



Adsorption of Cl₂ on pristine and Pd doped TiO₂ clusters: A transition state theory study

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ABSTRACT

The chlorine (Cl₂) sensitivity of pristine and Pd-doped titanium dioxide (TiO₂) clusters is investigated. Cl₂ gas and its compounds are known for their wide use in industry. However, the high toxicity of the gas forces its users to use sensors to detect its probable leakage. TiO₂ is one of the most stable oxides. The surface decoration or surface doping of TiO₂ with Pd or other catalysts increases its sensitivity to Cl₂, reduces response time, and reduces the temperature needed to best sensitivity to the gas. In the present work, transition state theory is used to simulate the reaction of Cl₂ with pristine and Pd-doped TiO₂ clusters. The three steps of physisorption, transition state, and chemisorption are described. A comparison of experimental and theoretical results assists the temperature-dependent Gibbs activation energy because of activation entropy. The comparison includes temperature-dependent sensitivity, concentration-dependent sensitivity, and response and recovery times. The evaluation of thermodynamic quantities, i.e., Gibbs free energy and entropy, are needed to perform present calculations using density functional theory. The present work is one of the rare applications of transition state theory in gas sensing.

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Keywords: TiO₂ Cluster; Cl₂ Gas; Transition State; Gas Sensor; Density Functional Theory.

1. Introduction

The number of accidents connected to chlorine leakage is relatively high compared with other gases, which induces more studies on the subject^[1-3]. Cl₂ and its compounds are also known as chemical war weapons^[4]. These factors encourage the building and improvements of Cl₂ gas sensors. Studies on using several materials for detecting Cl₂ is an ongoing contemporary subject. The materials that are usually investigated as a gas sensor for Cl₂ include ZnO^[5], In₂O₃^[6], SnO₂^[7], etc. These materials' surface doping or decoration with noble metals such as Pd, Pt, and Au increases their gas sensitivity^[8-11].

Arrhenius equations are applied to gas sensing in a few attempts^[12-14]. The same is true for the transition state theory^[8,15,16]. The results show that the calculated sensitivity at different temperatures may differ from the experiment^[12]. This deficiency is addressed in the present work by applying entropy-dependent variable activation energy, as will be discussed in the

theory section.

The current work theoretically investigates pristine and Pd-doped TiO₂ clusters as a Cl₂ gas sensor. Experimental data on pristine and Pd-doped TiO₂ sensitivity to Cl₂ gas are available in the literature^[17]. The three steps of physisorption, transition state, and chemisorption are described. A comparison of theoretical and available empirical results is conducted. The comparison includes sensitivity, response time, recovery time, and the effect of Cl₂ concentration. The present work is one of the rare applications of transition state theory in gas sensing.

2. Theory

Density functional theory (DFT) is employed to evaluate the reaction rate of chlorine with pristine and Pd-doped TiO₂ clusters. The B3LYP/6-311G** level and basis are used to evaluate and optimize the different structures encountered in this research. The B3LYP version of DFT is one of the most successful methods applied in gas sensing applications^[12,18]. The kind of basis set employed in a particular DFT calculation depends on the number of atoms and their atomic number. 6-311G** is suitable for present calculations containing more than 30 atoms, including Ti

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and O. Heavy metals like Pd are usually described using effective core potential states. GD3BJ dispersion corrections are added due to their importance in gas sensing^[12]. Gaussian 09 software is used to complete computations in the present work^[19].

TiO₂ clusters on the surface of TiO₂ nanoscale particles usually take pyramid shapes^[20,21]. These pyramids are shown in Fig. 1a for the cluster Ti₁₀O₂₀. The same should be valid for the Pd doped cluster as in Fig. 1b for the cluster Ti₉PdO₁₉. The doped TiO₂ cluster has less oxygen because, unlike Ti, the oxidation state of Pd is two, not four. The Ti₁₀O₂₀ cluster is suggested in reference^[22]. The weight ratio of titanium, oxygen, and palladium is as close as possible to experimental results considering the computational efforts needed to perform calculations. Interpolation of the Gibbs free energy between 0 Pd content in TiO₂ and 0.126 weight ratio in Ti₉PdO₁₉ is used to obtain the experimental Gibbs free energy value of 0.0601 Pb weight ratio^[17]. The general form for the reaction rate equation of TiO₂ cluster with Cl₂ can be given by the equations^[23–25]:

$$\frac{d[\text{Ti}_{10}\text{O}_{20}]}{dt} = -[\text{Ti}_{10}\text{O}_{20}] [\text{Cl}_2]_e k(T), \quad (1)$$

$$k(T) = A T^m \exp\left(\frac{-\Delta G^\ddagger}{k_B T}\right). \quad (2)$$

In the equations above, [Ti₁₀O₂₀] and [Cl₂]_e is the concentration of Ti₁₀O₂₀ clusters and effective Cl₂ gas molecules, respectively. The use of effective Cl₂ gas molecules concentration will be discussed shortly. k(T) is the temperature part of the rate of reaction equation. A is a pre-exponential factor (sometimes called a frequency factor). A is usually a fitting constant that depends on the sensor material's structure, dimensions, and geometry. ΔG[‡] is the Gibbs free energy of activation in transition state theory or activation energy in the Arrhenius equation. Finally, m equals zero in Arrhenius equation formalism or one in transition state theory. Both Arrhenius and transition state theory formalisms have been tried to apply Eqs. (1,2) to simulate gas reactions in sensors^[8,12]. However, the results of experiments show that the reaction rate is sometimes different than the theory in different temperatures^[12].

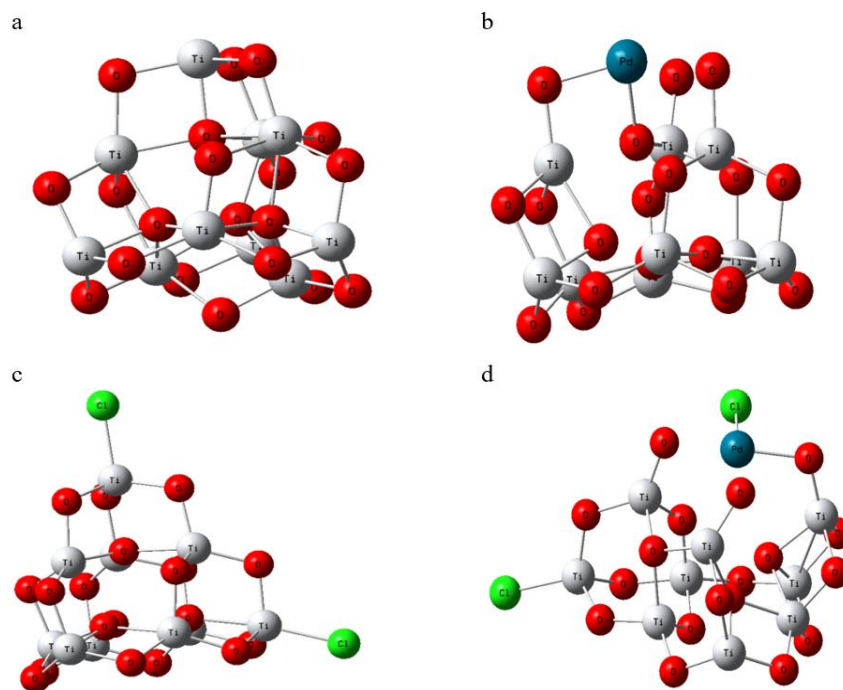
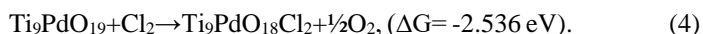
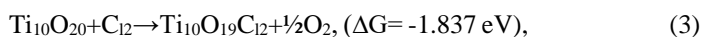


Figure 1: (a) The optimized Ti₁₀O₂₀ cluster [22]; (b) Pd doped cluster Ti₉PdO₁₉; (c) titanium oxide cluster after chemisorption reaction with Cl₂; (d) Pd doped cluster after chemisorption reaction with Cl₂.

TiO₂ clusters (Ti₁₀O₂₀) or its Pd doped version (Ti₉PdO₁₉) reaction with Cl₂ (chemisorption) is supposed to replace oxygen atoms in TiO₂ as in the reactions (all reaction energies are in normal temperature and pressure (25 °C and 1 bar) unless otherwise mentioned):



In the equations above, ΔG is the free energy of the reaction. The enthalpy (ΔH) of the reaction of the two above equations are -

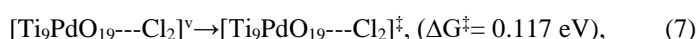
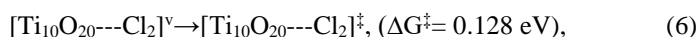
1.924 and -2.657 eV, respectively. We can see from the above equations that the doped TiO₂ cluster (Ti₉PdO₁₉) reaction is energetically more robust than the undoped cluster (Ti₁₀O₂₀). Using the Evans–Polanyi principle, we can determine the activation energy of the two reactions empirically from the equation:

$$E_a = E_0 + \alpha \Delta H. \quad (5)$$

E_a is the activation energy, ΔH is the enthalpy, and E₀ and α are empirical parameters (α is positive and less than 1) that can be determined from experimental results. From the values of

reaction enthalpies of Eq. (3,4), we can see that the activation energy of the Pd-doped TiO₂ cluster is less than the undoped cluster. Lower activation energy means a higher reaction rate of the doped cluster, as in Eqs. (1,2). This result is what one can expect from adding a catalyst like Pd.

Equations 1 and 2 can be used to determine the response (recovery) times of a pristine and Pd-doped TiO₂ sensor—however, all the variables in Eqs. (1,2) can be determined experimentally except for geometric and activation energy, which must be determined empirically in the Arrhenius equation. Transition state theory has the advantage of determining the activation energy theoretically. The activation energy is the minimum energy needed to overcome the potential barrier for the reaction. The activation Gibbs energy is calculated using the Bery optimization algorithm in the following equations^[26]:



In the above equations, $[\text{Ti}_{10}\text{O}_{20}\text{---Cl}_2]^v$ and $[\text{Ti}_9\text{PdO}_{19}\text{---Cl}_2]^v$ are the physisorption of chlorine molecules to the surface of pristine and Pd-doped TiO₂ clusters, respectively. This physisorption is characterized by the weak van der Waals forces (note the *v* superscript). The chlorine molecule climbs the transition state's hill, costing 0.128 and 0.117 eV for the pure and Pd-doped clusters, respectively. An indicator of the correct identification of the transition state is the occurrence of imaginary frequencies at -83.785 and -76.671 cm⁻¹ for the pristine and Pd-doped clusters, respectively. The physisorption of Cl₂ on the Ti₁₀O₂₀ cluster and the transition state of the reaction of Cl₂ with the TiO₂ cluster are shown in Fig. 2. As expected; the pristine cluster has higher transition state energy than the doped cluster that leads to a higher reaction rate of the doped cluster as in Eqs. (1,2). In addition, the free energy of activation (ΔG^\ddagger) is not constant with the variation of temperature:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (8)$$

In the equation above, ΔH^\ddagger and $T\Delta S^\ddagger$ are the activation enthalpy and entropy energies, respectively. From the equation above, the change in free energy of activation with temperature is associated with a non-zero value of activation entropy (ΔS^\ddagger).

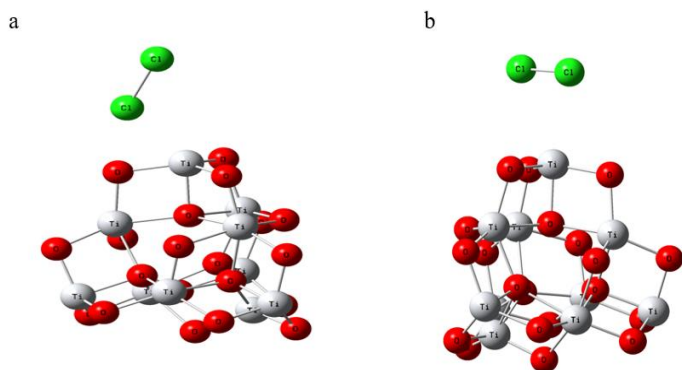


Figure 2: (a) Physisorption of Cl₂ on the Ti₁₀O₂₀ cluster $[\text{Ti}_{10}\text{O}_{20}\text{---Cl}_2]^v$; (b) transition state of the interaction of Cl₂ with the TiO₂ cluster $[\text{Ti}_{10}\text{O}_{20}\text{---Cl}_2]^\ddagger$.

The 90% response time ($t_{\text{res}(90\%)}$) is defined as the time needed to reduce (or increase) 90% of the current or resistivity before reaching its steady state. In the present case, this time can be given by^[27]:

$$t_{\text{res}(90\%)} = \frac{\ln(10)}{[\text{Cl}_2]_e A T \exp\left(\frac{-G^\ddagger}{k_B T}\right)} \quad (9)$$

In the same way, the 90% recovery time (that occurs after the response time) is given by^[12]:

$$t_{\text{rec}(90\%)} = \frac{\ln(10)}{[\text{O}_2]_e A T \exp\left(\frac{-G^\ddagger}{k_B T}\right)} \approx \frac{\ln(10)}{[\text{O}_2]_0 A T \exp\left(\frac{-G^\ddagger}{k_B T}\right)} + \sigma[\text{Cl}_2] \quad (10)$$

In the upper equation, $[\text{O}_2]_e$ is the effective oxygen concentration because the reaction product gases replace some oxygen in addition to the effect of produced gases themselves. Eq. (10) is further reduced regarding the normal oxygen concentration $[\text{O}_2]_0$ and Cl₂ concentration. The σ parameter shows that the deficiency of oxygen and the effect of reaction product gases is proportional to the initial chlorine concentration.

In Eq. (1), the effective concentration of chlorine is used since, at high temperatures, Cl₂ concentrations reduce due to various reaction channels, especially chlorine with oxygen or even nitrogen in the air that can be explosive at high temperatures^[28]. Most other gases behave the same way at high temperatures^[29]. The effective concentration of chlorine can be described using the logistic function^[29]:

$$f(T) = \frac{1}{1 + e^{k(T-T_0)}} \quad (11)$$

In the upper equation, *k* is the steepness of the consumption rate of Cl₂, and *T*₀ is the temperature at which Cl₂ concentration reaches 50% of its original concentration. From experimental results, *k* and *T*₀ are 0.06 (°C)⁻¹ and 275 °C, respectively, for pristine TiO₂. For the Pd doped clusters, *k* and *T*₀ are 0.04 (°C)⁻¹ and 175 °C, respectively^[17]. Fig. 3 shows the logistic function that describes the reacted Cl₂ ratio on the surface of the TiO₂ cluster in addition to the remaining fraction of Cl₂.

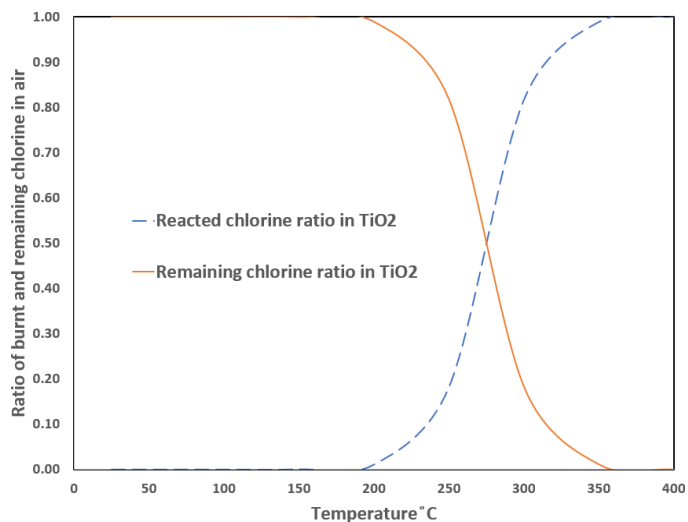


Figure 3: Logistic function describes the reacted Cl₂ ratio on the air above the TiO₂ cluster and the remaining fraction of Cl₂.

For the present calculations to be compatible with available experimental data, the theoretical gas response is calculated from the following equation for the pristine TiO_2 ^[17]:

$$\text{Response}(\text{theoretical}) = C \left| \frac{d[\text{Ti}_{10}\text{O}_{20}]}{dt} \right| \quad (12)$$

The factor C in the above equation is used to correlate between theoretical and the experimental ratio of the change in resistance between the air (R_a) and the resistance during the existence of detected chlorine gas (R_g) as in the equation:

$$\text{Response}(\text{experimental}) = \frac{R_a - R_g}{R_a} \times 100 \quad (13)$$

The best values of C for pristine and Pd doped clusters are 1750 and 900 seconds compared to experimental results^[17].

3. Results and discussion

Fig. 4 explains the energy scheme of the interaction of the Cl_2 molecule with the TiO_2 cluster. A similar scheme can be drawn for the interaction of Cl_2 with the Pd-doped cluster. The interaction starts with the physisorption of the Cl_2 molecule on the surface of the TiO_2 cluster. Van der Waals forces characterize the physisorption. A transition state is formed as the Cl_2 molecule dissociates, so chlorine atoms are attached to the TiO_2 cluster. Finally, one oxygen atom is released from the TiO_2 cluster, as in Eq. 3, for the final chemisorption step.

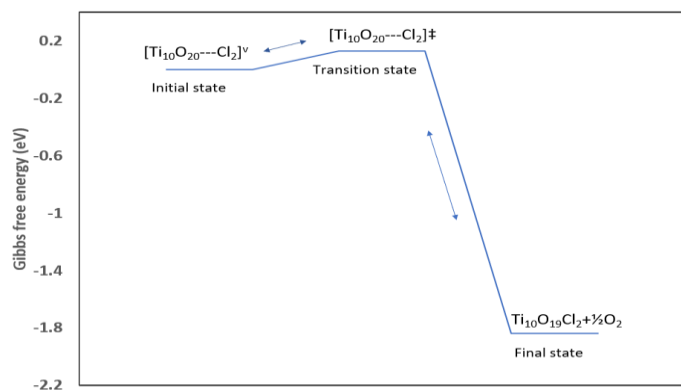


Figure 4: The energy scheme of the interaction of the Cl_2 molecule with the TiO_2 cluster.

Fig. 5 illustrates the variation of the free energy of activation with temperature for both pure and Pd-doped TiO_2 clusters. The free energy decreases with the temperature increase, as in Eq. (8), because of the positive value of the entropy of activation that is usually associated with dissociation processes^[30]. The value of the entropy of activation of doped TiO_2 is less than that of pristine TiO_2 , which results in a smaller decrease in the free energy of activation of the doped case.

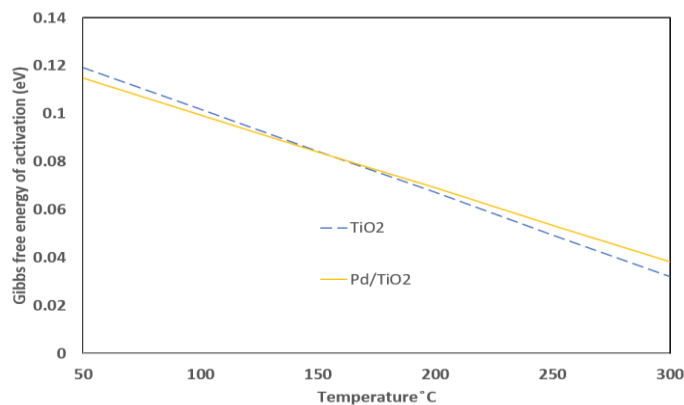


Figure 5: Variation with the temperature of free energy of activation or transition of pristine and Pd-doped TiO_2 clusters.

Fig. 6 shows the calculated responses in comparison with experimental results. The pristine TiO_2 calculated response is in excellent agreement with the experiment. However, the Pd doped cluster has less degree of agreement than the pristine case. This agreement can be attributed to the more complex Pd/ TiO_2 case that contains a single Pd atom, as in Fig 1b. Both calculated cases agree with the experiment on the position of the highest response at 250 and 150 °C for pristine and Pd-doped TiO_2 , respectively^[17].

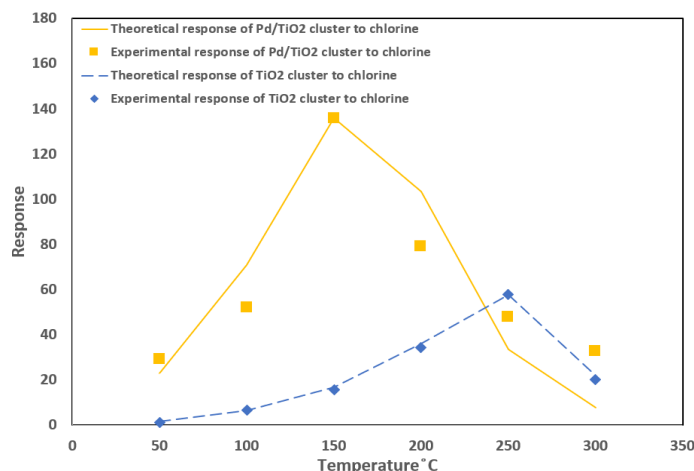


Figure 6: Pristine and Pd-doped TiO_2 clusters theoretical and experimental response to 100 ppm of Cl_2 as the temperature increases. Experimental points are from reference^[17].

Fig. 7 shows the calculated response time as in Eq. (9) compared to the experiment. The Pd-doped TiO_2 is in good agreement with the experimental results. This good agreement is not the case for the pristine TiO_2 cluster. The theoretical TiO_2 cluster results are steeper than the experimental results. This behavior is the reverse case compared to the response results in Fig. 6.

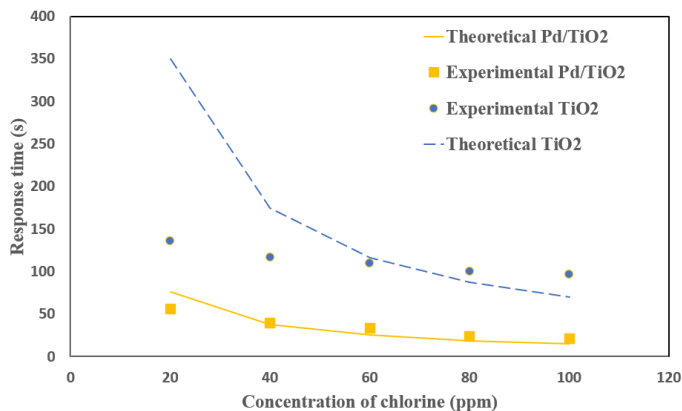


Figure 7: Pristine and Pd doped TiO₂ clusters theoretical and empirical response time as a function of Cl₂ concentration at 250 and 150 °C, respectively. Experimental results are from reference^[17].

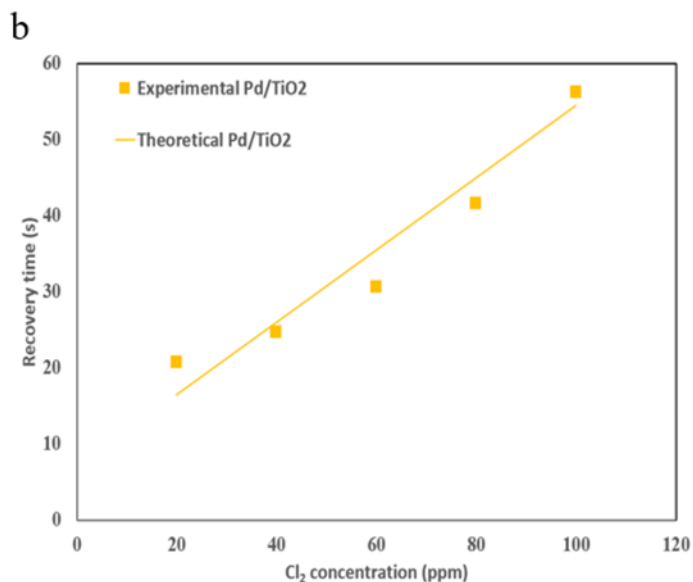
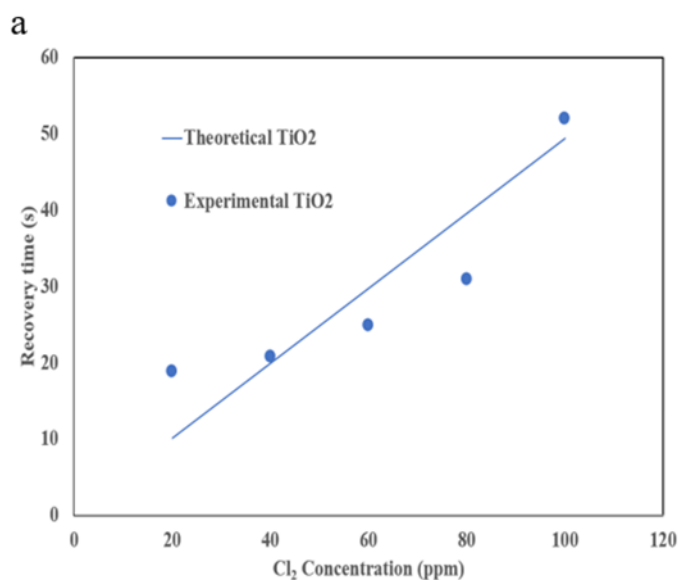


Figure 8: (a) Recovery time of TiO₂ cluster as a function of Cl₂ concentrations at 250 °C. (b) Recovery time of Pd-doped TiO₂ as a function of Cl₂ concentrations at 150 °C. Experimental points are from reference^[17].

Table 1 lists the parameters used in the present calculations. The first and third reactions are the response reactions, while the second and fourth reactions are the recovery reactions for the pristine and Pd-doped TiO₂, respectively. The A parameter is sometimes called the frequency parameter. This parameter's value is much smaller in the response step than in the recovery

step due to the large number of collisions of the high number of oxygen molecules compared to the relatively lower number of Cl₂ molecules. The σ parameter exists only for recovery reactions. The ΔG^\ddagger energy is determined using the Gaussian 09 program, while A and σ parameters are used for fitting the empirical results.

Table 1: Reaction parameters used in the present model. ΔG^\ddagger values are at normal temperature and pressure (25 °C and 1 bar).

	Transition	A (s.K) ⁻¹	ΔG^\ddagger (eV)	σ (s)
1	[Ti ₁₀ O ₂₀ ---Cl ₂] ^v →[Ti ₁₀ O ₂₀ ---Cl ₂] [‡]	2.3	0.128	-
2	[Ti ₁₀ O ₁₉ Cl ₂ ---O] ^v →[Ti ₁₀ O ₂₀ ---Cl ₂] [‡]	10 ¹⁷	1.886	600000
3	[Ti ₉ PdO ₁₉ ---Cl ₂] ^v →[Ti ₉ PdO ₁₉ ---Cl ₂] [‡]	49	0.117	-
4	[Ti ₉ PdO ₁₈ Cl ₂ ---O] ^v →[Ti ₉ PdO ₁₉ ---Cl ₂] [‡]	6×10 ²⁸	2.620	650000

Conclusions

Transition state theory simulates the reaction rate, response, and recovery times of pristine and Pd-doped TiO₂ with Cl₂. The results show acceptable agreement between theory and experiment. Density functional theory is used as a tool to perform

the present calculations. The free energy of activation is calculated using Bery optimization. The value of the activation energy changes with temperature due to the entropy positive value. The logistic function is used to consider other channels of chlorine reactions. The first step of the reaction of Cl₂ is to be physisorbed at the cluster's surface. The establishment of the

transition state follows this step. The final step is transforming the transition state to the chemisorption reaction products. The response, response time, and recovery time as a function of temperature or concentration of Cl₂ are in acceptable agreement with available empirical results. Future aspects of the present work might include complex reactions or multi-step transition states into account.

Conflict of interests

No.

Author contribution

Abdulsattar: Proposing the research, computational tasks, and writing the manuscript.

Khalil: Discussion and corrections.

Mahmood: Discussion, Figures, and Tables.

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