

Effective upgrade of CO2 and CH4 to high-value products over iron-containing Al-rich *BEA zeolite

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Significance and Relevance

The chemical recycling of CO_2 and CH_4 into platform chemicals has attracted considerable attention from industry and academia. Here, we demonstrate the direct and efficient conversion of these waste gases into acetic acid, with methyl acetate as a secondary product (both achieving 35% efficiency), using iron active centres in an Al-rich *BEA zeolite catalyst. The selected zeolitic matrix enhances reagent transport, while tailored synthesis achieves a high aluminum concentration, ensuring a substantial fraction of iron active species. Together, these factors deliver exceptional catalytic activity for the direct processing of CO_2 and CH_4 into valuable chemical products.

Preferred and 2^{nd} choice for the topic: CO_2 utilization and recycling / Fundamental advances in understanding catalysis

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Introduction and Motivations

Converting CO₂ and CH₄ into platform chemicals provides a sustainable way to utilize these abundant greenhouse gases, mitigating their environmental impact while reducing reliance on fossil feedstocks. This approach supports the transition to a circular carbon economy by transforming waste emissions into valuable chemical intermediates for industrial applications. CO₂ or CH₄ molecules can be effectively activated over transition metal ion-containing (TMI) zeolites as catalysts.¹⁻² TMI centres in zeolites exhibit unique electron-donating properties that can lower the energetic barrier for C-H bond cleavage and possess intrinsic acidity, facilitating the transfer of Brønsted acid protons. These two characteristics enable the formation of critical reaction intermediates, their subsequent conversion, and the efficient desorption of desired products.³⁻⁵ For this study, we selected a wide-pore zeolite with *BEA topology, focusing specifically on a sample with a low Si/Al molar ratio to maximize its capacity to host TMI centers. The Al-rich *BEA zeolite was synthesized using a template-free approach to minimize the environmental impact typically associated with zeolite production. The aim was to harness the catalytic potential of iron species, known for their high activity in redox processes.

Materials and Methods

For our study, we utilized laboratory-synthesized Al-rich *BEA zeolite (Si/Al = 4.5), characterized by a high concentration of aluminum pairs capable of stabilizing divalent iron ions. After synthesis, the zeolitic material underwent structural characterization by XRD. The state of Al atoms was analysed using 27 Al and 29 Si MAS NMR. The distribution of Al atoms in the synthesized sample was determined using a well-established, multi-spectroscopic method based on the analysis of its Co-form⁶. The sample was converted to its NH₄-form and subsequently impregnated with a solution of FeCl₃ in acetylacetonate to obtained three Fe-*BEA samples with Fe/Al varying between 0.06-0.3. Iron speciation in such prepared samples was characterized using FTIR, Mössbauer, UV-Vis, and XAS spectroscopies. The activity of iron centres embedded in Al-rich *BEA zeolite for CO₂ and CH₄ utilization was monitored using operando FTIR-MS. Prior to the catalytic process, the samples were dehydrated under a dynamic vacuum at 450 °C. Following this, a mixture of CO₂ and CH₄ in an equimolar ratio was introduced into the system. The reaction was studied over a temperature range of 250–450 °C.



Results and Discussion

The template-free synthesis of Al-rich *BEA zeolite yielded a sample with a Si/Al ratio of 4.5, exhibiting diffraction patterns characteristic of zeolites with this topology. NMR studies confirmed that all Al atoms are exclusively located in the tetrahedral positions of the framework. Analysis of Al atoms revealed that 30% of the Al atoms can stabilize divalent iron species. The introduction of iron produced materials with Fe/Al ratios ranging from 0.06 to 0.3. Spectroscopic analysis revealed the exclusive presence of bare Fe(II) in samples with Fe/Al ratios < 0.15. However, as the Fe loading increased, iron oxo mono- and binuclear species were observed. Iron oxide was also detected in the sample with the highest Fe/Al ratio, in addition to bare cations and iron oxo species. Hyperfine parameters obtained from Mössbauer spectroscopy of dehydrated Fe-*BEA samples, combined with pre-edge features from XAS spectra, confirmed that all studied samples contained a fraction of bare divalent iron cations, which are predominantly located within six-membered rings of the zeolitic framework. The presence of Fe(II) species in Al-rich Fe-*BEA was confirmed by FTIR analysis using CO as a probe molecule. The interaction of the studied iron-containing zeolites with CO resulted in the appearance of a new band in the FTIR spectrum around 2190 cm⁻¹, indicating the formation of a Fe(II)CO monocarbonyl complex. The interaction of equimolar CO₂ and CH₄ with Fe-*BEA zeolites was monitored in-situ by FTIR across a temperature range from RT to 300°C. The FTIR results confirmed the emergence of new bands in the region of 1750–1300 cm⁻¹, typical for CH₃, CHO, and COO⁻ groups. Additionally, a decrease in the intensity of bands corresponding to CH₄ and CO₂ was observed. The temperature range of 200–300°C



was selected for catalytic testing due to the formation of highintensity bands in the FTIR spectrum originating from acetic acid. Activity tests revealed signals with m/z values of 60 and 74 in the mass spectra (Figure 1) of reactor exhaust gases following the interaction of dehydrated Fe-*BEA samples with an equimolar CO_2 and CH₄ mixture. These signals, attributed to acetic acid and methyl acetate respectively, appeared at temperatures above 230 °C, with maximum concentrations observed at 450 °C. The catalytic efficiency for producing these products was 35%. In the catalytic process, both Fe(II) and easily reducible Fe(III) species played active roles. The presence of CH₄ reduced iron-oxo species, thereby integrating them into redox cycles. The results presented here offer an efficient and straightforward approach for processing CO_2 and CH₄ at low temperatures into value-added products.

Figure 1 Activity of Al-rich Fe-*BEA in direct transformation of carbon dioxide and methane into acetic acid (A) and methyl acetate (B).

References

- 1. Q. Zhang, J. H. Yu and A. Corma, Adv. Mater., 2020, 32, 2002927.
- 2. M. Zabilskiy, V. L. Sushkevich, M. A. Newton and J. A. van Bokhoven, ACS Catal., 2020, 10, 14240.
- 3. C. Tu, X. Nie and J. G. Chen, ACS Catal., 2021, 11, 3384.
- 4. G. Zhao, M. Drewery, J. Mackie, T. Oliver, E. M. Kennedy and M. Stockenhuber, Energy Technol., **2020**, 8, 1900665.
- 5. W. Zhou, K. Cheng, J. C. Kang, C. Zhou, V. Subramanian, Q. H. Zhang, Y. Wang, Chem. Soc. Rev., **2019**, 48, 3193.
- 6. J. Dedecek, E. Tabor, S. Sklenak, ChemSusChem, 2019, 12, 556.

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