Experimental report

14/09/2023

Proposal: **5-22-788** **Council:** 4/2020

Title: The direct conversion of methane to methanol by the copper-exchanged zeolites

Research area: Chemistry

This proposal is a new proposal

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Samples:
High copper Mazite
low copper Mordenite
high copper Mordenite
Low copper Mazite
High copper Faujasite
low copper Faujasite

Instrument	Requested days	Allocated days	From	To
D1B	6	2	03/09/2021	05/09/2021
D20	6	0		

Abstract:

In this project, we would like to use the neutron powder diffraction (NPD) technique for studying the process of the partial oxidation of methane to methanol (MtM) by active copper species in various Cu-zeolite structures. The objective is to determine whether the methoxy forms on copper monomers, dimers or higher nuclearity clusters, which is currently heavily debated in the scientific community. The positioning of hydrocarbon species will also show the distribution of copper species and elucidate if the activity increases only because of increased density of active species or structural differences in the zeolite framework. In situ neutron powder diffraction measurement should provide excellent contrasts for methane and methoxy species if labelled with deuterium (b= 6.67 fm).

Abstract:

In this study, we employed neutron powder diffraction to elucidate the nature of methoxy groups formed on copper sites during methane reactions and their spatial distribution within the zeolite Omega structure. By labeling methane with deuterium (D, with a neutron scattering length, b, of 6.67 fm) and conducting in-situ measurements, we aimed to achieve optimal contrast for detecting methoxy species formation.

Results expected from this proposal:

The direct and selective conversion of methane to methanol (MtM) holds significant promise as a sustainable alternative to methane flaring, particularly at remote oil and gas extraction sites. Copper-exchanged zeolites have emerged as a widely studied catalyst for this transformation. However, the precise nature of the interaction between active sites responsible for forming methoxy species remains elusive. Proposed models involve associating monomers,[1,2] di-copper species,[1,3] or tri-nuclear copper oxo entities.[4] In addition, it has been shown Cu-Omega (Cu-MAZ) can significantly outperform other zeolites in terms of the production yield.[5,6]

To address these knowledge gaps, our research aimed to conduct comprehensive investigations on copper Omega systems using the High-Resolution X-ray Diffraction technique (offered by ID22 proposal: CH-6224). This technique was chosen to probe the location and nuclearity of the active copper species. Furthermore, experiment at D1B was proposed to shed light on the electronic structure of methoxy species resulting from this reaction. By synergizing and cross-referencing these methodologies in an operando fashion, our objective was to provide a holistic understanding of the mechanisms underpinning methane-to-methanol conversion using copper zeolites. This research also lays the foundation for further catalyst development and optimization.

Results achieved from this proposal:

The sample selected to tests, of MAZ topology, is hexagonal structure composed with gmelinite (GME) cages. It displays similar Si:Al ratio (4.3) and was exchanged with 4.7wt% Cu. The experiment followed the isothermal MtM procedure outline at fig. 1. Temperature 473K was maintained at all steps of the stepwise reaction. The sample was heated at 473 K under vacuum and then backfilled with oxygen. After 6-8 h the excess oxygen was evacuated and deuterium-labeled methane (5mL/min) was fed for 1 h. The non-adsorbed methane was flushed out. The system was continuously monitored by collecting NPD data.

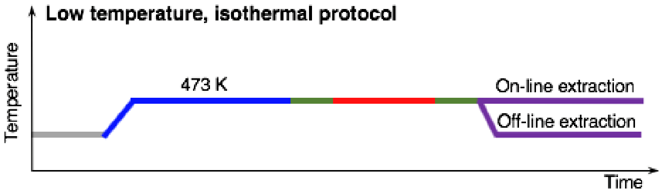

Figure 1. The isothermal MtM protocol designed for Cu-omega. Flow of O_2 (blue) and CH_4 (red).

Additionally to the NPD data the framework structure models of the zeolites were refined using complementary X-ray diffraction data collected at ID22. The positions and occupancies of copper species are optimized using resonant diffraction data (XPD collected across Cu absorption K-edge during the same experimental steps), while the methoxy groups positions were determined based on neutron data collected at D1B.

The refinement protocol is ongoing, but the preliminary model for the isothermal reaction at 473K is depicted in Figure 2.

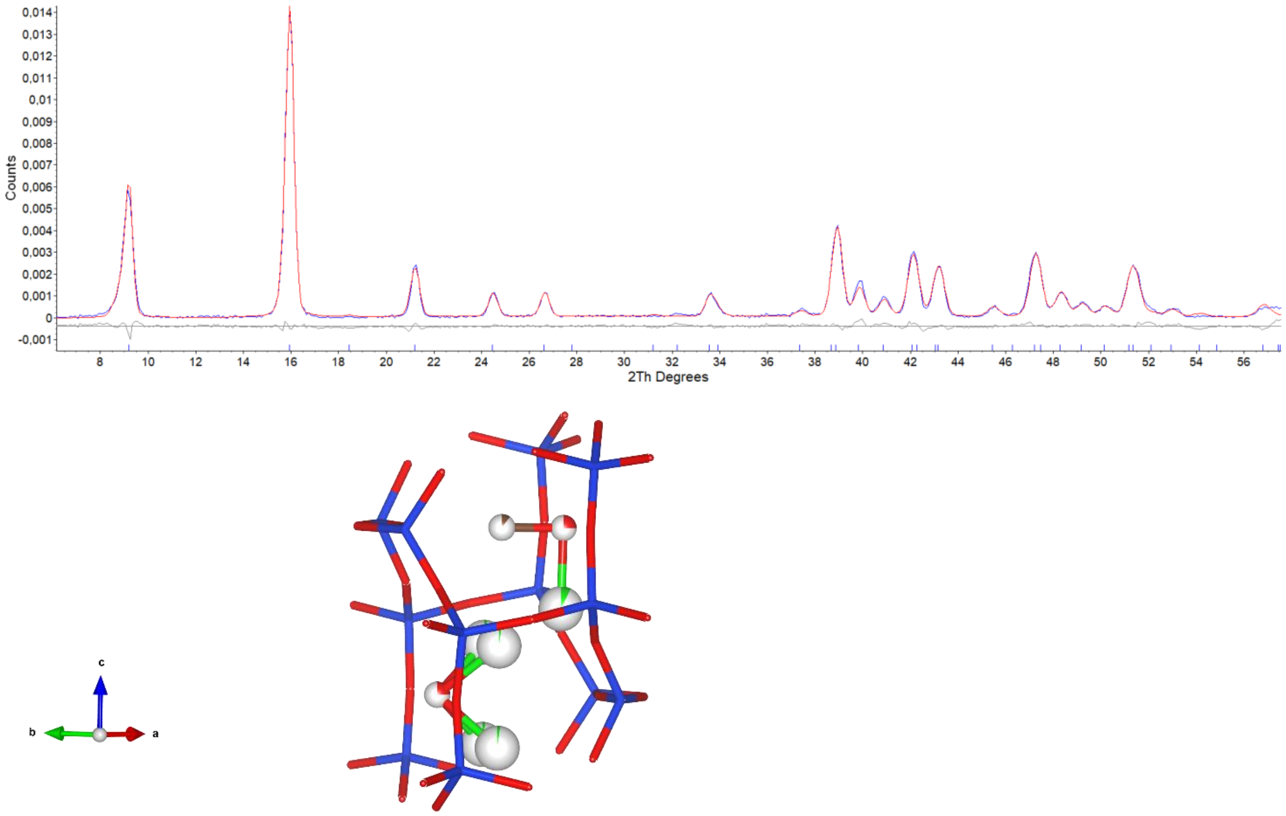

Figure 2. The refinement profile line (top) and the refined model of Cu-MAZ activated under oxygen flow and contacted with methane at 473K (bottom).

Bibliography:

(1) Sushkevich, V. L.; Palagin, D.; van Bokhoven, J. A. Angew. Chemie *130* (29), 2018.

(2) Knorpp, A. J.; Newton, M. A.; Mizuno, S. C. M.; Zhu, J.; Mebrate, H.; Pinar, A. B.; Van Bokhoven, J. A. Chem. Commun. *55* (78), 2019.

(3) Vanelderen, P.; Snyder, B. E. R.; Tsai, M. L.; Hadt, R. G.; Vancauwenbergh, J.; Coussens, O.; Schoonheydt, R. A.; et al. J. Am. Chem. Soc. *137* (19), 2015.

(4) Grundner, S.; Markovits, M. A. C.; Li, G.; Tromp, M.; Pidko, E. A.; Hensen, E. J. M.; Jentys, A.; et al. Nat. Commun. 2015.

(5) Knorpp, A. J.; Pinar, A. B.; Baerlocher, C.; Mccusker, L. B.; Casati, N.; Newton, M. A.; Checchia, S.; et al. Angew. Chemie *133* (11), 2021.

(6) Wieser, J.; Knorpp, A. J.; Stoian, D. C.; Rzepka, P.; Newton, M. A.; van Bokhoven, J. A. Angew. Chemie Int. Ed. 2023.