From molecular adsorption to decomposition of methanol on various ZnO facets: A Periodic DFT study.

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Abstract

Methanol is an interesting and important molecule to study because of its potential to replace existing fuels. It is also a prominent hydrogen source which can be used to generate hydrogen in-situ. ZnO is widely used as catalyst in synthesis of methanol from CO₂ at industrial scale. In this work, we demonstrate that the same catalyst could be used for MeOH decomposition. We have carried out a systematic study of interaction of methanol with various flat and stepped facets of ZnO by employing Density Functional Theory (DFT). Two flat [(10 $\bar{1}$ 0) and (11 $\bar{2}$ 0)] and two stepped [(10 $\bar{1}$ 3) and (11 $\bar{2}$ 2)] facets are investigated in detail for methanol adsorption. Chemisorption of MeOH with varying strength is common to all four facets. Most importantly spontaneous dissociation of O-H bond of methanol is observed on all facets except (11 $\bar{2}$ 0). Our DFT calculations reveal that molecular adsorption is favored on flat facets, while dissociation is favored on step facets. Also, (10 $\bar{1}$ 0) facet undergoes substantial reconstruction upon MeOH adsorption. Activation of C-H bond along with strengthening of C-O bond on ZnO facets suggest partial oxidation of methanol. With our DFT investigations, we dig deeper into the underlying electronic structure of various facets of ZnO and provide rationale for the observed facet dependent interaction of ZnO with MeOH.

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1. Introduction

Methanol is one of the most important chemical for industrial reactions and a primary feed-stock for energy production. Due to easier transportation and compatibility with the existing infrastructure, methanol attracts considerable
5 attention. Methanol is also a promising hydrogen source because of its high hydrogen content.[1, 2] However, use of methanol as a source of hydrogen requires breaking of its O-H and C-H bonds with substantial bond dissociation energies, viz. 96.1 kcal/mol and 104.6 kcal/mol respectively.[3] Over the past two decades, extensive studies of activation and decomposition of methanol on various metal
10 surfaces,[4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14] metal alloys,[15, 16, 17, 18, 19, 20] metal clusters,[21, 22, 23, 24] metal oxides,[25, 26, 27, 28, 29, 30, 31] mixed metal oxides,[32] and zeolites[33, 34, 35] have been carried out. In general metal oxides turn out to be better catalyst for activation of methanol due to the presence of oxygen on the surface, which acts as an active site.

15 ZnO is considered as a very active catalyst for many reactions because of its mixed covalent and ionic bonding.[36] Vo et.al. investigated the adsorption and decomposition of methanol on ZnO(10 $\bar{1}$ 0) by employing DFT and concluded that methanol strongly adsorbed on ZnO(10 $\bar{1}$ 0) surface as compared to CuCl(111), Cu(111), and Au(111) surfaces. Their results showed that decomposition of MeOH to CH₂O molecule has a barrier of 1.20 eV.[37] In another
20 interesting study, Abedi et.al. employed DFT to understand the conditions leading to monolayer formation of methanol on ZnO(10 $\bar{1}$ 0) surface. They reported breaking of the O-H bond, with a barrier of 0.5 eV, as the preferred mechanism over cleavage of C-O bond.[38] In a combined experimental and theoretical work, Ruan et.al, used high-resolution scanning tunnelling microscopy
25 in combination with density functional theory to identify both the physisorbed methanol species on the non-polar ZnO(10 $\bar{1}$ 0) surface. The physisorption of methanol dominates at liquid nitrogen temperature which trans-

form into chemisorption upon either thermal annealing or electron injection. Moreover, the chemisorbed methanol mostly retains an undissociated state and tends to form one-dimensional chain structure along the (0001) direction mediated by the intermolecular hydrogen bonding interactions.[39] A DFT study carried out by Smith et.al. demonstrated significantly lower reaction barrier (0.39 eV) towards methanol dissociation on ZnO (0001) compared to PdZn surfaces (0.54 eV).[40] Recently Jin et.al. studied the adsorption and reactions of CH₃OH on non-polar mixed-terminated ZnO(10 $\bar{1}$ 0), polar O terminated ZnO(000 $\bar{1}$) and Zn terminated ZnO(0001) surfaces using high-resolution electron energy loss spectroscopy (HREELS) in conjunction with temperature programmed desorption (TPD). They found that for all three ZnO surfaces, methanol adsorb dissociatively at room temperature which leads to the formation of hydroxyl and methoxy species. Upon heating to higher temperatures (370K and 440K), the dissociated and intact methanol species on ZnO(10 $\bar{1}$ 0) predominantly undergo molecular desorption releasing CH₃OH. While on both polar surfaces, thermal decomposition of CH₃OH occurs to produce CH₂O, H₂, CO, CO₂, and H₂O at temperatures higher than 500K.[41]

Although ZnO is used extensively as a catalyst in many reactions, its potential is not truly realized. To the best of our knowledge only non-polar (10 $\bar{1}$ 0) and polar (0001) facets of ZnO have been studied for methanol activation. XRD pattern shows that (11 $\bar{2}$ 0), (10 $\bar{1}$ 3), and (11 $\bar{2}$ 2) are also prominent facets. These facets are hardly studied for methanol activation. In the present work, we have systematically studied the interaction of methanol with various flat (10 $\bar{1}$ 0), (11 $\bar{2}$ 0) and stepped surfaces (10 $\bar{1}$ 3), (11 $\bar{2}$ 2) by employing periodic DFT. We report not only molecular adsorption and activation of O-H bond of methanol on these facets but also spontaneous dissociation of its O-H bond leading to formation of methoxy species. The quenched C-O bond-length in methanol along with partial double bond type character indicates onset of oxidation of methanol. Finally, we demonstrate various possibilities regarding interaction of MeOH with ZnO and bring out the rationale behind the reactivity in terms of electronic structure of these facets.

60 2. Computational Details

All the calculations are carried out within the Kohn-Sham formalism of Density Functional Theory. Projector Augmented Wave potential[42, 43] is used, with Perdew Burke Ernzerhof (PBE)[44] approximation for the exchange-correlation and generalized gradient approximation,[45] as implemented in planewave, pseudopotential based code, Vienna Ab initio Simulation Package (*VASP*).[46, 65 47, 48] The bulk unit cell is taken from the materials project.[49] The bulk lattice parameters upon optimization are $a = 3.28 \text{ \AA}$ and $c = 5.30 \text{ \AA}$ demonstrate excellent agreement with the experimentally measured ($a = 3.24 \text{ \AA}$, $c = 5.20 \text{ \AA}$) lattice parameters.[50, 51] Two flat facets, $(10\bar{1}0)$ and $(11\bar{2}0)$ of ZnO are modeled as slabs by cleaving a surface with 3x3 periodicity in x and y direction 70 with 4 layers using Quantumwise-VNL-2017.1.[52] Two stepped facets, $(10\bar{1}3)$ and $(11\bar{2}2)$ are also cleaved by taking 3x1 and 2x2 periodicity respectively in the x and y direction with 6 layers. In every model, bottom layer is fixed and rest all layers and adsorbate are fully relaxed. Van der Waals corrections are applied 75 to account for dynamic correlations between fluctuating charge distribution by employing Grimme method (DFT-D2).[53] It is observed that 20 $\text{\AA}$ of vacuum is sufficient to avoid interaction between adjacent images of planes along the z-direction. Geometry optimization is carried out with a force cutoff of 0.01 eV/ $\text{\AA}$ on the unfixed atoms and the total energies are converged below 10^{-4} eV 80 for each SCF cycle. A Monkhorst-Pack grid of 3x2x1 for $(10\bar{1}0)$ and 3x3x1 for $(11\bar{2}0)$ slabs is used. For both stepped surfaces, Monkhorst-Pack grid of 2x2x1 is used. The difference in energies is less than 4meV/atom for every system upon refining the K mesh further. Entire surface is scanned by placing MeOH molecule at all available unique sites. To compare the interaction of methanol at these sites, interaction energy is calculated using the formula: $E_{int} = E_{system}$ 85 - $(E_{surface} + E_{molecule})$ where E_{system} is energy of the system when MeOH is placed on the surface, $E_{surface}$ is energy of the bare surface and $E_{molecule}$ is energy of the MeOH molecule. To understand the electronic structure of these facets, total Density of States (*tDOS*) are calculated with denser k-mesh using

LOBSTER.[54, 55, 56, 57] Mulliken charges are computed for all the atoms on the surface.

3. Results and Discussion

Bulk ZnO crystallizes in the hexagonal wurtzite structure consisting of hexagonal Zn and O planes stacked alternately. Both oxygen and zinc atoms are coordinated by four zinc and oxygen atoms respectively. Polar ((0001) and (000 $\bar{1}$)) and non-polar ((10 $\bar{1}$ 0), (10 $\bar{1}$ 1), (11 $\bar{2}$ 0)), (10 $\bar{1}$ 3), and (11 $\bar{2}$ 2)) facets have prominent peaks in XRD.[58, 59] In this work, we have studied the interaction of methanol with two flat ((10 $\bar{1}$ 0), (11 $\bar{2}$ 0)) and two stepped ((10 $\bar{1}$ 3), (11 $\bar{2}$ 2)) facets of ZnO. The top and side view of all these facets are shown in Fig. SI1 and Fig. SI2. Each layer of (10 $\bar{1}$ 0) is divided into two sub-layers leading to various unique sites for methanol adsorption. All these unique sites such as top of Zn, bridge of Zn-Zn, O-O, Zn-O, and bridge positions of atoms of two sub-layers are scanned for methanol interaction. All the sites where MeOH is placed are shown schematically in Fig. SI3. The numbers in Fig. SI3-(a) represent the initial positions where MeOH is placed and final position of adsorbed methanol or dissociated methoxy group are shown in Fig. SI3-(b). The black numbers indicate molecular adsorption while the red numbers denote dissociated methoxy group.

On the (10 $\bar{1}$ 0) facet, methanol adsorbs either molecularly or dissociatively at different sites. The interaction energy, O-H bond-length, and Zn-O_{MeOH} bond-length are tabulated in Tab. 1. Molecular adsorption of MeOH is thermodynamically the most probable outcome at this facet. However as seen from the Tab. 1, dissociation of MeOH into methoxy is also a likely product at elevated temperatures considering the small energy difference between these two outcomes. We report strong chemisorption and spontaneous dissociation of O-H bond of MeOH. A weak chemisorption is also observed, consistent with previously reported work,[60] though it is not thermodynamically most favorable outcome. At this point, it is pertinent to note that a molecule like MeOH could

Table 1: Interaction energy (eV), O-H bond-length ($\text{\AA}$), C-O bond-length ($\text{\AA}$), and Zn-O_{MeOH} bond-length ($\text{\AA}$) for various sites on ZnO (10 $\bar{1}$ 0) facet. All these positions are indicated in Fig. SI3-(b). Dissociation is indicated in red color while molecular adsorption is shown in black color.

Positions	E_{int} (eV)	O-H BL ($\text{\AA}$)	C-O BL ($\text{\AA}$)	Zn-O _{MeOH} BL ($\text{\AA}$)
4	-1.58	1.04	1.44	2.05
3	-1.52	1.03	1.44	2.06
7	-1.36	3.09	1.43	1.96
6	-1.35	4.37	1.41	1.96
5	-1.25	1.61	1.41	1.93
1	-1.08	0.98	1.45	2.11
2	-0.69	1.00	1.39	3.54

be placed at the symmetry driven unique points on the surface in various different ways. A detail account of which could be found in our previous paper.[32]
A small change in MeOH orientation wrt surface leads to completely different result in terms of extent of O-H bond activation or even O-H bond dissociation. Considering this, any study of MeOH interaction is always limited by initial configurations one investigates and there is a dire need of formalizing a methodology for accounting of all possibilities.

Fig. 1 shows representative conformations of MeOH upon adsorption/dissociation on this facet. A closer look at the adsorbed conformations reveal certain patterns in MeOH interaction with the facet. For example, highly activated methanol always gets adsorbed through oxygen (refer Fig. 1-(b)) whereas in case of barely activated MeOH, sometimes it gets adsorb through methylic H (refer Fig. 1-(c)). Another interesting observation is that MeOH adsorption also leads to the surface reconstruction which results into formation of voids as evident in all the cases. However, the extent of reconstruction depends on the outcome i.e.

Figure 1: (a) side view of bare (10 $\bar{1}$ 0) facet, (b) Chemisorbed MeOH with highly activated O-H bond, (c) chemisorbed MeOH with barely activated O-H bond, (d) dissociated MeOH with methoxy group attached to Zn atom, and (e) dissociated MeOH with methoxy group at bridge of two Zn atoms. For clear view of adsorption of methoxy on the surface (d) and (e) figures are enlarged. The numbers in the bracket indicates configuration with other details listed in Tab. 1

chemisorption (Fig. 1-(b) and (c)) or dissociation (Fig. 1-(d) and (e)). It was
 135 also observed that the dissociated methoxy group can adsorb at a Zn site or at
 bridge of two Zn sites. Further we investigate the interaction of MeOH with
 reconstructed surface by introducing second MeOH molecule with the most stable
 configuration. We placed the second molecule at various sites in the vicinity
 of previously activated MeOH. This results into two outcomes, viz. chemisorp-
 140 tion and dissociation, depending on availability of oxygen atom near the second
 molecule for abstraction of proton of MeOH. Dissociation of O-H bond of second
 MeOH is thermodynamically the most favorable outcome of this interaction (as
 shown in Tab. SI1).

Another flat facet that we studied is $(11\bar{2}0)$. This is a highly symmetric facet
 145 with less number of inequivalent sites on the surface as shown in Fig. SI4-(a).
 Interestingly, when MeOH is placed on any sites except 4^{th} , upon optimization
 it gets chemisorbed at one specific site as schematically represented in Fig.
 SI4-(b). The orientation of methanol on this site is shown in Fig. SI4-(c).
 E_{ads} for methanol at this site is -1.24 eV and O-H bond of MeOH elongates to
 150 1.02 Å. Further adsorbing the second MeOH molecule on the surface, results in
 chemisorption of molecule with elongation in O-H bond up to 1.03 Å. This shows
 that $(11\bar{2}0)$ facet does not favor dissociation of methanol due to uniformity on
 the surface. Comparing adsorption of MeOH on flat facets underlines the fact
 that nonuniform facet provides multiple possibilities.

Table 2: Interaction energy (eV), O-H bond-length (Å), C-O bond-length (Å), and Zn- O_{MeOH}
 bond-length (Å) for various sites on ZnO ($10\bar{1}3$) facet. All these position are indicated in Fig.
 SI5-(b). Dissociation of MeOH is shown in red color while molecular adsorption is shown in
 black color.

Positions	E_{int} (eV)	O-H BL (Å)	C-O BL (Å)	Zn- O_{MeOH} BL (Å)
2,7	-3.88	1.57	1.44	1.88
10	-3.70	1.73	1.39	1.89
6,8	-2.87	1.46	1.43	1.90
4,5,9	-1.71	1.03	1.37	3.49
1	-1.54	0.99	1.45	2.17
3	-1.42	0.99	1.45	2.21

155 Next we investigate a stepped facet $(10\bar{1}3)$. Various available unique sites,
 where MeOH is placed are shown in Fig. SI5-(a). Those sites where methanol/methoxy
 adsorb upon optimization are shown in Fig. SI5-(b). Interaction energy, O-H
 bond-length and Zn- O_{MeOH} bond-length are tabulated in Tab. 2. As evident
 from the interaction energy, dissociation of methanol is thermodynamically the

Figure 2: Various conformers of MeOH interaction with $(10\bar{1}3)$ facet. Upper panel shows chemisorption of MeOH and lower panel shows dissociation of MeOH at the facet. (a) weak chemisorption, (b) strong chemisorption, (c) monodentate adsorption of methoxy group, and (d) bidentate adsorption of methoxy group. The numbers in the bracket indicates configuration and the details are listed in Tab. 2.

most favorable outcome on this facet. Fig. 2 shows the representative cases of chemisorption as well as dissociation of methanol on $(10\bar{1}3)$ facet. It is observed that generally MeOH/methoxy group adsorb via its O at Zn site, but in few cases, it adsorbs through its methylic H (refer Fig. 2-(b)). Contrary to $(10\bar{1}0)$ facet, this methylic adsorption shows higher activation of O-H bond. The dissociated methoxy group adsorbs on the surface in two different ways, either through O_{MeOH} (monodentate as shown in Fig. 2-(c)) or via two atoms i.e. O_{MeOH} and methylic H (bidentate as shown in Fig. 2-(d)). Interestingly, coordination number of surface sites where MeOH/methoxy group adsorbs governs the stability of any configuration. Due to the presence of step, extent of reconstruction upon methanol adsorption is less on this facet as compared to

(10 $\bar{1}$ 0) facet.

Table 3: Interaction energy (eV), O-H bond-length ($\text{\AA}$), C-O bond-length ($\text{\AA}$), and Zn-O_{MeOH} bond-length ($\text{\AA}$) for various sites on ZnO (11 $\bar{2}$ 2) facet. All these position are indicated in Fig. SI6-(b). Dissociation is indicated in red color while molecular adsorption is shown in black color.

Positions	E_{int} (eV)	O-H BL ($\text{\AA}$)	C-O BL ($\text{\AA}$)	Zn-O _{MeOH} BL ($\text{\AA}$)
3,9	-6.24	2.25	1.44	1.98
1,2,7,11,12	-3.10	2.04	1.44	1.98
6,8	-2.95	2.01	1.45	1.99
13	-2.86	1.94	1.45	1.98
5	-1.78	1.00	1.45	2.04
10	-1.77	0.98	1.47	2.26
4	-1.56	0.98	1.46	2.08

Next, we discuss another stepped facet (11 $\bar{2}$ 2) which is more symmetric than (10 $\bar{1}$ 3) facet. Methanol is placed at all available unique sites as shown schematically in Fig. SI6-(a) and its interaction with the ZnO surface has been
175 studied. In majority of the cases, irrespective of initial positions of methanol, it diffuses to a single position upon optimization, as indicated by red triangle in Fig. SI6-(b). Similar to the previous stepped facet, this facet also shows two outcomes of MeOH interaction viz. dissociation as well as chemisorption. However, dissociation is highly favored over its molecular adsorption as evident
180 from Tab. 3. Distinct conformations of adsorption as well as dissociation of methanol on this facet are shown in Fig. 3. A careful look at the adsorbed conformations reveals that depending on the sites of adsorption viz. bridge (refer Fig. 3-(a)) or on-top site (refer Fig. 3-(b)), activation of O-H bond of methanol differs. The dissociated cases have methoxy adsorbed at Zn site with Zn-O_{MeOH}
185 bond-length (1.98 $\text{\AA}$) comparable to bulk Zn-O bond-length. Further, second

Figure 3: Upper panel shows adsorption of MeOH at $(11\bar{2}2)$ facet and lower panel shows dissociation of MeOH. (a) barely activated MeOH (b) highly activated MeOH (c) adsorption of methoxy group at bridge of two Zn atoms. The enlarged figure is shown to provide a clear view of methoxy group adsorption on Zn site. The numbers in the bracket indicates configuration and the details are listed in Tab. 3

Figure 4: The *tDOS* of four facets are plotted. The inset figure shows the enlarged *tDOS* near Fermi level. Only for $(11\bar{2}0)$ facet *tDOS* is zero at Fermi.

molecule also chemisorbs on the surface with O-H bond elongation up to 1.01 Å. In short, dissociation of MeOH is thermodynamically the most favorable outcome on stepped facets while molecular adsorption is favorable on the flat facets.

190 So far, we have observed that different facets of ZnO interact differently with
methanol resulting into molecular adsorption and/or activation and/or dissoci-
ation of O-H bond. This difference in behavior is correlated with underlying
electronic structure of these facets. Coordination number and Mulliken charges
of surface Zn and O atoms of all the facets are noted in Tab. SI2. For all
195 facets but $(10\bar{1}3)$, all the surface Zn or O atoms are identical. $(10\bar{1}3)$ facet
has two types of Zn and O atoms on the surface experiencing the difference in
their neighboring environment and hence Mulliken charges. It is also evident
that higher coordination of surface atoms leads to higher effective charges and

hence reduced reactivity. For example, in the case of $(11\bar{2}0)$ facet, Zn and O
 200 atoms with highest coordination and Mulliken charges do not show dissociation
 of methanol. The inhibition of O-H bond breaking of MeOH at $(11\bar{2}0)$
 facet could be explained by analyzing the total density of states ($tDOS$) plot as
 shown in Fig. 4. The $tDOS$ plot for $(11\bar{2}0)$ facet clearly shows non availability
 of energy states near Fermi level, which makes it least reactive. Remaining all
 205 facets with energy states available near Fermi level enhance reactivity of the
 facet and explain the observed dissociation of methanol on these facets. Next
 we plot projected density of states ($pDOS$) of surface atoms for all facets. 3d

Figure 5: (a) $pDOS$ of Zn-3d orbitals of flat and stepped facets. As expected, 3d in Zn being completely filled are much away from Fermi level. (b) Zn-4s of flat and stepped facets. It is interesting to note that for flat facets $pDOS$ of surface Zn atoms show unavailability of states near Fermi as opposed to case of stepped facet

and 4s states of surface Zn atoms are shown in Fig. 5. Zn, being a late transition metal with fully filled 3d states lying much below the Fermi level (refer

Fig. 5-a), does not participate in reactivity. While its 4s states, lying near the Fermi level, participate in reactivity of the surface. It is clearly seen in the Fig. 5-b that for flat facets, 4s states of surface Zn atoms are zero near Fermi level while it is non-zero for stepped facets. The presence of non-zero 4s states near Fermi for stepped facets favors dissociation of MeOH, which is most favorable on these facets.

4. Conclusion

We have carried out a systematic study of methanol adsorption on various facets of ZnO which includes two flat $[(10\bar{1}0)$ and $(11\bar{2}0)]$ and two stepped $[(10\bar{1}3)$ and $(11\bar{2}2)]$ surfaces. O-H bond dissociation is thermodynamically the most favorable outcome on stepped facets where on chemisorption of MeOH with 7-10% O-H bond activation is observed on the flat facets. We also report considerable surface reconstruction upon MeOH adsorption. However, the reconstruction is lesser on the stepped surfaces compared to the flat facets. Further, partial oxidation of MeOH is favored on ZnO facets. Our detailed electronic structure analysis brings out the rationale behind the surface dependent interaction of MeOH. Analysis of pDOS, tDOS along with Mulliken charges on surface atoms explains the facet dependent reactivity observed in case of ZnO. Facets with available empty states near Fermi leads to O-H bond dissociation whereas absence of empty states near Fermi leads to O-H bond activation. Considering the role of ZnO in various reactions and importance of MeOH in the current energy scenario we believe our study shade light on some important aspects of interaction of ZnO with MeOH.

Conflicts of interest

“There are no conflicts to declare”.

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