

DFT Analysis of Metal Complexes for Selective Nitrogen Removal from the Syngas Based on Binding Energy Criteria

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ABSTRACT

The presence of nitrogen in air gasification adversely affects the product gas heating value. The present work deals with the Density Functional Theory analysis of FeMo cofactor, ruthenium complex and the products formed when they react with syngas. The compounds are modelled using Chemcraft software and Density Functional Theory analysis of the modelled compounds using Gaussian software. The results show that the binding energy of ruthenium nitrogen complex is low when compared to its corresponding hydrogen and CO complexes, whereas FeMo cofactor can produce a stable complex with nitrogen than that with hydrogen and CO. The binding energies obtained for the products of FeMo cofactor when it reacted with N₂, CO, H₂ are 4.1 a.u, 3.57 a.u, 2.33 a.u respectively. Thus, FeMo cofactor can be considered as a potential compound that can selectively remove nitrogen from the gas mixture.

KEYWORDS: Binding energy, DFT analysis, Gasification, Hydrogen-palladium, Syngas.

INTRODUCTION

The exponentially increasing energy demand, depleting conventional energy sources and environmental issues associated with fossil fuels encouraged mankind to depend on renewable energy sources like biomass. Besides its renewability and wide availability, it is bulk in nature with low energy density. Therefore to utilise biomass economically, it is necessary to improve its properties, which can be achieved by biomass gasification. Gasification is the conversion of biomass into a combustible gas mixture by partial oxidation at high temperature, in the presence of gasifying agents such as air, oxygen or steam[1]. Although air gasification is the most economical and widely used gasifying method, the presence of nitrogen in the product gas adversely affects the quality of syngas[2]. In addition to its extremely strong triple bond, nitrogen is nonpolar with tightly bounded σ and π electrons and hence it is a poor ligand. Due to these intrinsic properties of nitrogen, a catalyst is necessary for its activation. The DFT (Density Functional Theory) is a potential tool to predict the possibility of a reaction and relative stability of the optimised compound, by comparing the binding energies. Yadav and Mookerjee [3] studied the nitrogen absorption on tantalum clusters by DFT analysis and predicted that such clusters can be used as catalysts for nitrogen dissociation. Mackay and Fryzuk [4] provided a review on the various metal complexes that can activate and make bond with nitrogen molecule. Guimaraes *et al.* [5] studied the dissociation of nitrogen on Cr based bimetallic alloy by DFT calculation and found that Fermi level can be shifted by doping with 3d element to increase dissociation efficiency. From kinetic and spectroscopic analysis of FeMo cofactor Thomas Spatzal *et al.* [6] Suggested that the central iron atoms that are bound to carbon and sulphur atoms are the substrate binding sites. Coric and Mercado [7] described a synthetic complex with sulphur

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rich coordination sphere that breaks a Fe-S bond to combine with N₂. Thus, they demonstrated that breaking a Fe-S bond is a chemically reasonable route to bind N₂ with FeMo cofactor. Rochana *et al.* [8] studied the absorption and dissociation of nitrogen on vanadium surface by DFT analysis and compared it with the hydrogen-palladium system. The results demonstrated that diffusion barrier for nitrogen vanadium system is very large and suggested that alloying with Ru will reduce the diffusion barrier. Cao *et al.* [9] studied the interaction of N₂ with Ru clusters using DFT calculations and indicated that Ru clusters have high activity for N₂ activation. The present work deals with the DFT analysis of metal complexes and products formed when they react with syngas constituents and to suggest the suitable metal complex that can selectively remove nitrogen from the syngas.

II. Computational Method:

The Schrodinger equation describes the variation of quantum state of a physical system with time. It is a partial differential equation describing the time evolution of the system's wave function, given by Eq. 1.

$$\hat{H}\Psi_i = [\hat{T} + \hat{V} + \hat{U}] = E_i\Psi_i \quad (1)$$

where \hat{T} is the kinetic energy, \hat{V} is the potential energy from the external field due to positively charged nuclei, \hat{U} is the electron-electron energy and E_i is the total energy.

The ground state energy of a compound can be determined by solving Schrodinger equation. The Density functional theory based electronic structure calculation is used to solve Schrodinger equation computationally, as it possesses very good predictability for various structural and thermodynamic properties of a molecular system. Nuclei of selected molecules are considered as fixed based on Born-Oppenheimer approximation. The binding energy (ΔE) of a compound formed by chemical reaction can be calculated as the difference between the energy of the compound formed and the sum of energies of the reactants. The compound with highest binding energy is the most stable one. The unstable complex can be dissociated by giving bond dissociation energy and reaction components such as CO and H₂ can be retrieved. The metal complex which produces a product with higher binding energy with N₂, than that with H₂ and CO, can be considered as a potential compound that can selectively remove nitrogen from the gas mixture. Chemcraft software is used to model the compounds using electron spectrographic details available from the earlier works [7,8]. DFT analysis of the modelled compounds is done using Gaussian software. In this work, the computational method is divided into two section, Structure and DFT analysis. In the structure part, modelling of the compounds using chemcraft software is discussed. In the DFT analysis section, criteria for the selection of parameters in the Gaussian software for DFT analysis of the compounds is discussed.

2.1. Structures:

Based on the literature survey FeMo cofactor and ruthenium metal complexes are selected for the analysis because of their greater potential for activation of triple bond in nitrogen. The structures of the complexes are developed using the available electron spectrographic details [7,8].

2.1.1. FeMo cofactor:

The structure of FeMo cofactor and the product when it reacted with nitrogen are developed and is shown in Fig.1. The central iron sites that are coordinated to sulphur and carbon atoms is the ligand for N₂ activation. The structure of product compound is developed by breaking a Fe-S bond and binding N₂ to the unpaired electron thus produced [7].

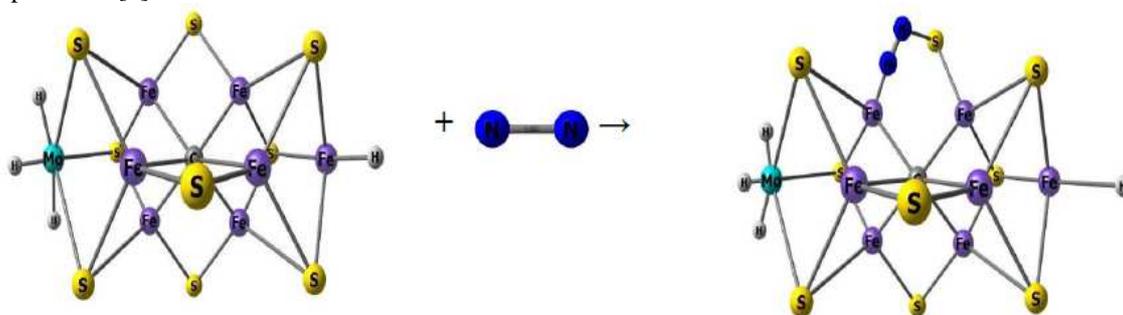


Fig. 1: Reaction between FeMoco and N₂

Spatzal et al. [6] reported a crystal structure of carbon monoxide (CO) inhibited nitrogenase FeMo protein in which CO displaces sulphur from FeMo cofactor and bridges Fe2 and Fe6. The structure of product formed when CO reacts with FeMo cofactor is modelled by displacing sulphur atom bounded to Fe2 and Fe6 with CO molecule. The modelled structure is shown in Fig.2.

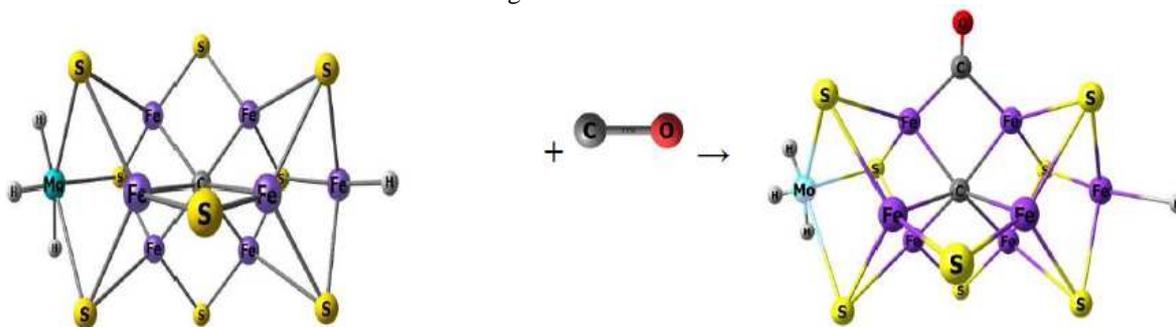


Fig. 2: Reaction between FeMoco and CO

Similarly, the structure of product formed when hydrogen reacts with FeMo cofactor is developed by breaking Fe-S bond and binding to the unpaired electrons of iron and sulphur. The structure of modelled compound is shown in Fig.3.

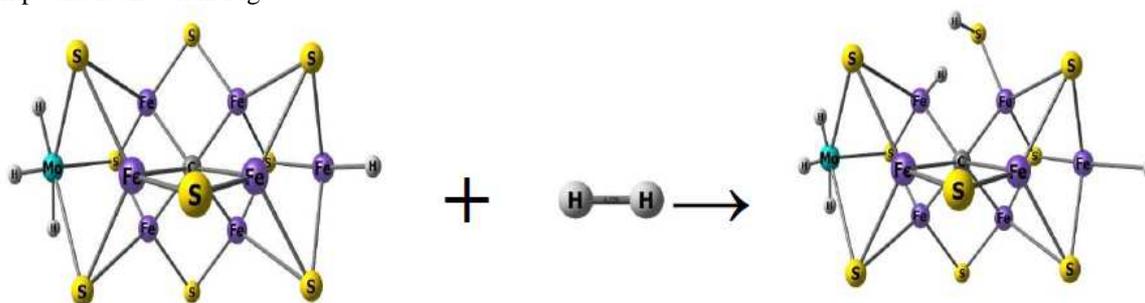


Fig. 3: Reaction between FeMoco and H₂

Similarly, the ruthenium complex $[(S-C_6H_4-N(Me)CH_2CH_2N(Me)-C_6H_4-S)(P^iPr_3)Ru(NCMe)]$ is also modelled using available spectrographic data.

2.1.2. Ruthenium complex:

Ruthenium complex $[(S-C_6H_4-N(Me)CH_2CH_2N(Me)-C_6H_4-S)(P^iPr_3)Ru(NCMe)]$ reacts spontaneously with dinitrogen, where N₂ reversibly displaces acetonitrile to form the linear monometallic N₂ complex $[(S-C_6H_4-N(Me)CH_2CH_2N(Me)-C_6H_4-S)(P^iPr_3)Ru(N_2)]$, as shown in Fig.4.

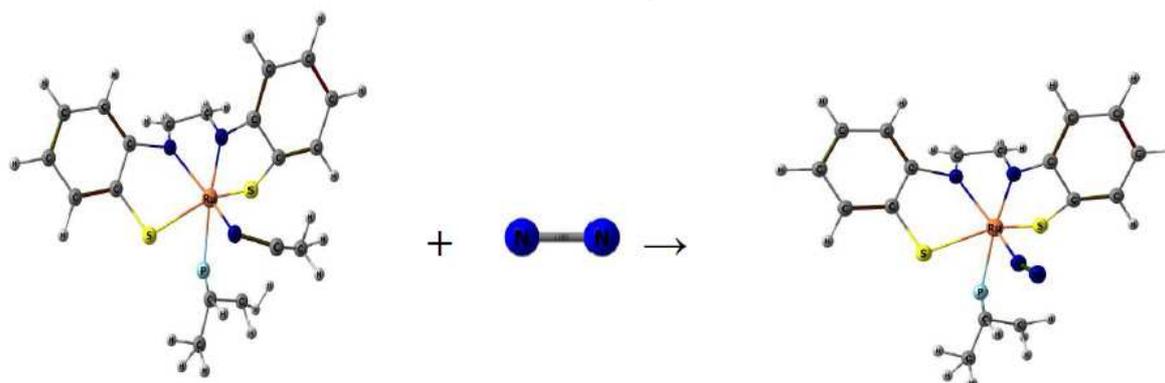


Fig. 4: Reaction between Ruthenium complex and N₂

CO can displace acetonitrile from the ruthenium complex and form bond with the ruthenium. The resultant compound is optimised by ground state energy minimization technique. The modelled compound is shown in Fig.5.

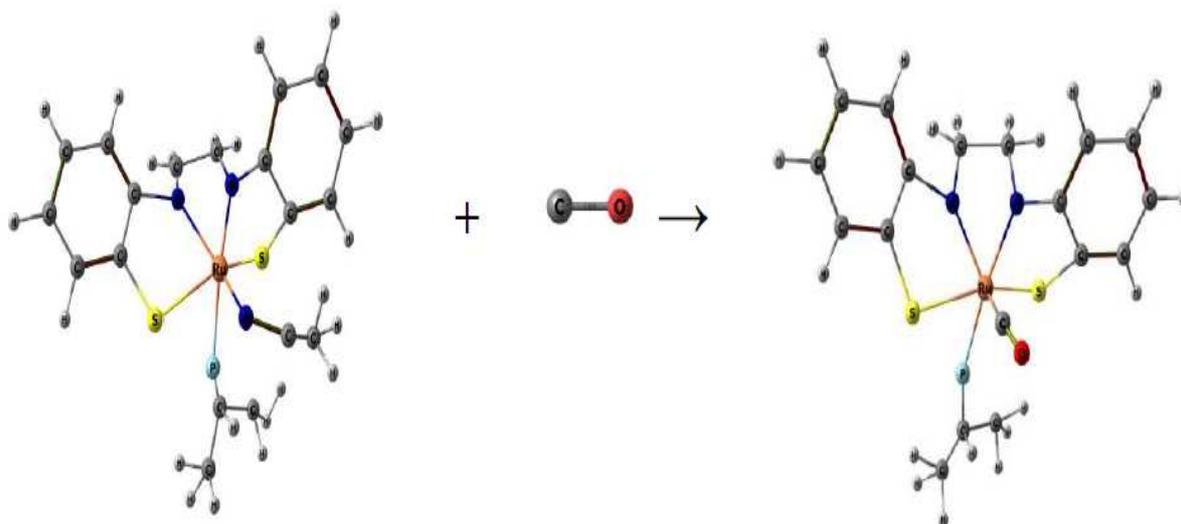


Fig. 5: Reaction between Ruthenium complex and CO

The structure of product formed when hydrogen reacts with ruthenium complex is modelled by displacing acetonitrile from the ruthenium complex using H_2 . The modelled compound is shown in Fig.6.

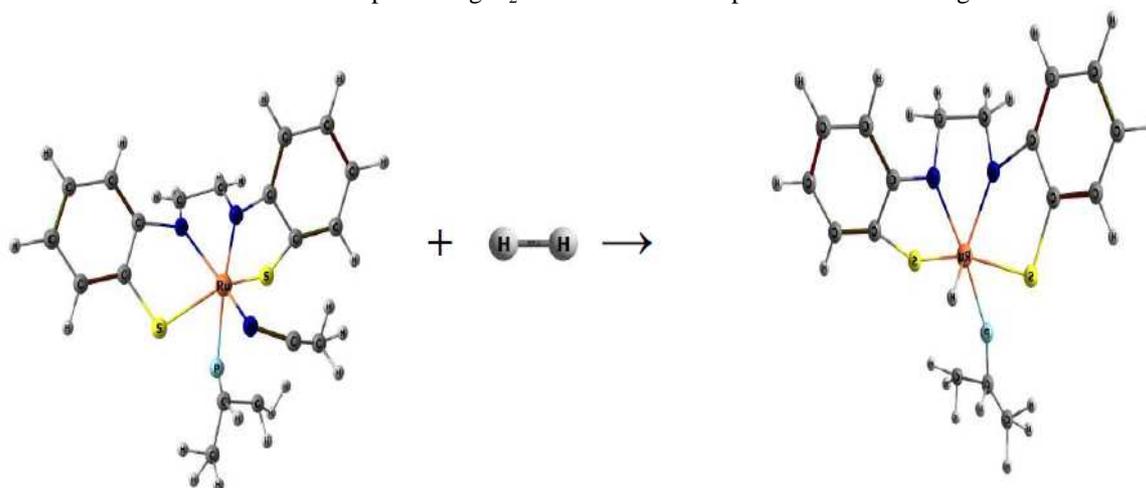


Fig. 6: Reaction between Ruthenium complex and H_2

2.2. DFT Analysis:

The following parameters are selected for the DFT analysis:

- BP86 Density functional method is selected as it gives values close to the experimental results as compared to the Becke's three parameter nonlocal hybrid exchange–correlation functional (B3LYP) [10].
- LANL2DZ basis set is chosen for the analysis for better approximation.
- Charge is taken as zero as all the molecules considered are neutral.
- The spin multiplicity is taken as one by Hund's rule as there are no unpaired electrons in the compounds.

$$\text{Spin Multiplicity} = \{2s+1\} \quad (2)$$

where s denotes the spin of the electrons,

$$S = \left(\frac{1}{2}\right) \text{ if unpaired electron moves in anticlockwise direction}$$

$$S = -\left(\frac{1}{2}\right) \text{ if unpaired electron moves in clockwise direction}$$

$$S = (0) \text{ if there are no unpaired electrons.}$$

RESULTS AND DISCUSSION

The ground state energies of the modelled compounds are calculated by DFT analysis using Gaussian software and are given in Table 1.

Table 1: Ground States Energies of the optimised compounds

Compound	Ground State Energy (a.u)
FeMoco	-16349.21
N ₂	-108.30
CO	-112.09
H ₂	-1.12
FeMoco-N	-16453.40
FeMoco-CO	-16457.73
FeMoco-H	-16348.00
Ru complex	-6439.23
Ru complex-N	-6418.56
Ru complex-CO	-6422.48
Ru complex-H	-6310.15

The binding energies of the compounds formed are calculated by the relation Binding energy(ΔE)= Energy of product - Sum of energies of reactants (3), The calculated binding energies are given in TABLE 2.

Table 2: Binding energies of the products

Compound	Binding Energy(a.u)
FeMoco-N	4.1
FeMoco-CO	3.575
FeMoco-H	2.332
Ru complex-N	128.969
Ru complex-CO	128.837
Ru complex-H	130.199

The results show that higher binding energies for the products formed are when the ruthenium complex reacted with the syngas. The binding energies obtained for products of ruthenium complex when it reacted with N₂, CO, H₂ are 128.96 a.u, 128.83 a.u, 130.19 a.u respectively. Even though the nitrogen complex has high binding energy but it is less than the binding energy of hydrogen complex, so hydrogen complex is more stable compared to nitrogen complex. Therefore, retrieval of hydrogen from the reaction products is not possible. On the other hand binding energies of the products formed, when the FeMo cofactor reacted with the syngas constituents are low. The binding energies obtained for the products of FeMo cofactor when it reacted with N₂, CO, H₂ are 4.1 a.u, 3.57 a.u, 2.33a.u respectively. Even though the nitrogen complex has low binding energy still it is much more than binding energies of hydrogen and CO complexes, so nitrogen complex is more stable compared to hydrogen and CO complexes and hence the retrieval of H₂ and CO complexes is possible.

Conclusions:

The DFT analysis of metal complexes for the selective nitrogen removal from the syngas based on binding energy criteria are done. The results show that the binding energy of ruthenium nitrogen complex is low when compared to its corresponding hydrogen and CO complexes. Therefore, ruthenium complex could not be used as a compound that can selectively remove nitrogen from the gas mixture. FeMo cofactor can produce a more stable complex with nitrogen than that with hydrogen and CO. The binding energies obtained for the products of FeMo cofactor when it reacted with N₂, CO, H₂ are 4.1 a.u, 3.57 a.u, 2.33 a.u respectively. Thus, FeMo cofactor can be considered as a potential compound that can selectively remove nitrogen from the gas mixture.

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