

# Site-specific monomeric Fe sites catalyze the N<sub>2</sub>O decomposition reaction

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#### Significance and Relevance

Determining the nature of active sites in complex catalysts such as Fe-exchanged zeolites is challenging due to the variety of coordination environments Fe ions can adopt. In this work, we present an *operando* multi-spectroscopy investigation, complemented by spectroscopic-based kinetic analyses, to elucidate the mechanistic details of N<sub>2</sub>O decomposition over Fe-SSZ-13. We demonstrate the site selectivity of the process, involving the redox of specific Fe ions, where the reduction half cycle is the rate-determining step. We highlight the value of *operando* spectroscopy to draw structure-activity relations and elucidate kinetic details, offering insights to guide efforts in the development of Fe-zeolites for use in advanced after-treatment processes, such as N<sub>2</sub>O abatement in NH<sub>3</sub> engines.

Preferred and 2<sup>nd</sup> choice for the topic: Fundamental advances in understanding catalysis, Automotive and stationary emission control.

Preferred presentation: Oral preferred or Short Oral

#### **Introduction and Motivations**

In the context of energy transition and new frontiers in environmental catalysis, N<sub>2</sub>O has emerged as a significant challenge for next-generation emission control technologies. Fe-containing zeolite catalysts exhibit remarkable activity for the decomposition of N<sub>2</sub>O and the selective catalytic reduction of nitrogen oxides by NH<sub>3.</sub><sup>1</sup> Extensive research has been dedicated to these materials,<sup>2</sup> yet most characterizations, assignment of active sites, and structure-activity relationships relied predominantly on ex situ experiments. This often led to conflicting interpretations and assignments, due to the presence of numerous spectator species and the dynamic nature of the active centers under operando conditions. To address these challenges, we have dedicated efforts to the investigation of Fe-exchanged zeolites using a comprehensive set of bulk, site-selective, and vibrational spectroscopies, combined with modulated excitation (ME) and phase-sensitive detection (PSD). This approach allowed us to precisely track Fe species, identify intermediate species, and unambiguously assign the active sites.

## **Materials and Methods**

Fe-SSZ-13 was synthesized via a one-pot hydrothermal method and thoroughly characterized.<sup>3</sup> Catalyst performance was evaluated in a plug-flow reactor. The dynamics, speciation, and nature of Fe under conditions representative of N<sub>2</sub>O decomposition were elucidated using *operando* resonance inelastic X-ray scattering (RIXS), high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS), X-ray emission spectroscopy (XES), electron paramagnetic resonance (EPR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and diffuse reflectance UV-Vis spectroscopy (DRUV). ME experiments consisted in the periodic variation of the concentration of N<sub>2</sub>O while recording spectra simultaneously.

## **Results and Discussion**

Ex situ EPR and DRUV revealed the coexistence of distinct Fe species within the zeolite. Despite this complex speciation, *operando* DRUV experiments enabled tracking of the redox dynamics ( $Fe^{2+} \leftrightarrow Fe^{3+}$ ) and further indicating that only a fraction of the species participates actively in the full catalytic cycle (**Fig 1a**). Kinetic analyses of *operando* DRUV and EPR data showed that both oxidation half-cycle (OHC) and reduction half-cycle (RHC) proceed via 1<sup>st</sup> order reactions, with the kinetic constant of oxidation ( $k_{ox}$ = 0.034 s<sup>-1</sup>) exceeding the reduction rate constant ( $k_{red}$ = 0.013 s<sup>-1</sup>), thus confirming the



rate-determining nature of the RHC. Quantitative pre-edge analysis of the HERFD-XAS data suggests that Fe may adopt an octahedral coordination, which appeared to be distorted in the presence of N<sub>2</sub>O, as evidenced by the feature at 7.12 keV in the PSD data (**Fig. 1b**). *Operando* EPR further demonstrated that the N<sub>2</sub>O decomposition reaction is site-selective, involving only the isolated Fe species located in the 6-membered rings of the  $\beta$  cationic exchange sites of the zeolite (Fe<sub> $\beta$ </sub><sup>2+</sup>  $\leftrightarrow$  Fe<sub> $\beta$ </sub><sup>3+</sup>; **Fig. 1b**). DRIFTS identified Fe<sub> $\beta$ </sub><sup>3+</sup>-OH (**Fig. 1b**), likely as manifestation of the [FeO]<sup>2+</sup> moiety, previously reported as intermediate species.<sup>4</sup> Additionally, spin-selective HERFD-XAS ruled out the presence of Fe<sup>4+</sup>=O, suggesting a radical intermediate of oxidation state 3+ (Fe<sub> $\beta$ </sub><sup>2+</sup>  $\leftrightarrow$  Fe<sub> $\beta$ </sub><sup>3+</sup>-OH). The evolution of isolated high-spin Fe<sub> $\beta$ </sub><sup>3+</sup> sites in the OHC and the RHC was further probed using high-time resolution *operando* EPR (**Fig. 1c**), which gave access to the apparent activation energies (Ea<sub>app</sub>) of the RHC (ca. 138 kJ·mol<sup>-1</sup>) and the OHC (ca. 34 kJ·mol<sup>-1</sup>).

Our results reveal a strong correlation between the kinetics of the monomeric Fe centers and the N<sub>2</sub>O decomposition kinetics (ca. 138 kJ·mol<sup>-1</sup>), thus allowing the consistent assignment of the global reactivity of the catalyst to the Fe<sub> $\beta$ </sub> centers.



**Figure 1.** Characterization of catalytic N<sub>2</sub>O decomposition. (a) temporal evolution of UV-vis spectra at 400°C; (b) time and phase-resolved HERFD-XAS, EPR, DRIFTS spectra obtained during the ME experiment at 400°C; (c) Arrhenius plots obtained from selectively monitoring  $Fe_{\beta}$  by EPR.

## References

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