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Elucidation of the Mechanism for Ethene Hydrogenation over Single Metal Cation Catalysts: A Combined Modeling and Experimental Study

Hafeera Shabbir
Clemson University

Steven Pellizzeri
Clemson University

Magali Ferrandon
Argonne National Lab

Massimiliano Delferro
Northwestern University

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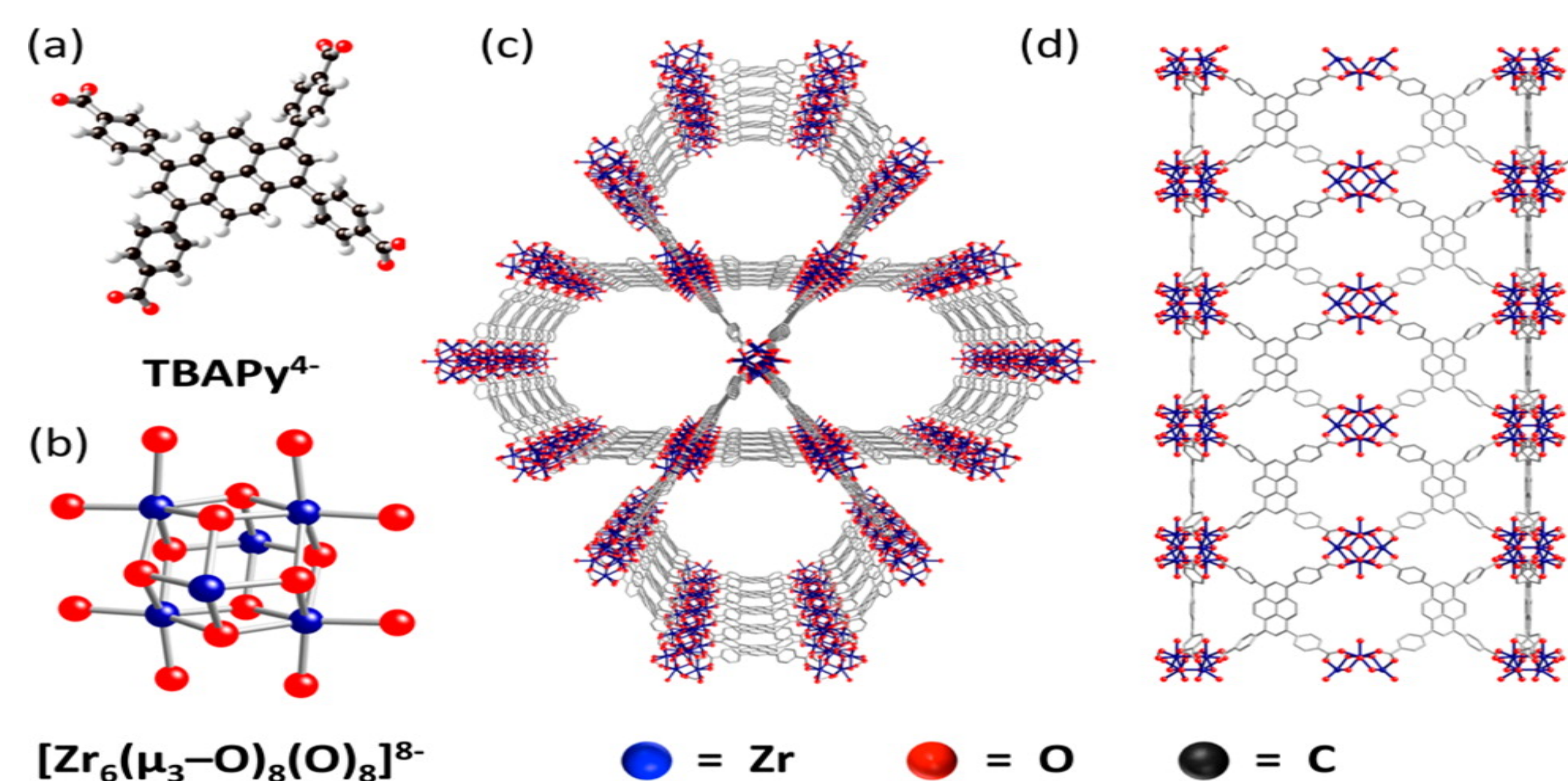
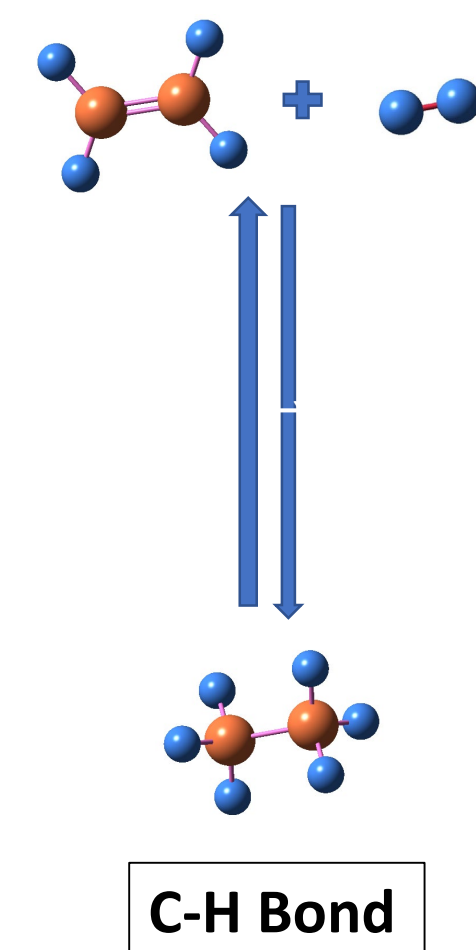
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Hafeera Shabbir^a, Steven Pellizzeri^b, Magali Ferrandon^c, Massimiliano Delferro^d, In Soo Kim^{e,f}, Alex Martinson^{e,*}, Rachel Getman^a
^a Department of Chemical and Biomolecular Engineering, Clemson University. ^b Department of Chemistry, Clemson University. ^c Chemical Sciences and Engineering Division, Argonne National Lab. ^d Department of Chemistry, Northwestern University ^e Materials Science Division, Argonne National Lab. ^f Nanophotonics Center, Korea Institute of Science and Technology. *corresponding authors

INTRODUCTION

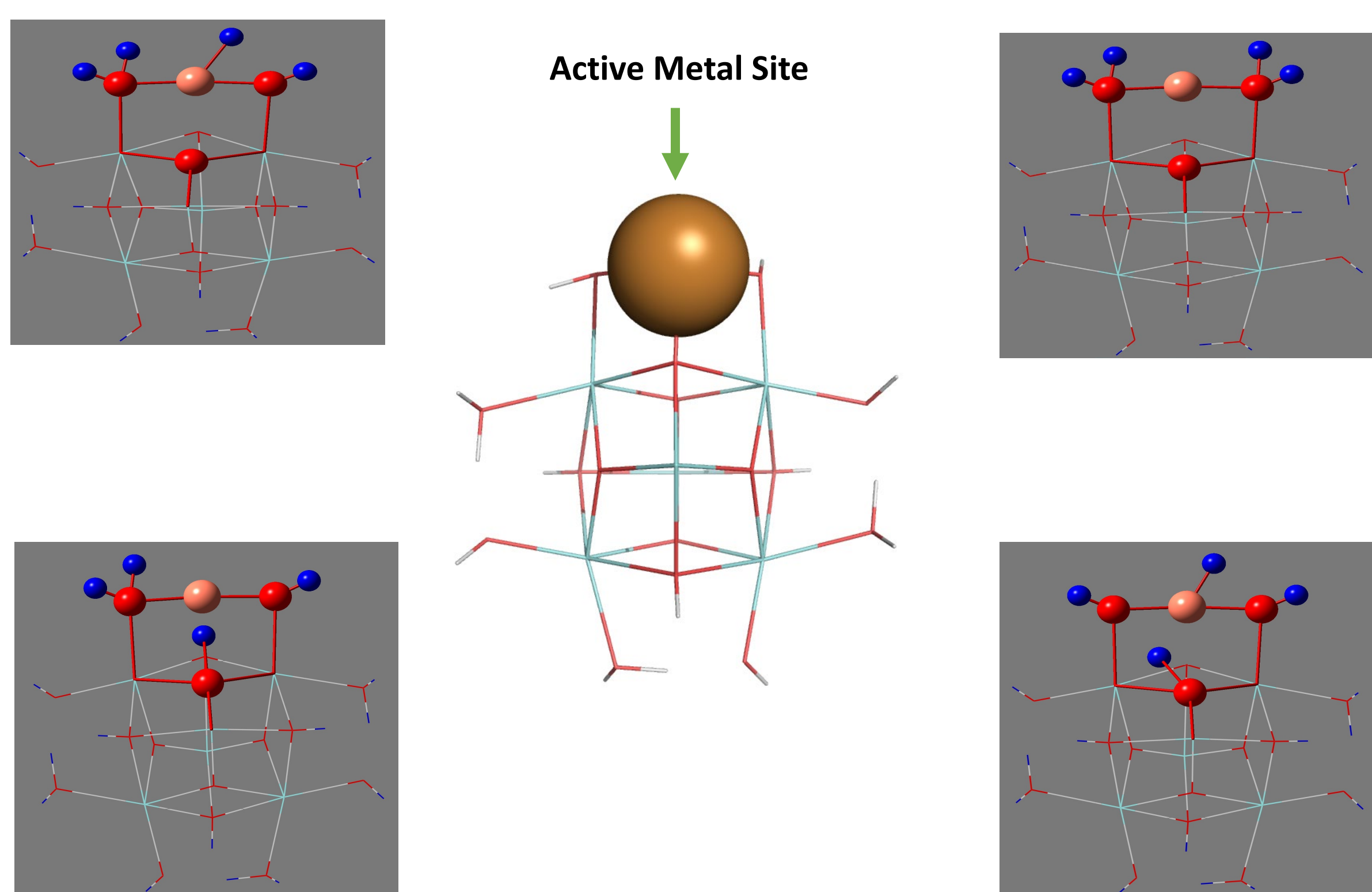
According to figures in 2014, The shale gas flared
 5.5 BCM/year = 350 Peta Joules /year = Residential energy demand in SC

- Single-site cation catalysts can catalyze C-H bond formation and scission reactions for transforming shale gas to liquids.
- NU-1000 a metal organic framework (MOF) support can spatially and electronically isolate single-site metal cations for catalysis.
- Mn, Ni, Cu and Zn catalysts on NU-1000 have been explored in this study for the test reaction of hydrogenation of Ethene to Ethane.



1,3,6,8-Tetrakis(p-benzoic acid)pyrene linker, TBAPy⁴⁻ (a) and the [Zr₆(μ₃-O)₈(O)₈]⁸⁻ node (b) of the Zr₆-based framework NU-1000 (c and d) Ref: *J. Phys. Chem. Lett.* 5, 21, 3716-3723

CATALYST MODEL AND COMPUTATIONAL METHODS

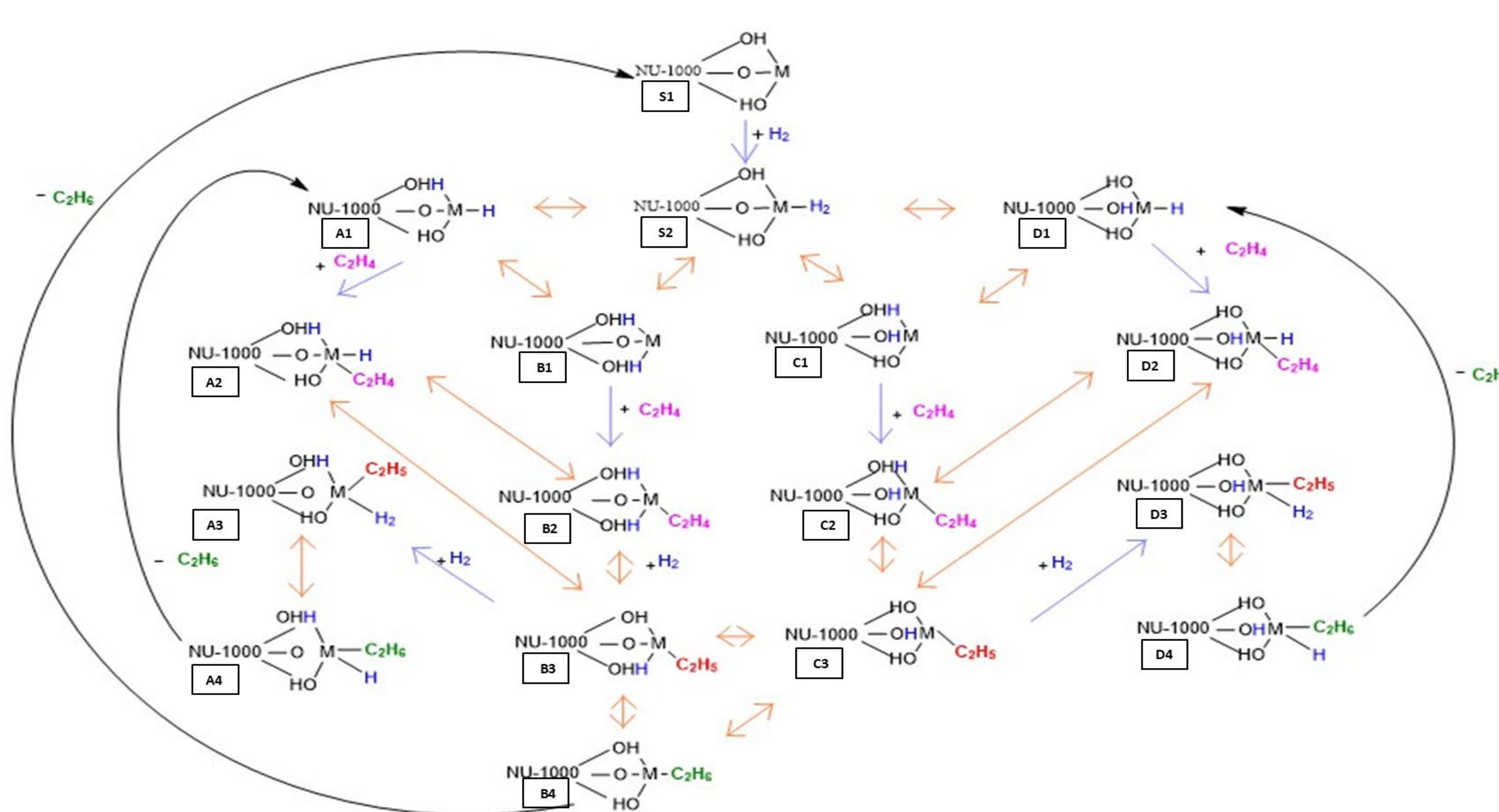


DETAILS OF CALCULATION

- DFT with Gaussian09 to get Energy.
- Functional: M06-L
- Basis set: Def2-SVP (H,C,O) Def2-TZVPP (Zr, Metals)
- Carbon atoms of the formate linker were held fixed.
- MKMCXX for microkinetic modelling.

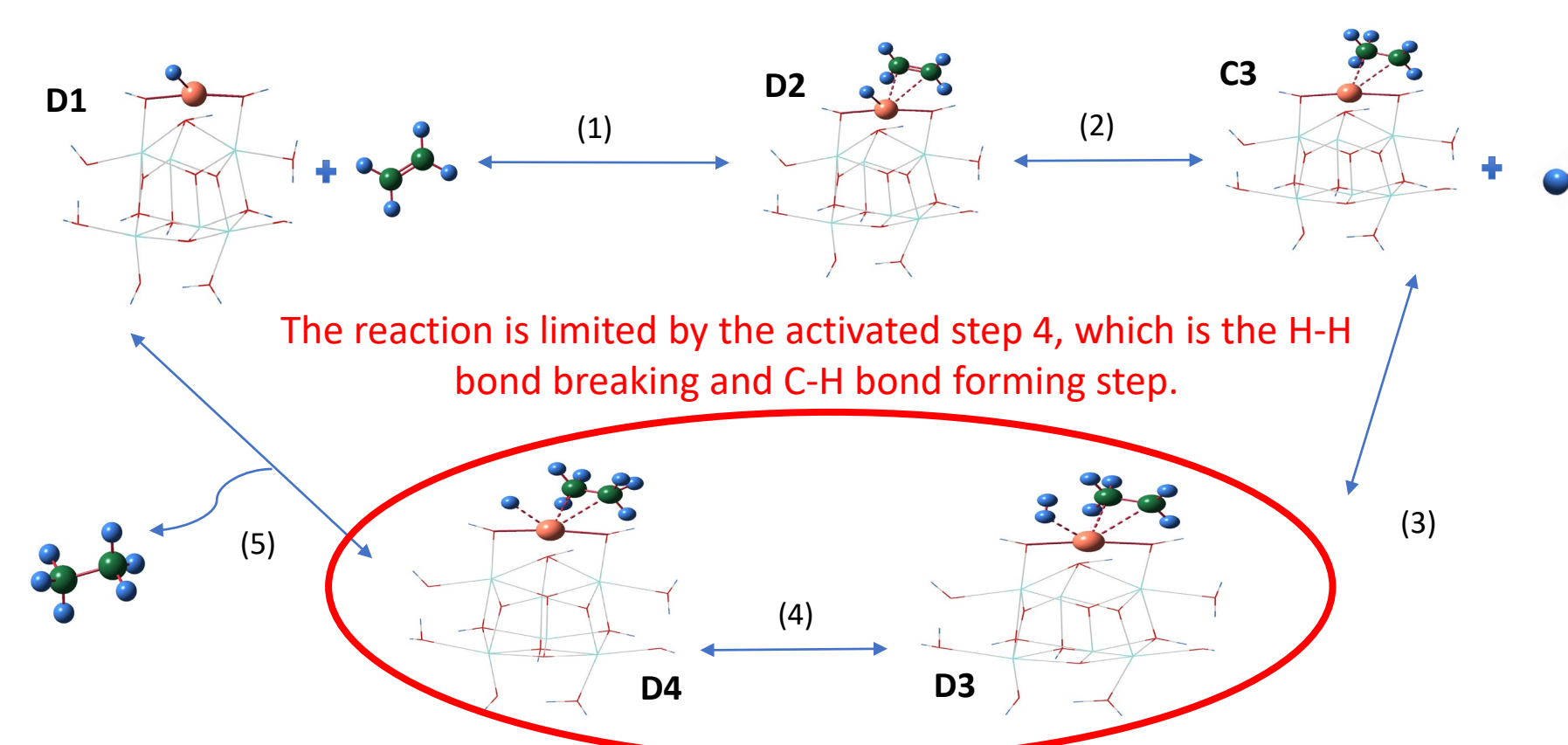
RESULTS AND DISCUSSION

PROPOSED REACTION MECHANISM

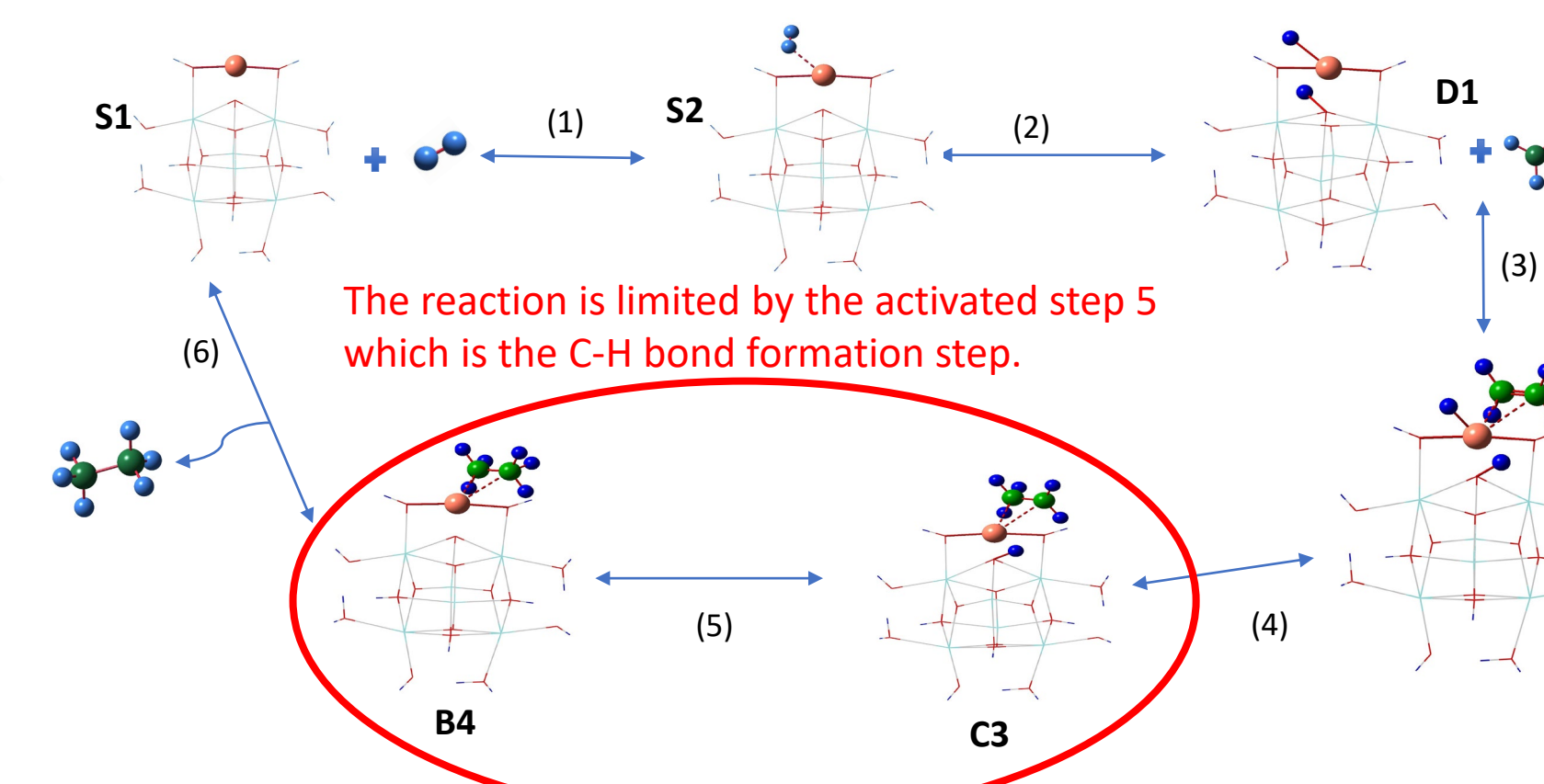


DEGREE OF RATE CONTROL ANALYSIS

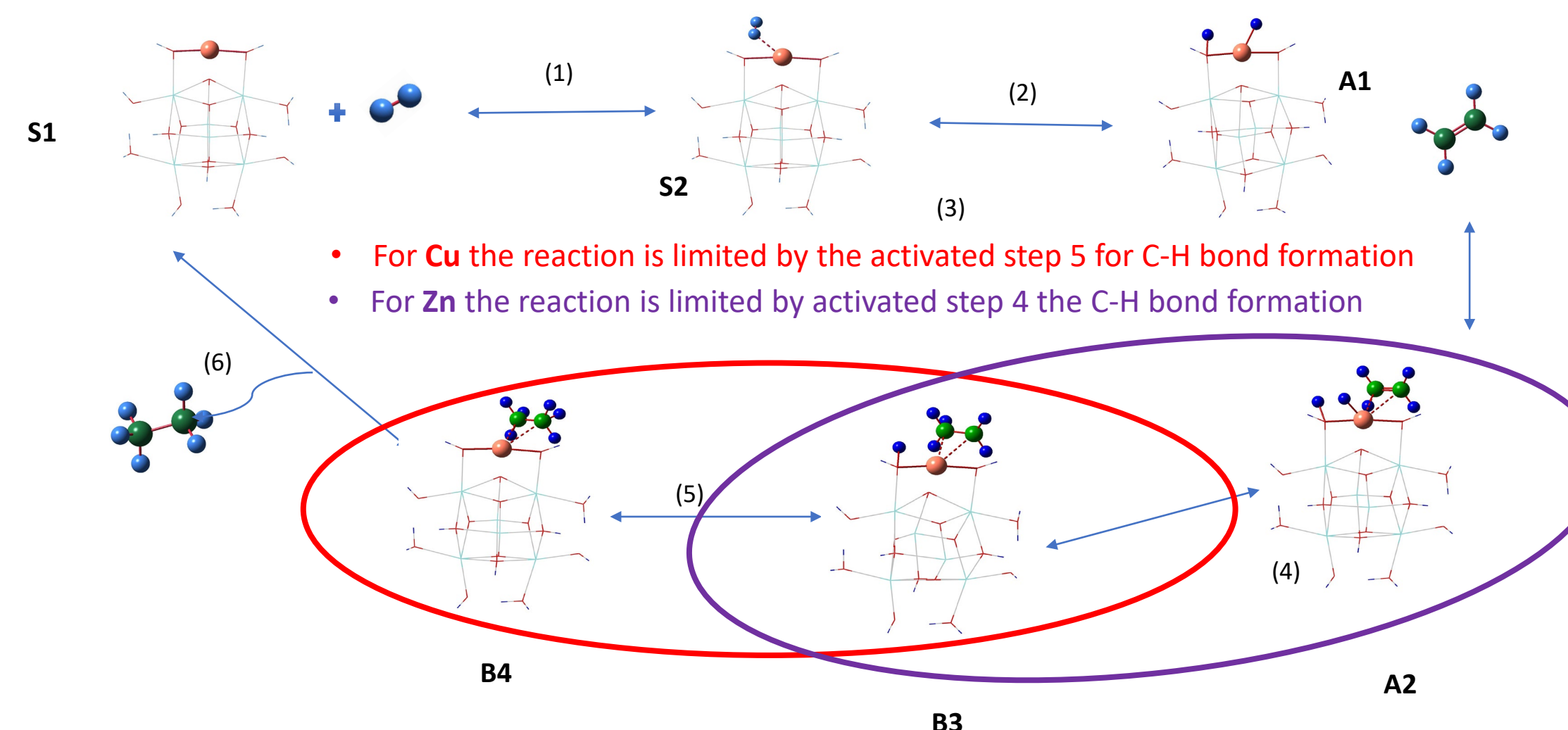
Degree of Rate control : Pathway I is Dominant for Nickel T=273K to 773K, Copper T=273-423K and Zinc T=273-573K and P=1-10 atm



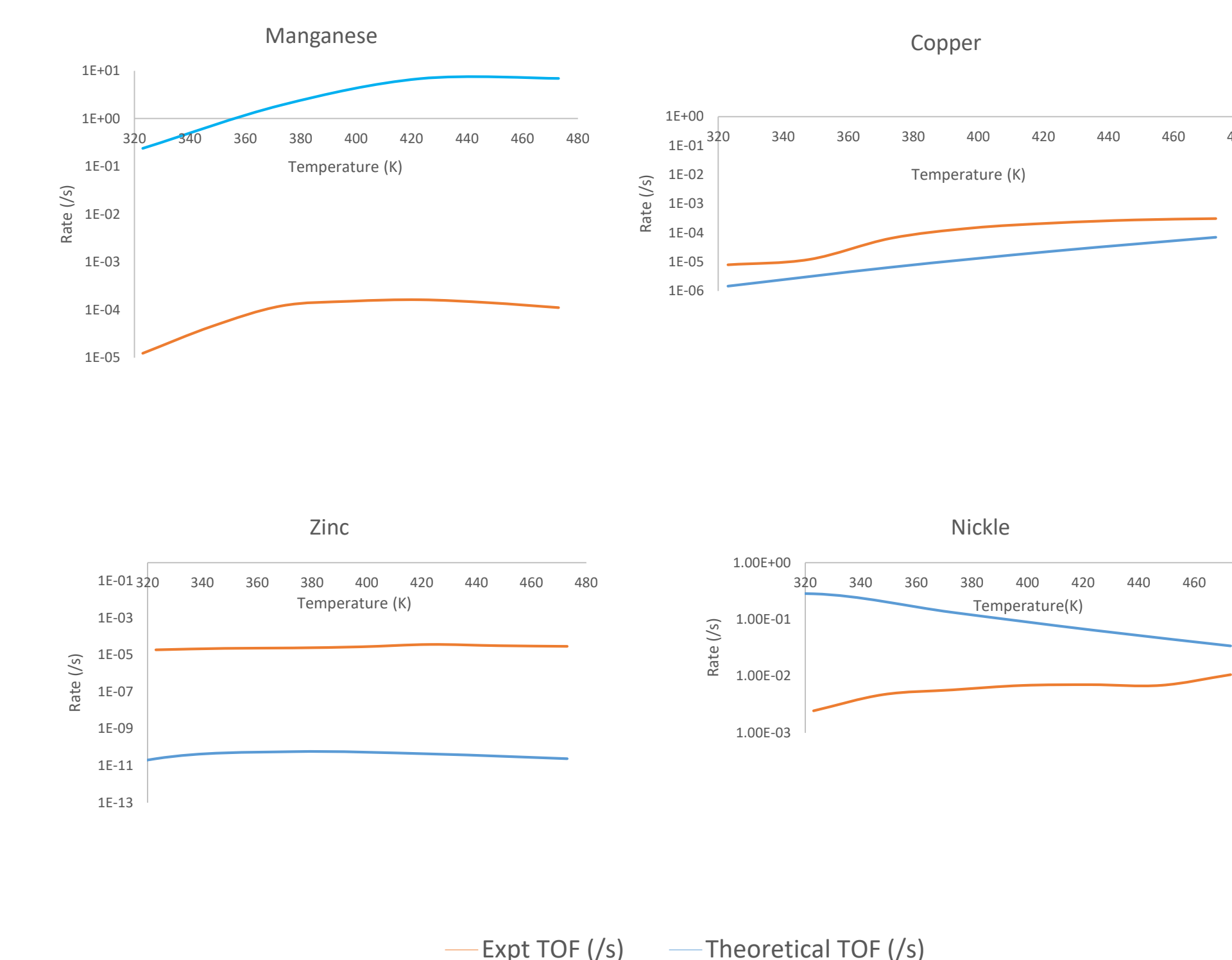
Degree of Rate control : Pathway II is Dominant for Manganese T=273K to 773K and P=1-10 atm



Degree of Rate control : Pathway-III for Copper T=423K to 773K and Zinc T=573K to 773K and P=1-10 atm



COMPARISON WITH EXPERIMENTAL RESULTS



1. The Metal catalysts follow different reaction pathways dependent on temperature.
2. The rich proton topology of NU-1000 support plays a role as a hydrogen shuttle for the hydrogen dissociation step.
3. The rate determining steps vary with the metals and condition of operation.
4. The C-H bond formation is the RDS for Cu, Zn (at high temperature) and Mn
5. Both H-H dissociation and C-H bond formation step are rate determining steps for Cu and Zn at low temperatures and Ni.

CONCLUSION AND FURTHER WORK

1. Copper gives excellent agreement with the order of magnitudes of activities.
2. All metals except Nickel follow the experimental trends.
 - Possible reasons for this could be missing steps in the mechanism or the single site assumption in our model could also be an incorrect.
 - Another source of error could be experimental data not being taken at steady state and structural deformities in the catalyst.

Revisit the assumption of single-site metal catalyst and examine multi-nuclear catalyst sites mechanism for metals that don't agree well with the current mechanism.