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Selective promotion of different modes of methanol adsorption via the cation substitutional doping of a ZnO($10\bar{1}0$) surface

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Abstract

We used density functional theory to examine how doping the surface of an oxide (i.e., substituting a cation in the surface layer of the metal oxide with a different cation) modifies its chemical properties. As an example, we used the ZnO($10\bar{1}0$) surface doped with Na, K, Au, Ag, Cu, Ti, Al, or Mg and the adsorption of methanol to probe the chemistry of the doped surface. We calculated the binding energies of the possible adsorption products. When we say that methanol preferred to form a certain product, we mean that the product had the lowest energy of formation from gas-phase methanol and the surface. We found that on a surface doped with Na or K, CH_3OH preferred to dissociate into adsorbed formaldehyde and two hydroxyls on the surface. On the Ti- or Al-doped surfaces, methanol dissociated by forming a methoxy radical bound to the dopant and a hydroxyl on an oxygen atom near the dopant. On the undoped oxide or on ZnO doped with Au, Cu, Ag, or Mg, methanol preferred to adsorb molecularly. The Au, Cu, Ag, or Mg dopants exhibited no significant preference for one adsorption mode over the others. Our most important qualitative conclusion is that doping can significantly alter the chemistry of an oxide surface, offering an avenue for designing catalysts that have better performance than undoped oxides.

1. Introduction

Oxides are widely used in industry and in academic research for performing oxidation, oxidative dehydrogenation, and ammoxidation reactions [1–3]. Recent experimental [4–20] and theoretical [21–32] research has examined the possibility that the catalytic properties of oxides might be improved by replacing a small fraction of the cations at their surface with other cations. An example of such a compound is $Cu_xCe_{1-x}O_2$ (with $x < 0.2$), in which some Ce atoms on the surface are replaced with Cu. We call $Cu_xCe_{1-x}O_2$ a doped oxide, the Cu atom a dopant, and CeO_2 the host oxide or the host. Oxides also have been doped to modify their electrical, mechanical, and sintering properties or their oxygen conductivity [33], but these properties are not of interest here. The goal of the present study was to investigate how doping the surface modifies its chemical properties.

Doped oxides are difficult to characterize experimentally; it is hard to prove that a doped oxide has been prepared (as opposed to a mixture of oxides), that the dopant is at the surface, and that the doped oxide is stable under reaction conditions. This creates an opportunity for theory that can easily "prepare" doped oxides and help clarify how doping can affect the chemical properties of the surface.

Numerous oxide–dopant combinations can be formed, with a rich and varied chemistry. It is therefore reasonable to expect that some of these compounds might be better oxidation or oxidative dehydrogenation catalysts than the host oxides. Creating isolated, atomic-sized centers on the surface may improve selectivity, because it reduces the number of reactions that can occur at the small center.

In the present work, we used methanol as a probe molecule to investigate to what extent doping ZnO($10\bar{1}0$) can modify the chemistry occurring on the surface. We did not examine any particular catalytic reaction in detail. We chose methanol because it is frequently used to a as probe in investigating the chemistry of oxide surfaces [34–48]. Its oxidative dehydrogenation is used industrially to produce formaldehyde [43,49–54] and dimethyl ether [55], and its catalytic decomposition is being evaluated as a possible source of clean hydrogen [56–70]. We chose ZnO because it is used as a catalyst by itself [8,71–76]

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and in combination with other oxides [77–90] and also as a support for the water–gas shift reaction and methanol synthesis [1,78,91,92].

Methanol can adsorb on the surface of a doped oxide molecularly or dissociatively. The dissociation can occur in several ways: The OH bond can be broken to form a methoxy radical bound to the dopant and a hydroxyl with an oxygen atom on the surface, the C–O bond can be broken to form a hydroxyl bound to the dopant and a $-CH_3$ radical bound to a surface oxygen atom, or methanol may lose two hydrogen atoms, one from the methyl and one from the –OH group, to make two surface hydroxyls and formaldehyde. In what follows, we refer to these dissociation modes as molecular adsorption, methoxy formation, methyl formation, and formaldehyde formation, respectively. We investigated whether different dopants of the ZnO surface can be used to control the preference for one of the aforementioned adsorption modes, whether the chemistry of methanol on the doped ZnO is strongly dependent on the dopant, and whether the chemical activity of the doped oxide is higher than that of the host oxide.

In previous work, we showed that some dopants weaken the bond of some of the surface oxygen atoms in their neighborhood, making them more reactive [21,22]. In those studies, we concentrated on the activation of one surface oxygen atom by the dopant and used CO oxidation as a probe to investigate the ability of the doped surface to perform oxidation reactions. The DFT calculations presented herein investigate the dissociative adsorption of CH_3OH, which requires the participation of two adsorption sites, the dopant and an oxygen atom near it.

We only calculated the binding energies of various methanol dissociation products to the doped (and the undoped) ZnO surface; we provide no kinetic information regarding dissociation. Nevertheless, these calculations indicate that doping can dramatically change the chemistry of the surface. We hope that these results will stimulate experimental work in this field.

2. Computational methodology

The calculations presented here use DFT as implemented in the VASP program [93]. The electron–ion interactions are treated with the projector augmented wave method, in which all the electrons except the valence ones are kept frozen [94]. Exchange-correlation energy was calculated using the PW-91 GGA functional [95]. The computed bulk lattice constants of ZnO were found to be $a = 3.282$ Å, $c/a = 1.6176$, and $u = 0.378$. The calculated heat of formation was -3.41 eV, close to that observed in previous experiments [96,97] and computations [98–100]. A (2×3)-ZnO $(10\bar{1}0)$ surface supercell with three double layers was used for all calculations. The dopants were in a substitutional position (see Appendix A), replacing one Zn atom for every 6 Zn atoms in the surface layer of ZnO. Tests performed with slabs with five double layers and a (3×4) supercell found that increasing the slab thickness and supercell size changed the relative adsorption energies by <0.05 eV. A plane-wave cutoff of 400 eV and a $2 \times 2 \times 1$ k-points grid was used for all calculations. For a few systems, we increased the k-points grid to $4 \times 4 \times 1$, which changed the relative adsorption energies by <0.05 eV. The total energy was converged to within 10^{-3} eV/supercell. We allowed fractional occupancy of bands by using Gaussian smearing with an energy window of 0.05 eV. Spin-polarized DFT was used for all calculations, because doping the oxide surface may produce radical species with different spin multiplicities. The adsorption energy for different modes was computed by fixing the net spin of the reactant and the products. The Bader charges on atoms were calculated using a method proposed by Henkelman et al. [101].

3. Results

3.1. *Methanol adsorption on the undoped ZnO$(10\bar{1}0)$ surface*

Adsorption of CH_3OH on doped ZnO or ZnO mixed with other oxides has been studied experimentally [34,37,39,43,45–48,56–70]. In the absence of oxygen vacancies, CH_3OH adsorbs on ZnO$(10\bar{1}0)$ molecularly, but a small amount of methoxide is also formed [48].

Our calculations for the undoped ZnO$(10\bar{1}0)$ surface show that the molecularly adsorbed CH_3OH (Fig. 1a) was the most stable, with a adsorption energy of $E_{\text{ads}} = -1.1$ eV (Table 1). Methanol also adsorbed by breaking the bond between O and H to form an adsorbed methoxy and surface hydroxyl, with an adsorption energy of -0.8 eV (Fig. 1b). It also dissociated by breaking the bond between C and O to give an adsorbed methyl and adsorbed OH, with a release of -0.4 eV (Fig. 1c).

3.2. *Molecular adsorption on a doped ZnO surface*

The binding energy of molecular CH_3OH on ZnO doped with Na or K was less than that to pure ZnO; the binding to ZnO doped with Au, Ag, or Cu was about the same as that to clean ZnO; and the binding on Mg-, Al-, or Ti-doped ZnO was stronger than that on pure ZnO (Table 1). For ZnO doped with Na, K, Al, or Ti, molecular adsorption was no longer the most stable adsorption state. The structure of molecularly adsorbed CH_3OH on Na-doped ZnO is shown in Fig. 2. The presence of Na significantly changed the binding site of the CH_3OH molecule. On pure ZnO, the oxygen in CH_3OH was bound to a Zn atom on the surface, whereas on the Na-doped surface, the hydrogen in the OH group in CH_3OH was bound to a surface oxygen atom. In previous work [23], we found that doping with Na (or K) weakened the bond of an oxygen atom to the surface. We used the energy for forming an oxygen vacancy at the surface (EFOVS) as a measure of the strength of the oxygen bond to the oxide, and found that doping ZnO with Na or K decreased EFOVS by ∼1.3 eV. This makes the O atom more reactive and may be why methanol binds to it rather than to Zn. The structure of molecularly adsorbed CH_3OH on K-doped ZnO is very similar to that shown in Fig. 2a.

In the case of ZnO doped with Ti, Al, or Mg, the oxygen atom in CH_3OH was bound to the dopant (Fig. 2b). In previous work [23], we showed that doping with Al or Ti strengthened the bond of the neighboring oxygen atoms to the oxide, making the oxygen atoms less reactive. Doping with Al or Ti increased EFOVS above the value for undoped ZnO by 0.8 eV for Al and

Table 1
Adsorption energies (in eV) of different modes of CH_3OH adsorption on various doped $ZnO(10\bar{1}0)$ surfaces. The energy of the most stable adsorbed structure is shown in a bold font

Dopants	Molecular adsorption	Formaldehyde formation	Methoxy formation	Methyl formation	CH_3O adsorption on the dopant
Na	−0.6	**−1.2**	−0.3	0.0	−0.5
K	−0.7	**−1.1**	−0.3	0.4	−0.2
Au	**−1.0**	−0.7	**−1.0**	**−1.1**	−1.3
Ag	**−1.1**	−0.6	−0.9	−1.0	−1.1
Cu	**−1.0**	−0.2	−0.8	−0.9	−1.4
Undoped ZnO	**−1.1**	1.4	−0.8	−0.4	−1.0
Mg	**−1.5**	1.2	−0.8	−0.8	−1.3
Al	−1.4	2.5	**−2.2**	−1.7	−4.1
Ti	−1.1	2.5	**−2.4**	−1.2	−4.7

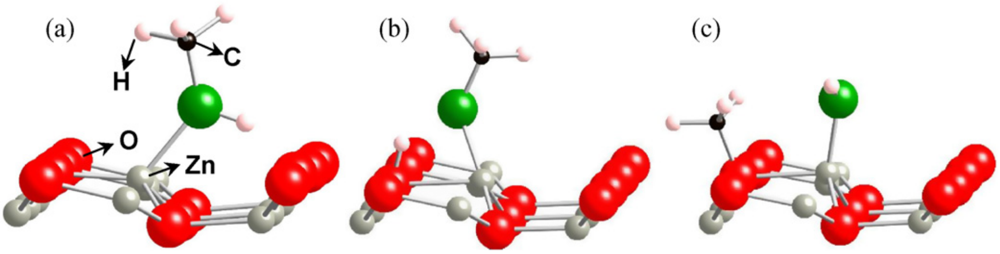

Fig. 1. Possible adsorption modes of CH_3OH on the $ZnO(10\bar{1}0)$ surface. The pink spheres represent the hydrogen, the gray ones the Zn atoms, the red ones the oxygen atoms on the oxide surface, the black one is carbon and the green one is the oxygen atom in methanol. The most stable structure is shown in (a) and is exothermic by −1.1 eV. Methoxy formation (b) is exothermic by −0.8 eV and methyl formation (c) by −0.4 eV. The lines joining the atoms in all figures in this article are drawn to make it easier to understand the structure; a line does not necessarily indicate the existence of a chemical bond.

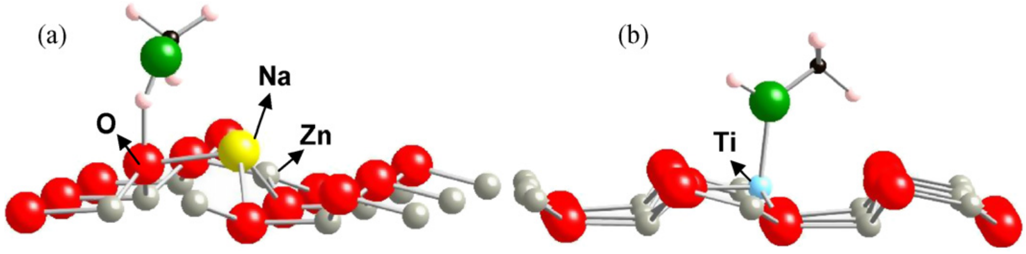

Fig. 2. The structure of the molecularly adsorbed CH_3OH on a Na-doped $ZnO(10\bar{1}0)$ surface is shown in (a). The structure of the molecularly adsorbed CH_3OH in a K-doped $ZnO(10\bar{1}0)$ surface is quite similar. The structure of the molecularly adsorbed CH_3OH on a Ti-doped $ZnO(10\bar{1}0)$ surface is shown in (b). The structure of the molecularly adsorbed CH_3OH on an Al- or Mg-doped $ZnO(10\bar{1}0)$ surface is quite similar.

by 1.2 eV for Ti. We take this as an indication that the dopant is undercoordinated, and thus this explains why it binds methanol more efficiently than the surface Zn atoms.

3.3. Adsorption on doped ZnO, with formaldehyde formation

The energies of CH_3OH dissociative adsorption by the simultaneous breaking of the CH and the OH bonds (Fig. 3a) on the doped $ZnO(10\bar{1}0)$ surface are given in column 3 of Table 1. This hydrogen abstraction produced adsorbed CH_2O. In gas phase, the reaction $CH_3OH \rightarrow H_2CO + H_2$ was endothermic by $\sim$1.5 eV (computed by density functional theory), and on the undoped ZnO surface, the energy of reaction was $\sim$1.4 eV. On the $ZnO(10\bar{1}0)$ surface doped with Na and K, this reaction was exothermic (−1.2 eV for the Na-doped $ZnO(10\bar{1}0)$ surface and −1.1 eV for the K-doped $ZnO(10\bar{1}0)$ surface). Doping with Au or Ag also made this reaction exothermic, but not as much as doping with Na or K.

In previous work [23], we showed that the presence of Na or K weakens the bond of the oxygen atoms to the oxide and increases their reactivity, making them more "willing" to bond the hydrogen produced by formaldehyde formation. This interpretation is supported, qualitatively, by the Bader charges on the atoms. The charge on a Zn atom in the surface layer of undoped $ZnO(10\bar{1}0)$ was +1.21, whereas that on the Na (or K) atom substituting a Zn atom in the surface was +0.88 (or +0.84). Thus, fewer electrons were available to the oxygen atoms when the oxide was doped. The surface O atoms in a $ZnO(10\bar{1}0)$ surface had a Bader charge of ~ -1.19, compared with ~ -1.15 for oxygen at the surface of Na-doped ZnO or of K-doped ZnO surface. To compensate for this electron deficit, the O atom abstracted two H atoms, which act as electron donors (the Bader charge on the H atom in the hydroxyl is $\sim +1$). The electron deficit introduced by doping ZnO surface with Na or K was also reflected in the band structure of doped ZnO, which exhibited an empty, delocalized orbital at the top of the valence band.

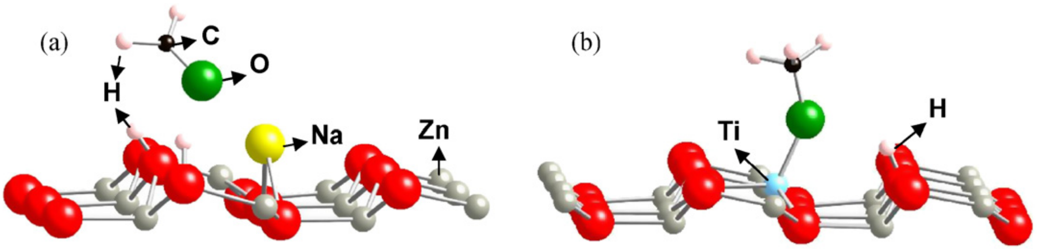

Fig. 3. The dissociative adsorption of CH_3OH via the simultaneous breaking of the CH and OH bonds to form an H_2CO and two hydroxyls on the Na-doped ZnO($10\bar{1}0$) surface is shown in (a). The structures obtained by this adsorption mode on Na-, K-, Au-, Ag-, or Cu-doped ZnO($10\bar{1}0$) surfaces are similar. (b) shows the structure of the dissociatively adsorbed CH_3OH by breaking the O–H bond to form a methoxy radical bound to the dopant and a surface hydroxyl on a Ti-doped ZnO($10\bar{1}0$) surface. The structures for this adsorption mode on Al- and Mg-doped ZnO($10\bar{1}0$) surfaces are similar.

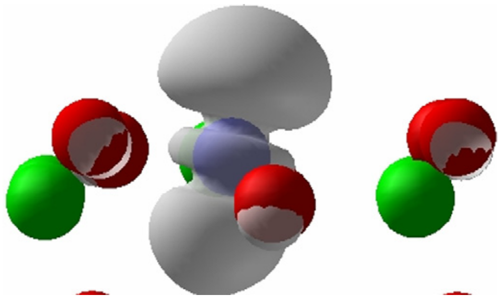

Fig. 4. A side view of the ZnO($10\bar{1}0$) surface with the red, green and blue spheres denoting O, Zn, and Ti, respectively. Electronic density (diffuse grey lobe) of the HOMO of Ti-doped ZnO is localized over Ti atom.

The activation energy for converting the molecularly adsorbed CH_3OH (Fig. 2a) to an adsorbed H_2CO and two surface hydroxyls (Fig. 3a), computed using the nudged elastic band method [102], was 0.22 eV for the Na-doped ZnO($10\bar{1}0$) surface and 0.23 eV for the K-doped ZnO($10\bar{1}0$) surface. Unfortunately, the desorption energy of formaldehyde was ∼0.8 eV for the Na-doped surface and ∼0.5 eV for the K-doped surface, which means that one had to operate at relatively high temperature to desorb the formaldehyde from the reactive center.

When Au, Ag, and Cu is substituted for Zn in the ZnO($10\bar{1}0$) surface, the Bader charges on the dopant were +0.54, +0.68, and +0.9, respectively, all lower than the Bader charge of +1.21 on Zn in the undoped ZnO($10\bar{1}0$) surface. These dopants also causes an electron deficit in the doped ZnO($10\bar{1}0$) surface, and their presence decreases the energy needed for forming an oxygen vacancy on the surface [23]. These doped oxides also have a delocalized, empty state at the top of the valence band. The surfaces doped with Ag, Ag, and Cu could dissociate CH_3OH into H_2CO and two hydroxyls, but the exothermicity for these systems was lower than that for the alkali-doped surfaces (Table 1, column 3).

Doping ZnO($10\bar{1}0$) with Al or Ti increases the energy required for removing an oxygen atom from the neighborhood of the dopant [23]. The Bader charge on Ti (Al) for a Ti- (Al-) doped ZnO($10\bar{1}0$) surface, was +1.76 (+1.53), exceeding the charge of +1.2 on a Zn atom in the surface layer of an undoped ZnO($10\bar{1}0$) surface. These dopants cause an excess of electrons in the oxide. Doping with Ti created a HOMO ∼0.3 eV below the conduction band edge, whereas doping with Al created a HOMO at the conduction band edge. A distinct electron lobe was localized over Ti (Fig. 4). Projecting the HOMO in its contributing atoms confirmed that HOMO of Ti-doped ZnO was localized on the Ti, whereas in HOMO of Al-doped ZnO was more delocalized. The excess electrons introduced by doping ZnO with Al or Ti presumably decreased the tendency of the oxygen atoms to form bonds with H atoms abstracted from CH_3OH. This rendered the dissociation of CH_3OH on these surfaces into H_2CO and two surface hydroxyls highly endothermic (see Table 1, column 3). The little energy gained by forming two hydroxyls did not compensate for the energy required to break the CH and OH bonds.

3.4. *Dissociative adsorption with methoxy radical formation*

The energies of CH_3OH adsorption in forming a methoxy radical bound to the dopant and a surface hydroxyl are given in column 4 of Table 1. This reaction is very exothermic on the ZnO surface doped with Ti or Al (−2.4 and −2.2 eV, respectively). Doping with Na or K lowered the methoxy energy compared with that on an undoped ZnO surface. Doping with Au, Ag, or Cu increased the reaction energy slightly over the value found on the undoped surface.

The energy required by this dissociative adsorption was decreased, compared with that required by the same reaction in the gas phase, by formation of a bond between the methoxy radical and the dopant and of a bond between O and H in the surface hydroxyl. To determine which of these two energies plays the more important role, we calculated the energy for adsorbing the OCH_3 radical from the gas phase onto the dopant (sixth column of Table 1). The adsorption of OCH_3 on the dopant was very exothermic in Ti- or Al-doped ZnO($10\bar{1}0$). The substitution of Zn with Ti or Al likely produced an excess of electrons around the dopant, increasing the affinity of the dopant to the methoxy radical. The Ti and Al dopants also strengthened the bond of the surface oxygen atoms surrounding the dopant to the oxide [23]. This is why hydroxyl formation near the dopant did not produce much energy.

3.5. *Dissociative adsorption with CH_3 formation*

On the undoped ZnO, adsorption of CH_3OH with the formation of a methyl group bound to oxygen and a hydroxyl bound to the Zn atom (Fig. 1c) was exothermic (−0.4 eV). However, molecular binding is preferred; experiments studying CH_3OH adsorption on the ZnO surface have shown that the CO bond is not broken [103,104]. Doping with Na and K made this reaction energetically less favorable compared with that on the undoped ZnO surface. All of the other dopants made this reaction energetically more favorable than that on the undoped surface, with Al and Ti having the greatest effect; however, this dissociation was never the most likely thermodynamically on any of the surfaces studied here.

3.6. Selectivity

In principle, the products of these dissociation modes coexist on any given surface. For all practical applications, a catalyst that clearly favors one product (selectivity) is preferred. As a rough approximation, we can ignore entropy and use the energy of formation of various products as a criterion for the concentration of various products on the surface. We found that molecular adsorption is favored on undoped ZnO and also on ZnO doped with Mg, Cu, Ag, or Au. On undoped ZnO, the energy released during molecular adsorption of CH_3OH was 0.3 eV greater than that of methoxide radical formation. Doping ZnO with Au made the energy of molecular adsorption of CH_3OH equal to that of the formation of the methoxide radical. Therefore, within the computational approximations used here, the methoxy and the CH_3OH concentrations on the surface were equal on a Au-doped ZnO surface. Taking the entropy into account will change the fractions of methoxy and CH_3OH on the surface, but they will still coexist. The concentration of CH_3OH on Ag- or Cu-doped surfaces was higher than that of methoxy, but the presence of the latter on the surface cannot be ruled out. Formation of the methoxide radical was greatly favored on the Al- and Ti-doped surfaces. The Na- and K-doped surfaces favored formaldehyde formation. Because we calculated only the binding energies, these are approximate statements about the equilibrium concentrations. In Na- and K-doped ZnO, we also found low activation energy for formaldehyde formation.

4. Conclusions

Previous theoretical work on doped oxides [21,22] focused on the activation of the oxygen atoms around the dopant. We were interested in using dopants to facilitate reactions, abstracting one oxygen atom from the surface (e.g., CO oxidation, perhaps epoxidation). Subsequent work has shown [23] that some dopants strengthen the bond of the oxygen atoms to the oxide, making it a poorer oxidant than the undoped oxide. In the present work, we studied a system in which both the dopant and its surrounding oxygen atoms participate in the chemistry, because they are both activated when the cation of the host oxide is replaced with another cation. To explore this idea, we studied the adsorption of methanol, which can adsorb molecularly and/or dissociatively. In the latter case, both the dopant and the surrounding oxygen must be "willing" to bond with the dissociation products.

The main question that we posed is qualitative: To what extent does doping modify the chemistry of the surface? Our calculations show that doping is a very versatile method for significantly changing the preference for a specific dissociation mode. The undoped oxide and oxides doped with Au, Ag, Cu, and Mg prefer to adsorb methanol molecularly. On surfaces doped with Na or K, methanol prefers to form formaldehyde and two adsorbed H atoms (to form hydroxyls with surface oxygen). On the Al- and Ti-doped surfaces, methanol decomposes into a methoxide radical bound to the dopant and a surface hydroxyl. These findings demonstrate that doping can cause very substantial changes in the chemistry of the surface.

The results presented here are qualitative for two reasons. First, the single-crystal surfaces may not represent the dispersed catalysts. Second, there are reasons to worry that DFT may not give accurate results for narrow-band oxides [105]. Our main conclusion—that doping is an excellent method for modifying surface chemistry—is not likely to be affected by possible errors in DFT calculations or by the fact that we worked with single-crystal surfaces. The classification of the dopants into those that favor aldehyde formation and those that favor methoxide formation is likely to be safe in those cases in which the energy differences on which these conclusions are based are large.

Given the fact that so many oxides can be combined with so many dopants, and the fact that the dopants strongly affect surface chemistry, it is likely that there are some good oxidation catalysts among these compounds. We hope that our calculations will stimulate more experimental research on doped oxides.

Acknowledgments

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Appendix A. Position of the dopant in the doped ZnO($10\bar{1}0$) surface

We have examined in this article the chemistry of dopants that substitute a Zn atom in the surface layer of ZnO. It is possible that during the synthesis the dopant may occupy an interstitial position or form a single neutral atom on the surface. In this appendix we examine these other possibilities. Numerous vapor deposition studies have shown that single atoms diffuse readily on the surface to form large, neutral metal clusters. If the concentration of dopant atoms on the surface is very low it is possible that many of them are trapped as single atoms at oxygen vacancy sites. We have not examined the chemistry of such atoms here. There is no doubt that during synthesis some dopant atoms are trapped in interstitial sites in the bulk [106,107]. However, they do not affect catalysis unless they are present under the surface layer. We have calculated the energies of a dopant in an interstitial position closest to the surface and compared it to the energy of the same dopant adsorbed on the surface. Ti, Al, and Mg, in an interstitial position in the subsurface layer, are unstable: they displace a Zn atom, pushing it onto the surface, and take its place in the lattice (ending as substitutional dopants). The energy of Na, K, Au, Ag, and Cu in the interstitial position is much higher than when the dopant is adsorbed on the surface. Therefore one expects that a dopant trapped accidentally in an interstitial position during synthesis will move onto the surface and will migrate to join other adsorbed dopants to form neutral, metallic clusters.

One must keep in mind that the preparation methods of mixed oxides involve very complex liquid phase and solid state chemistry and the final product is not in thermodynamic equilibrium. To make doped oxides one must make sure that the host oxide is made rapidly and the dopant gets trapped in the host lattice without having time to migrate in the system and join other dopant atoms to form its own oxide. Dopant atoms will be occasionally trapped in an interstitial position in the bulk, but they are not stable near the surface. A more difficult question to answer (for both theory and experiment) is whether during the synthesis the dopant forms a very small oxide cluster on the surface of the host. It is well known that such clusters are chemically active and their chemistry is different from that of bulk oxides. It is therefore very difficult to distinguish small oxide clusters supported on oxide from the doped oxide.

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