Summer Undergraduate Research Fellowship (SURF) USA

Photocatalytic Methane Coupling over Gold-Heteropoly Acids

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***The following example SURF proposal has been adapted from a longer original proposal written by Jack Sullivan/Chemical Engineering (Faculty Mentor: Nan Yi). The example has been modified and edited to fit the current, more concise SURF proposal guidelines.**

Proposal prompts in blue are included for instructional purposes only, based on the SURF proposal guidelines. Applicants should not include these prompts when submitting a final application.

Project Summary (one page maximum, single-spaced)

1. Abstract (200 words maximum): concisely summarize your project and its goals

Catalytic conversion of methane to more valuable chemicals such as fuels is a promising process that offers economic incentive and environmental benefits. Industrial methane conversion still currently faces multiple challenges, notably high energy being required to maximize the methane conversion. However, high reaction temperature leads to a random distribution of products. This proposal investigates a photocatalytic approach to convert methane to ethane and hydrogen, which are two useful platform chemicals. The developments of gold-modified heteropoly acid catalysts, particularly silicotungstic acid, makes it possible to achieve higher methane conversion under variable wavelengths of light. This project focuses on synthesis variables and operation conditions to optimize photocatalytic activity and selectivity at a lower temperature. The success of this project will make photocatalysis become a viable and economic approach to mitigate the environmental impact of methane.

2. Outcomes (list 2-5, one bullet point each): tangible products of your project (e.g. report, database, results of quantitative/qualitative/textual analysis, paper, thesis, presentation, production, exhibition, film, article submitted for conference or publication, etc.); also include at least one outcome stating how this project contributes to your personal, educational, and/or professional goals

- Produce data for catalyst synthesis, characterization testing, and activity testing
- Data analysis and presentation of results at 2024 AIChE National Conference and 2025 Undergraduate Research conference
- Advance my coursework knowledge, research interest, and problem solving and critical thinking skills toward a Ph.D. in chemical engineering and a future career in the area of energy sectors

3. Timetable (one line or row per week maximum): using bullet points or a table, list your planned research activities and specific goals for each week of the project

Weeks 1-10: Catalyst Synthesis: Synthesis variables, such as the ratio of gold and support, the structure of support, and pretreatment conditions will be studied.

Weeks 2-10: Activity Tests: Operational conditions, including the intensity of light power, the choices of wavelength, and reaction temperature will be optimized to boost methane conversion and improve the selectivity of products.

Weeks 2-10: Characterizations: Surface and structural properties will be evaluated with a variety of instruments in order to identify the relationship between catalyst properties and activity performance.

Project Background **(two pages maximum, single-spaced)**

1. Project History, Definition, and Significance

- general problem, theme, or issue to be addressed
- historical context: i.e., most relevant previous research, scholarship, or artistry on this topic by other researchers, scholars, or artists (cite sources)
- project's specific question, hypothesis, or objective
- contribution of your project to the problem and your field
- broader significance or importance of your research (e.g., social, cultural, intellectual, creative, practical, theoretical)

Methane is an abundant hydrocarbon that is the primary component of natural gas as well as produced by many livestock, but has a significant negative impact on the environment as it is responsible for around 30% of the recent rise in global temperature. The abundance of methane makes it an ideal feedstock for catalytic conversion, where methane can be used to produce more valuable chemicals and fuels while minimizing the environmental impact of methane emissions [1]. While catalytic conversion of methane is promising, multiple challenges limit its industrial potential, such as the need for high reaction temperatures and the possibility of side reactions [2]. The photocatalytic approach (Scheme 1), which replaces thermal energy with light energy, requires a far lower energy demand and might be more economically viable, but has a low conversion yield and selectivity of the resulting products. To optimize conversion and selectivity, various catalysts have been studied for photocatalytic conversion of methane to ethane and hydrogen [4,5], such as heteropoly acid [6]. My literature review identified a lesser studied heteropoly acid as an effective catalyst for my research: silicotungstic acid. Silicotungstic acid can absorb a wider range of electromagnetic wavelengths compared with other photocatalysts [6], so we can design and optimize the photocatalytic process [4]. Adding a precious metal such as gold to the surface of the catalyst may also improve methane conversion by delaying the recombination of electrons. With the goal of improved methane conversion and yields to ethane and hydrogen, this project aims to answer the following research questions: 1) How effective is gold modified silicotungstic acid as catalyst for methane conversion, and what synthesis variables are important to improve photocatalytic conversion? 2) How do various wavelengths, namely visible light or UV light, affect the conversion rate of methane over gold modified silicotungstic acid? 3) How do we identify the key properties related to optimized methane conversion? Is it possible to correlate chemical/physical properties with the reaction rate?

2. Approach and Methodology

- methods, theories, procedures, or lines of thinking and/or creating you will use to address your research topic and answer the question(s) you pose
- if you plan to conduct interviews or surveys: what assumption/hypothesis/general principle you will test; the number of participants you will seek and how you will recruit/select them; sample interview/survey questions (to be included in Appendices)
- materials and sources needed to pursue your project
- how you will analyze, interpret, and/or evaluate your findings – including how/why this mode of analysis will enable you to accomplish your project objectives and/or answer your research question(s)
- foreseeable challenges, obstacles, or difficulties – and how you are prepared to address them

I will pursue three methods: catalyst synthesis, activity testing, and characterizations.
(1) <u>Catalyst synthesis</u>: Silicotungstic acid lacks higher surface area compared to other photocatalysts. To increase surface area significantly (up to up to 200 m^2/g), I plan to introduce

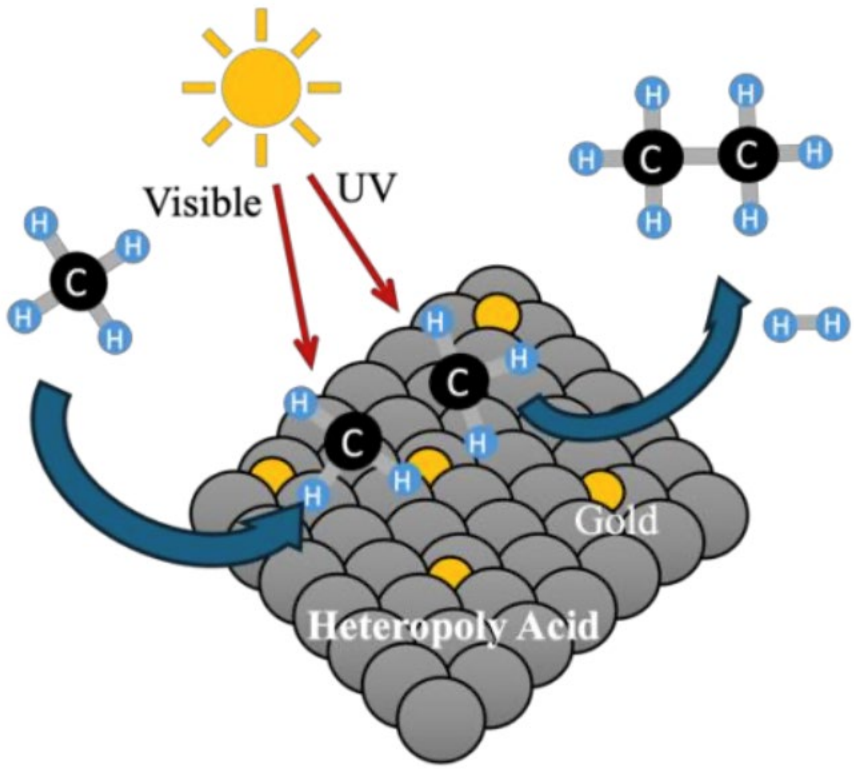
group-1 metal cations, especially cesium, to replace the protons from silicotungstic acid. The gold-modified silicotungstic acid catalyst will be synthesized in a two-step process: first, adding soluble cesium salts into the aqueous silicotungstic acid solution, and second, introducing gold into the cesium modified silicotungstic acid using impregnation method. Variables such as the gold weight loadings, the ratio between gold and modified support, and calculation temperature, will be studied. (2) Activity Testing: Testing will be conducted using a homemade photocatalytic reactor with methane flowing continuously over the catalyst. The intensity of light will be adjusted to maximize methane conversion with optimized operation conditions. Gas chromatography is used to analyze the products, allowing the calculation of conversion and selectivity of ethane. The research fund is budgeted to purchase a mass flow rate controller for photoactivity testing. (3) Characterizations: I will explore surface area and surface properties of gold-heteropoly acids. First, I will measure surface area using a Brunauer-Emmet-Teller (BET) method with a Micromeritics instrument. Second, I will measure temperature programmed reactions: Hydrogen-Temperature Programmed Reduction (H2-TPR) will be used to determine the oxidation states of gold by tracking hydrogen being reduced by the gold nanoparticles, and Methane-Temperature Programmed Desorption (CH_4-TPD) will be performed to determine the amount of methane absorbed on the surface of the catalyst. Third, I will perform an *In-situ* Infrared experiment, which allows us to understand the bond interaction between methane and the catalyst. The spectrum, especially the infrared peaks, collected from an IR-spectrometer can reveal how individual methane molecules form different bonds with catalysts. Fourth, using UV-VIS spectroscopy, I will measure the response to absorption with wavelength. Absorption will be plotted against wavelength to find the band gap.

3. My Role/Preparation/Experience

- your preparation and qualifications to undertake the project (e.g., previous coursework, jobs, extracurricular experiences, other research or training)
- your plans for further preparing yourself before undertaking the project, prior to the start date
- your unique role in the project as compared to the role of your faulty mentor and others (graduate students, technicians, collaborators), including your plan for regular communication with your mentor
- if a group project, the unique role of each student on the project (use an additional paragraph if necessary for this question)

Starting early January 2024, I worked with my mentor to prepare for the Summer Undergraduate Research Fellowship. Having read through review papers and research articles, I was able to understand the fundamentals of photocatalysis and challenges related to methane conversion. In preparation for this project, I have presented my findings from relevant literatures in our lab group meetings, and I have taken proactive steps to familiar myself with our lab, including integrating ongoing research into my weekly schedule. This spring, I will continue working with Dr.[A] and his students to learn how to operate instruments for catalyst synthesis, characterizations and activity test. I am confident that lab skills acquired from my organic chemistry and physical chemistry courses will facilitate my training on all required instrumentation, such as an IR-spectrometer and temperature controller. My knowledge from chemistry courses, general physics and differential equation courses enables me to have fundamental understandings of data analysis and interpretation. In conjunction with this training, I will continue reading literature to further my knowledge of photocatalysis and methane conversion. This summer, I plan to meet with Dr. [A] two to three times per week to discuss my research progress.

Appendices



Scheme 1. Photocatalytic Methane Conversion Mechanism. Methane is absorbed and is transformed into ethane and hydrogen

References

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