ESRF	**Experiment title:** Exploiting anomalous (resonant) scattering at the Cu K-edge to elucidate the structure of the copper species present during the partial oxidation of methane to methanol (MtM)	**Experiment number**: CH-5872
Beamline: BM28	**Date of experiment**: from: 10 Nov 2021 to: 16 Nov 2021	**Date of report**: *03.05.2023*
Shifts: 18	**Local contact(s)**: Paul Thompson	

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Report:

Results expected from this proposal:

The combined measurements of high resolution XPD and Cu XANES were exploited to study the long-range order and the local structure of the copper species acting in the partial oxidation of methane to methanol (MtM) by copper-exchanged Mazzite. This well-recognized zeolite-type catalyst outperforms many other topologies. The cooper positions forming active sites in MtM were have been characterized during high temperate variant of the reaction (450°C) (1). It remains unknown however how the copper species perform at isothermal route (200-300°C) upon the presence of H_2O. The major objective of the experiment was then to pinpoint the positions and geometry of both active and inactive copper species in 4.7wt% Cu-MAZ exploited in isothermal route to MtM to understand whether the species are comprised of copper monomers, di-copper species, or higher nuclearity clusters.

Results achieved from this proposal:

The Cu-MAZ sample was placed in 0.5mm quartz capillary cell. The experiment followed the isothermal approach (1) to MtM protocol with the same temperature (200-300°C) for all experimental steps: (a) activation by the oxygen flow under given T (b) purification using an inert gas and (c) feeding with methane flow. The reaction's outcomes were monitored with the mass spectrometer. All gas supplies were provided by BM28 and the sample environment brought by the users.

Cu-MAZ sample was isothermally tested under 175, 250°C and 275°C. Each experimental step was probed by measuring diffraction data at the conventional, off-resonance energy 17.5keV (Figure 1A) and near Cu absorption edge followed by XANES scans (Figure 1C). Data obtained by mean of both methods show the diminishing hydration of the sample in function of temperature. The framework structure models were refined against the conventional diffraction data and only the positions and occupancies of copper species against anomalous diffraction data. The refinement procedure continues but the initial results are already presented in Figure 1B.

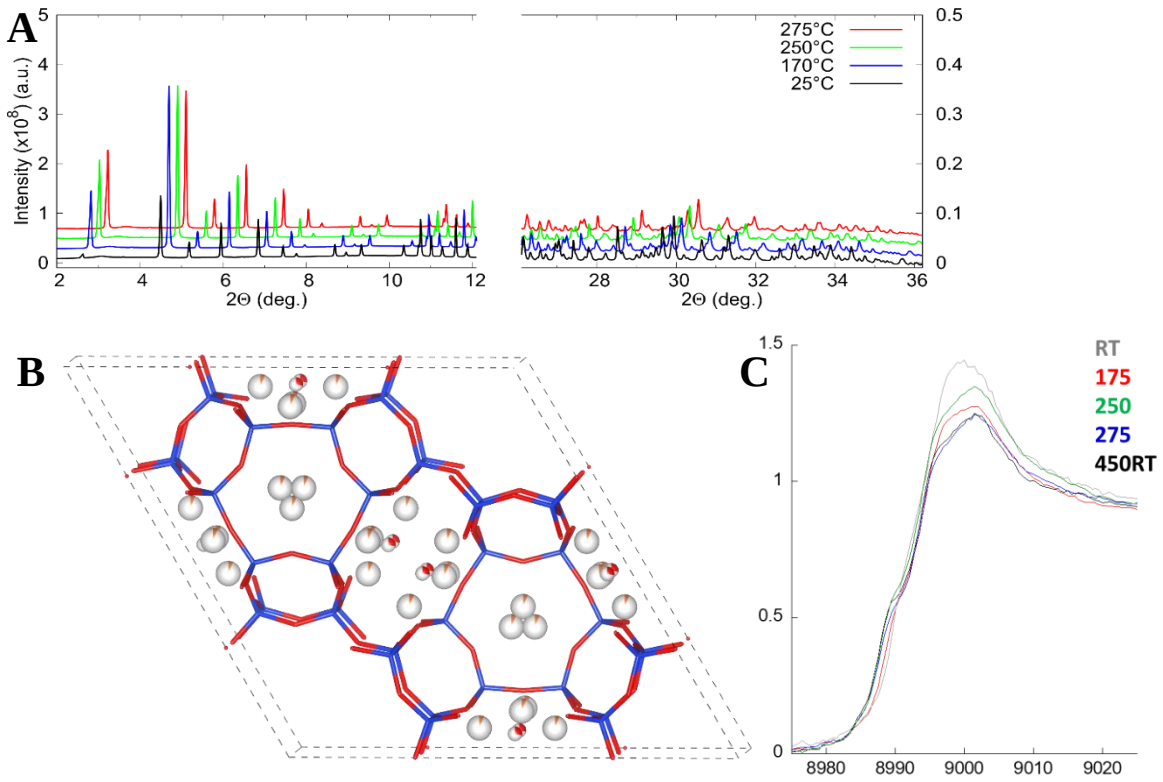

Figure 1. The X-ray diffraction data collected at Cu-MAZ activated under oxygen flow at different temperatures (A). The refined structure of Cu-MAZ activated under oxygen flow and 230°C (B). Normalized Cu XANES as a function of temperature under oxygen flow.

Bibliography

1. Knorpp, A. J., et al., Angew. Chem. Intl. Ed., (2021), 133(11), 5918-59222