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Analysis of the Pyrolysis of Methane Reaction over Molten Metals for CO_2-Free Hydrogen Production: An Application of DFT and Machine Learning †

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Abstract: The co-production of CO_2 continues to remain the bane of several hydrogen production technologies, including the steam reforming of methane and the dry reforming of methane processes. Efficient utilization of abundant greenhouse gas in the form of methane provides opportunities for the design of an innovative system that will maximize the use of such a raw material in the most environmentally friendly manner. The study of the mechanism of the pyrolysis of methane reactions over molten metals provides promise for improved hydrogen yield and methane conversion with a greater turnover frequency. Catalyst electronic properties computed via Density Functional Theory using the Quantum Espresso code provided data that were built into a database. Using Bismuth as the base metal, active transition metals including Ni, Cu, Pd, Pt, Ag, and Au of different concentrations of 5, 10, 15, and 25% were placed on 96 atoms of the base metal and relaxed to obtain the optimized geometric structures for the catalytic reaction studies. The kinetics of the individual elementary steps of the pyrolysis reaction at preset temperatures over the bi-metals were calculated using the Car-Parinello (CP) method and Nudge Elastic Band (NEB) computations. The collated data of the various pyrolysis of methane reactions over the different bi-metals was used to train machine learning models for the prediction of reaction outcome, catalytic performance, and efficient operating conditions for the pyrolysis of methane over molten metals. The turnover frequency, which is determined using the transition state energies of the fundamental reaction cycles, will be used to simulate the stability of the catalyst.

Keywords: methane; catalyst; DFT; Car-Parinello simulation; hydrogen; methane pyrolysis; machine learning

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1. Introduction

Global demand for energy continues to increase, and hydrogen has become a promising fuel to power our industrial machines [1]. Hydrogen can be produced by water electrolysis, thermochemical, and biological methods. Among these, the biological process can be the most favorable because it requires less energy. The method of electrolysis of water requires a lot of energy and hence cannot be a viable alternative. Notwithstanding, it is often used when hydrogen is required in a highly pure form. Steam reforming, a type of thermochemical method, is often used to produce hydrogen, and steam reforming of methane is most commonly employed. Steam methane reforming (SMR) is the current industrial method of choice for hydrogen production. However, the SMR process still has disadvantages from reactant properties and thermodynamic conditions of the reaction,

which include insufficient catalytic activity, low long-term stability of reactant (methane), high production cost, and high energy consumption, mostly because of the management of large amounts of CO_2 co-produced [2].

With the growing need for hydrogen production and the need to adopt a process that is sustainable and environmentally friendly, it becomes necessary to upgrade some of the existing industrial processes used for hydrogen production for effective management of raw materials, such as methane, while adopting technologies that are environmentally sustainable. Furthermore, catalysts with higher activity and stability necessary to control the reaction routes and efficient reaction conditions, including temperature, pressure, feeding rate, type of reactor, etc., have to be improved for efficient hydrogen production [2,3].

The pyrolysis of methane over molten metals provides an opportunity for carbon dioxide-free hydrogen production while co-producing solid carbon that has several industrial applications as shown in Figure 1.

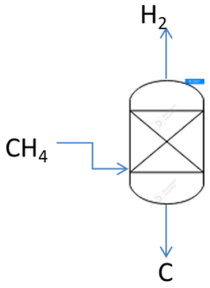


Figure 1. Schematic of pyrolysis of methane.

2. Methodology

This work involves an ab initio investigation of molten metals as catalysts for the heterogeneous catalysis of hydrogen production via methane pyrolysis. It has been reported that metals considered functional catalysts for methane (Ni, Pt, Pd, Cu, Ag, Au) when doped in Bi, an inactive low-melting temperature metal, yield stable molten metal alloy catalysts for the pyrolysis of methane into hydrogen gas and solid carbon [4,5].

$$CH_{4(g)} \rightarrow 2H_{2(g)} + C_{(s)} \qquad \Delta H^0 = 75\ \frac{\text{kJ}}{\text{mol}} \tag{1}$$

Experimental reports indicate the deactivation of solid catalysts, while the insoluble carbon would float to the surface in molten alloy systems in the reactor [4]. Hence, the aim of this work is to simulate the structural and chemical properties of molten alloy systems of varying concentrations of active and inactive metals using the ab initio molecular dynamics (MD) code of Car-Parinello (CP) implemented in Quantum Espresso.

The specific objectives being carried out in the study include:

- Determine the kinetic and wavefunction cut-offs for the separate metal and metal alloy systems.
- Perform variable cell relaxation for separate active (Ni, Pt, Pd, Cu, Ag, Au), inactive (In, Ga, Sn, and Pb), and molten metal alloy systems containing different concentrations.
- Determination of density of states (DOS), projected DOS, D-band, etc., to characterize the metal systems.
- Calculate the pair distribution functions, the local concentrations, and Bader charges for the constituent metal atoms as one approaches the surface of the liquid.
- Calculate the activation parameters for the dissociative adsorption of methane using a nudged elastic band (NEB).
- Calculate the adsorption energies of the adsorbate on the catalyst surface.
- Correlation of parameters such as concentrations with turnover frequency (TOF).
- Simulate the effect of temperature and pressure on the molten catalyst systems for the pyrolysis of methane.

- Predict catalytic performance and optimum operating conditions using machine learning models.

The procedures for carrying out the tasks above include:

1. Generation and optimization of catalyst constituents' crystal structures.
2. Variable cell relaxation SCF calculation for Bismuth base metal doped with varying proportions (0%, 5%, 10%, 15%, 25%) of Ni, Pt, and Pd.
3. Variable cell relaxation SCF calculation for Bismuth base metal doped with varying proportions (0%, 5%, 10%, 15%, 25%) of Ni, Pt, Pd, Cu, Ag, and Au using the PBE form of the generalized gradient approximation for the electron exchange and correlation and the electron core interaction described using projector augmented wave (PAW), ultrasoft (US) pseudopotentials (PPs), and norm-conserving (NC) methods.
4. Cell Molecular Dynamics was calculated using the Car-Parinello Method for thermostat-varied temperatures with a cell vacuum thickness of 12A for the simulation. Electron and ion dynamics were simulated using the Verlet algorithm.
5. Computation of adsorption energies with the formulae:

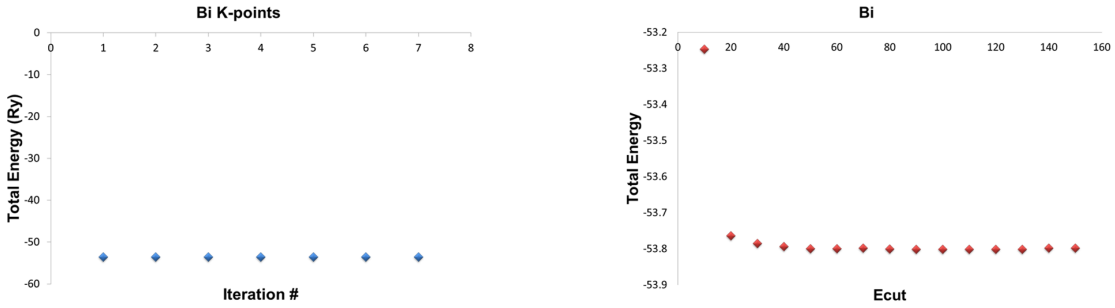
$$E_{ads} = E_{surface+adsorbate} - (E_{surface} + E_{adsorbate})$$

6. The transition state will be found via a two-step approach using the nudged elastic band (NEB).
7. Computation of catalyst TOF/TON
8. Creation of and comparison of ML models for the prediction of efficient catalyst compositions and optimum operating conditions using the computed adsorption energies, binding energies, and reaction kinetics. The models will be compared on the basis of their MAE, MSE, and R^2 for the selection of the most accurate models for the prediction

3. Results and Discussion

3.1. Computational Parameters Optimization

The selection of the K-points for the description of the Brillouin zone of the crystal structures created from the doping of the base Bismuth crystal structure with varying percentages (0%, 5%, 10%, 15%, and 25%) of Ni, Pt, Pd, Cu, Ag, and Au was conducted by comparing the total atomic energies of the structures using varying K-points ranging from 7 | 7 | 7 to 1 | 1 | 1. The 5 | 5 | 5 K-point was seen to produce the lowest atomic energy and considered the optimum K-point for the un-doped Bismuth structures, as shown in Figure 2a. Similarly, the kinetic energy cut-off (Ecut) was decided upon using the same optimization method. Varying Ecuts produced varying total energy outputs. The Ecut of 90Ry was found to be the optimum Ecut for the un-doped Bismuth, as shown in Figure 2b. The relaxed Bismuth structures were further doped using Ni, Pt, Pd, Cu, Ag, and Au. Figure 3a,b illustrate the visual distribution of atoms in the base Bismuth structure when non-relaxed and when relaxed, while Figure 3a,b illustrate the visual distribution of atoms in the relaxed base Bismuth structure doped with 5% gold and 10% gold, respectively.



(**a**) (**b**)

Figure 2. (**a**) K-point optimization for 100% Bi crystal; (**b**) kinetic energy cut-off for charge density of Bi crystal.

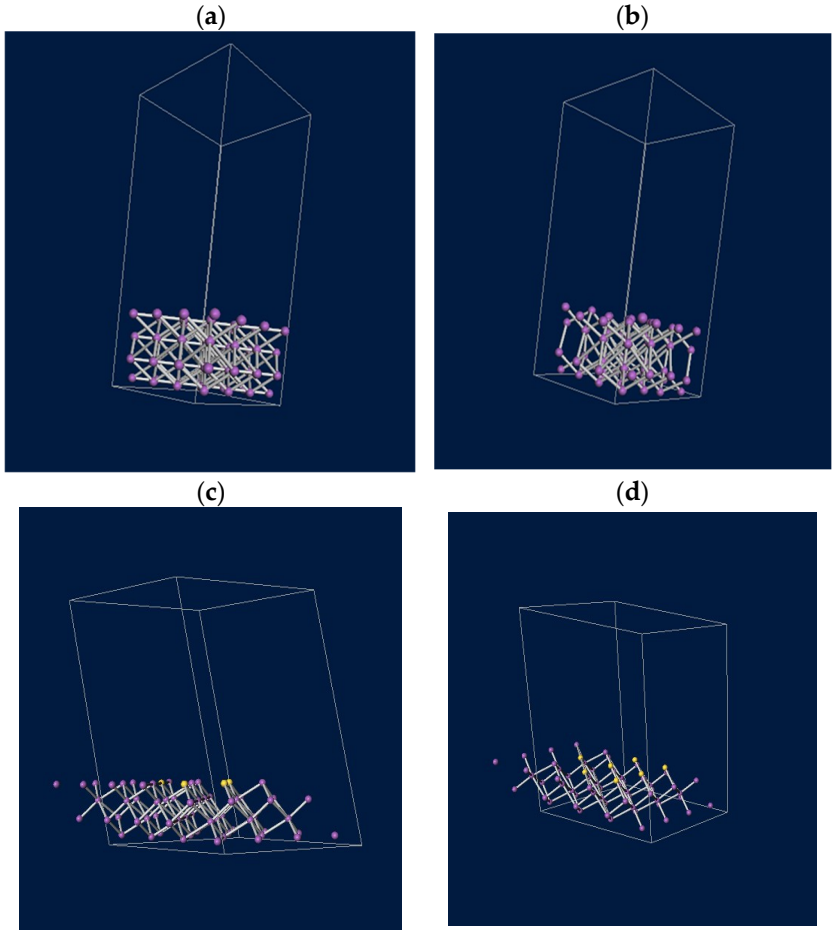
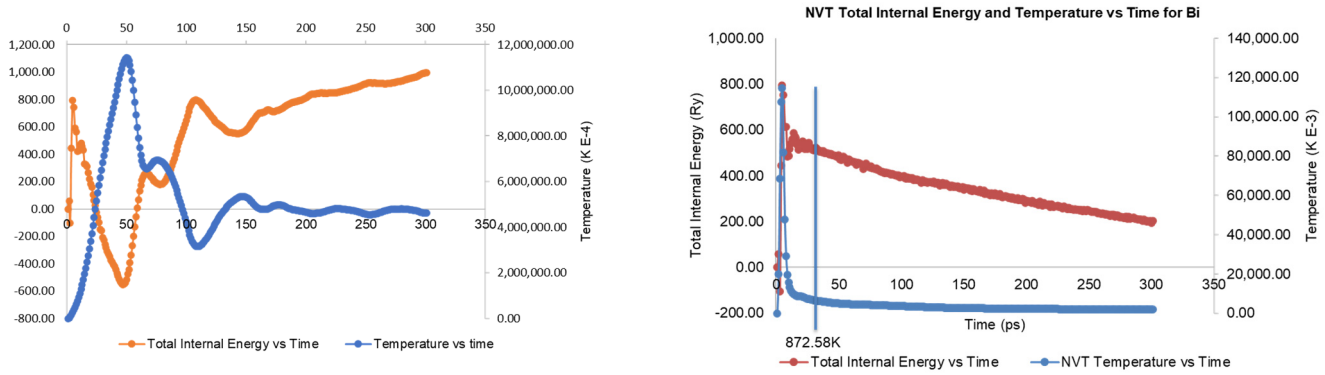


Figure 3. (**a**) Non-relaxed Bi crystal; (**b**) relaxed Bi crystal; (**c**) relaxed Bi 0.95Au0.05 crystal; (**d**) relaxed Bi 0.95Au0.10 crystal.

3.2. Molecular Dynamics of Bismuth Base Metal

The NVE ensemble of the Bismuth base metal system corresponds to the microcanonical ensemble, where the system is isolated and exchanges neither energy nor particles with its surroundings. This isolation allows for the study of the system's intrinsic properties without interference from external factors. Using the Car-Parinello method for molecular dynamics of the Bismuth base structure comprising 64 atoms, the system is seen to commence relaxation in 90 ps with a ground state energy of 210 Ry. Similarly, the NVT ensemble allows for the simulation of the Bismuth systems at specified temperatures. Simulations in the NVT ensemble enable the calculation of various thermodynamic properties, such as energy fluctuations, heat capacity, entropy, and other temperature-dependent quantities.

These properties are essential for understanding the behavior of materials under different temperature regimes. The pure Bismuth system was seen to stabilize at an internal energy of 545 Ry and a temperature of 872.58 K using an ion temperature set at 460 K using a "Nose" thermostat. Figure 4a is an illustration of the NVE ensemble internal energy and temperature vs. time for Bi crystal, while Figure 4b is a graph of the NVT ensemble internal total internal energy and temperature vs. time for Bi, signifying the nature of the stabilization of the Bismuth system with varying temperatures. The stabilization temperature for molten Bismuth well below its melting point confirms the suitability of the Bismuth as a base metal for methane pyrolysis.



(**a**) (**b**)

Figure 4. (**a**) NVE ensemble internal energy and temperature vs. time for Bi crystal, indicative that Bi crystal with 64 atoms relaxes within 90 ps; (**b**) NVT ensemble internal total internal energy and temperature vs. time for Bi.

4. Conclusions

At the current level of the study, the following preliminary conclusions have been reached:

1. Bi crystal with 64 atoms relaxes within 90 ps with a ground state energy of 210 Ry, which is a suitable base metal for pyrolysis of methane, as confirmed by an NVE simulation.
2. NVT simulation is indicative that in connection with a heat bath, the optimum temperature for MD is 872.58 K, which is above the melting point of Bi. Hence, its suitability as a molten base metal carrier for active metals for CH4 pyrolysis.

Based on the above observations, Bismuth is a suitable base metal for carrying active metal catalysts for the pyrolysis of methane. Hence, the computational modeling of bimetallic catalysts for the pyrolysis of methane over molten metals will proceed in line with the methodology laid down.

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Conflicts of Interest: The authors declare no conflicts of interest.

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