Computational insights into crystal plane dependence of thermal and photoresponse of pure and palladium-substituted titania

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ABSTRACT

Shape effects have caught attention of researchers worldwide with attempts to synthesize catalytic materials with well-defined exposed facets to obtain high activity being the central idea. In this study, we have dedicated our attention to develop structure-property relationships in TiO_2-based solid solutions with particular reference to net oxygen activation. Density functional theory calculations were implemented on (001) and (100) planes of anatase TiO_2 with anionic vacancy defects ($TiO_{2-\delta}$), cationic substitution ($Ti_{1-x}Pd_xO_2$) and solid solutions with anionic vacancy defects ($Ti_{1-x}Pd_xO_{2-\delta}$). (100) plane was found to show higher oxygen activation with smaller rigidity towards surface relaxations. Vacancy formation energy was found to decrease with an introduction of cationic defects with the net oxygen activation reaching up to 26% in $Ti_{1-x}Pd_xO_2$. Different vacancy sites on the two planes were observed to show different oxygen activations. Formation of surface hydroxyl groups, envisaged as dissociative adsorption of H_2 over oxidized catalyst or dissociative adsorption of H_2O over reduced catalyst, was found to be influenced by cation substitution with the stability of surface hydroxyls being compromised by substitution. Synergism of surface hydroxyl groups and lattice oxygen activation for the water-gas shift reaction was identified. Photocatalytic response was found to be higher for $TiO_{2-\delta}$ catalysts as it narrowed the band gap via formation of mid-gap states and shifting the valence band maximum closer to the conduction band minimum.

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1. Introduction

TiO$_2$ has been extensively studied during the last few decades in heterogeneous catalysis due to its wide application window. It finds application as a photocatalyst, high temperature gas sensing material and selective NO_x reduction catalyst [1–9]. High thermal stability, non-toxicity and high reactivity of TiO_2 makes it an important heterogeneous catalyst. TiO_2 occurs in nature in three phases namely, anatase, rutile and brookite. Rutile is the most thermodynamically stable polymorph of TiO_2 at standard pressure and a temperature range of 300–1000 K [10]. It is formed from coarsening of anatase phase at moderate temperatures [11]. The crystallite size of rutile TiO_2 depends on the degree of coarsening and is readily available in the form of single crystals. Albeit, the anatase phase is thermodynamically lesser stable than the rutile phase, it is widely used catalytic material as well as a support material in several processes due to its highly reactive nature [1,5]. Both rutile and anatase phases of TiO_2 have been widely studied previously for catalytic conversion of CO to CO_2 [9,12], photocatalytic

reduction of CO_2 with water vapor [13], formation of nitrates by oxidation of NO_x, formaldehyde adsorption [14,15] and photocatalytic degradation of organics [16–18].

In recent years, metal ion doped TiO_2 nanoparticles have proven to be prominent catalysts and photocatalysts in systems where metal-support interactions play a key role. Improved photoanode performance of 12.1% for Sn-doped TiO_2 dye-sensitized solar cells synthesized via hydrothermal method with 8.31% of optimium efficiency for 0.5 mol% Sn doping was reported by Duan et al. [19]. Increased photocatalytic activity of W-N co-doped TiO_2 was demonstrated by Choi et al. [20] when W was doped for Ti and N was doped for O, respectively. The increased photocatalytic activity of W-N co-doped TiO_2 was due to the band gap narrowing between the valence band maximum (VBM) and conduction band minimum (CBM). Various transition metal ion substituted solid solutions of TiO_2 with enhanced catalytic activities have been reported by Hegde and co-workers in the recent past [21–25]. A series of studies conducted by Roy et al. [22–25] on substitutional solid solutions of TiO_2 with several metal ions including Pd^{2+}, Pt^{2+}, Rh^{3+}, Ru^{4+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} and Cu^{2+} has established the superiority of metal ion doped TiO_2 over the conventional metal nanoparticle impregnated catalysts. Pd^{2+} ion substituted solid solution

($Ti_{0.99}Pd_{0.01}O_{1.99}$) has been reported to show higher activity for CO and hydrocarbon oxidation reactions than Pd nanoparticle-impregnated TiO_2. Similarly, NO_x reduction has been shown to take place over such solid solutions with selectivity towards N_2 reaching nearly 100% at 350 °C [22]. Among various metal ion substituted TiO_2 catalysts, Pd^{2+}-substituted TiO_2 has been reported to show superior catalytic activities for NO_x reduction, CO oxidation and hydrocarbon oxidation [22,23,26]. Further, solid solution formation with Pd^{2+}-substituted TiO_2 is easier and cost of synthesis is lesser when compared to platinum and other metal ion substitution [26–31]. This makes the understanding of structure–property relationships in TiO_2-based solid solutions important. In this study, we attempt to develop insights into the activity of Pd^{2+}-doped TiO_2 via a thorough structural analysis developed using density functional theory (DFT).

In addition to the crystalline phases [11,32] and size of the crystallites [10], catalytic activity and photoresponse of a material also depends on the exposed crystal planes [1,2,33,34]. Different planes have different atomic/ionic arrangements [33–35] and, hence, they exhibit different reactivities due to differences in surface active sites and the coordination environment. Therefore, it is important to synthesize a metal oxide nanoparticle with reactive crystal plane exposed for high catalytic and photocatalytic activity. (001) and (101) planes have been extensively studied for the anatase phase [7–9] whereas (011) plane has been studied in case of the rutile phase [36,37]. Roy et al. [38] have reported that TiO_2 nanorods with (100)/(010) facets exhibited the highest photocatalytic activity when compared to (001) and (101) facets due to their unique surface chemistry. According to their reports, the photocatalytic activities were found to be higher for a combination of (101), (100) and (001) planes when compared to (101), (100) and (001) planes alone. Enhanced the activities of co-exposed (001)-(101) crystal planes of TiO_2 with oxygen vacancies towards the photoreduction of CO_2 to CO under visible light compared to the individual planes of (001) and (101) was demonstrated by Liu et al. [39]. The increase in photocatalytic activity of co-exposed (001)-(101) planes was due to higher exposure of active sites, significant electrons transfer between the two facets and the formation of mid-gap states of Ti^{3+} in the band gap of TiO_2. Liu et al. [35] have synthesized Au/TiO_2 catalysts with several crystal planes exposed on anatase TiO_2 for the deposition of Au and have tested the catalytic properties of Au/TiO_2 for CO oxidation reaction over (001), (100) and (101) planes at various temperatures. The authors reported higher catalytic activities of Au/TiO_2 for the CO oxidation over (100) and (101) planes when compared to (001) plane. Wanbayor and Ruangpornvisuti [40], reported the adsorption of CO, H_2, N_2O, NH_3 and CH_4 and co-adsorption of CO/H_2, CO/N_2O and N_2O/H_2 over anatase TiO_2 (001) and (101) surfaces. Adsorption of NH_3 was energetically more favoured over (001) and (101) surfaces of TiO_2 (−26.6 and −24.3 kcal/mol) when compared to other gases. Adsorption of CO (−9.7 and −6.8 kcal/mol) was also observed on (001) and (101) surfaces where as in case of H_2 adsorption, (001) was the only favorable plane for weak adsorption. Guo et al. [41] investigated the photocatalytic dissociation of methanol and H_2O on the surface of (110) plane of TiO_2. They reported a stepwise mechanism of dissociation of methanol and H_2O on TiO_2. Mino et al. [42] studied CO_2 adsorption and formation of carbonate species over the anatase TiO_2(001) and (101) planes. (001) plane was found to be more active to adsorb CO_2 and was more reactive to form surface carbonate species when compared to the (101) plane. Appreciating the importance of the identity of exposed crystal planes on the catalytic activity and photoresponse, we have analyzed the activities of different low index face planes in TiO_2-based solid solutions. As highlighted in the foregoing discussion, cationic substitution imparts vital

characteristics which alter the thermal and photoresponse of TiO_2, as highlighted in this paper.

In heterogeneous catalysis, metal-support interactions have a significant impact on the catalytic activity and photoresponse of various adsorption and surface reaction steps. Metal-support interactions depend on the type of metal ions doped, oxidation state and the nature of the metal oxide surface [35,43]. The present work focuses on DFT analysis of anatase TiO_2 (001) and (100) planes. The effects of oxygen vacancy formation, Pd ion substitution and H_2 adsorption on the stabilities and catalytic activites of anatase TiO_2 (001) and (100) surfaces were investigated. Various unique sites were identified for the creation of oxygen vacancies on the two surfaces and the effect of oxygen vacancy on bond length distribution was studied. Further, the synergistic effect of vacancy formation along with Pd ion substitution and H_2 adsorption on the surface was also examined for the two surfaces. DFT calculations were performed for bulk and surface in order to compare the thermodynamic stabilities and the feasibilities of anion vacancy and foreign metal ion substitution in anatase TiO_2 (001) and (100) planes on the surface with the bulk. Photocatalytic response was also studied in this work for TiO_2, $TiO_{2-\delta}$, $Ti_{1-x}Pd_xO_2$ and $Ti_{1-x}Pd_xO_{2-\delta}$ catalysts from thorough band structure analyses. The study provides insights into the reactivities and metal-support synergism on different crystal planes of TiO_2 explaining the reason for different activities and providing a motivation and rationale to the experimentalists to synthesize nanocrystalline TiO_2 with a desired crystal plane exposed.

2. Computational details

DFT was used to obtain all equilibrium structures reported in this study. Structural optimizations were performed using Quantum Espresso package [44]. Plane wave basis sets and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional with ultrasoft pseudopotentials [45] were employed in the PWscf code implemented in the Quantum Espresso package. A kinetic energy cutoff for the plane wave expansion of the wave function was set to 40 Ry [46] and the Fourier expansion of charge density was set to 400 Ry. A (3×3) supercell of anatase TiO_2 was chosen as the molecular model, as shown in Fig. 1, comprising of total 108 atoms in which 36 Ti atoms and 72 oxygen atoms leading to 36 unit cells of TiO_2 were present. TiO_2 periodic slab hence developed consisted of total 12 atomic layers, out of which 8 were oxygen layers and remaining 4 were Ti layers. The Brillouin zone integrations were sampled by a $5 \times 5 \times 1$ Monkhorst-Pack k-point mesh.

TiO_2 used in the rest of the text refers to anatase TiO_2. Bulk calculations of TiO_2, $TiO_{2-\delta}$, $Ti_{1-x}Pd_xO_2$ and $Ti_{1-x}Pd_xO_{2-\delta}$ were performed by relaxing all the atoms present in the aforementioned supercell. Surface calculations of (001) plane were carried out by relaxing top Ti layer and corresponding two oxygen layers while the remaining nine layers were kept frozen at their crystallographic coordinates (Fig. 1). Atoms colored with cyan represent the frozen atoms and the layers corresponding to these are denoted as frozen layers. The layers with brown and red colored atoms represent the relaxed ones for surface optimizations. For (100) plane, top two Ti layers and corresponding four oxygen layers were relaxed while the remaining six layers were kept frozen. Vacuum of 10 Å was applied to the unit cell in order to eliminate the interaction of atoms between the adjacent surface slabs during geometry optimizations. The convergence criteria based on the total energy difference were set to 1×10^{-4} a.u. between the two consecutive optimization steps and 1×10^{-8} a.u. for self-consistency.