Aluminum-rich small-pore Cu-zeolites applied for NH_3-SCR of NOx

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Significance and Relevance

Indicate in 5-6 lines (max. 80-100 words) the main relevant results and why they are novel.

High-performance selective catalytic reduction (SCR) catalysts have garnered significant attention for the abatement of NOx emissions from both stationary and mobile sources in the past decades. The formation of dimer-Cu species, which serve as the active sites of the low-temperature SCR, relies on the mobility of Cu^I species in the channels of the Cu-SSZ-13 catalysts. We found that framework Brønsted acid sites influence the intercage diffusion and reactivity of $[Cu(NH_3)_2]^+$ complexes in Cu-SSZ-13 catalysts and provide new insights for the development of zeolite-based catalysts with excellent SCR activity by regulating the aluminum distribution by using Aluminum-rich zeolites.

Preferred and 2nd choice for the topic: Automotive and stationary emission control
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral preferred of Short Oral

Introduction and Motivations

A short description of the background and motivations.[1] Limit to a few lines, and indicate refs with an apex.[2] …………

The reaction atmosphere is capable of dynamically regulating the structure of active sites and forming active multinuclear species at low temperatures, thereby realizing quasi-homogeneous reactions over Cu-SSZ-13 zeolites in the selective catalytic reduction of NOx with NH_3 (NH_3-SCR).[1] Under the standard SCR conditions, a large number of linear $[Cu^I(NH_3)_2]^+$ complexes are generated through the coordination with NH_3 and form dimer Cu species to activate O_2 molecules, which is thought as rate-limiting step of the SCR reaction over Cu-SSZ-13.[1-3] Therefore, the dynamic characteristics of $[Cu^I(NH_3)_2]^+$ is significantly important for the low-temperature NH_3-SCR reaction. The electrostatic interaction between Cu species and the negatively charged zeolite framework Al significantly influence the $[Cu^I(NH_3)_2]^+$ mobility. However, the mechanism by which the microscopic features of the Al spatial distribution (i.e., local Al-poor or Al-rich) affect the intercage diffusion of reactive Cu species remains highly uncertain.

Results and Discussion

Describe the main scientific results and methodologies used. Add a relevant Figure that highlights the more relevant result. A final statement overviews the main conclusions and advances.

In this study,[4] the key role of framework Brønsted acid sites in the mobility of reactive Cu ions during the NH_3-SCR reaction was elucidated via a combination of density functional theory calculations, in situ impedance spectroscopy, and in situ diffuse reflectance ultraviolet-visible spectroscopy. When the number of framework Al sites decreases, the Brønsted acid sites decrease, leading to a systematic increase in the diffusion barrier for $[Cu^I(NH_3)_2]^+$ and less formation of highly reactive dimer-Cu species, which inhibits the low-temperature NH3-SCR reactivity, and vice versa. When the spatial distribution of Al sites is uneven, due to the difference in the interaction between the $[Cu^I(NH_3)_2]^+$ and the zeolite framework during the intercage diffusion of Cu species, the migration of $[Cu^I(NH_3)_2]^+$ from an Al-poor cage to an Al-rich cage (e.g., cha cage with paired Al sites) has a lower diffusion barrier, which effectively accelerates the formation of dimer-Cu species and hence promotes the SCR reaction. These findings unveil the mechanism by which framework Brønsted acid sites influence the intercage diffusion and reactivity of $[Cu^I(NH_3)_2]^+$ complexes in Cu-SSZ-13 catalysts, and provide an effective strategy for the development of zeolite-based catalysts with high-efficiency de-NOx performance.

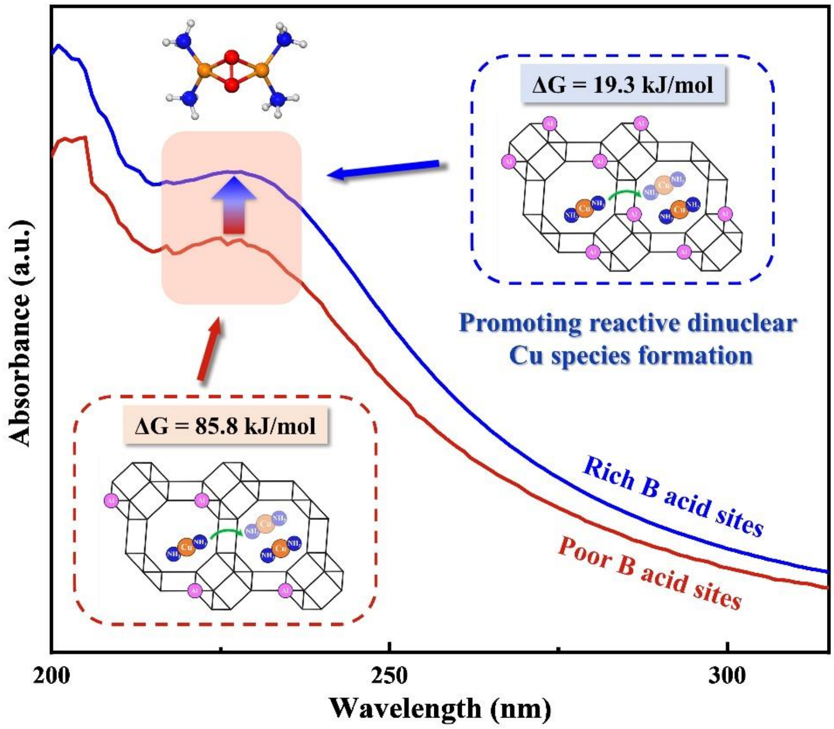

Figure 1 In situ DRUVS spectra of Cu-SSZ-13 with poor and rich Bronsted acid sites and its intercage diffusion energy barrier.

References

1. C. Paolucci, I. Khurana, A. A. Parekh et al., Science 2017, 357, 898.
2. L. Chen, H. Falsig, H. Grönbeck et al., J. Catal., 2018, 358, 179.
3. F. Gao, D. Mei, Y. Wang et al., J. Am. Chem. Soc., 2017, 139, 4935.
4. Y. Fu, W. Ding, H. Lei et al., J. Am. Chem. Soc., 2024, 146, 11141.

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