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Structure and Chemical Activity of Transition Metal and Metal Oxide Catalysts: An Insight from Theoretical DFT Studies[1]

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Abstract—The present theoretical DFT study discusses the structure and chemical activity of transition metal and metal oxide catalysts within the well-known cluster approach. Selective oxidation of carbon monoxide on gold supported on titania (Au/TiO_2 (110)) as well as some key points in understanding the effect of non-metal doping on TiO_2 with the aim to increase its photocatalytic functionality have been briefly discussed. It was shown that Au (with formal oxidation state equal to plus one) stabilized on water-assisted and vacancy containing TiO_2 (110) can explain selective oxidation of CO. Here binding of O_2 with the vacancy site is energetically preferable than its adsorption on an Au site. Conversely, CO adsorbs on an Au center of Au/TiO_2 (110) which is energetically much more profitable than its interaction with the oxygen vacancy site. Also, carbon and nitrogen doping on TiO_2 (110) leads to two different structures. Energetically most profitable is that carbon occupies an interstitial position in deep bulk while nitrogen replaces the protruded oxygen atom and forms a surface N–H group.

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Quantum chemical modeling of the adsorption and catalysis of reactant molecules with transition metal containing oxide materials are computationally very demanding due to their three-dimensional infinite structures. As a result the use of the finite cluster approach has been found as a solution to the problem in which one deals with a part of the large system and the influence of the crystalline environment is mostly neglected or only included approximately [1–5]. Therefore it is particularly suited to describe local phenomena and local character of interactions, i.e. interactions on catalytically active sites, defects at a broken space and/or translation symmetry, strong host—guest interactions, etc. However, the use of such kind of finite cluster models has well-documented disadvantages in describing extended surfaces, though the latter can be effectively undertaken by either through the increase of the cluster size or by introducing different kinds of embedding techniques. Since cutting substructures from oxides generates dangling bonds, they must be saturated in such a way that the final cluster models should obey for the overall stoichiometry, boundary terminations, and for electroneutrality [4–7]. Most widely used border H atoms to account for proper boundary terminations stand also to mimic the remaining part of oxide lattice when a cluster is formed, so that the formation of an artificial net of intramolecular H-bonds should be effectively excluded from the considerations.

We have recently shown an ultimate importance of proper modeling of structure and chemical activity of transition metal and metal oxide catalysts to proper understanding of the experimental findings [6–8]. First the formation of oxygen vacancy site on rutile TiO_2 (110) and its interaction with molecular oxygen were considered [6]. It was shown that to explain the experimental temperature-programmed desorption (TPD) observations on triply exceeding concentration of O_2 per vacancy site at low temperature saturation coverage [9, 10], one does not need to make an assumption on the formation of O_4 particle at the vacancy site [11], if one properly address the mechanism of formation of precursor defect sites on rutile TiO_2 (110). Next we have shown elsewhere [7], that not only the active site structures but also support structures should be properly modeled for reliable description the mechanism of the selective oxidation of methanol into formaldehyde over vanadia supported on silica and titania catalysts. An improper use of cluster models mimicking an intrinsic support structure may result in the failure [12] to explain the experimental findings on selective oxidation of methanol into formaldehyde over these modified oxide catalysts. Finally, the importance of proper consideration of spin state of the selected cluster models to describe an attractive bonding interaction not only for bromine and Pt (111) but also for all the three adsorption modes of NO on the Pt (111) surface have been also explained [8]. In agreement with experimental observations [13], the calculations have predicted that the first peak in the IR spectra appears at ca. 1515 cm^{-1} at the initial

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stage of low NO coverage, while it would shift to 1707 cm^{-1} at high NO coverage [8]. The results obtained gave some insight in understanding the target phenomena as well as offer some recipe on molecular modeling on related other systems when one uses cluster approach.

In present paper, we would like extend these considerations to deal with selective oxidation of carbon monoxide on gold supported on titania (Au/TiO_2) as well as on some key points in understanding the effect of non-metal doping on TiO_2 with the aim to increase its photocatalytic functionality for light-harvesting purposes [14].

CALCULATION METHOD AND CLUSTER MODELS

DFT calculations were carried out with the use of Becke's three-parameter hybrid method with the Lee, Yang, and Parr (B3LYP) gradient-corrected correlation functional [15, 16] and combined basis sets. The latter basis sets include the standard 6-31G* ones for the Ti, O, C, N, and H atoms and Lanl2dz basis sets for all the Au atoms. As a result, they can be denoted as B3LYP/(Lanl2dz + 6-31G*) level for all calculations involving Au/TiO_2, B3LYP/Lanl2dz level for isolated Au clusters, and B3LYP/6-31G* level for interactions of adsorbates on defect-free and/or reduced TiO_2. The rutile TiO_2 (110) surface is modeled either by two-layer cluster of $H_{38}O_{53}Ti_{17}$ or one-layer cluster of $H_{34}O_{43}Ti_{13}$, respectively. These molecular clusters are formed through cutting the substructures from rutile while properly taking into account their boundary terminations, electroneutrality and stoichiometry [4, 6, 7]. The geometry optimizations were carried out taking into account symmetry restrictions for rutile structure motif and followed by estimation of vibration fundamentals via performing harmonic frequency calculations.

RESULTS AND DISCUSSION

Selective Oxidation of CO on Au/TiO_2 (110)

Selective oxidation of carbon monoxide on Au/TiO_2 has been the subject of many experimental and theoretical investigations because of considerable interest in the field of heterogeneous catalysis and various catalytic processes [17]. One of the important examples is a reduction of CO and/or NO from the flue gases emitted by stationary and mobile sources, coal-fired power plants, electric power generators, nitric acid factories, etc. Despite of general agreement on molecularly adsorption feature of CO on an Au surface at low temperatures, there are still controversial discussions on the nature of target interactions and stable adsorption sites on the Au/TiO_2 surface. Also, either of the isolated Au or TiO_2 is relatively inactive for the selective oxidation of CO, but the combination of the two produces excellent catalyst for low temperature CO oxidation, water-gas shift reaction, propylene epoxidation, nitrogen oxide reduction, etc. [17].

First we have found that on defect-free rutile surface, neither neutral Au nor molecular oxygen have stably bound state underlining relative inertness of the surface for the activation of dioxygen molecule [6]. Our calculations have shown that the adsorption energy for the most active singlet dioxygen on TiO_2 (110) is slightly endothermic (−13.5 kcal/mol) compared to the isolated non-interacting TiO_2 (110) and dioxygen in its triplet electronic ground state [6]. Also in the unbound state, spin density is mostly localized on Au and nearby bridging protruded O atom of Au/TiO_2 (110). CO can be equally adsorbed either on Lewis acid five-fold coordinated Ti_{5c} or on an Au site with adsorption energies estimated as 19 and 20.5 kcal/mol, respectively (see, Fig. 1). However, the former complex results in blue-shift of 65 cm^{-1} while the latter complex produces red-shift of 62 cm^{-1} in the ν_{CO} stretching frequency of CO. Similarly, for an isolated gold mimicked by a cubic cluster of Au_{14} the interaction of CO on three-fold coordinated Au_{3c} results in an adsorption energy (ΔE) of 10.4 kcal/mol with a red-shift of ca. 37 cm^{-1} in ν_{CO}. Evidently, adsorption of CO on Au_{4c} is energetically less profitable ($\Delta E = 6$ kcal/mol) while red-shift in ν_{CO} does not practically altered (see, Fig. 1d). In overall, these findings shows that the neutral state of the Au center of Au/TiO_2 (110) cannot be reliable to explain the experimental findings on selective CO oxidation [17].

Recently we have shown that water assisted vacancy formation on TiO_2 (110) can resolve experimental TPD observation on triply exceeding concentration of O_2 per vacancy site [6]. Note that the neutral oxygen vacancy is accompanied here with additional hydroxyl groups located nearby on the two Ti_{5C} sites from both sides of the vacancy. One may bolster this idea also for selective oxidation of CO on Au/TiO_2 (110) where water presence also enhances the target reaction [17]. In this case, either one or both O–H groups is replaced by O–Au groups, where Au center(s) becomes nominally in plus one oxidation state(s) (Fig. 2). Note Au has two-fold coordination with bond lengths equal to 2.054 and 2.224 Å, respectively. Thus, Au mobility is low and as consequence of this, the surface would have an isolated Au centers on TiO_2 (110) surface. Now it is easy to explain the selective oxidation of CO using this model cluster. For molecular oxygen, bonding with the vacancy site is energetically preferable than its adsorption on an Au site. Conversely, CO adsorbs on an Au center of Au/TiO_2 (110) which is energetically much more profitable than its interaction with the oxygen vacancy site. The selective oxidation takes then place through a Langmuir–Hinshelwood mechanism.

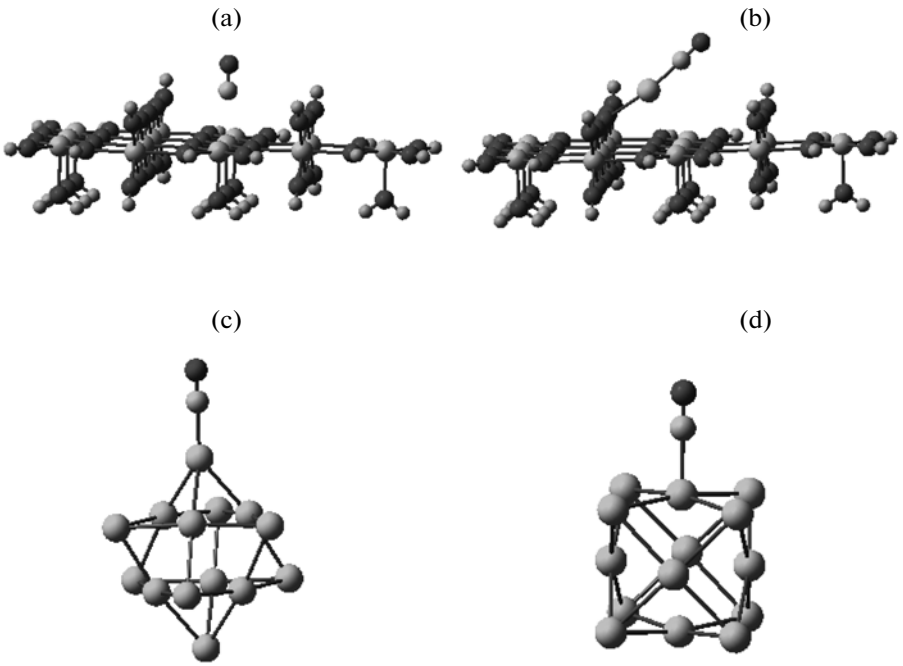

Fig. 1. The ball and stick optimized adsorption complexes of CO on Ti_{5c} (a) and on Au site (b) of Au/TiO_2 (110) as well as on Au_{3c} (c) and Au_{4c} (d) sites of Au_{14} nanocluster.

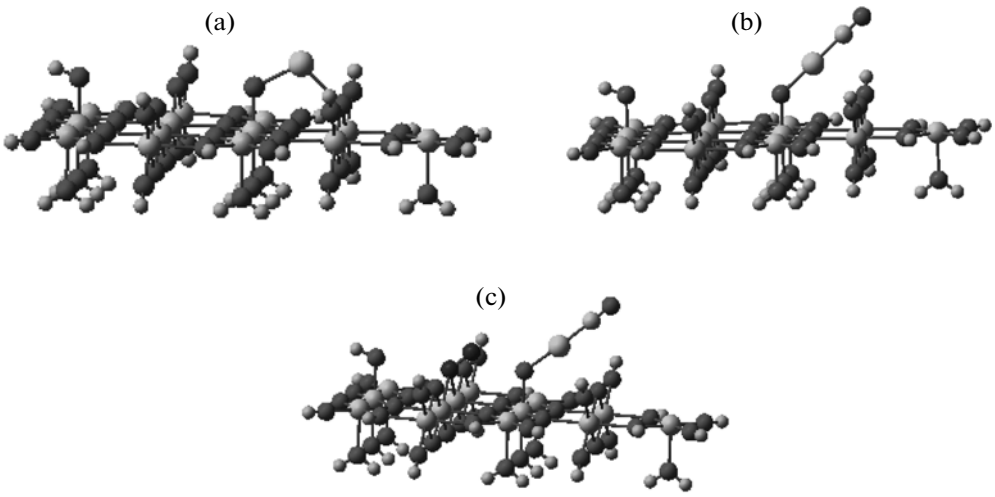

Fig. 2. The ball and stick optimized structure for Au stabilized on vacancy containing TiO_2 (110) surface (a), its adsorption complex with CO (b) as well as with both CO and molecular oxygen (c).

Carbon or Nitrogen Doped TiO_2

Titanium dioxide, either as rutile or anatase, is well-known photocatalyst for the removal of pollutant NO and other nitrogen oxides, purification of air and waste waters, in degrading organics and inorganic pollutants in environmental catalysis, because of its high resistance for photocorrosion, biologically and chemically inertness, relatively inexpensive prices, non-toxicity, high thermal and photostability, etc. [18, 19]. However, it can only adsorb about 3–5% of the solar beams (UV fraction only) reached the earth, leaving enormous part of the solar energy ineffective [19–22]. Thus attempts to increase the above threshold are highly attractive and important. In this case, one deals with doping of TiO_2 by organic dye molecules, noble metals (Au, Pt, Ir), by transition metal (V, Cr) ions, non-metals (C, N, F, S) as well as by inclusion of mixture of both metals and non-metals (like $LaTiO_2N$) [18–23]. The incorporation of non-metals into the

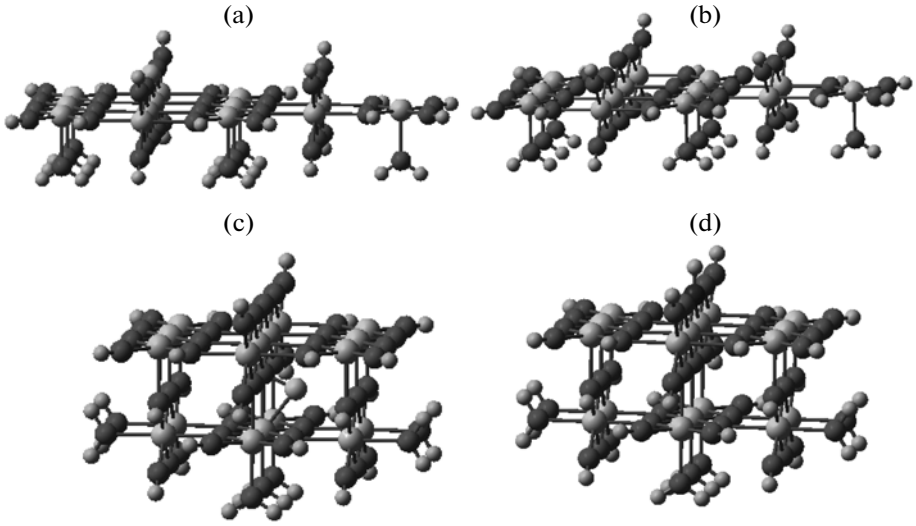

Fig. 3. The ball and stick optimized structures for substitution C doping on the precursor O site (a) and Ti_{6c} (b) of one-layer TiO_2 (110) as well as the most energetically feasible structures for interstitial C (c) and N-doping (d).

lattice structure of titania is just one of the possible ways to decrease the large band gap of titania catalyst. Below we would like to consider just two cases of nonmetal doping on rutile TiO_2 (110).

First, carbon doping is considered using one-layer and two-layer molecular clusters that mimic rutile TiO_2 (110). It was found that the substitution of the Ti_{5c} (or Ti_{6c}) by C_{5c} (or C_{6c}) is highly endothermic process and accompanies by consuming more than 280 kcal/mol extra energy. This means that the substitution of Ti^{4+} by C^{4+} cannot proceed and it should be simply ruled out. A simple reason for that is just structural dissimilarity that arise from large difference in ionic radii of these ions: an average Ti–O bond distance in TiO_2 is ca. 2.1 Å while that for a single C–O bond is ca. 1.4 Å, much smaller than the Ti–O one. Conversely, substitution of protruded oxygen by carbon is energetically slightly feasible but still endothermic process (needs ca. 40 kcal/mol extra energy). Substitution at deep bulk position of oxygen by carbon is attractive but still energetically costly process and it is less stable. Among the different structures considered, the only possibility to get reliable catalyst here is the incorporation of carbon at the interstitial position (see, Fig. 3) that needs only ca. 5 kcal/mol extra energy. In this structure, the HOMO–LUMO band gap amounts only 0.0485 atomic units (a.u.), a substantial decrease from the value of 0.0898 a.u. for pure TiO_2.

In the case of substitution nitrogen doping, one must take into account charge imbalance that arises from the replacement of O^{2-} by N^{3-}: either three O^{2-} should be replaced by two N^{3-} (formation of oxygen vacancy) or additional H^+ should be added for charge neutrality. Evidently, the former process with double N-substitution and with oxygen vacancy formation was found to be energetically too costly while the formation of the surface N–H fragment on the precursor protruded oxygen atom site is energetically feasible for the latter process among other possible structures. Also, the structure with N–H group leads to a feasible decrease in the band gap (i.e., decrease in the HOMO–LUMO energy difference from 0.0898 a.u. for pure TiO_2 to 0.0769 a.u. for N-doped TiO_2) that shifts the excitations into longer wavelengths [19, 20, 23].

The presented results of DFT calculations for the selected representative systems show the ultimate importance of proper modeling of structure and chemical activity of transition metal and metal oxide catalysts within the well-known cluster approach. Not only active site structures but also intrinsic support structures become highly important for the proper description of available experimental findings.

It was shown that the neutral state of the Au center of Au/TiO_2 (110) cannot be reliable to explain the experimental findings on selective CO oxidation. Instead, the strongly bound state of Au (with formal oxidation state equal to plus one) on water-assisted and vacancy containing TiO_2 (110) can explain this phenomenon. Here binding of O_2 with the vacancy site is energetically preferable than its adsorption on an Au site. Conversely, CO adsorbs on an Au center of Au/TiO_2 (110) which is energetically much more profitable than its interaction with the oxygen vacancy site.

Carbon and nitrogen doping on TiO_2 (110) leads to two different structures. Energetically most profitable is that where carbon occupies an interstitial position in deep bulk while nitrogen replaces the protruded oxygen atom and forms a surface N–H group.

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