Doubly-Charged Negative Ions of Triple-Hybrid Atomic-Metal, Super-benzene, Fullerene, and Nanotube as Novel Catalysts for Clean Air through SO_2 Reduction by CO

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Abstract

Sulfur dioxide (SO_2) reduction remains an area of global necessity further enhanced by the current international focus on pandemic diseases mitigation, elimination of air pollution, and promotion of renewable green energy. The dynamics of chemical bond-strength breaking and reformation in the transition state (TS) is a fundamental process in the reduction of SO_2 by CO. Density Functional Theory (DFT) has been used to determine optimal TS reaction pathway via a novel triple-hybrid catalyst utilizing doubly-charged negative atomic V, Mn, and Au. The triple-hybrid catalyst is furthermore tailored to the subsequent minimization of each individual step of the 3-Step SO_2 reduction by CO chemical reaction. Each optimized step 1, 2, and 3 is minimized with doubly-charged V, Mn, and Au, respectively, with TS barrier reductions ranging from 1.18 eV to 0.002 eV. Super-benzene, armchair (6, 6) single wall carbon nanotube, and fullerene TS reaction pathways have also been calculated to compare the nanoscale catalytic effectiveness with that of the atomic scale transition metals.

***Keywords*:** Sulfur dioxide reduction; doubly-charged anions; triple-hybrid catalyst; super-benzene; fullerene; atomic metals; tunable catalysts; carbon nanotube

1. Introduction

Sulfur dioxide (SO_2), produced in large quantities in the combustion of coal and other fuels in domestic and industrial activities is important due to its toxicity and in large quantities as a common air pollutant. Sulfur dioxide is rapidly oxidized in heterogenous and homogeneous reaction mechanisms. Sulfur is largely found as SO_2 and its high reactivity with CO is further heightened through humidity as well as combustive conditions. Furthermore, SO_2 is typically inhaled by industrial workers as well as the general population residing near industrial sites. This represents a primary vehicle for human exposure. A recent study of the current state of environmental SO_2 pollution concluded that pine needles present in industrialized and urban ecological sites contained the highest concentrations of sulfur [1].

Therefore, SO_2 reduction by CO remains generally an area of great interest globally due to the current need for cleaner air, mitigation of unwanted bacterial growth, and further environmental impedance of viral transmissions such as the now ravaging COVID-19. The understanding of the sulfur evolution mechanism during the reduction reaction of SO_2 with CO over carbon materials is also essential for the development of innovative methods to recover elemental sulfur [2]. Importantly, in the investigation [2] it was discovered that in the reaction with a CO/SO_2 ratio of 3, COS resulted as the primary sulfur-containing product rather than elemental sulfur. The effect of alkali/alkaline earth metals on the adsorption-desorption cycle of activated carbon (AC), which provides a deeper understanding of sulfur migration in the AC flue gas desulfurization process, has been elucidated [3]. Porous carbon materials have emerged as a new technology with tremendous potential as energy-saving and environmentally friendly pathways for SO_2 removal [4]. The use of model adsorbents and Density Functional Theory (DFT) calculations has yielded a new insight into the SO_2 adsorption behavior of oxidized carbon materials [5].

Compared with other gases, the SO_2 reduction by CO is expected to yield a higher conversion rate when the temperature is relatively low provided an appropriate catalyst is utilized [6]. SO_2 and CO coexist in petrochemical waste gases [6]. Previously, catalysts such as the bimetal Pt-Au [7], alumina supported

transition metals [6] and La_2O_2S [8] have been developed for the selective reduction of SO_2 using CO. More recently the Au_5Cu^- has been proposed as an ideal catalyst for the simultaneous removal of SO_2 and CO [9]. The main reaction considered in [9] for the removal of both SO_2 and CO was $SO_2 + 2CO \rightarrow S + 2CO_2$; it is represented here as a multistep process. Negative ion catalysis involves anionic molecular complex formation in the transition state (TS), with the anion weakening/breaking the bond strength [10]. In [11] DFT was used to determine the best catalyst among Fullerene anions, for both water oxidation to peroxide and water synthesis from H_2 and O_2. The effectiveness in catalyzing the oxidation of water to peroxide of the doubly-charged Fullerene C_{60}^{-2} anion, the negative metal ions Sn^{-2}, Pd^{-2}, Ag^{-2}, and Au^{-2}, the lanthanide anions La^{-2}, Ce^{-2}, Eu^{-2}, and Tm^{-2} and the actinide anions Th^{-2}, Pa^{-2}, Pu^{-2}, and U^{-2} has been investigated recently [12].

2. Results

Herein, we report activation energy barrier reductions supporting the potential production of doubly-charged negative ion hybrid nanoparticle catalysts utilizing the atomic metals V, Mn, and Au, Fullerene C_{60}, armchair (6, 6) carbon nanotube (CNT), and Super-benzene (C-24). A novel hybridized atomic catalytic triple metal optimal 3-Step TS pathway for the SO_2 reduction by CO is predicted to be 1.175eV, 0.002eV, and 0.003eV for the transition metals V^{-2}, Mn^{-2}, and Au^{-2}, respectively. Moreover, these are optimized predicted values for the SO_2 reduction by CO consistent with those reported in [9]. Our DFT results further suggest that the permutated combination of nanoscale catalysts may prove to be efficacious in further catalytic tuning and reaction mechanism optimization for a wide array of environmental and industrial applications requiring the neutralization of SO_2 and CO. We further demonstrate an optimal permutated carbon allotrope 3-Step reaction pathway of 0.141eV, 0.135eV, 0.45eV for TS-1, TS-2, and TS-3 using C-24, C-24, and armchair CNT (6, 6), respectively. It is important to note that for C-24 we utilized the (2+1) cyclo-addition approach to achieve the oxidation reduction for the system [13]. Furthermore, the persulfurated version of the C-24 molecule has been featured as the premiere molecule in C&EN's "Molecules of The Year" for 2017 as synthesized by Dong and Pfeffermann et. al.[14,15]. Conclusively, the TS values for doubly-charged negative Fullerene C_{60} catalysis of SO_2 reduction mechanism are predicted to attenuate the speed of the reaction by comparison as seen in Table II.

The multistep reaction pathway of SO_2 reduction by CO of interest here is described by:

$$\mathbf{SO_2 + CO \xrightarrow{catalyst} SO + CO_2} \qquad \mathbf{(1)}$$

$$\mathbf{SO + CO \xrightarrow{catalyst} S + CO_2} \qquad \mathbf{(2)}$$

$$\mathbf{S + CO \xrightarrow{catalyst} COS} \qquad \mathbf{(3)}$$

We have applied typical doubly-charged transition metal atoms and nanoscale carbon allotrope molecules to the 3-Step SO_2 reduction by CO synthesis reaction in order to predict optimized minimum transition state pathways TS-1, TS-2, and TS-3 utilizing DFT. Our results indicate that the atomic scale combination of doubly-charged V-23, Mn-25, and Au-79 is overall the most efficient pathway as compared to the nanoscale carbon allotrope systems for TS-1, TS-2, and TS-3, as shown in Figure 1 and Table I. Notably, Super-benzene (C-24) exhibits almost a factor of 10 catalytic superiority strength over Fullerene C_{60} and CNT (6, 6) for both TS-1 and TS-2. However, for the TS-3 the three nanoscale molecules C-24, CNT (6, 6) and Fullerene C_{60} yield almost the same energy reduction as demonstrated by Figure 2, Figure 3, and Table II.

Element (doubly charged)	Transition State Energy (eV)	Reaction Steps
V-23	1.175	Step 1 (TS-1)
Mn-25	0.002	Step 2 (TS-2)
Au-79	0.003	Step 3 (TS-3)

Table I: Transition state barrier minima calculated in units of (eV) associated with the optimal reaction steps for the 3-step reaction of the synthesis of COS from SO_2 utilizing the proposed triple-hybrid catalyst tuned by atomic Vanadium, Manganese, and Gold, respectively.

Carbon Allotrope (doubly-charged)	TS-1 (eV)	TS-2 (eV)	TS-3 (eV)
C60	2.79	3.47	0.47
CNT (6,6)	1.35	2.52	0.416
C-24	0.141	0.135	0.45

Table II: Transition state barrier minima calculated in units of (eV) for the intermediate reaction steps TS-1, TS-2 and TS-3 for the 3-step reaction of the synthesis of COS from SO_2 utilizing the doubly-charged nanoscale catalyst molecules Fullerene (C60), armchair carbon nanotube CNT (6,6), and Super-benzene (C-24), respectively.

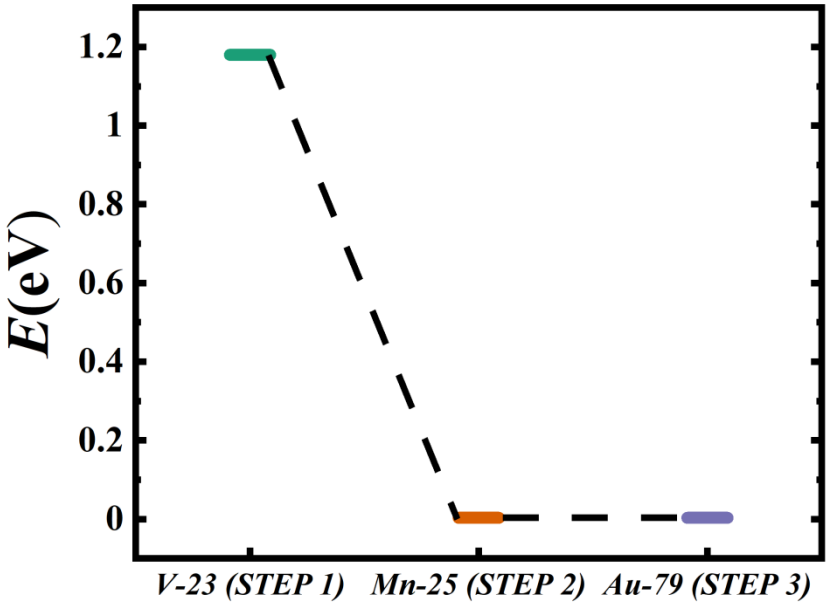

Figure 1a: Calculated transition state reaction barriers of the doubly-charged V-23, Mn-25, and Au-79 for the optimized 3-step SO_2 reduction reaction by CO, represented by the cyan, orange, and purple bars, respectively.

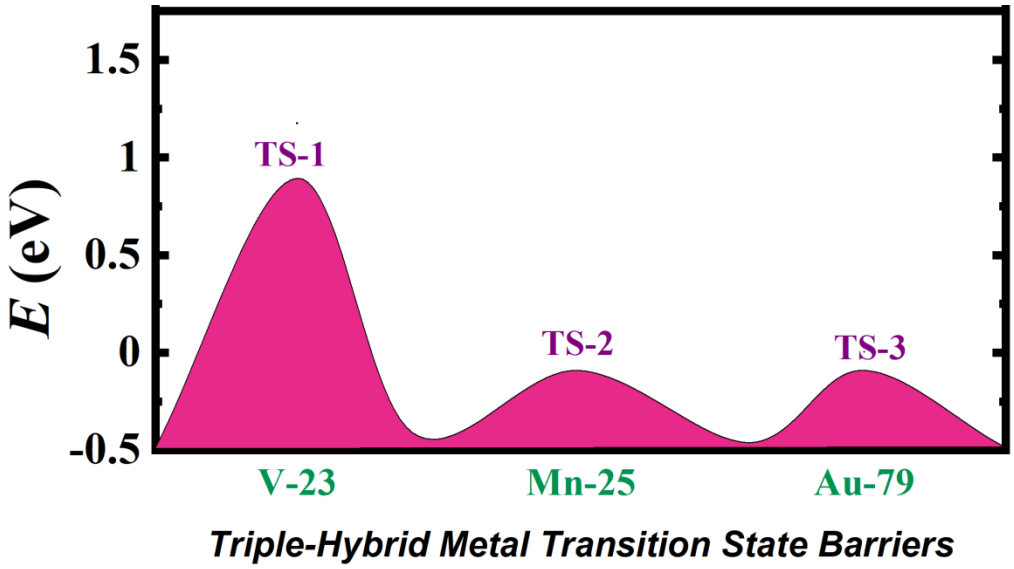

Figure 1b: Calculated transition state reaction barriers of the doubly-charged V-23, Mn-25, and Au-79 for the optimized 3-step SO_2 reduction reaction by CO, represented by proposed conceptual oscillating pink reaction space.

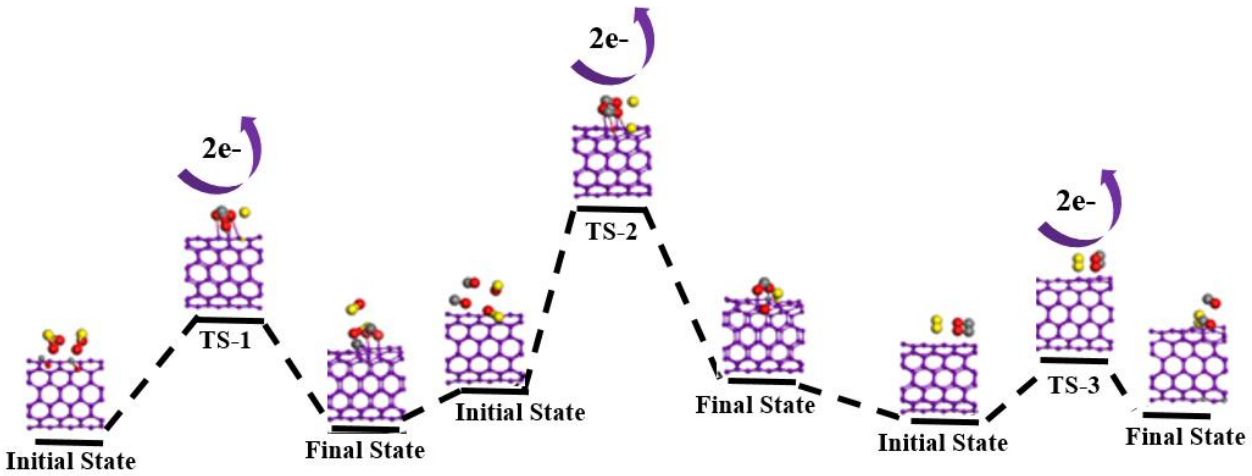

Figure 2: Calculated intermediate transition state energy barriers of the doubly-charged anions of (6, 6) armchair carbon nanotube (CNT) allotrope for the catalysis of the 3-step (TS-1, TS-2, TS-3) SO_2 oxidation reduction reaction where Sulfur, Oxygen, Carbon, and CNT (6,6) are represented by the yellow, red, gray, and purple spheres, respectively.

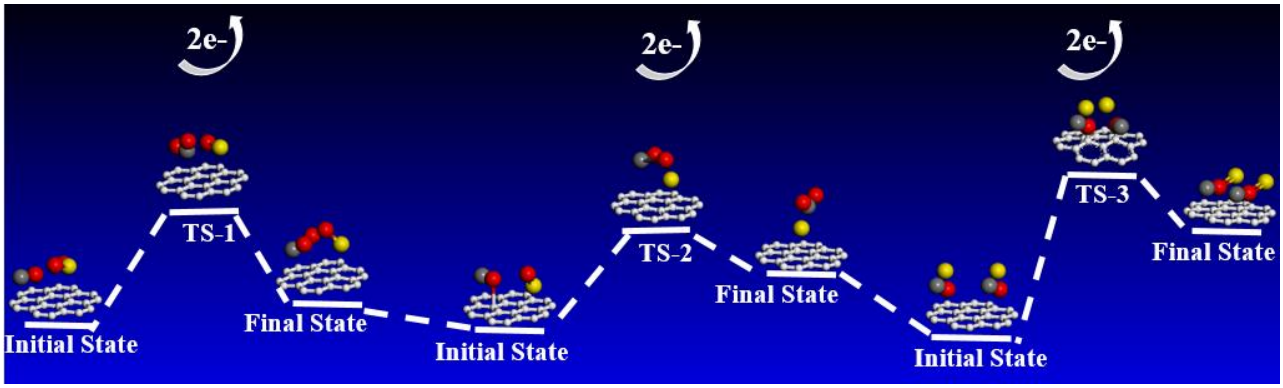

Figure 3: Optimized geometric structures for Super-benzene (C-24) of relative (not-to-scale) transition state (TS) pathway calculations for the 3-Steps 1, 2, and 3 of the SO_2 reduction reaction by CO indicated by TS-1, TS-2, and TS-3, as well as the renderings for the associated initial and final states. Carbon, Oxygen, and Sulfur are represented by the gray, red, and yellow spheres, respectively.

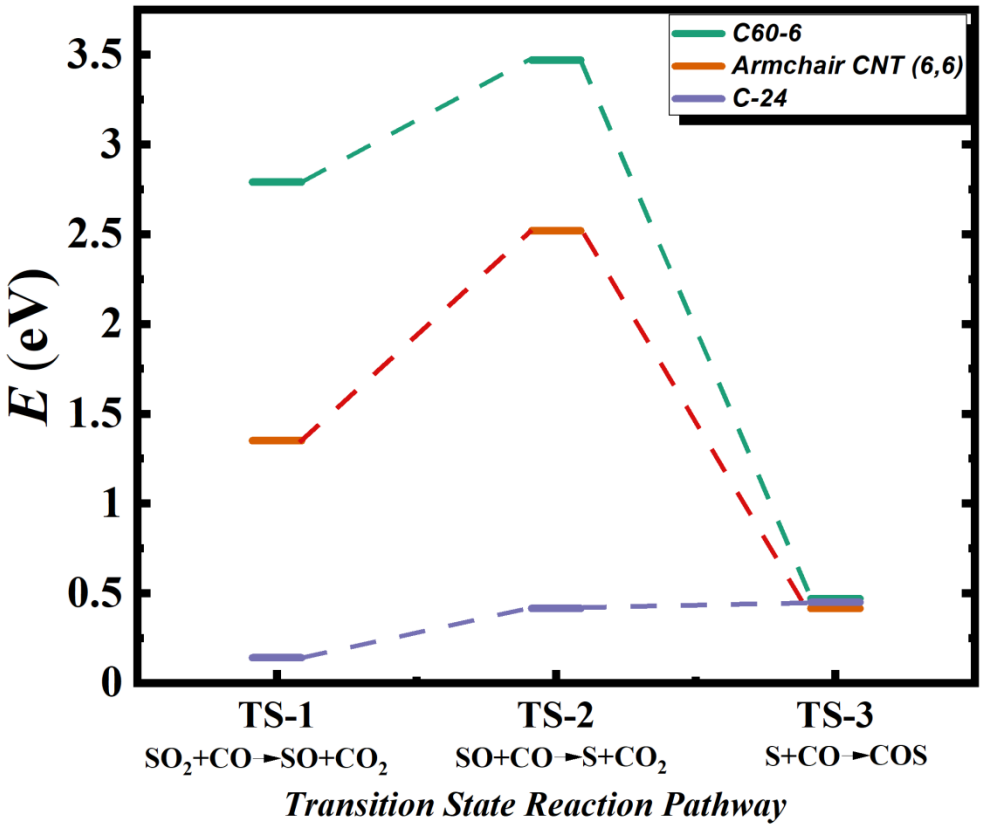

Figure 4: Calculated transition state reaction barriers of the doubly-charged Fullerene (C60), armchair carbon nanotube (6, 6), and Super-benzene consisting of 24 carbon atoms (C-24) for the optimized 3-step SO_2 reduction reaction by CO, represented by the cyan, orange, and purple bars, respectively.

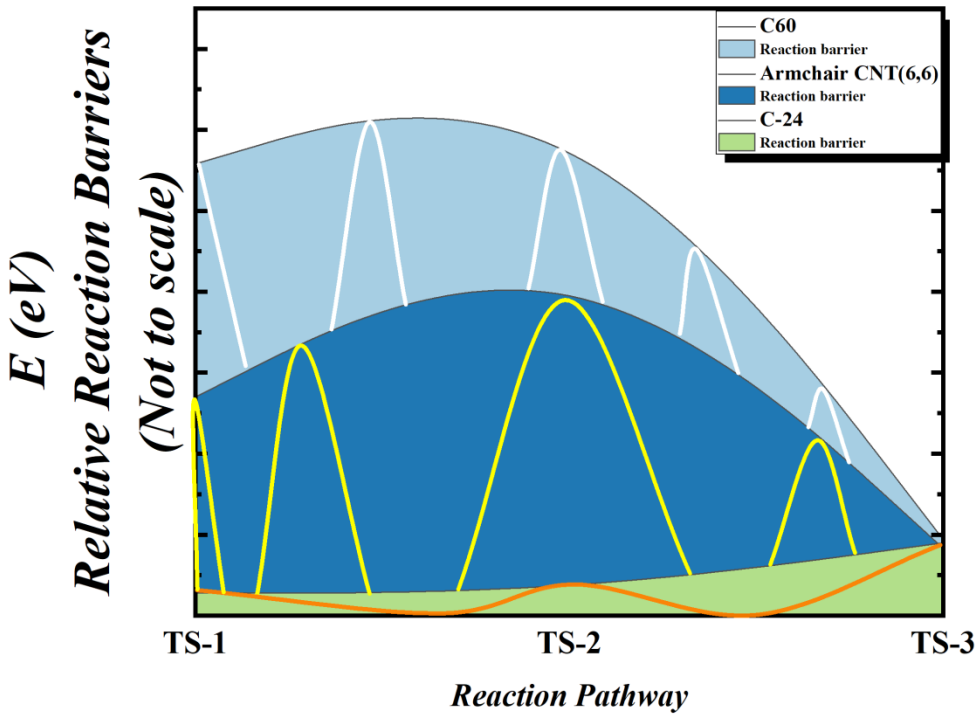

Figure 5: Calculated transition state reaction barriers of the doubly-charged Fullerene (C60), armchair carbon nanotube (6, 6), and graphene consisting of 24 atoms (C-24) for the optimized 3-step SO_2 reduction reaction by CO, represented by light blue, blue, and light green reaction barrier space, respectively. The white, yellow, and orange curves are conceptual renderings for the tendency of the chemical reactions to oscillate within the reaction barriers.

The overall results suggest that atomic scale systems tend to accelerate the catalytic reaction processes whereas nanoscale molecules can be used to relatively slow down the reactive transition states resulting in plausible tunable systems tailored to the potential specifications of industrial processes involving SO_2 reduction by CO mechanism.

Method

The atomic and nanoscale molecules have been geometrically optimized via the DFT of Burke-Lee-Yang-Parr (BLYP) approximation [16, 17]. The initial and final states for the 3-Step reaction of the SO_2 synthesis to COS are calculated with a self- consistent field (SCF) tolerance of 0.01Ha for the TS-1, TS-2, and TS-3 activation energy barriers. Subsequently, the linear synchronous transit approach has been utilized for the approximation of the relative doubly-charged transition states [18, 19].

3. Conclusion

Nanoparticles formed from doubly-charged negative atomic metals are proposed for novel highly efficient acceleration of the catalysis of SO_2 conversion to COS consistent with the previous predictions of similar oxidation reduction reactions such as water conversion to peroxide [11, 12]. Our findings suggest that hybridizing the proposed catalyst using doubly-charged V-23, Mn-25, and Au-79 for the steps TS-1, TS-2, and TS-3, respectively could prove to be optimal for "Step-tuning" the chemical reaction pathways. Furthermore, nanoscale molecules Super-benzene (C-24), armchair nanotube CNT (6,6), and Fullerene C_{60} have been demonstrated to relatively slow down the synthesis reaction with Super-benzene predicted to be an excellent nanoscale accelerative candidate. This suggests further tunable catalytic properties among the doubly-charged negative multiscale atomic and nanoscale molecular systems. The presented

novel approach to SO_2 conversion to COS could accelerate the effort toward the elimination of its air pollution effect, and promotion of renewable green energy.

Author Contributions:
K. Suggs and A. Z. Msezane are responsible for conceptualization, methodology, investigation, formal analysis and writing of the original draft as well as rewriting and editing. A. Z. Msezane is also responsible for securing the funding for the research.

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Conflict of Interest:
The authors declare no conflict of interest or state

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