

Spectroscopic Investigation of the Role of Water in Copper Zeolite Methane Oxidation

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Significance and Relevance

For the first time, a mononuclear copper site ([CuOH]⁺) was identified as an active site for selective methane oxidation to methanol over Cu-exchanged zeolites. This active site was thoroughly characterized with a combination of site-selective spectroscopic methods (UV-Vis, resonance Raman, EPR...). Additionally, an important but contentious claim in literature stating that water can reoxidize Cu(I) in methane-reacted Cu-zeolites, has been disproven, and an alternative explanation is offered for the observed phenomena.

Preferred choice for the topic: Fundamental advances in understanding catalysis. Preferred presentation: Oral only.

Introduction and Motivations

A mild, selective conversion of methane to methanol is a major goal in modern chemistry, sparking considerable interest in methane-oxidizing metal sites among heterogeneous and (bio)inorganic chemists. Cu-exchanged zeolites show promise for this direct methane-to-methanol oxidation through a typical non-catalytic, three-step cyclic process: formation of active sites at elevated temperature, methane reaction at 200°C, and methanol extraction with water (steam) at 200°C.^{1,2} The extraction step, however, deactivates the material, requiring high-temperature reactivation before each subsequent methane reaction. This poses a substantial hurdle for industrial application, and thus considerable research efforts are focused on developing a catalytic process (with sufficient selectivity and yield) and on improving the efficiency and speed of the current cyclic process.

In this context, an interesting study on Cu-MOR zeolites, published in *Science* in 2017, proposed that the water/steam used for methanol extraction could simultaneously reoxidize Cu(I) to Cu(II) in the methane-reacted material.³ Amongst other, this claim was supported by the detection of hydrogen gas during steam extraction, thought to result from water reduction. Nonetheless, the claim that water can oxidize Cu(I) remains contentious, with some authors questioning the overall reaction's thermodynamic feasibility.^{4,5} This work identifies, for the first time, a mononuclear copper site ([CuOH]⁺) as the active site for selective methane oxidation, and then investigates whether water can indeed reoxidize Cu(I) in methane-reacted Cu-MOR zeolites.

Materials and Methods

After ion exchange with copper(II) acetate and calcination, the Cu-MOR material proceeded through a three-step cycle: 1) autoreduction in helium at 500°C, 2) reaction with methane at 200°C and 3) extraction of the produced methanol with water-saturated helium (steam) at 200°C. Active site characterization and quantification after each of the 3 steps occurred via a combination of spectroscopic methods, including diffuse reflectance (DR) UV-Vis, in-situ resonance Raman, electron paramagnetic resonance (EPR), and X-ray absorption spectroscopy (XAS). Online mass spectrometry (MS) was used to analyze the gas mixture during steam extraction of the methane-reacted Cu-MOR.

Results and Discussion

First, we identified the methane-oxidizing active site in autoreduced Cu-MOR zeolites as a [CuOH]⁺ species, characterized by a broad OH⁻ to Cu(II) charge transfer band at 20700 cm⁻¹ in the DR-UV-Vis spectra, a $g_{\parallel} = 2.27$ feature in EPR and a Cu-O stretch of 750 cm⁻¹ in resonance Raman.⁶

With the active site identified, we studied all three steps of the methane oxidation cycle (autoreduction, methane reaction, and steam extraction) using XAS and EPR to quantify Cu(I) and Cu(II)



amounts, respectively. Copper oxidation was not observed upon exposing methane-reacted Cu-MOR to steam at 200°C. Despite the lack of Cu(I) oxidation, H₂ evolution was detected during the steaming step with MS. Quantification of H₂, HD and D₂ evolution during MS isotope experiments with all four combinations of CH₄/CD₄ reaction followed by H₂O/D₂O steaming, elucidates that the hydrogen in H₂ mainly stems from the [Cu(II)OH]⁺ active site and from methane.⁷

A plausible explanation is the decomposition of formic acid, produced from methane overoxidation over $[Cu(II)OH]^+$, into CO_2 and H_2 : HCOOH $\rightarrow CO_2 + H_2$. This is supported by the near-equal amounts of CO_2 and H_2 observed with MS during steam extraction. In addition, the fraction of $[Cu(II)OH]^+$ not contributing to the measured methanol yield (and thus available for overoxidation) is around 6 times the produced CO_2/H_2 yield.⁷ This corresponds to the fact that 6 equivalents of Cu(II) need to be reduced to oxidize methane to formic acid: $CH_4 + 6 [Cu(II)OH]^+ \rightarrow HCOOH + 6 Cu(I) + 4 H_2O$.

In summary, we find that a mononuclear $[CuOH]^+$ is the active site for methane oxidation in autoreduced Cu-MOR. This site reduces to Cu(I) during methane reaction, after which water/steam is not able to reoxidize Cu(I) to Cu(II). The observed H₂ does not result from water reduction, but instead from formic acid decomposition after methane overoxidation.⁷ The fact that water facilitates the conversion of the methane reaction products to CO₂ offers promise for the pursuit of a lowtemperature oxidation process of atmospheric CH₄ to CO₂ (with a lower global warming potential) as a negative emission technology. This is an active area of research, with the most promising results so far involving a dry stream of methane and O₂ at 300°C.^{8,9} Adding water could potentially lower the temperature required for complete methane oxidation, improving its feasibility for real-world applications.

References

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