxygen-bonded hydroxymethylene species. Thus the oxygen vacancies play a 2-fold role in this step: they activate H_2 by the heterolytic adsorption and they stabilize the reaction product. Together these two effects reduce the barrier for the H^- transfer to about $\lesssim$100 kJ/mol. Either after (or simultaneous with) a heterolytic chemisorption of another H_2 molecule or diffusion to another vacancy site formaldehyde is further reduced via zinc-bonded hydroxymethylene to methoxy anions or directly to methanol, which desorbes from the surface after a reduction of the binding site. The barriers for the reaction of formaldehyde to methanol are 100−125 kJ/mol, depending on the distribution of the OH groups next to the vacancy.

The reactions to formate and possibly also to the oxygen-bonded hydroxymethylene species seem to be only side reactions. All considered paths which would lead to further reduction of these species have significantly higher barriers than the decomposition of formate to CO and of hydroxymethylene to formaldehyde and methanol.

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Supporting Information Available: The total electronic energies, zero point vibrational energies, entropies, and the Cartesian coordinates of the stationary points (intermediates and transition states) described in this paper are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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