Sn-adopted fullerene (C₆₀) nanocage as acceptable catalyst for silicon monoxide oxidation

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Abstract. In recent years, the discovery of metal catalysts for the oxidation of silicon monoxide (SiO) has become extremely important. In first step, the Sn adoption of fullerene (C₆₀) was investigated and then activation of surface of Sn-C₆₀ via O₂ molecule was examined. In second step, the SiO oxidation on surface of Sn-C₆₀ via Langmuir Hinshelwood (LH) and Eley Rideal (ER) mechanisms was investigated. Results show that O₂-Sn-C₆₀ can oxidize the SiO molecule via Sn-C₆₀-O-O* + SiO → Sn-C₆₀-O-O*-SiO → Sn-C₆₀-O* + SiO₂ and Sn-C₆₀-O* + SiO → Sn-C₆₀ + SiO₂ reactions. Results show that SiO oxidation via the LH mechanism has lower energy barrier than ER mechanism. Finally, Sn-C₆₀ is an acceptable catalyst with high performance for SiO oxidation in normal temperature.

Keywords. Catalyst; nanostructure; metal adoption; oxidation reaction; adsorption energy.

1. Introduction

Some of the factories produced the toxic gases and these factories increased the air pollution. In recent years, many works on oxidation of toxic gases via metal catalysts to reduce the air pollution were investigated. In industry, metal catalysts were used in vital chemical reactions and they have high performance [1–6].

Previous works proved that metal catalysts were expensive and they have high energy barrier and also these reactions required high temperature to have appropriate efficiency [7–12]. To discover the novel catalyst with low price and high activity in normal temperature; the ability of nanocatalysts to oxidation of toxic gases were investigated [13–18].

Many of the nanostructures because of their remarkable properties, such as big surface-to-volume relationship, comfort of adopting and functionalization, high efficiency in normal temperature were used as sensor of toxic gases [19–21]. Previous studies show that functionalization and adoption of nanostructures via metal atoms improved the sensitivity of nanostructures to toxic gases [22–27].

The oxidation of silicon monoxide (SiO) significantly reduced the environmental complications. Nanocatalysts can oxidize the SiO molecule via Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms [28–30]. In previous studies, the oxidation of toxic gases on surfaces of nanostructures

via LH and ER mechanisms was investigated. Results show that these mechanisms depended on the type of metal nanostructures and these catalysts improved the rate and quality of oxidation reaction of toxic gases [31–33].

In LH mechanism, the oxygen molecule (O₂) and SiO were adsorbed on the surface of catalyst and also in surface of catalyst and an intermediate state was formed and finally, silicon dioxide (SiO₂) was separated. In ER mechanism, straightforward reaction between the pre-adsorbed O₂ and adsorbed SiO was performed [34–36].

In previous studies, the potential of metal-adopted nanostructure as catalysts for oxidation of toxic gases via LH and ER mechanisms was investigated. Results proved that metal-adopted nanostructures were acceptable catalysts with lower energy barrier [37–40]. Therefore, metal-adopted nanostructures can be novel catalysts to oxidation of toxic gases at normal temperature [41–43].

In this study, the surface of fullerene (C₆₀) was adopted by Sn atom and the SiO oxidation on the surface of Sn-C₆₀ via LH and ER mechanisms was investigated by theoretical methods. The main questions were answered in this work are: (1) How much energy is needed to adopt Sn on C₆₀ surface? (2) How much energy is needed to O₂ and SiO adsorption on Sn-C₆₀ surface? (3) Can Sn-C₆₀ be a catalyst for SiO oxidation in normal temperature? (4) How much barrier and adsorption energies are needed to SiO oxidation on Sn-C₆₀ surface?

(5) Which mechanisms are more appropriate to SiO oxidation on Sn-C₆₀ surface?

2. Computational details

In this study, the geometries of C₆₀ and Sn-C₆₀ and their complexes with SiO and O₂ molecules were optimized via GAMESS software via DFT/ M06-2X theory and 6-311+G (2d, 2p) basis set [44–48]. In this study, the vibrational frequency calculations of all the studied structures via DFT/ M06-2X theory and 6-311+G (2d, 2p) basis set were done to evidence that all the optimized geometries are factual local minima and also thermodynamic parameters of studied reactions were calculated by using vibrational frequency analysis [46–50]. In this study, natural bond orbital (NBO) analysis was performed to calculate the charge transfers and orbital energies of studied C₆₀, Sn-C₆₀ and their complexes with SiO and O₂ [49–51]. The adsorption energy (E_{ad}) values of SiO and O₂ on Sn-C₆₀ surfaces were equal with difference energies between Sn-C₆₀ and SiO and O₂, respectively [49,50]. Corresponding to E_{ad} values, the

adsorption enthalpy (H_{ad}) and Gibbs free energy (G_{ad}) for adsorption of SiO and O₂ on Sn-C₆₀ surface were calculated and the negative G_{ad} values correspond to an exothermic process.

3. Results and discussion

3.1 Sn adoption of C₆₀

In previous studies, results show that adoption of nanocages with metal atoms can efficiently modify their electrical properties, chemical activity and reaction potential [22–27]. In this study, the structures of C₆₀ and Sn-C₆₀ were optimized and their binding distances are reported in figure 1.

In figure 1, the Sn atom was adopted to C₆₀ and then, Sn atom was formed three bonds by bordering C atoms. Figure 1 shows that calculated bond lengths of Sn atom with three bordering C atoms are *ca.* 1.95 Å. Calculated bond lengths of each C atom with three bordering C atoms are *ca.* 1.45 Å. These growths in the Sn–C rather than C–C were interpreted by forcing of bordering C atoms via the Sn atom

Figure 1. Structures of C₆₀, Sn-C₆₀, Sn-C₆₀-O₂ and Sn-C₆₀-SiO (bond distances (Å)).

Table 1. Calculated values for Sn adoption of C₆₀ and calculated parameters for SiO and O₂ adsorption on Sn-C₆₀ surface.

Nanoparticles	ΔE_{ad} (eV)	ΔH_{ad} (eV)	ΔG_{ad} (eV)	q (e)	E_{HLG} (eV)
Sn-C ₆₀	-1.09	-1.04	-0.56	0.48	2.13
Sn-C ₆₀ -SiO	-0.47	-0.42	0.29	0.12	2.14
Sn-C ₆₀ -OSi	-0.50	-0.45	0.27	0.14	2.16
Sn-C ₆₀ -O ₂	-1.02	-0.99	-0.38	0.62	2.53

and so the locations of the Sn atom and bordering C atoms were perturbed toward out of the main plane.

In this study, the adoption energy (ΔE_{ad}), enthalpy (ΔH_{ad}), Gibbs free energy (ΔG_{ad}) and energy of HOMO–LUMO gap (E_{HLG}) of Sn-C₆₀ were calculated. The transferred charge (q) between the Sn atom and C₆₀ were calculated and obtained results are reported in table 1. Results show that the calculated ΔE_{ad} , ΔH_{ad} , ΔG_{ad} , E_{HLG} and q values of Sn-C₆₀ were -1.09, -1.04, -0.56, 2.13 eV and 0.48 electron, respectively. Results show that in Sn-C₆₀, there are three strong covalent bonds between Sn atom and bordering C atoms.

3.2 Adsorption of SiO and O₂ on Sn-C₆₀ surface

The study of SiO and O₂ adsorption on Sn-C₆₀ surface is highly important to study SiO oxidation. In this step, the adsorption of SiO and O₂ on Sn-C₆₀ surface was investigated and the most stable Sn-C₆₀-SiO and Sn-C₆₀-O₂ complexes from thermodynamic view point is shown in figure 1.

In figure 1, structure of Sn-C₆₀-SiO complex show that the distance between the SiO and Sn-C₆₀ was 3.57 Å. The results in table 1 show that the calculated ΔE_{ad} , ΔH_{ad} , ΔG_{ad} values of Sn-C₆₀-SiO were -0.47, -0.42 and 0.29 eV, respectively. The calculated q value for interaction between the SiO and Sn-C₆₀ is *ca.* 0.12 electron. Additionally, E_{HLG} parameter to determine the changes in electronic properties of Sn-C₆₀ after SiO adsorption was calculated and obtained results are reported in table 1. Results indicated that Sn-C₆₀ and Sn-C₆₀-SiO have same E_{HLG} values.

In this section also, interactions between the Sn-C₆₀ and OSi from Sn-C₆₀-OSi direction were investigated and the calculated ΔE_{ad} , ΔH_{ad} , ΔG_{ad} , E_{HLG} and q values are reported in the fourth column of table 1. Here, calculated ΔE_{ad} , ΔH_{ad} , ΔG_{ad} values of Sn-C₆₀-OSi were -0.50, -0.45 and 0.27 eV, respectively. In the fourth column of table 1, transferred q value for Sn-C₆₀-OSi interaction is *ca.* 0.14 electron and E_{HLG} values of Sn-C₆₀ (2.13 eV) and Sn-C₆₀-OSi (2.16 eV) are almost equal.

The transferred charge from Sn-C₆₀ to SiO shows that SiO adsorption on Sn-C₆₀ surface cannot modify the activity of Sn-C₆₀ significantly. The low ΔE_{ad} and ΔH_{ad} values and positive ΔG_{ad} values of Sn-C₆₀-SiO show that interactions of SiO with Sn-C₆₀ were weak and SiO adsorption on Sn-C₆₀ surface was impossible from thermodynamic view point.

As seen in figure 1, in Sn-C₆₀-O₂, the distance between the O₂ and Sn-C₆₀ was 1.98 Å. The adsorption parameters in table 1 show that the calculated ΔE_{ad} , ΔH_{ad} , ΔG_{ad} values of Sn-C₆₀-O₂ are -1.02, -0.99 and -0.38 eV, respectively. The calculated ΔE_{ad} , ΔH_{ad} and ΔG_{ad} values confirmed that O₂ and Sn-C₆₀ have appropriate chemical interactions.

The O₂ bond length in Sn-C₆₀-O₂ is 1.31 Å and it is longer than bond length in single O₂ *ca.* 0.10 Å. Results show that when Sn-C₆₀-O₂ is formed, the O₂ bond length is elongated and O₂ on Sn-C₆₀ surface is activated. The obtained q value of interaction between the O₂ and Sn-C₆₀ is *ca.* 0.62 electron. Calculated E_{HLG} value shows that Sn-C₆₀-O₂ has higher E_{HLG} values than Sn-C₆₀ *ca.* 0.40 eV. Therefore, results show that O₂ adsorption on Sn-C₆₀ surface can modify the chemical structure of Sn-C₆₀ and O₂ adsorption can improve the activity of Sn-C₆₀ efficiently.

Finally, results in table 1 show that O₂ adsorption on Sn-C₆₀ surface improved the chemical properties of Sn-C₆₀ because of large q , ΔE_{ad} and ΔH_{ad} values. Also, results confirmed that when the equal amount of SiO and O₂ molecules were nearby to Sn-C₆₀ structure, the Sn-C₆₀ surface was covered by O₂ molecule exactly. So, the formation of Sn-C₆₀-O₂ can be considered as the first step in SiO oxidation reaction.

3.3 SiO oxidation on Sn-C₆₀ surface via ER and LH mechanisms

As illustrated in Section 1, the ER and LH were possible mechanisms to SiO oxidation on surface of nanostructures. In ER mechanism, SiO molecule was moved near to the surface of Sn-C₆₀, but in LH mechanism, first SiO and O₂ groups were adsorbed and then, oxidation occurred on Sn-C₆₀ surface. In previous studies, the ER and LH mechanisms for toxic gas oxidation on metal-adopted nanostructures were investigated. Results indicated that metal-adopted nanostructures were acceptable catalysts to toxic gas oxidation [28–36].

In this section, the potential of Sn-C₆₀ surface for SiO oxidation was investigated and energy pathways for SiO oxidation in both ER and LH mechanisms were examined. The SiO oxidation pathways on Sn-C₆₀ surface is shown in figures 2 and 3. The calculated activation energies (E_{ac}) and thermodynamic indices (ΔE_{ad} , ΔH_{ad} and ΔG_{ad}) of the studied pathways are reported in table 2.

Results in table 2 show that the energy barriers of SiO oxidation on O₂-activated Sn-C₆₀ surface via LH mechanism

Figure 2. Plan of $\text{Sn-C}_{60}\text{-O-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O} + \text{SiO}_2$ reaction (bond distances (Å) and relative energies (eV)).

were lower than the corresponding values of ER mechanism. Therefore, the LH mechanism was considered in the following two reactions: first reaction is $\text{Sn-C}_{60}\text{-O-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O-O-SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$, and second reaction is $\text{Sn-C}_{60}\text{-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60} + \text{SiO}_2$. The geometry of important structures in the pathways of above two reactions were optimized and corresponding structures of initial state (IS), final state (P) and transition state (TS) are shown in figures 2 and 3.

In the first reaction ($\text{Sn-C}_{60}\text{-O-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O-O}^* \text{-SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$), the $\text{Sn-C}_{60}\text{-O-O}^* \text{-SiO}$, $\text{Sn-C}_{60}\text{-O}^*$ and $\text{Sn-C}_{60}\text{-O-O}^*$ were TS, P and IS structures, respectively (structures are shown in figure 2). Calculated results in table 2 show that E_{ac} , ΔE_{ad} , ΔH_{ad} and ΔG_{ad} values of first reaction were 0.79, -3.67 , -3.61 and -3.52 eV, respectively.

Figure 2 shows that in IS structure, the SiO was close to $\text{Sn-C}_{60}\text{-O-O}^*$ and the O-O was lengthened from 1.31 to 1.43 Å and in IS structure, the distance between SiO and O_2 was 3.15 Å. Figure 2 shows that in TS structure, the $\text{Sn-C}_{60}\text{-O-O}^* \text{-SiO}$ was designed and the O-O* and O*-Si were 1.57 and 1.67 Å, respectively. Therefore, results in the first reaction show that

a SiO_2 molecule was formed at room temperature because of interaction of $\text{Sn-C}_{60}\text{-O}^*$ with SiO_2 , which was weak.

In the second reaction ($\text{Sn-C}_{60}\text{-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60} + \text{SiO}_2$), the $\text{Sn-C}_{60}\text{-O}^* \text{-SiO}$, Sn-C_{60} and $\text{Sn-C}_{60}\text{-O}^*$ were TS, P and IS structures, respectively (structures shown in figure 3). Calculated results in table 2 show that E_{ac} , ΔE_{ad} , ΔH_{ad} and ΔG_{ad} values of the second reaction were 0.22, -3.02 , -2.98 and -2.91 eV, respectively.

Figure 3 shows that in IS structure, the SiO was close to $\text{Sn-C}_{60}\text{-O}^*$ and the O*-Si and Sn-O* bonds were 2.97 and 1.82 Å, respectively. Figure 3 shows that in TS structure, the $\text{Sn-C}_{60}\text{-O}^* \text{-SiO}$ was designed and the Sn-O* and O*-Si were 1.85 and 2.35 Å, respectively. Therefore, results show that in the second reaction, a SiO_2 molecule was formed at room temperature because of interaction of Sn-C_{60} with SiO_2 , which was weak.

In this study, first, the adsorption of O_2 and SiO on Sn-C_{60} surface were investigated and results indicated that interactions of the SiO with Sn-C_{60} were weak and O_2 adsorption on Sn-C_{60} surface was strong from energy view point. So when the equal amount of SiO and O_2 molecules were nearby

Figure 3. Plan of $\text{Sn-C}_{60}\text{-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60} + \text{SiO}_2$ reaction (bond distances (Å) and relative energies (eV)).

Table 2. Calculated parameters for $\text{Sn-C}_{60}\text{-O-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O} + \text{SiO}_2$, $\text{Sn-C}_{60}\text{-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60} + \text{SiO}_2$ and $\text{Sn-C}_{60} + \text{O}_2 + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$ reactions.

Reactions	E_{ac} (eV)	ΔE_{ad} (eV)	ΔH_{ad} (eV)	ΔG_{ad} (eV)
$\text{Sn-C}_{60}\text{-O-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O} + \text{SiO}_2$	0.79	−3.67	−3.61	−3.52
$\text{Sn-C}_{60}\text{-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60} + \text{SiO}_2$	0.22	−3.02	−2.98	−2.91
$\text{Sn-C}_{60} + \text{O}_2 + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$	0.75	−3.64	−3.58	−3.48

of Sn-C_{60} structure, the Sn-C_{60} surface was exactly covered by adsorbed O_2 molecule. Hence, we considered the LH reaction, i.e., $\text{Sn-C}_{60} + \text{O}_2 + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O-O-SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$ (structures shown in figure 4 and data reported in table 2) as a starting point, followed by the ER reaction, $\text{O}^* + \text{SiO} \rightarrow \text{SiO}_2$. Figure 4 shows that in IS structure, the O_2 and SiO was near to Sn-C_{60} and in IS structure, the distance between the Sn-C_{60} and SiO and O_2 were 2.39 and 2.24 Å, respectively. Figure 4 shows that in TS structure, the $\text{Sn-C}_{60}\text{-O-O}^*\text{-SiO}$ was designed and the O-O^* and $\text{O}^*\text{-Si}$ were 1.63 and 1.61 Å, respectively. Calculated results in

table 2 show that E_{ac} , ΔE_{ad} , ΔH_{ad} and ΔG_{ad} values of second reaction were 0.75, −3.64, −3.85 and −3.48 eV, respectively.

It is remarkable that two investigated reactions ($\text{Sn-C}_{60}\text{-O-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O-O-SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$ and $\text{Sn-C}_{60}\text{-O}^* + \text{SiO} \rightarrow \text{Sn-C}_{60} + \text{SiO}_2$) in figures 2 and 3 were exothermic. In table 2, the calculated ΔG_{ad} proposed that the two studied reactions were negative in normal temperature and so the SiO oxidation via $\text{Sn-C}_{60}\text{-O}^*$ and $\text{Sn-C}_{60}\text{-O-O}^*$ was favourable from the thermodynamic view point. Finally, results show that Sn-C_{60} can be remarkable catalyst for SiO oxidation via LH mechanism

Figure 4. Plan of $\text{Sn-C}_{60} + \text{O}_2 + \text{SiO} \rightarrow \text{Sn-C}_{60}\text{-O}^* + \text{SiO}_2$ reaction (bond distances (Å) and relative energies (eV)).

with high efficiency due to low barrier energy in normal temperature.

4. Conclusion

The DFT method was used to SiO oxidation on activated Sn-C_{60} surface via LH and ER mechanisms. Results indicated that Sn-C_{60} can be an efficient catalyst to SiO oxidation in normal temperature. Results show that O_2 adsorption on Sn-C_{60} surface increased the chemical activity of Sn-C_{60} . Results show that ΔE_{ad} and q values of $\text{Sn-C}_{60}\text{-O}_2$ were higher than

$\text{Sn-C}_{60}\text{-SiO}$. When the SiO and O_2 reached Sn-C_{60} , the Sn-C_{60} surface was concurrently surrounded by O_2 . Results show that SiO oxidation on Sn-C_{60} via the LH mechanism has lower energy barrier than ER mechanism. Finally, results propose that Sn-C_{60} can be a novel catalyst to SiO oxidation with high efficiency in normal temperature.

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