Nature of Cu active centres in ferrierite based catalysts responsible for direct CO_2 transformation to platform chemicals

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Significance and Relevance

Here, we present highly active copper (Cu) zeolite-based catalysts for producing acetic acid or methanol through the direct interaction of carbon dioxide (CO_2) and methane (CH_4) at 220 °C. The studied Cu-zeolites exhibit significant differences in the types and populations of copper species involved in transforming CO_2 and CH_4 into various oxygen-containing products. By combining results from in-situ spectroscopic methods (IR, UV-Vis), synchrotron techniques (XAS), and mass spectrometry, we identified the nature of the Cu active centers responsible for producing acetic acid or methanol. Our study revealed that CO_2 and CH_4 were preferentially converted into methanol by Cu-oxo species present in Cu-zeolites, whereas acetic acid production was primarily facilitated by Cu bare cations.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling and 2nd choice: Fundamental advances in understanding catalysis
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Introduction and Motivations

Carbon dioxide and methane are the primary compounds contributing to Earth's escalating global warming.[1] The abundance of these gases has spurred efforts to convert them into valuable products, such as methanol and acetic acid, which serve as critical materials in industrial and chemical processes. Copper-containing zeolites represent a group of catalysts capable of effectively converting methane into methanol using O_2 in a cyclic regime.[2] Methanol is extracted from the system by using water. Moreover, studies have shown that copper species within zeolites play a significant role in CH_4/CO_2 interactions, leading to the formation of acetic acid. However, the nature of the active copper centers and the mechanism of CO_2/CH_4 transformation remain subjects of ongoing debate.

This paper presents research on the conversion of methane and carbon dioxide into acetic acid and methanol over Cu-FER zeolites, using advanced operando spectroscopic techniques (UV-Vis, FTIR, XAS, and mass spectrometry). The study aims to experimentally analyze copper species within FER zeolites, examining their roles in the selective formation of CH_3COOH or CH_3OH from the CO_2/CH_4 reaction mixture. The results obtained could significantly contribute to the design of catalysts dedicated to processing CO_2 and CH_4 into value-added products.

Results and Discussion

Two Cu-FER samples differing in the types of copper species were prepared by ion-exchange procedure. The sample with low copper loading (Cu/Al ratio 0.06) was denoted as Cu-FER-L and high loaded Cu-FER with (Cu/Al ratio 0.4) was denoted as Cu-FER-H. Analysis combining FTIR, UV-Vis, and XAS results confirmed the presence of a high fraction of Cu(II) species and a smaller population of Cu(I) species in both samples. In Cu-FER-L, copper is primarily located in cationic positions, whereas the copper-rich Cu-FER-H contains copper species in both cationic positions and various forms of Cu-oxo species. The evaluation of CH_4 and CO_2 interaction products on Cu-FER catalysts, monitored in the

temperature range of 25–450 °C using coupled FTIR and mass spectrometry techniques, allowed for the detection of reaction products adsorbed on the catalyst surface (via FTIR) as well as the composition of the gas phase (via mass spectrometry). The FTIR spectra of Cu-FER-L confirmed acetic acid formation at temperatures above 200°C, evidenced by the appearance of new bands at 1580 and 1490 cm^{-1} (indicative of acetic acid) and 1334 cm^{-1} (associated with the CH_3 group). Detailed analysis of the FTIR spectra revealed that acetic acid production occurs in two stages, at 210°C and 280°C. The FTIR spectra of Cu-FER-H also showed the formation of bands characteristic of acetic acid following CO_2/CH_4 interaction. Furthermore, in both samples, the presence of acetic acid among the reaction products was confirmed by the detection of an m/z = 60 signal.

To characterize the catalytic behavior of Cu-FER-L and Cu-FER-H in CO_2 and CH_4 transformation, the reaction was carried out at a constant temperature of 200 °C. Figure 1 shows the time dependence of FTIR spectra (upper part) in a top-down projection, alongside the evolution (bottom part) of mass spectrometry signals for acetic acid (m/z = 60), carbon dioxide (m/z = 44), methanol (m/z = 31), water (m/z = 18), and methane (m/z = 16). For the Cu-FER-L zeolite, bands corresponding to acetate ions (1580–90 and 1490 cm^{-1}) and CH_3 groups (1334 cm^{-1}) appeared within the first few minutes, with product accumulation on the surface intensifying after 30 minutes. From that point, the increasing intensities of bands associated with acetates and water molecules (1615 cm^{-1}) were accompanied by a marked decrease in CO_2 (2350 cm^{-1}) and CH_4 gas-phase bands (3100–2800 cm^{-1}). The m/z = 60 signal over time indicates acetic acid generation for 60 minutes, after which production attenuates, corresponding to a substantial accumulation of acetate ions on the catalyst surface. Acetic acid production is also associated with the formation of methanol and water, likely resulting from the oxidation of CH_4 by copper(II) oxo-forms. As the reaction progresses, methanol and water production decrease, probably due to the strong adsorption of acetate ions on active copper sites. In the case of Cu-FER-H zeolite, with a high content of copper(II) oxo-species, only methanol and water are produced in large quantities, while acetic acid formation remains minimal. This finding suggests that the presence of copper(II) oxo-forms is unfavorable for acetic acid production, as these centers tend to consume methane by oxidizing it to methanol. Integration of the m/z signals for acetic acid over the entire reaction duration revealed that acetic acid was formed with 20% efficiency in the Cu-FER-L catalyst, compared to 3.5% for Cu-FER-H.

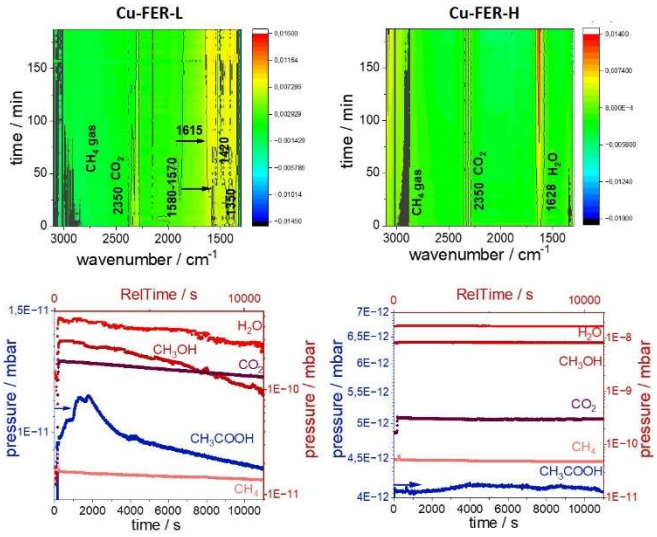

Figure 1. (Upper part) Top-down projection of difference spectra. (Bottom part) Time dependence of the signal intensity (ion currents) of CH_3COOH, CO_2, CH_3OH, H_2O, and CH_4.

These findings clearly indicate that Cu cations are primarily responsible for acetic acid production, while Cu-oxo species facilitate the transformation of CO_2 and CH_4 into methanol in the catalytic regime.

References

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