

# **Noble Metal Supported GeS Monolayer as Promising Single Atom Catalyst for CO Oxidation**

Sharmistha Karmakar, Chandra Chowdhury and Ayan Datta\*

*Department of Spectroscopy, Indian Association for the Cultivation of Science, 2A  
and 2B Raja S. C. Mullick Road, Jadavpur – 700032, Kolkata, WestBengal, India.*

\*Email: [spad@iacs.res.in](mailto:spad@iacs.res.in)

# Supporting Information File

## Available Information:

- PDOS plots for free metal atoms.
- AIMD results for Ir-GeS system at 300K
- Microkinetic analysis.

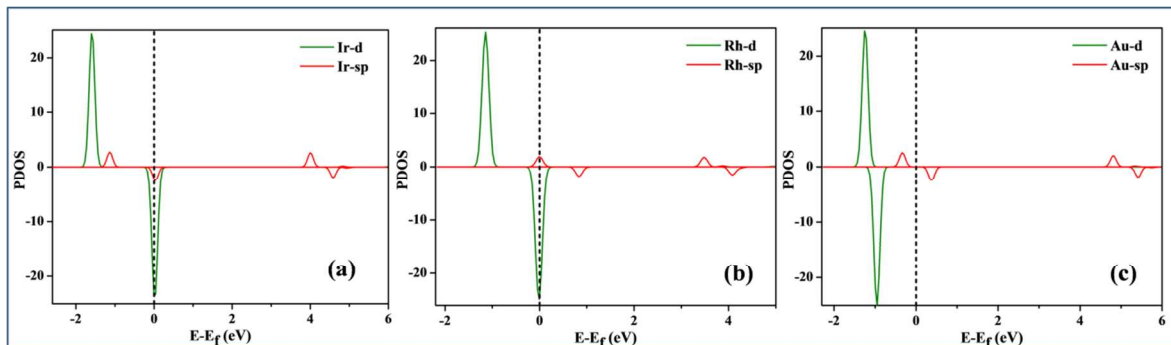


Figure S1: The spin-polarized PDOS plots of selected metal orbitals ( $4d$ ,  $5s$  and  $5p$  for Rh and  $5d$ ,  $6s$  and  $6p$  for Au and Ir) for free metal atoms (a) Ir, (e) Rh and (f) Au.

### AIMD analysis for Ir-GeS at 300K:

#### Computational methodology for AIMD calculations:

Ab – initio molecular dynamics (AIMD) simulations are carried out using the QUICKSTEP program implanted in CP2K package.<sup>1</sup> This algorithm uses a Gaussian plane-wave (GPW) approach where Kohn-Sham orbitals are generated in an atom-centered Gaussian basis. Auxiliary plane wave basis sets are used to describe electronic charge density. Under GPW approach, the norm-conserving Goedecker, Teter, and Hutter (GTH) pseudopotentials have been used to describe the core electrons as well as nuclei, double  $-\zeta$  valance polarized basis set (DZVP-MOLOPT-SR-GTH) are used to treat electrons in the valence shell. We employed Grimme's DFT-D3 method to incorporate non-covalent interactions. All simulations are carried out at 300K in the NVT ensemble where isothermal condition is maintained using Nosé-Hoover thermostat. Velocity-Verlet algorithm is used to integrate the equations of motion taking 0.5 fs as the time step and all the trajectories were propagated for at least 25 ps.

### Plot of RMSD and radial distribution function

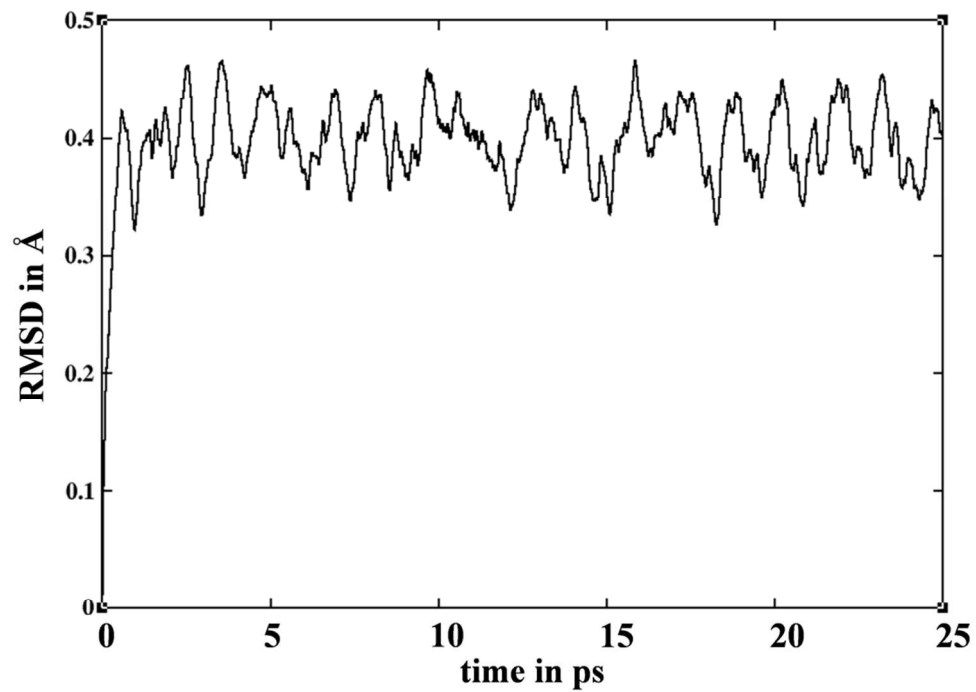


Figure S2: Plot of RMSD with time for Ir supported GeS monolayer at 300 K.

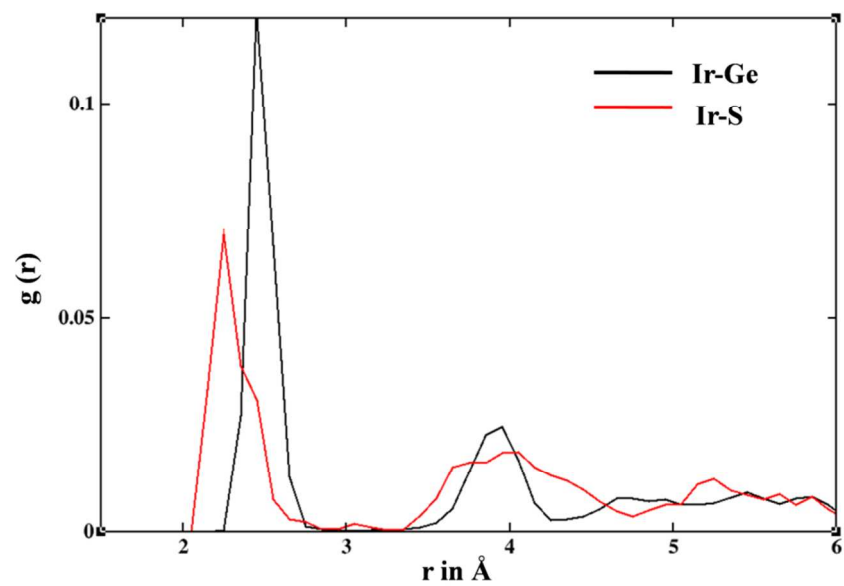


Figure S3: Plots of radial distribution function [ $g(r)$ ] between Ir-Ge and Ir-S pairs for Ir-GeS SAC at 300 K.

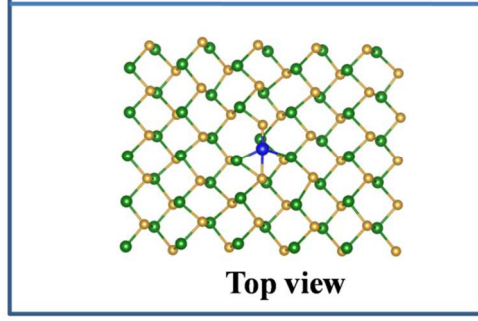


Figure S4: Equilibrated structure of Ir-GeS system 300 K.

### Microkinetic analysis for CO oxidation:

A microkinetic analysis was carried out from the DFT calculated values to get further insight about the surface coverage, partial pressure of the reactant and product and reaction temperature. CO oxidation can occur through three distinct mechanisms namely, Eley–Rideal (ER) and bimolecular Langmuir–Hinshelwood (BLH) and trimolecular Eley–Rideal (TER) mechanism. We have evaluated the maximum CO oxidation rate for all three mechanisms. The elementary steps considered for CO oxidation following TER mechanism (Figure 5) are summarized as following



Here, the labels " \* " and "  $\ddagger$  " symbolize the bare Ir site and Ir site with one adsorbed CO. We need to consider also the competitive adsorption of  $O_2$  molecule on site " \* " and "  $\ddagger$  ". The adsorption of CO and  $O_2$  molecules on site " \* " and "  $\ddagger$  " (step R1, R2, R5 and R6) are

highly exothermic and, therefore, they are assumed to be in equilibrium. The equilibrium constants ( $K_{CO}^*$ ,  $K_{CO}^\ddagger$ ,  $K_{O_2}^*$ ,  $K_{O_2}^\ddagger$ ) are calculated as following

$$K_{eq} = \exp[-(\Delta E_{ad} - T\Delta S_{ad})/k_B T]$$

where,  $\Delta E_{ad}$  is the CO or O<sub>2</sub> adsorption energy at site " \* " or " ‡ ",  $\Delta S_{ad}$  is the entropy change upon adsorption, T represents temperature and  $k_B$  is the Boltzmann constant. The gas phase entropies for CO and O<sub>2</sub> are obtained from NIST database. All the exothermic reactions are assumed to be irreversible; hence only forward steps are considered. All the rate constants are calculated using harmonic transition state theory

$$k = \frac{k_B T}{h} \times \frac{Q_{TS}}{Q_A Q_B} \times \exp-(\Delta E^\ddagger/k_B T)$$

Here,  $Q_{TS}$  is the transition state partition function,  $Q_A$  and  $Q_B$  are the partition functions for the reactants.  $\Delta E^\ddagger$  represents the activation barrier for that step. For step R3 and R4, we have considered only the forward rate constants as the reverse rate constants are negligible due to large activation barrier. The term  $\frac{Q_{TS}}{Q_A Q_B} \approx 1$ , when both the reactants and the transition state are adsorbed species (as for step R4). However, when one of the reactant molecules reacts from the gas phase as the case with ER mechanism (step R3), the contribution from the translational and rotational partition functions for the gas phase species makes the overall pre-exponential factor lower. Campbell's degree of rate control (DRC) analysis<sup>2</sup> was used to identify the elementary step that controls the overall CO oxidation rate. The degree of rate control coefficient ( $\chi_{RC,i}$ ) for a specific elementary step (i) is calculated as following

$$\chi_{RC,i} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}$$

where,  $r$  is the overall reaction rate,  $k_i$  is the forward rate constant and  $K_i$  is the equilibrium constant for step i.

The coverage of CO ( $\theta_{CO}^*$  and  $\theta_{CO}^\ddagger$ ) and O<sub>2</sub> ( $\theta_{O_2}^*$  and  $\theta_{O_2}^\ddagger$ ) at different sites are obtained by the following equations

$$\theta_{CO}^* = K_{CO}^* p(CO)\theta_*, \quad \theta_{CO}^\ddagger = K_{CO}^\ddagger p(CO)\theta_\ddagger, \quad \theta_{O_2}^* = K_{O_2}^* p(O_2)\theta_*, \quad \theta_{O_2}^\ddagger = K_{O_2}^\ddagger p(O_2)\theta_\ddagger$$

where,  $p(CO)$  and  $p(O_2)$  are the partial pressures of CO and O<sub>2</sub>.  $\theta_*$  and  $\theta_\ddagger$  represent the free active sites. The coverage of the intermediate species, i.e. MS1-TER ( $\theta_{MS1-TER}$ ) is obtained by applying steady-state approximation. The sum of coverage of adsorbents (CO, O<sub>2</sub>, MS1-TER) and free active sites should be 1 for both site \* and ‡, respectively. Hence,  $\theta_*$  and  $\theta_\ddagger$  are calculated as following for TER mechanism

$$\theta_* + \theta_{CO}^* + \theta_{O_2}^* + \theta_{MS1-TER} = 1 \quad ; \quad \theta_\ddagger + \theta_{CO}^\ddagger + \theta_{O_2}^\ddagger = 1$$

The maximum rate for CO<sub>2</sub> formation can be obtained as following

$$r_{CO_2} = 2k_2\theta_{MS1-TER}, \text{ where } \theta_{MS1-TER} = \frac{k_1}{k_2} p(O_2)\theta_{CO}^\ddagger\theta_{CO}^*$$

The CO oxidation rate following the TER mechanism at 298 K was found to be  $5.34 \times 10^3 \text{ s}^{-1}$  for  $p(CO) = 0.01$  bar and  $p(O_2) = 0.21$  bar. Here, step R3 i.e. formation of MS1-TER intermediate is the rate determining step according to Campbell's degree of rate control analysis.

The elementary steps considered for CO oxidation following BLH mechanism (Figure 4) are summarized as following:





The coverage of the intermediate species, i.e. MS1-BLH ( $\theta_{MS1-BLH}$ ), FS1 ( $\theta_{FS1}$ ) and MS1-ER ( $\theta_{MS1-ER}$ ) are obtained by applying steady-state approximation. The sum of coverage of adsorbents (CO, O<sub>2</sub>, MS1-BLH, FS1 and MS1-ER) and free active sites should be 1 for both site ‡ and \*, respectively. Hence,  $\theta_*$  and  $\theta_{\ddagger}$  are calculated as following for BLH mechanism

$$\theta_* + \theta_{CO}^* + \theta_{O_2}^* + \theta_{MS1-BLH} + \theta_{FS1} + \theta_{MS1-ER} = 1 \quad ; \quad \theta_{\ddagger} + \theta_{CO}^\dagger + \theta_{O_2}^\dagger = 1$$

The maximum rate for CO<sub>2</sub> formation following BLH mechanism can be obtained as following

$$r_{CO_2} = 2k_2\theta_{MS1-BLH}, \text{ where } \theta_{MS1-BLH} = \frac{k_1}{k_2}\theta_{O_2}^\dagger\theta_{CO}^*$$

The CO oxidation rate following the BLH mechanism at 298 K was found to be  $4.7 \times 10^{-3} \text{ s}^{-1}$  for  $p(CO) = 0.01 \text{ bar}$  and  $p(O_2) = 0.21 \text{ bar}$ . Here, step R7 i.e. formation of MS1-ER intermediate is the rate determining step according to DRC analysis.

The elementary steps considered for CO oxidation following ER mechanism (Figure 6) are summarized as following:



The coverage of the intermediate species, i.e. MS1-ER ( $\theta_{MS1-ER}$ ) and FS1 ( $\theta_{FS1}$ ) are obtained by applying steady-state approximation. The sum of coverage of adsorbents (CO, O<sub>2</sub>, FS1 and MS1-ER) and free active sites should be 1 for site \*. Hence,  $\theta_*$  is calculated as following for ER mechanism



$$\theta_* + \theta_{CO}^* + \theta_{O_2}^* + \theta_{FS1} + \theta_{MS1-ER} = 1$$

The maximum rate for CO<sub>2</sub> formation following ER mechanism can be obtained as following

$$r_{CO_2} = 2k_1\theta_{O_2}^*p(CO)$$

The CO oxidation rate following the ER mechanism at 298 K was found to be  $1.8 \times 10^{-15} \text{ s}^{-1}$  for  $p(CO) = 0.01$  bar and  $p(O_2) = 0.21$  bar. Here, step R3 i.e. formation of FS1 and physisorbed CO<sub>2</sub> is the rate determining step according to Campbell's degree of rate control theory.

Reference:

1. Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. CP2K: atomistic simulations of condensed matter systems. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2014**, 4, 15-25.
2. Stegeimann, C.; Andreasen, A.; Campbell, C. T. Degree of Rate Control: How Much the Energies of Intermediates and Transition States Control Rates. *J. Am. Chem. Soc.* **2009**, 131, 8077-8082.