Effect of FeRu Core-shell Catalysts Size and Temperature on Fischer-Tropsch Reactions

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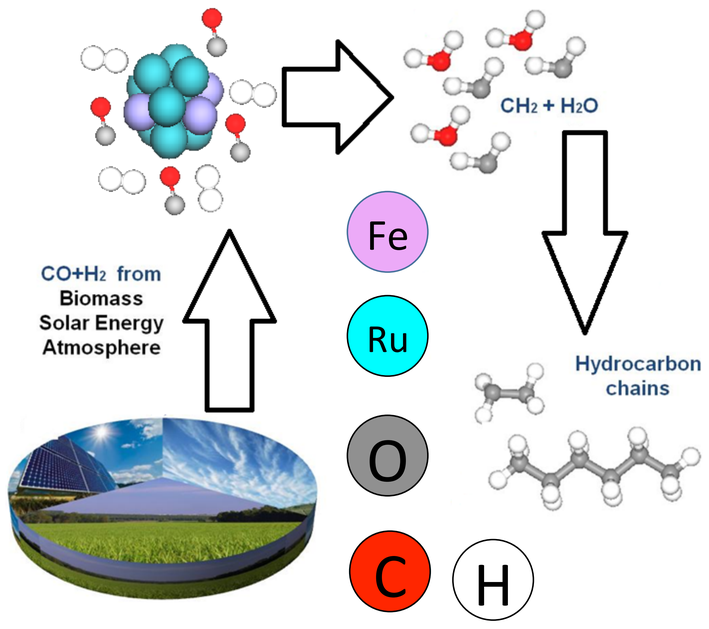
Abstract

Density Functional Theory is employed to study the adsorption of Carbon Monoxide (CO) on Iron Ruthenium (FeRu) nanoclusters. The RPBE functional in combination with DNP basis set under the Generalized Gradient Approximation (GGA) method was employed for nanocluster structural stability analysis and CO adsorption and dissociation studies. The nanocluster with highest Cohesion energy was next tested upon CO adsorption and dissociation using DFT at all different possible catalytic sites (top, bridge, hollow).

Introduction

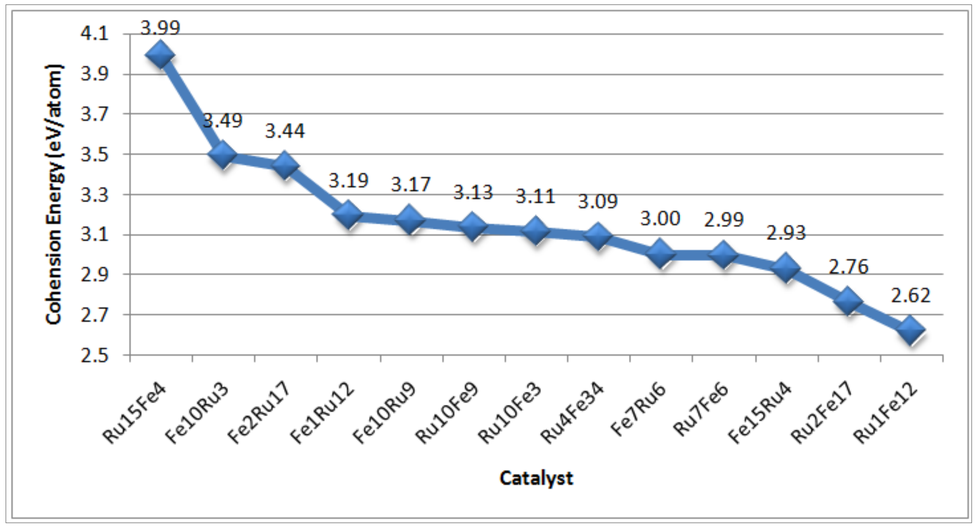
Fischer-Tropsch (FT) Process



Results

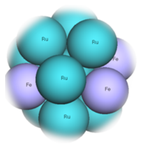
The Density Functional Theory (DFT), and DFT-coupled Molecular Dynamics (DFT-MD) calculations were used to study Fischer-Tropsch reactions on FeRu core-shell nanostructured catalysts. After building core shell models of Iron Ruthenium of different sizes(13 and 19) they were then optimized. For each cluster size mixtures containing approximately 10%, 50%, and 80% of each element was considered.

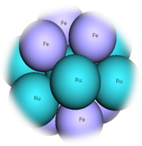
The Cohesion Energy was then calculated using a formula. Our results show that $Ru_{15}Fe_4$, a 19 atom cluster, has the greatest cohesion energy at 3.99 eV/atom. The second highest Cohesion Energy was $Fe_{10}Ru_3$, a 13 atom cluster, at 3.49 eV/atom.

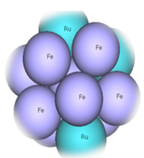


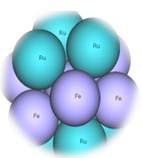
Core-Shell Models

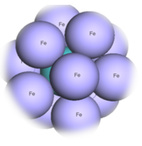
13 Atom Clusters

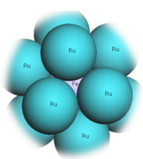




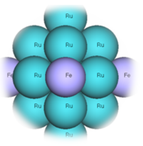


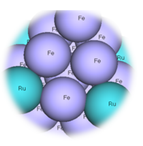


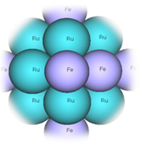


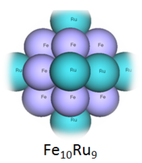


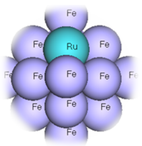
19 Atom Clusters

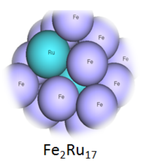












Future Work

These clusters will then be put into a system containing one CO molecule to determine the preferred adsorption site. There are three possibilities top, bridge, and hollow. These simulations are still being run. The CO adsorption energy per atom will be calculated.

$$E_{ads}(CO) = \frac{(E(CO*) - E(A_nB_m) - E(CO))}{N}$$

The hope is to get a negative binding energy, this would mean that the CO is stable when adsorbed to the surface of the catalyst.

After determining the most stable adsorption sites, then run the DFT-MD simulations at 25 and 200 degrees Celsius to investigate the conversion of CO and $2H_2$ molecules to octane over the most favorable FeRu core-shell catalyst.

Methods

DFT Calculations were carried out using DMOL3 module of the Materials Studio. Using the RPBE functional in combination with DNP basis set under the GGA method. DIIS was used to speed up the SCF convergence.

The cohesive energy of the binary clusters was determined by the equation below. Where $E(A_nB_m)$ is the energy of the A_nB_m binary core (A)-shell(B) catalysts (A,B: Fe, and Ru) containing N=n+m total number of atoms, E(A) and E(B) are the energies of the pure elements A and B, and n and m are the total numbers of atoms of A and B respectively.

$$E_{coh}(A_nB_m) = \frac{(nE(A) + mE(B) - E(AnBm))}{N}$$

Acknowledgements

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