

# Iron-catalyzed cooperative red-ox mechanism for the simultaneous conversion of nitrous oxide and nitric oxide

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## Significance and Relevance

Our work demonstrates i) that the simultaneous Selective Catalytic Reduction of  $N_2O$  and NO ( $N_2O$ -NO-SCR) is a feasible and promising strategy for concomitant conversion of these pollutants, ii) that dynamic *operando* spectroscopic experiments are essential to extract valuable molecular insights and draw reliable mechanistic considerations and iii) that the reactivity of Fe centers in Fe-exchanged zeolites can be disentangled.

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

## **Introduction and Motivations**

The individual abatement of nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) has received tremendous scientific attention owing to their effects on human health and the environment. Differently, their concomitant conversion under selective catalytic reduction (SCR) conditions was far less investigated despite being crucial to control emissions from NH<sub>3</sub> internal combustion engines and from industrial plants devoted to the production of caprolactam as well as nitric and adipic acids.<sup>1</sup> In order to explore the feasibility of the combined SCR of N<sub>2</sub>O and NO by NH<sub>3</sub> (N<sub>2</sub>O-NO-SCR), to rationalize its reaction mechanism and to isolate the reactivity of active Fe centers in a commercial Fe-exchanged zeolite catalyst (Fe-FER), we monitored the red-ox processes and the dynamics of adsorbed species combining catalytic and transient spectroscopic experiments employing the modulated excitation (ME) approach.<sup>2</sup>

## **Materials and Methods**

The Fe-FER catalyst was provided by CASALE SA.<sup>3</sup> Activity tests were conducted between 200 and 500 °C in a feed of 500 ppm NO, 500 ppm NH<sub>3</sub>, 3 vol% O<sub>2</sub> and 0.3 vol% H<sub>2</sub>O/N<sub>2</sub> with no N<sub>2</sub>O (NO-SCR) or 300 ppm N<sub>2</sub>O (N<sub>2</sub>O-NO-SCR). N<sub>2</sub>O conversion was also monitored under reference conditions of 300 ppm N<sub>2</sub>O/N<sub>2</sub> in i) N<sub>2</sub> ii) 500 ppm NO/N<sub>2</sub> and iii) 500 ppm NH<sub>3</sub>/N<sub>2</sub>. Reactants and products were analyzed using an FTIR spectrometer. Equivalent *operando* X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR) and infrared spectroscopy in diffuse reflectance mode (DRIFTS) experiments were performed by repeatedly adding or cutting-off 1000 ppm NH<sub>3</sub> + 3 vol% O<sub>2</sub>/Ar at 400 °C. An on-line mass spectrometer (MS) monitored the gas concentrations.

#### **Results and Discussion**

Catalytic experiments indicated enhanced NO conversion above 300 °C in presence of N<sub>2</sub>O. The onset of this beneficial effect of N<sub>2</sub>O coincided with the on-set of N<sub>2</sub>O conversion under N<sub>2</sub>O-NO-SCR conditions, which also provided highest N<sub>2</sub>O conversion compared to reference conditions. Timeresolved XAS spectra (Fe K-edge) showed a shift of the absorption edge towards high energy upon N<sub>2</sub>O addition to the NO-SCR feed (Fig. 1a). The spectra obtained by phase sensitive detection,<sup>4</sup> showed an increased contribution of the pre-edge associated with Fe<sup>3+</sup> species (7115 eV) at the expenses of Fe<sup>2+</sup>



thus indicating a higher average oxidation state in the presence of N<sub>2</sub>O (Fig. 1b). The complementary EPR spectra demonstrated that this phenomenon is related to the Fe<sup>2+</sup>/Fe<sup>3+</sup> oxidation of monomeric Fe centers in β- and γ-cationic positions (Fe<sub>β</sub> and Fe<sub>γ</sub>) possessing a distorted square planar and a tetrahedral coordination, respectively (Fig. 1c),<sup>5</sup> and which are also kept in a reversible red-ox active state during N<sub>2</sub>O-NO-SCR (Fig. 1d). Reference experiments showed that this reversible red-ox dynamics occurs because of their involvement in processes of N<sub>2</sub>O activation (Fe<sub>β</sub>) and NO oxidative transformation (Fe<sub>γ</sub>). Equal phase-resolved DRIFTS experiments (Fig. 1f) revealed the formation of Fe<sub>β</sub><sup>3+</sup>-OH and simultaneous consumption of NO adsorbed on Fe<sub>γ</sub><sup>2+</sup> during N<sub>2</sub>O addition. Enhanced consumption of NH<sub>3</sub> adsorbed on Brønsted sites (NH<sub>3,BAS</sub>) also occurred, but was delayed compared to the kinetics of the Fe<sub>γ</sub><sup>2+</sup>-NO and Fe<sub>β</sub><sup>3+</sup>-OH signals.

The combination of these results enables to propose the following rationale: i) N<sub>2</sub>O is activated on square planar isolated  $Fe_{\beta}^{2+}$  sites in form of  $Fe_{\beta}^{3+}$ -OH, ii)  $Fe_{\gamma}^{2+}$ -NO species drives utilization of  $Fe_{\beta}^{3+}$ -OH, promoting iii) the  $Fe_{\beta}^{3+}$ -OH/  $Fe_{\beta}^{2+}$  red-ox transition and the oxidative activation of  $Fe_{\gamma}^{2+}$ -NO to  $Fe_{\gamma}^{3+}$ -HONO. Finally, iv)  $Fe_{\gamma}^{3+}$ -HONO is reduced to  $Fe_{\gamma}^{2+}$  by reactive NH<sub>3,BAS</sub> producing N<sub>2</sub> and water through NH<sub>4</sub>NO<sub>2</sub> and closing the catalytic cycle.<sup>2</sup>



**Figure 1**. Averaged time-resolved (a, c, e) and phase-resolved (b, d, f) operando XAS (a, b), EPR (c, d) and DRIFT (e, f) spectra of Fe-FER during pulses of 1000 ppm N<sub>2</sub>O/Ar in 1000 ppm NO, 1000 ppm NH<sub>3</sub> and 3 vol%  $O_2$ /Ar at 400 °C. The coloured spectra in b), d) and f) serve to guide the eye. The red spectrum in f) emphasizes kinetic differences.

## References

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