EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

EILERS FELLOW:	Yujia Wang
FACULTY ADVISOR:	William F. Schneider
REPORT PERIOD:	Jan 2021 - Dec 2021
PROJECT TITLE:	Computational investigation of the identity and reactivity if exchanged Cu sites in zeolites for selective activation of methane
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(×) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **( ) Transformation Solar** **(×) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS:
List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Identify for CH_4 activation	Identified relevant species in Cu-CHA under CH_4 activation conditions by supercell density functional theory (DFT) calculations and thermodynamic analysis.	100%
Predict the quantities of Cu species using statistical analysis	Developed statistical simulation protocols to predict quantities of Cu monomer and dimer species. Also predicted the influence of different Al distributions on the quantities of Cu species.	100%
Compare Cu reduction with CH_4 for various relevant Cu species	Cu reduction reaction with CH_4 was compared among Cu dimer species. More comparisons will further be conducted for Cu reduction with other reductants, such as H_2, NO + NH_3, CO, and Cu auto-reduction under inert conditions.	80%

RESEARCH OUTPUT:
Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) 1. "Quantitative connections between copper site proximity and binuclear active sites for partial methane oxidation to methanol in Cu-CHA zeolites", Laura N. Wilcox, Yujia Wang, William F. Schneider, Rajamani Gounder, *in preparation*. 2. "First-principles analysis of dicopper species in zeolites for O_2 activation and implications for catalyst optimization", Yujia Wang, Sichi Li, Tong Wu, William F. Schneider, *in preparation*.
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location) 1. ND Energy Postdoc and Grad Student Seminar, "Computational investigation and quantification of active Cu sites in Cu-SSZ-13 zeolite for selective activation of methane", October 2021, Notre Dame 2. 42nd Annual Symposium of Michigan Catalysis Society, "Computational investigation and quantification of active Cu sites in Cu-SSZ-13 zeolite for selective activation of methane", September 2021, virtual

	3. Fall 2021 ACS National Meeting, "Computational investigation and quantification of active Cu sites in Cu-SSZ-13 zeolite for selective activation of methane", August 2021, hybrid 4. Spring 2021 ACS National Meeting, "Computational investigation of Al distribution in SSZ-13 zeolites and its influence on Cu speciation", April 2021, virtual 5. Women ExceLling in COmputational Molecular Engineering (WELCOME) seminar, "First-principles analysis of dicopper species in zeolites for O_2 activation and implications for catalyst optimization", February 2021, virtual
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) Prof. Rajamani Gounder's group, Purdue University, Performing experiments to isolate the origins of reactivity and evaluate the mechanistic behavior of catalysts.
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL) https://energy.nd.edu/about/associated-researchers/yujia-wang/
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

1. Identify relevant copper species for CH_4 activation

Dimeric Cu species have been proposed in literature to facilitate O_2 and CH_4 activation for selective hydrocarbon oxidation. In this project, we systematically investigate the formation of Cu dimers in Cu-SSZ-13 zeolite to identify relevant Cu species under O_2 and CH_4 activation conditions.

Supercell density functional theory (DFT) calculations and thermodynamic analysis are applied to identify relevant species under O_2 and CH_4 activation conditions. We consider the influence of local Al proximity on Cu dimer speciation, considering potential ligands (-O, -O_2, -OH) and Cu formal charges from 1+ to 3+. Free energies of Cu species shown in Figure 1 are computed at several Al sites with harmonic approximation for entropy estimation. We find the formation of Cu dimers is highly associated with framework Al proximity. The results show under high temperature oxidation treatment conditions, $[CuOH]^+$ monomers are found to have a strong thermodynamic driving force to form a manifold of O/O_2/OH-bridged Cu site types at eight-membered ring (8MR) Al pair sites. The finding agrees with experimental observations that SSZ-13 samples prepared to contain only $[CuOH]^+$ always contain a confounding subset of O- or OH-bridged Cu dimers and/or larger aggregates. Furthermore, compared to $[CuOH]^+$, Z_2Cu (Z represents an Al-substituted Si site in the zeolite framework) species in 6MR Al pair sites are found to be thermodynamically unfavorable to form Cu dimer species. The results rationalize what has been observed experimentally that for Cu-CHA samples containing solely Z_2Cu sites, they do not have partial methane oxidation to methanol (PMO) activity; however, Cu-CHA samples containing ZCuOH sites show methanol yields from PMO cycles.

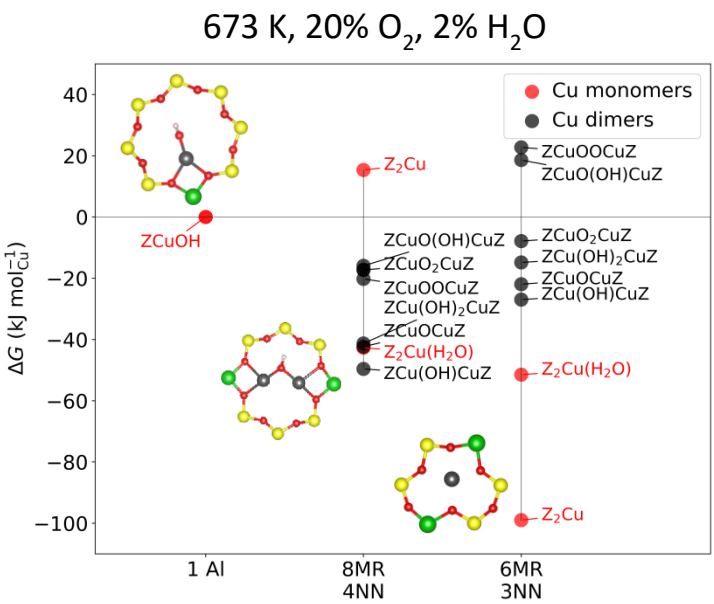

Figure 1: Free energy comparison of Cu monomer and dimer species (Z represents an Al-substituted Si site in the zeolite framework) in 1 Al (isolate Al site), 8MR 4NN (eight-membered ring 4th-nearest-neighbor Al-Al pair site) and 6MR 3NN (six-membered ring 3rd-nearest-neighbor Al-Al pair site) sites in CHA at high temperature oxidation condition in experiment (673 K, 20% O_2, 2% H_2O).

2. Predict quantities of copper species using statistical analysis

We subsequently predict Cu-SSZ-13 composition phase diagrams by predicting the number of Al sites for hosting Cu^{2+}, Cu dimers and $[CuOH]^+$ species as a function of Si:Al and Cu:Al ratios using numerical simulations (Figure 2). We find, under Löwenstein's rule (no Al-O-Al linkage), a significant number of 8MR Al pair sites exist which prefer hosting Cu dimers over monomers, over the tested Si:Al ratios ranging from 3 to 40. We also find the number of 8MR Al pair sites maximizes at Si:Al around 10, which qualitatively agrees with reported methanol productivity in Cu-SSZ-13 in partial methane oxidation to methanol reactions in literature, where Cu dimers are proposed to be responsible for the conversion.

Besides Löwenstein's rule, we explore the Al distribution rule where the repulsion between Al and Al is considered when distributing Al in numerical simulations. In the previous project, the resulting Al distribution predicted using Al-Al repulsion has shown an agreement with Al distribution in CHA samples that are synthesized using organic structure-directing agents (SDA) only without any inorganic SDA. We find the predicted composition phase diagrams are sensitive to Al distribution rules applied, thus, sensitive to zeolite synthesis conditions (the use of organic and inorganic structure-directing agents). This workflow can be applied broadly to other zeolites to predict speciation and composition of exchange cations.

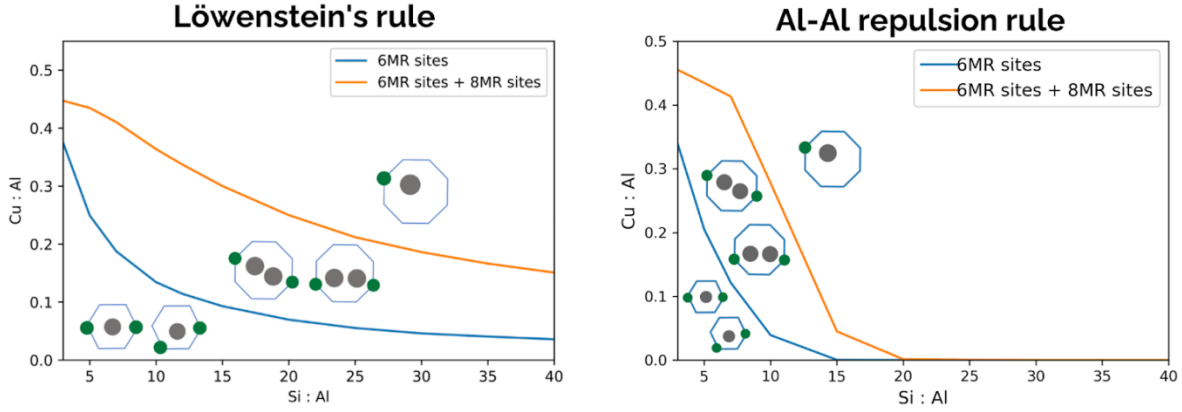

Figure 2: Predicted Cu-SSZ-13 composition phase diagrams under different Al distribution rules. Left: Löwenstein's rule, right: "Al-Al repulsion" rule.

3. Compare Cu reduction with CH_4 for various relevant Cu species

To compare the ability to activate CH_4 of the manifold of O/O_2/OH-bridged Cu site types shown in Figure 1, we constructed a H-abstraction reaction, and use the computed reaction energy as a descriptor for measuring the ability of a Cu dimer to abstract H atom from CH_4 and thus to activate CH_4:

$$ZCuO_xH_yCuZ + CH_4 \rightarrow ZCuO_xH_{y+1}CuZ + \cdot CH_3 \ (x = 1 \text{ or } 2, y = 0 \text{ or } 1)$$

We find the ability to break C-H bond in CH_4 and to form O-H depends on the type of the Cu dimer and the Al-Al configuration the Cu dimer is associated with. Further analysis of the reactions of these Cu dimers with different reductants (such as H_2, NO + NH_3, CO, and Cu auto-reduction under inert conditions) will be conducted to better understand the function of the Cu dimer sites and the selective oxidation mechanisms in order to design catalysts that have the optimal compositions to perform methane to methanol conversion, and eventually diversify the strategies available to use the world's abundant hydrocarbon resources.