Plan Overview

A Data Management Plan created using DMPTool

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Title: STUDY OF REDOX REVERSIBILITY OF COPPER-BASED CATALYSTS FOR APPLICATION IN A PHOTO-THERMOCATALYTIC SYSTEM FOR “DAY-AND-NIGHT” CO2 HYDROGENATION

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Project abstract:

The increasing concentration of atmospheric CO2 from anthropogenic sources is generating great concern for worldwide organizations. Therefore, the hydrogenation of this residue, which is obtained in high purity in agro-industrial processes, can be a promising alternative for generating high-value hydrocarbons. In this context, the present project aims to understand the hydrogenation process catalyzed by copper-based catalysts, comparing the mechanisms present in the photoactivated and thermoactivated routes. The main motivation lies in the fact that the effective incidence of sunlight to favor the electron transfer between the chemical species is limited to a few hours a day, requiring the development of an interchangeable system that acts during the day and night, that has not yet been investigated. Thus, as the mechanisms of CO2 reduction on copper catalysts might coexist in photo and thermocatalysis, this study aims to investigate the best conditions and similarities in these two isolated reaction pathways. In the future, it will be proposed the application of a day-and-night system in the same uninterrupted reactor, seeking to achieve an optimal yield window for products. For this, this scientific project will develop a fundamental study to understand how Cu0/Cu+/Cu+2 species can favor the application of the material which might, reversibly, act as a reforming catalyst and a photocatalyst.

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STUDY OF REDOX REVERSIBILITY OF COPPER-BASED CATALYSTS FOR APPLICATION IN A PHOTO-THERMOCATALYTIC SYSTEM FOR “DAY-AND-NIGHT” CO2 HYDROGENATION

In the Project Scope, data will refer to any equipment result, including those intended for graphical plots (e.g., spectroscopic data) or images (e.g. transmission electron microscopy). These data will be collected in different experiments regarded to the produced samples and their characterizations, mainly in digital format.

Data on the synthesized catalysts will be obtained from characterization techniques, such as: X-ray diffraction (XRD) for phase identification; Raman spectroscopy for verification of possible impurities measured by Fourier transform infrared spectroscopy (FTIR).; N2 physisorption at -196 °C when investigating the surface (surface area, pore volume and diameter, etc.); scanning electron microscopy (SEM) to observe the morphology; and UV-Vis and photoluminescence spectroscopy for electronic properties. In order to monitor the copper oxidation states before and between each catalytic process, it is intended to use the following techniques: X-ray photoelectron spectroscopy (XPS), electronic paramagnetic resonance spectroscopy (EPR), in-situ FTIR (DRIFT), and temperature programmed reduction with H2 (H2 -TPR). The catalytic data will be obtained from periodic measurements of a valve system, and the products generated will be quantified by the gas chromatography (GC) equipment. The mechanisms of photo and thermocatalytic reactions will be investigated using 13C markers to identify the reaction pathways of each process and, in the future, of both processes concomitantly. All data generated in the equipments will be treated by applying specific equations for each case with the help of appropriate software, such as Origin-Pro software.

Along to Storage and Backup and Selection and Preservation procedures, all information about equipment model, experiment setup, calibration and accessory data will be kept in Repository. Information management will be done by the Project software using the structure of Laboratory digital notebooks.

Each project member should sign an Ethical and Legal Responsibility term, which will be kept by Project Coordination. This term will follow the general guidelines promoted by FAPESP, including data ownership, responsibility and absence of plagiarism declarations. Plagiarism software support will be provided by Project Coordination using Technical Reserve resources. Plagiarism reports for each produced document will be kept together to the final documents in Data Repository.

Core IT systems to secure IP, includes all input/output devices that store the documents they process, and they are typically networked and connected to remote management systems. Also, cloud applications and file-sharing services.

All produced data will be stored in a Data Repository, based in digital servers (to be acquired using Technical Reserve resource) provided by the Project Coordination and located in UFSCar TI Support, with remote backup in Embrapa TI Support. For data organization, project management software will be provided to all users keeping basic information about acquisition date, equipment and measurement conditions. Free software alternatives will be analyzed by Project Coordination but keeping all the information encrypted in a physical server, for data reliability and confidentiality.
Management software will include a digital Laboratory Notebook, which will be used by all project members. Related sub-projects (e.g. PhD thesis, posdoc projects, etc) will be registered using the same system. Raw data from equipments will be linked to the digital Notebook and physical versions (paper-based) will be scanned and also stored in digital format. Project Coordination will keep physical notebooks after each sub-project ending at least for 3 years after Project completion.

All data will be registered in a standard Laboratory Notebook, to be provided by the Project Coordination to all project members. This Laboratory Notebook (see below), in both physical and digital format, is aimed to keep all the information protected and easily available for Coordinators (for checking or validation).

Several experiments proposed in this Project are destructive analyses and, in some cases, as-produced catalysts are unstable for a long-term storage. Therefore, methods for sample preparation and characterization will be preserved in digital server for experiment reproduction in a detailed format. When possible, representative samples will be stored and classified by Project Coordination for cross-checking and validation if necessary. As described above, data and methods should be preserved in Repository at least for 10 years.

A Project webpage will be built for public information about main proposal, members, sub-proposals and achievements. A contact email will be provided in webpage. This webpage will be prepared using support from UFSCar and Embrapa TI services and features will be used to help accessing of project members to restricted areas.

Papers and published content will be freely provided in Project webpage using preprint documents or final papers in case of open access options. These will strictly follow Journals' policies and, in cases of restricted data access, Project Coordination will ask FAPESP about any specific event. Raw data will be provided by request to Project Coordination, in Project contact email. The wide range of possible new knowledge requests a continuous approach of integration and discussion among researchers, which is only possible through regular meetings. Since all the groups are based in Sao Paulo state, dislocations and travels are not a major problem to the group keep in contact. These activities will be supported by the Team experience in research networks as well as supporting structures such as AgroNano Network.
To access information about each Project achievements, Public Yearly Meetings will be promoted, structured for 2-days meeting. The meeting structure will comprise a public part in the 1st day and a closed session in the 2nd day with project members. During the 1st day each principal investigator will be invited to present to the general public the main achievements through oral presentations and poster discussion about specific topics. The events will follow the general structure of scientific meetings, with invited presentations (generally by important researchers in related areas, not necessarily working on the project) and regular talks. A public document will be produced reporting the main achievements and highlights of the research, such as important papers (in high impact factor journals), patents or technology transfer processes. In this document only the public information will be widespread taking care about language (intended to be accessible for all publics) and structure (visually-attractive). In the 2nd day, the closed meeting will take place to discuss the main problems in the course of research activities and present technologic achievements under protection processes. This closed meeting is intended to help researchers to share their experience in confidential topics and, also, to avoid any unintentional information disclosure which may compromise patent requests. The Public Yearly Meetings will be important to start cooperation among groups but this will be stimulated by other means, such as
regular web-based forums. To that a project webpage will be developed with thematic forums to promote continuous discussion about specific topics and sharing of research results.

Also, Embrapa Instrumentação has the Open Access Repository to Embrapa Scientific Information (Alice) designed to gather, organize, store, preserve and disseminate, in full, scientific information produced by Embrapa researchers and edited in book chapters, articles in indexed journals , articles in conference proceedings, theses and dissertations, technical notes, among others. As it uses standardized technologies adopted by the world scientific community, it is interoperable with other open access systems and, therefore, integrates a global network of scientific information. Thus, in addition to being able to contribute directly and automatically to increasing the impact of research results, it will also provide greater visibility for Embrapa and its researchers. Access to the repository can be made through the link: https://www.alice.cnptia.embrapa.br/

Access will be restricted to project members until paper publication or any other information disclosure (patent, meetings, etc). As published, raw data will be available to anyone who formally requests to Project Coordination. Raw data will be stored by digital format at least for 10 years after Project completion.

Data management will be responsibility of Project Coordination (Coordinator and PIs). TI support from institutions will be provided as Institutional Support. A Data curator will be yearly indicated by Project Coordinator as a contact point from TI support, researchers and community. To help the Proponent to organize information about equipment and data
sources, a project secretariat will be provided with general support for project management (acquisitions, payments, etc) and to provide information about multiuser facility. All the equipment acquired in this proposal will be asked to operate as multiuser facilities and the Secretariat will be responsible to propose and manage a system for easy access. The involved costs (including maintenance, consumables and operational people) of each technique will be studied by the Secretariat aiming to support researchers to propose sustainable conditions for shared usage. A general web-based scheduling system for equipment accessing will be discussed with all investigators. The previous experience of Embrapa Instrumentation in the management of LNNA (Nanotechnology National Laboratory for Agriculture), as member of SISNano (Brazilian System of Nanotechnology Laboratories) will support this discussion. The equipment, book and database acquisition processes will be preferably done by the project secretariat. The Secretariat will be supported by the previous experience of FAI-UFSCar and Embrapa Instrumentation Project Management Office in international acquisitions. In any case, all the equipments financed by this proposal will be offered as multiuser facility according to FAPESP guidance lines. A wide discussion in the participants institutions will be done to define a specific person for secretariat, according to the local availability and as an additional resource (not paid by FAPESP).

The approval of the Research Internship Abroad Scholarship (BEPE), funded by FAPESP will be enough to achieve the mentioned goals.

Planned Research Outputs

Data paper - "Development of photocatalysts based on zeolite A with copper oxide (CuO) for application in the artificial photosynthesis process"

This study explores the CO2 photoreduction process and its importance as a potential solution to mitigate carbon emissions. The co-precipitation method was used to produce composites formed between zeolite A and varying mass percentages of CuO, which demonstrated good activity and selectivity in CO2 photoreduction. The selectivity of the composites was linked to the presence of Lewis acid and base sites, with the predominance of Lewis base sites favoring the conversion of CO2 to CH4. Increased CuO content in the composite structure led to enhanced selectivity, reaching 100 % with ZE/CuO10 %. The presence of both Lewis acid and base sites facilitated the formation of two-carbon compounds such as ethylene, making the process of dimerization more accessible. Additionally, the study suggests that methanol and acetic acid can also be produced alongside other gaseous products such as CO, C2H4, and CH4. These findings highlight the potential of zeolite-based composites containing different active sites important during CO2 photoreduction for the production of valuable chemicals.

Event - "Estudo da evolução da atividade de fotorredução de CO2 com SnO2/Cu sob o armazenamento à baixas temperaturas: ativação e desativação para produtos C2"

A busca por catalisadores seletivos para a conversão de CO2 é um assunto de suma importância para mitigar esse gás estufa da atmosfera. Nesse cenário, este trabalho discorre sobre a atividade de catalisadores de SnO2 à base de Cu e sua estabilidade sob o armazenamento em baixas temperaturas. Os resultados demonstraram que quanto maior o teor de Cu no material, maior a produção em fase gasosa. Em adjunto, possivelmente houve uma estabilização das espécies ativas em duas semanas de armazenamento, aumentando a produção de moléculas C2 de interesse. Porém, após 1 mês de armazenamento houve o decréscimo significativo da atividade que pode ter sido ocasionada pela aglomeração das nanopartículas de Cu, que presumivelmente impede a intercambialidade dos estados redox desse metal e diminui sua atividade catalítica para fotorredução
de CO2.

Event - "Análise da atividade fotocatalítica de SnO2/Cu para redução de CO2 em água: mudança estrutural com o tempo"

O aumento de temperatura global é diretamente relacionado a altas taxas de emissão de CO2 atmosférico, e uma das maneiras mais viáveis para mitigar esse gás é a partir do desenvolvimento de processos catalíticos altamente seletivos para converter o grande volume desse gás estufa em produtos. Nesse sentido, este trabalho estuda a atividade fotocatalítica das espécies de cobre em diferentes proporções mássicas (1, 10, 20, 30 wt. %) suportadas em SnO2, sintetizado e comercial, para a redução de CO2 em água.
A síntese de SnO2 utilizou do método de co-precipitação publicado recentemente pelo grupo de pesquisa, bem como a dopagem de cobre, mas nesse caso substituindo o TiO2 pelo SnO2 sintetizado e comercial (Aldrich, 99,99% trace metal basis). A reação foi realizada em um reator quatzo irradiado por UVC durante 6h após a saturação de CO2 que foi borbulhado no meio aquoso (100 mL). Os produtos do headspace foram quantificados por cromatografia gasosa. Para mensurar o teor de cobre em cada material, a análise de absorção atômica foi utilizada e a técnica de difração de raios-X foi empregada para avaliar a alteração estrutural do fotocatalisador. O procedimento de adição de Cu foi realizado analogamente para o SnO2 comercial
Os materiais sintetizados apresentaram resultados fotocatalíticos promissores com a produção de até 217 umol g-1 de CH4 para o material com SnO2-co/Cu-10%. Em comparação

ao suporte comercial, produziu-se muito mais CO e CH4 e etileno. No entanto, a dificuldade de reprodutibilidade das reações foi o que chamou atenção neste trabalho. Exceto para o material SnO2-co/Cu-20%, não foi possível obter boas réplicas dos ensaios realizados nas mesmas condições reacionais, independente do suporte utilizado, dado a considerável variação para menores valores dos resultados das amostras com maior porcentagem mássica de Cu, e o aumento considerável para materiais com menor teor de Cu. A taxa de cobre detectada em todos os materiais foi próxima da quantidade adicionada nas sínteses, exceto para os materiais com 30%, os quais demonstraram valores próximos a 20%, porém, os resultados catalíticos se diferem consideravelmente comparados aos materiais com essa quantidade mássica adicionada, sendo necessário outras técnicas de caracterização para elucidar a distribuição das espécies de cobre. Os difratogramas dos materiais recém-sintetizados comparados aos que foram realizados aproximadamente 1 mês após a síntese, apresentaram um aumento considerável das espécies de óxidos de cobre, e isso ocorreu tanto com a utilização do suporte comercial quanto para o sintetizado. Logo, o armazenamento do material passa ser um objeto de estudo de suma importância para aplicação desses fotocatalisadores, implicando que a instabilidade de cobre deve ser considerada ao correlacionar dados de caracterizações com os de reação. Ademais, o controle das espécies de Cu2O e CuO pode ser essencial para garantir a maior atividade fotocatalítica na redução de CO2 à produtos

Data paper - "CO2 Photoreduction Product Selectivity with TiO2-Cu Nanocatalysts under Different Reaction Media"

This study explores photocatalytic conversion of CO2 using TiO2-Cu heterojunctions with different Cu contents and investigates influence of different reaction media on the process efficiency. The use of KOH favored liquid products, especially ethanol. An analysis of H2 production as the main competitive reaction was done. Sodium oxalate led to an increase in H2 evolution by approximately 600 μmol g-1 compared to pure water, in the presence of CO2 in the reaction medium, but the blank test (without CO2) indicates a lower H2 yield (~136 μmol g-1), which suggests that the competitive reaction with CO2 also plays a role in H2 production. This role was related to the decrease of the initial pH from approximately 8.5 to 5.2, stabilizing at 5.5 at the end of the 6h reaction. In an environment saturated with N2, the pH increases to 9 and stabilizes at 7.8 at the end of the process. In the presence of acetic acid, both CO and H2 production were suppressed, with a significant increase in the selectivity for methane via cleavage of the acid's carbon bond. The findings underscore the importance of optimizing reaction conditions to achieve higher yields of desired products in the photocatalytic conversion of CO2.

Planned research output details

Title	Type	Anticipated release date	Initial access level	Intended repository(ies)	Anticipated file size	License	Metadata standard(s)	May contain sensitive data?	May contain PII?
Development of photocatalysts based on zeolite A w ...	Data paper	2023-09-07	Restricted	Embrapa Instrumentation Server		None specified	None specified	No	No
Estudo da evolução da atividade de fotorredução de ...	Event	2023-09-28	Restricted	Embrapa Instrumentation Server		None specified	None specified	No	No
Análise da atividade fotocatalítica de SnO2/Cu par ...	Event	2023-03-09	Restricted	Embrapa Instrumentation Server		None specified	None specified	No	No
CO2 Photoreduction Product Selectivity with TiO2-C ...	Data paper	2024-02-12	Restricted	Embrapa Instrumentation Server		None specified	None specified	No	No