Reduction of HCHO with OH⁻ on Pt loading Anatase TiO₂ (001)

Surface: A DFT Calculation

Zongbao Li^{1,3,*}, Xia Wang¹, Lichao Jia², Xiaobo Xing³

¹ School of Material and Chemical Engineering, Tongren University, Guizhou 554300, China

² School of Materials Science and Engineering, State Key Lab of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

³ South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou, Guangdong, 510631, China

*Corresponding Author, Tel: +86 08565230914 E-mail address: zongbaoli1982@163.com.

Abstract:

Using the first principle density function theory, based on the stabilized Pt/TiO₂ (001) structure, the adsorptions and reactions of the substances that may be involved in the reactions have been calculated. The most possible reaction path and reaction mechanism are obtained by the analysis of the adsorption energies and formation energies in reaction. The results indicate that the OH⁻ plays an important role in the HCHO degradation process. The reaction can be expressed as $\text{HCHO} + 2\text{OH}^- \rightarrow \text{HCOOH} + \text{H}_2\text{O}$ and $\text{HCOOH} + 2\text{OH}^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, which is carried out continuously with a large heat release.

Keywords: Pt/TiO₂ (001); HCOOH; DFT; Formation energy ; photocatalytic processes;

1 Introduction

Room temperature catalytic oxidation decomposition of formaldehyde (HCHO) to H₂O and CO₂ has drawn much attentions due to the environmental friendly reaction conditions.^[1-4] For the appropriate band gap to visible light, TiO₂ is the semiconductor that most widely studied and used in the photocatalytic processes for the higher degradation rates to HCHO. Hence, many attempts have been conducted to improve the photocatalytic performance for HCHO degradation by controlling geometry, optimizing particle size, and loading metal co-catalysts of TiO₂. Through the methods, noble metal atoms (Ag^[5], Au^[6], and Pt^[7]) or particles supported on TiO₂ surfaces are scientifically and technologically important because of their excellent catalytic

activity.^[8]

To improve the microstructural and chemical properties, some synthetic routes have been reported about Pt loading on TiO₂ with a large surface area and nanometric sizes.^[9-16] Based on the strong photocatalytic activity under UV and visible light irradiation, Pt/TiO₂ is widely used in the catalytic degradation of organic compounds. For the HCHO degradation, Fornari^[13] revealed that the hydrogen production rate increased with the Pt deposited increasing on the TiO₂ surface. It was observed that the presence of Pt on TiO₂ surface enhanced the photodegradation efficiency of patent blue V dye.^[14] For the organic pollutant of C₂H₄, C₂H₆, C₃H₆ and C₃H₈, it was found that the significantly improved photoactivity of Pt/TiO₂ could be reached even by loading a very small amount of Pt.^[17] Recently, for significant role of Pt in the decomposition, the experimental results demonstrated that TiO₂ surface loaded with Pt nanoparticles could greatly enhance the photocatalytic activity for HCHO degradation.^[18-21] In spite of the experimental results, there is no report theoretically studying the facts and specific reaction mechanism at present. In addition, for the stronger photocatalytic activity of anatase than rutile^[22], the natural crystallographic anatase (001) surface is the most often considered for catalytic applications.^[23]

In this study, we investigate the effects of a Pt atom on anatase TiO₂ (001) surface, relative stability of HCHO and OH⁻ chemisorption over H₂O and CO₂ physisorption. As role of the electron reservoir^[24-25], the adsorptions and reactions of HCHO and OH⁻ are calculated on Pt/TiO₂ (001). We restrict our investigation to the energetics of initial and final states, and any intermediate states are discussed.

2 Theoretical Calculations

Based on the density function theory (DFT), the optimized lattice structures and electronic structures are calculated by using the Vienna ab initio simulation package (VASP)^[26-27]. The spin-polarized with the GGA+PBE function are performed to calculate the ground states and energies.^[28-29] The cutoff energy of 400eV is used in the plane-wave basis set expansion. Monkhorst-Pack k-point sets of 4×4×4 are adopted for the anatase TiO₂. The stoichiometric slabs with 3 TiO₂-layers are adopted and periodic boundary conditions are applied in all three dimensions. With keeping

the lowest TiO₂ layers fixed, the slab is sandwiched by vacuum layers with a thickness of 15 Å while the convergence criteria force is set to 0.01 eV/Å for all surface calculations.

For the interstitial atom absorbing on the surface, the adsorption energies (E_{ads}) are defined as:

$$E_{ads} = E_{total} - E_{substrate} - E_{origin} \quad (1)$$

where E_{total} , $E_{substrate}$ and E_{origin} represent the total energies of adsorption configuration, substrate configuration, and original absorbed species. For the reactions, the formation energies (E_{form}) are calculated according to

$$E_{form} = E_{total} - E_{stable} - E_{dissociation} \quad (2)$$

where $E_{dissociation}$ and E_{stable} are the energies of the dissociated molecule and residual stable structure.

3 Results and discussion

Based on the former experimental results, for the purpose to obtain the degradation reaction mechanism and further guide for experimental design, the adsorptions of HCHO, OH⁻ and O₂ on different surface sites are considered by using the first principles calculations. With the lowest adsorption energy, the optimized structures are obtained for the three adsorbates. Before studying the adsorptions on the surface, the Pt modified anatase TiO₂ (001) surface at different sites are optimized^[24] and the prefect case is shown in Fig. 1. In the optimized structure, Pt binds with both Ti and O atoms at the bridge position, and forms a 52.7° Ti-Pt-O angle with the bonds of Pt-Ti = 2.62 Å and Pt-O = 2.05 Å, which is good agreement with the former result (∠ Ti-Pt-O = 51°, Pt-Ti = 2.55 Å & Pt-O = 1.97 Å).^[24]

Based on the stabilized TiO₂ (001) configuration, the adsorption of OH⁻ ions, HCHO, and O₂ molecules on different surface sites are calculated, and the stabilized structures are shown in Fig. 2. The adsorption energies and geometrical parameters are listed in Table 1. From Fig. 2 and Table 1, the following results are found: (1) O₂

and HCHO molecules prefer to absorb on Pt site while OH⁻ to the nearest Ti site. (2) A triangle forms with the oxygen absorbing while OH⁻ and HCHO perpendicular to the surface. (3) The adsorption of three adsorbates on the surface are all weak, keeping the original structures and with a long bond lengths between the adatoms to the substrate. (4) The adsorptions of three molecules are exothermic reactions for the negative adsorption energies values. (5) The adsorption of OH⁻ on Pt/TiO₂ (001) has the priority for the highest adsorption energy (0.1182eV), and next to be oxygen and HCHO with the energies as 0.0386 and 0.0363eV.

For the alkaline conditions of the experiment carried out, a large number of OH⁻ ions absorb on the surface and convenient in the photocatalytic reaction. As the main bodies of the reaction and for the similar adsorption energies, in the following calculations, we give out the possible reaction paths for HCHO and O₂ adsorption and reaction based on the stabilized adsorption structures of OH⁻ on Pt/TiO₂ (001) surface (marked as OH-Pt/TiO₂ (001)). As the intermediate step in the process of the HCHO degradation, two possible intermediate reactions of the three substances are O₂+OH-Pt/TiO₂ (001) and HCHO+OH-Pt/TiO₂ (001) cases. Base on the two co-absorbing models, the optimized structures and formation energies are calculated as shown in Fig. 3 and Table 2. From the formation energies comparisons of the two reactants in Table 2, the results are as follow as: (1) The two cases of HCHO+O₂-Pt/TiO₂ (001) and OH+HCHO-Pt/TiO₂ (001) are the most likely reaction process with the highest release energy of 0.0473eV and 0.05eV. (2) On the stabilized OH-Pt/TiO₂ (001), the adsorptions of HCHO and O₂ become weaker for the early hydroxyl adsorption, which inhibiting the occurrence of the chemical reactions. (3) The negative values of the formation energies reveal the exothermic reaction with Pt loading, which is good agreement with the experimental reaction essentials^[24]. (4) For the large energies release, the more stable chemical substances generate than that of the previous adsorption in the above two cases with the appropriate bonding. Figure 3 shows that, for the adsorption of HCHO on the stabilized O₂-Pt/TiO₂ (001) surface, a new bond forms between oxygen and HCHO. In the case of OH+HCHO-Pt/TiO₂ (001), a water molecular and a new chemical group appear because of the lowest

formation energy.

Nevertheless, for the above two possible reaction paths, the final complete chemical reaction of HCHO degeneration is energetically preferred and the proposed potential energies are calculated. The reaction processes can constructively occur and catalytic oxidation of the HCHO molecule on the Pt/TiO₂ (001) in the alkaline environment with different ways is proposed in Fig. 4. For the two possible reactions occur, Fig. 4 shows that there are two chemical intermediates of formic acid (HCOOH) and over formic acid (HCOOOH) with the similar formation energies, while the reaction of HCOOOH cannot continue due to the non cyclic reaction process (shown in blue color in Fig. 4). The real possible reaction path of the experiment ^[20-21] can be noted as:

The results show that the OH⁻ acts an important role in the reactions and the sufficient alkaline environment makes the positive responses of the HCHO photocatalytic degradation. With the adsorption of the chemical substances on the surface, the entire process is energetically downhill with the larger heat release (0.2134 eV in reaction RI) due to chemical reaction with less reactive substances. And then, with the excess OH⁻ ions, the HCOOH losses an H⁺ and then reacts with OH⁻ to produce CO₂ and H₂O. With the H₂O removing in the experiment, more OH⁻ is introduced on the surface. When the excess OH⁻ participates in the reaction with H₂O dissociation, the degradation efficiency of HCHO tends to steadiness, which is in good agreement with the experimental results ^[15, 20-21]. Therefore, it is concluded that the primary role of the Pt loading surface can provide electrons from the surface oxygen to Pt, and then induce the reactions between surface adsorptions. In the above reaction, the photocatalytic oxidation process of formaldehyde can be accomplished without oxygen.

4. Conclusions

Base on the stabilized Pt loading TiO₂ (001) surface, the adsorptions and the reactions of HCHO, OH⁻, and oxygen are calculated by the DFT. Meanwhile, the

adsorption energies and formation energies are calculated. The calculation results clearly show that the OH⁻ prefers to absorb on the surface Ti site with high adsorption energy while the HCHO and O₂ are absorb on Pt site. For the degeneration of HCHO, the OH⁻ plays an important role in the reaction paths, as well as the sufficient alkaline environment makes the positive responses of the HCHO photocatalytic degradation. With the large heat releasing, the reaction way of HCHO can be expressed as $\text{HCHO} + 2\text{OH}^- \rightarrow \text{HCOOH} + \text{H}_2\text{O}$ & $\text{HCOOH} + 2\text{OH}^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$. The calculation results give out the clear picture of the degradation mechanism of HCHO, which are good agreement with the experiment results.

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Figure Captions:

Fig. 1 The side view of the optimized structure of Pt loading on $\text{TiO}_2(001)$ surface. The steel blue sphere stands for Pt atom, the red one for O atoms and the grey one for Ti atoms.

Fig. 2 The optimized stabilized structures of O_2 , OH^- , and HCHO adsorb on the Pt/ $\text{TiO}_2(001)$ surface. (a) O_2 absorbs on the Pt site and forms a stable triangular structure; (b) with OH^- adsorptions, the O prefers to absorb on Ti than Pt atom while a stable chemisorption with a Pt-O bonding formed for HCHO adsorption.

Fig. 2 The optimized structures of two substances reaction on the Pt loading surface: $\text{HCHO} + \text{O}_2\text{-Pt/TiO}_2(001)$ (left) and $\text{OH} + \text{HCHO-Pt/TiO}_2(001)$ (right). The atoms in TiO_2 cell turn smaller in order to highlight the atoms in the surface reaction.

Fig. 4 Reaction diagram for catalytic oxidation of the HCHO molecule on the Pt/ $\text{TiO}_2(001)$ in the alkaline environment with different ways. The plus(+) and minus (-) signs represent the adsorption and desorption of the molecules in reactions, respectively. The one marked in red is the real reaction path of the experiment while the blue cannot continue due to the non cyclic reaction process.

Table 1 The adsorption energies (E_{ads}) and bond length of HCHO, OH⁻, and O₂ absorb on the Pt/TiO₂(001) surface

	HCHO			OH-		O ₂	
	Pt site	Ti _s site	O _s site	Ti _s site	O _s site	Pt site	Ti _s
E_{ads} (eV)	-0.0363	-0.0361	-0.0266	-0.1182	-0.0934	-0.0386	-0.0175
Bond length (Å)	Pt-O			O _{HO} -O _s	O-Pt	Pt-O	
	2.210	2.232	2.212	2.028	2.244	2.133	2.107

Table 2 The optimized lattice structures, formation energies (eV), and bond lengths (Å) of possible reactions of the two substances

Reacting substances			E_{form}	Bond length		
				Pt-O _{HCHO}		
OH- & HCHO	HCHO+OH-Pt/TiO ₂ (001) [†]		-0.0194	--		
	HCHO-Pt	OH-Ti [*]	-0.0091	--		
OH- & O ₂			E_{form}	Bond length		
				Pt-O _{oxygen}	Pt-O _s	
	O ₂ +OH-Pt/TiO ₂ (001)		-0.0095	2.245	2.175/2.201	
	OH-Ti	O ₂ -Pt	-0.0341	2.066	2.263/2.255	
O ₂ & HCHO			E_{form}	Bond length		
				Pt-O _{HCHO}	Pt-O _s	Pt-O _{oxygen}
	HCHO+O ₂ -Pt/TiO ₂ (001)		-0.0473	2.187	2.178/2.207	2.056
	O ₂ -Ti	HCHO-Pt	-0.0178	2.211	2.127	2.138
OH- & HCHO			E_{form}	Bond length		
				Pt-O _{HCHO}	Pt-O _s	Ti-O _{OH}
	OH+HCHO-Pt/TiO ₂ (001)		-0.05	2.231	2.213	--
	OH-Ti	HCHO-Pt	-0.0177	2.217	2.238	2.033

* HCHO-Pt and OH-Ti: denote a HCHO molecular adsorbing on the Pt site while a OH on Ti site on the Pt-TiO₂(001) surface without reaction.

† HCHO+OH-Pt/TiO₂(001): denotes HCHO molecular adsorbs and reacts with OH- on the stable structure of Pt/TiO₂(001).

The other similar cases are characterized by the same stoichiometric method in the table.

Figure(s)

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