Transition state application to simulate CO gas sensor of pristine and Pt doped tin dioxide clusters

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Abstract. Carbon monoxide sensitivity of pristine and Pt doped tin dioxide (SnO₂) is investigated in the present work using transition state theory. The use of transition state theory leads to a double exponent function formula for the concentration and sensitivity of the material. The method uses Gibbs free energy, enthalpy, and entropy of activation to formulate sensitivity, response time, and recovery time. The results showed that the activation energy of Pt doped SnO₂ nanocluster is lower than the pristine SnO₂ nanocluster. The Pt doped clusters promote higher reaction rates than pristine clusters. However, the activation energy of recovery with oxygen reaction is lower for the pristine cluster. The results also showed that the activation energy and reaction rates increase with temperature. The concentration of oxygen-deficient molecules in pristine and doped tin oxide as a function of temperature that represents the sensitivity of the sensor has the highest value at 225 °C. The theoretical results also show that response time decreases while recovery time increases with the increase of CO concentration. The results agree with experimental results.

1. Introduction
Doped tin dioxide is one of the best choices in gas sensor selection for many gases [1–9]. Pristine SnO₂ nanostructures can also be sensitive to many gases [10–12]. The surface loading with catalysts such as platinum group metals, other Nobel elements, and many common elements and compounds can make large differences in the sensitivity of the SnO₂ sensor [13,14]. Platinum is one of the frequently used catalysts in the gas sensor and other chemical reactions [1–5]. Platinum is one of the platinum group metals that include Ru, Rh, Pd, Os, and Ir. All these elements have the property of reducing the activation energy needed to be overcome during a reaction between different materials.

Carbon monoxide is one of the most dangerous gases that emerge from many industrial and daily uses of cars and other hydrocarbon burning tools. The toxicity of CO reaches low gas concentration in the air [15]. Regulations forbid CO concentration of more than 50 ppm in workplaces [16].

A lot of experimental data had accumulated regarding gas sensors; however, theoretical explanations are lacking in many of the experimental works. In general, gas sensing is regarded as an experimental science, with the theoretical part being less explained or tackled. Gas sensing is essentially a reaction or absorption phenomenon that takes place between certain gas and a solid surface. The solid materials used in gas sensing are usually semiconductor oxides such as SnO₂, ZnO, WO₃...etc. Reactions are usually treated using theories such as transition state theory. However, the application of transition state theory is limited to a small number of gas sensor researches [17–20].
In the present work, we investigate the use of transition state theory to explain the gas sensing behavior of SnO$_2$ nanoclusters to CO gas. The investigation includes the effect of Pt doping on SnO$_2$ nanoclusters sensitivity. The recovery of the sensor to its original condition must include the O$_2$ reaction with the oxygen-depleted sensor material. Gibbs free energy, enthalpy, and entropy of activation and reaction are the quantities that must be evaluated to evaluate reaction rates, sensitivity, response, and recovery times at the gas sensor temperatures, usually covering the range from room temperature to 500 °C.

2. Theory
Tin dioxide is known to have pyramid structures at its surface [21–23]. It is also observed that it has oxygen deficiency so that its stoichiometry is between Sn$_2$O$_3$ and SnO$_2$ [24,25]. The optimum stoichiometry was tested theoretically by adding or removing consecutive oxygen molecules to the suggested tin oxide cluster and observing the value of the calculated Gibbs free energy of the reaction. As we add an oxygen molecule to the suggested Sn$_{10}$O$_{16}$ cluster, the resultant Gibbs free energy of the reaction is positive, indicating that this reaction is non-spontaneous. The addition of an oxygen molecule to the Sn$_{10}$O$_{14}$ cluster results in a negative Gibbs free energy of reaction, indicating that this reaction is spontaneous. Thus, the optimum cluster stoichiometry is the Sn$_{10}$O$_{16}$ pyramid cluster in our calculations. This cluster is shown in figure 1(a) in addition to the optimized transition state of a CO molecule. Replacing one of the Sn atoms by a Pt atom results in the doped molecule in figure 2(b) with the stoichiometry Sn$_9$PtO$_{16}$. B3LYP hybrid functional in density functional theory with SDD basis for heavy atoms (Sn and Pt) and 6-311G** basis for the lighter ones was used [26] to optimize molecular geometries. The asterisks indicate that a set of polarizing functions is included to supplement the basis. Program Gaussian 9 was used to perform present computation [27]. The SDD basis is an effective core potential (ECP) basis or sometimes called a (pseudopotential) that serves to reduce the high computational time of core electrons without reducing the accuracy of these calculations [28,29]. The transition state was calculated by positioning the CO molecule at 3 Å from the SnO$_2$ molecule so that the dipole-dipole forces act between the two molecules, as in figure 1a and b. The program Gaussian 9 then proceeds to optimize the positions of the atoms of the two molecules [27] using transition state optimization procedures.

The reaction of the Sn$_{10}$O$_{16}$ cluster with carbon monoxide results in oxygen reduction in the cluster as in the equation:

$$\text{Sn}_{10}\text{O}_{16} + \text{CO} \rightarrow \text{Sn}_{10}\text{O}_{15} + \text{CO}_2$$ (1)

However, the CO molecule must overcome a potential barrier before it can reach the Sn$_{10}$O$_{16}$ cluster as in the equation:

$$\text{Sn}_{10}\text{O}_{16} + \text{CO} \rightarrow \text{Sn}_{10}\text{O}_{16-\text{CO}}$$ (2)

The state of the CO molecule at the top of this potential barrier is called the transition state and designated by (Sn$_{10}$O$_{16-\text{CO}}$), as in figure 1(a) and figure 2. The pristine and Pt doping schemes are shown in figures 2 and 3. When oxygen passes over the oxygen-deficient cluster, the cluster will retrieve its lost oxygen:

$$\text{Sn}_{10}\text{O}_{15} + \frac{1}{2}\text{O}_2 \rightarrow \text{Sn}_{10}\text{O}_{16}$$ (3)

However, in this reaction, the oxygen molecule must also overcome a potential barrier as in the equation:

$$\text{Sn}_{10}\text{O}_{15} + \frac{1}{2}\text{O}_2 \rightarrow \text{Sn}_{10}\text{O}_{15-\text{O}}$$ (4)
The attachment of oxygen to undoped and doped clusters is shown in figures 1(c) and 1(d), respectively, and the schemes of figure 2 and figure 3.

**Figure 1.** (a) shows the transition state of CO molecule with Sn$_{10}$O$_{16}$ cluster, (b) shows the transition state of CO molecule with Sn$_{9}$PtO$_{16}$ cluster, (c) and (d) shows the transition state of an oxygen atom with oxygen-reduced clusters Sn$_{10}$O$_{15}$ and Sn$_{9}$PtO$_{15}$ of pristine and Pt doped clusters, respectively.
The variation of the surface material composition due to the reaction in Eq. 1 is given by [27]:

\[
\frac{d[\text{Sn}_{10}\text{O}_{16}]}{dt} = -C_{\text{CO}}[\text{Sn}_{10}\text{O}_{16}][\text{CO}]k(T).
\]  

([Sn\text{O}_{16}] and [CO] are the concentration of Sn\text{O}_{16} and CO molecules, respectively. T is the temperature, and t is time. C_{\text{CO}} is the reaction proportionality constant in the case of CO gas reaction. k(T) is the reaction rate constant and is given by:

\[
k(T) = T \exp\left(-\frac{\Delta G}{k_BT}\right).
\]
ΔG_a is the Gibbs free energy of activation, and k_B is Boltzmann constant. In the above equation for the reaction rate constant, a pre-factor of the division of Boltzmann constant by Planck constant (k_B/h) is absorbed by the C_CO parameter in Eq. (5). Solving Eq. (5) for [Sn_{10}O_{16}], we have:

\[
[\text{Sn}_{10}\text{O}_{16}] = [\text{Sn}_{10}\text{O}_{16}]_0 \exp^{-C_{\text{CO}}[\text{CO}]k(B)T}t
\]  

(7)

The 90% response time can be evaluated from the above equation as [30]:

\[
\text{t}_{\text{response}} = \frac{\ln(10)}{C_{\text{CO}}[\text{CO}]T \exp\left(-\Delta G_a k_B T\right)} = \frac{D}{[\text{CO}]}
\]  

(8)

Recovery time (t_{recovery}) can also have the following:

\[
\frac{d[\text{Sn}_{10}\text{O}_{16-x}]}{dt} = -C_{\text{O}_2}[\text{Sn}_{10}\text{O}_{16-x}]_0[\text{O}_2]k(T)
\]  

(9)

x in above is the number of oxygen atoms removed from the original molecule [Sn_{10}O_{16}]. C_{O_2} is the proportionality constant in the case of the O_2 gas reaction. [O_2]_e is the effective concentration of oxygen. Solving for [Sn_{10}O_{16-x}] we have:

\[
[\text{Sn}_{10}\text{O}_{16-x}] = [\text{Sn}_{10}\text{O}_{16-x}]_0 \exp^{-C_{\text{O}_2}[\text{O}_2]_e k(T)}
\]  

(10)

For a given temperature and comparing with Eq. (8), we can see that the recovery time depends on the concentration of oxygen in the air [O_2]. However, O_2 must diffuse to the same depth that was previously reached by CO to reach oxygen vacancies removed previously by CO. As a result, the concentration of oxygen should reach its concentration in air (21%) at the surface and less concentration at the inside; the effective concentration of O_2 can be written by the equation:

\[
[\text{O}_2]_e = [\text{O}_2]_0 - \sigma[\text{CO}]
\]  

(11)

In Eq. (11), σ is called the screening parameter. Substituting the value of [O_2]_e in Eq. (10) and evaluating the recovery time we have [30]:

\[
\text{t}_{\text{recovery}} = \frac{\ln(10)}{C_{\text{O}_2}(0)_{0-}[\text{CO}]T \exp\left(-\Delta G_a k_B T\right)} = \frac{E}{[O]_0 - \sigma[CO]}
\]  

(12)

We can see from Eqs. (8) and (12) the inverse proportionality of response time to the concentration of CO while the recovery time is approximately linearly proportional to the CO concentration (after using Taylor series approximation of (1-x)^{-1} for the dominator of Eq (12)).

The electrical conductivity of a material can be expressed in terms of the energy gap by the following equation [31]

\[
\sigma_e = \sigma_0 \exp\left(-\frac{E_g}{2k_B T}\right)
\]  

(13)

Assuming \( \sigma_0 \) (conductivity preexponential factor) is constant, we can approximate the response (S) of a gas sensor by the equation:

\[
S = \frac{R_s}{R_a} = \exp\left(\frac{E_g - E_{\text{gap}}}{k_B T}\right)
\]  

(14)
R_a and E_g are the resistance and energy gap in the existence of air only while R_g and E_y are for the case of existing CO gas over the Sn_{10}O_{16} molecules. Using the energy gaps of Sn_{10}O_{16}, Sn_{9}O_{15}, and Sn_{9}O_{14} calculated in the present work (3.841, 3.537, and 3.127) eV, respectively, we can get the following responses 1.355 and 2.043 for the depletion of one and two oxygen atoms from the initial molecule Sn_{10}O_{16} respectively.

3. Results and discussion

Gibbs free energy of activation and reaction of CO gas as a function of temperature is shown in figure 4. This includes pristine (Sn_{10}O_{16}) and Pt doped (Sn_{9}PtO_{16}) clusters. This figure shows that the reaction energies are nearly constant and always have negative Gibbs free energy. The activation energy of the Pt doped cluster is always less than the pristine cluster. The activation energy is always positive and increases with temperature.

Figure 5 shows the Gibbs free energy of activation and reaction of O_2 gas as a function of temperature with oxygen-reduced pristine (Sn_{10}O_{13}) and Pt doped (Sn_{9}PtO_{15}) clusters. Oxygen reaction and activation energies increase with temperature. Also, the doped activation energy is higher than the pristine. This is in agreement with the fact that Pt plays a role in protecting against oxidation [32].

Figure 6 shows the reaction rate constant of pristine Sn_{10}O_{16} and Pt doped Sn_{9}PtO_{16} clusters with CO molecules as a function of temperature. This figure shows that the doped cluster has higher reaction rates as expected experimentally. This figure and the previous two figures have been obtained from ab initio calculations and do not involve any empirical parametrization.

Figure 7 shows the concentration of oxygen-deficient molecules [Sn_{10}O_{16-x}] in pristine tin oxide as a function of temperature that represents the sensitivity of the sensor. The concentration is compared with the average experimental operating temperature of reference [1] at 225 °C. Most references refer to the 100-300 °C as the preferred operating temperature range [33–35] for CO sensors. Higher temperatures are used to reduce response and recovery times, as in Eqs. (8) and (12), while low temperatures are used to reduce heating power.

Figure 8 shows the experimental and theoretical results of response time using the transition state method described by Eq. (8). The transition state method predicts the response time to be inversely proportional to the CO gas concentration. Simulation curve is obtained by using the proportionality constant D in Eq. (8) to fit the 50 ppm value of response time at 225 °C. The simulation curve is in a qualitative agreement with the experimental values. The value of the reaction coefficient C_{CO} is temperature-dependent and is given by:

\[ C_{CO} (T) = 7.425 \times 10^{-9} \ T^3 - 1.568 \times 10^{-5} \ T^2 + 0.0101 \ T - 1.763 \] (15)

The resistivity is expected to be a function of the number of oxygen-depleted atoms so that:

\[ R_a = R([Sn_{10}O_{16}]), \quad R_g = R([Sn_{10}O_{16-x}]) \] (16)

It is natural to assume that the resistivity decreases as a function of [Sn_{10}O_{16-x}] as in the equation:

\[ R_g = R_a (1 - S_0[Sn_{10}O_{16-x}]) \] (17)

In the above equation, S_0 is an empirical parameter that correlates between resistivity and concentration of oxygen-deficient molecules with the value 1.5 in the present work. We can see from the above equation that R_g will be equal R_a when the concentration of Sn_{10}O_{16-x} molecules vanishes. Finally, the response or sensitivity can be given by:

\[ S = \frac{R([Sn_{10}O_{16}])}{R([Sn_{10}O_{16-x}])} = \frac{R_a}{R_a(1-S_0[Sn_{10}O_{16-x}])} \approx 1 + S_0[Sn_{10}O_{16-x}] + \cdots \] (18)
Figure 9 shows the experimental [1] and the calculated theoretical responses as a function of CO gas concentration. We can see that in the present model, the response of Sn_{10}O_{16} molecules is to lose only one oxygen atom from the pristine Sn_{10}O_{16} molecule for concentrations less than 50 ppm. For larger concentrations of CO, the depleted oxygen atoms are between one and two atoms. The depletion of a high number of oxygen atoms is expected in the case of Pt doped case [36].

Comparison with Pt doped experimental results is limited in the present work. The doped simulating molecule Sn_{9}PtO_{16} has a Pt percentage of more than 12% of the molecule weight. The available experimental Pt concentrations are less than 5% [1,2]. However, the effect of Pt doping is obvious from figures 2, 4, and 6. Lower activation energies in figures 2 and 4 combined with higher reaction rate constants in figure 6 all indicate higher sensitivities and lower response time, which is the trend of experimental results [1,2]. To decrease the weight percentage in our model, we have to increase the number of Sn and O atoms more than twice the present number, which is out of the capacity of our computational facilities.

**Figure 4.** Gibbs free energy of activation and reaction of CO gas as a function of temperature with pristine (Sn_{10}O_{16}) and Pt doped (Sn_{9}PtO_{16}) clusters.

**Figure 5.** Gibbs free energy of activation and reaction of O_{2} gas as a function of temperature with oxygen-reduced pristine (Sn_{10}O_{15}) and Pt doped (Sn_{9}PtO_{15}) clusters.
Figure 6. The reaction rate constant of pristine Sn$_{10}$O$_{16}$ and Pt doped Sn$_{9}$PtO$_{16}$ clusters with CO molecules as a function of temperature.

Figure 7. The normalized concentration of oxygen-deficient molecules in pristine tin oxide as a function of temperature. The concentration is compared with the average experimental operating temperature of reference [1].
Figure 8. Experimental and theoretical results of response time using the transition state method at 225 °C of pristine tin oxide [1].

Figure 9. Experimental and calculated theoretical responses as a function of CO gas concentration at 225 °C [1]. The 1st and 2nd oxygen atom depletion are shown.
Figure 10. Theoretical responses as a function of time for three CO concentrations at 225 °C.

Figure 10 shows the theoretical responses as a function of time for three CO concentrations using the above transition state method. The figure is constructed from the response time, recovery time, and theoretical response in Eqs (8, 12, 18), respectively. The figure simulates the gas sensing operation by exposing the SnO$_2$ surface to CO gas in different concentrations 50, 100, and 200 ppm. Atmospheric air is passed between CO exposures to recover depleted oxygen. The shape of figure 10 is frequently encountered in gas sensing results [37].

Gibbs free energy has two components:

$$
\Delta G = \Delta H - \Delta ST
$$

(19)

The first component in Eq. (19) is the enthalpy ($\Delta H$), while the second is the entropy ($\Delta S$) and temperature (T). Table 1 shows the values of Gibbs free energies of reaction and activation accompanied by its components mentioned in Eq. (19) at standard conditions. The activation energies are given first for all interactions followed by reaction energies. A common feature of all activation energies is that all entropy changes have negative values. The negative value of the entropy change in energy is due to the reduction of the number of reaction products with respect to the number of reactants. When the number of product molecules is equal to the number of reactant molecules, the entropy change is positive, as in reaction numbers 5 and 6 in table 1. All enthalpies are negative, except for the enthalpy of activation number 4 in table 1. All changes in activation Gibbs free energies are positive (number 1 to 4), while all reactions are negative (number 5 to 8). As we mentioned before, the activation energies control the reaction rate. However, the reaction enthalpies determine the heat absorbed or released due to the reaction. This has great importance in determining the amount of increase or decrease of temperature and the amount of external heating needed to keep the reaction running at the same temperature and rate.

Table 1: Gibbs free energies, enthalpy and entropy of reaction and activation (temperature 298.15 Kelvin and pressure 1 atm).

| n  | Reaction                          | $\Delta G$ (eV) | $\Delta H$ (eV) | $\Delta ST$ (eV) |
|----|----------------------------------|-----------------|-----------------|-----------------|
| 1  | Sn$_{10}$O$_{16}$+CO$\rightarrow$Sn$_{10}$O$_{16}$---CO | 0.261           | -0.0423         | -0.303          |
| 2  | Sn$_9$PtO$_{16}$+CO$\rightarrow$Sn$_9$PtO$_{16}$---CO  | 0.128           | -0.0463         | -0.175          |
| 3  | Sn$_{10}$O$_{15}$+$\frac{1}{2}$O$_2$$\rightarrow$Sn$_{10}$O$_{15}$---O  | 0.240           | -0.0792         | -0.320          |
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