

# Investigating the Reduction Half-Cycle of Standard SCR at Low and High Temperature: Influence of HTA and H<sub>2</sub>O

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## Highlights

- The overall reducible Cu<sup>II</sup> fraction and the RHC rates are unaffected by HTA.
- H<sub>2</sub>O inhibits the Cu<sup>II</sup> reduction rate.
- At low- and high-T, the reduction of Cu<sup>II</sup> sites proceeds according to the same mechanism.
- Transient response methods effectively assess the RHC mechanism.

## 1. Introduction

Despite the recent strides in meeting the strict environmental standards, nitrogen oxides (NO<sub>x</sub>) emissions from Diesel engines still represent a concern. Nowadays, their reduction is accomplished through the so-called NH<sub>3</sub>-SCR (Selective Catalytic Reduction) technology: this involves the injection of a urea-based solution in the presence of a metal-exchanged zeolite [1,2]. Notably, copper-based catalytic systems are preferred for applications demanding high de-NO<sub>x</sub> activity, selectivity, and hydrothermal stability. While the involvement of Cu sites in a redox cycle (*Reduction Half Cycle*, RHC: Cu<sup>II</sup> → Cu<sup>I</sup>; *Oxidation Half Cycle*, OHC: Cu<sup>I</sup> → Cu<sup>II</sup>) during the Standard SCR reaction is widely acknowledged [1-4], certain aspects, such as the influence of temperature, hydrothermal aging (HTA) and H<sub>2</sub>O content still require further clarification. In this context, we systematically explore the effects of such parameters on a Cu-SSZ-13 catalyst in order to enhance the understanding of the RHC.

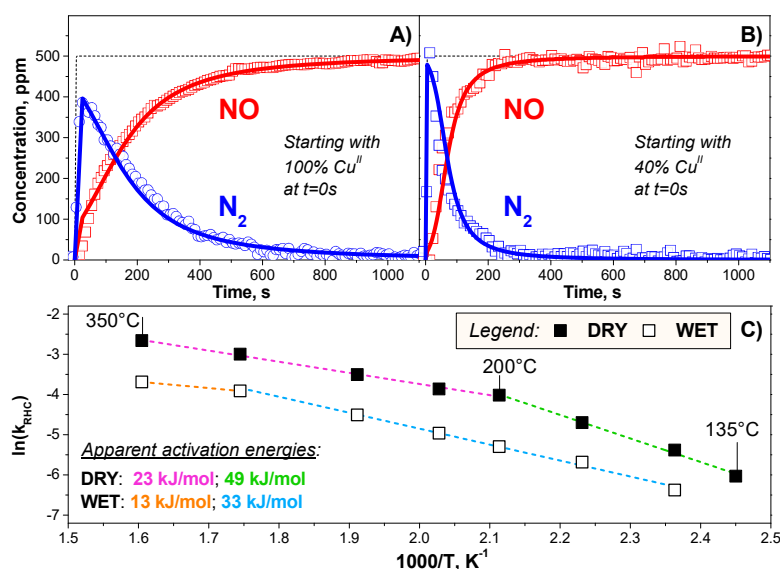
## 2. Methods

In this work, an experimental campaign is performed on a state-of-the-art Cu-SSZ-13 catalyst (Cu<sub>tot</sub> by ICP-analysis: ~2.4% w/w) subjected to three different hydrothermal aging levels: i) *degreened* sample (DG) - 550°C for 5h; ii) *mild-aged* sample (MA) - 650°C for 5h; iii) *aged* sample (AG) - 650°C for 50h. The samples are tested in the form of powder (32 mg mixed with cordierite up to 130 mg; placed in a quartz tubular microflow reactor) according to the following protocol: i) pre-oxidation at 550°C in 8% O<sub>2</sub> to clean and oxidize the catalyst; ii) isothermal pre-adsorption of NH<sub>3</sub> (500 ppm) until saturation; iii) NO+NH<sub>3</sub> (both 500 ppm) isothermal reduction of Cu<sup>II</sup> sites. Both dry and wet conditions (H<sub>2</sub>O=0-2-5% v/v) are adopted to assess the role of water in RHC across the 135-350°C T-range. A gas hourly space velocity (GHSV) of 266250 Ncc/h/g<sub>cat</sub> is selected. Consistent with previous publications [3,4], we kinetically analyze the obtained experimental data by means of a transient integral redox model which considers the RHC rate as: i) 0<sup>th</sup> order dependent on the NH<sub>3</sub> concentration; ii) 1<sup>st</sup> order dependent on the NO concentration; iii) 2<sup>nd</sup> order dependent on the Cu<sup>II</sup> fraction.

## 3. Results and discussion

Figure 1A shows the outlet concentration profiles of NO and N<sub>2</sub> obtained from NO+NH<sub>3</sub> reduction of Cu<sup>II</sup> sites at low-T (example at 150°C, DG sample). As observed, after NH<sub>3</sub> preadsorption (t=0 s), NO is consumed along with a mirror-like production of N<sub>2</sub> (peak of ~400 ppm). In line with the literature [2-4], we confirm the ability of the NO+NH<sub>3</sub> mixture to completely reduce the catalyst sites according to a well-established equimolar stoichiometry (Cu<sup>II</sup>:NO:N<sub>2</sub>=1:1:1). Also, the kinetic analysis reveals an excellent correspondence between experimental data (*symbols*) and model fit (*solid lines*) upon assuming the RHC rate equation described in Section 2. The same methodology is applied at higher

temperatures (up to 350°C). The NO+NH<sub>3</sub> mixture is still able to fully reduce the catalyst according to the same equimolar stoichiometry, even if with a higher rate. Notably, as long as enough NH<sub>3</sub> is adsorbed on the catalyst surface, the same kinetic dependencies already validated at low-T also apply at higher temperature, where a good match between experimental and model profiles is still observed. See Figure 1B for an example at 300°C on the DG sample (similar results are obtained on all the tested samples). The estimates of the apparent reduction rate constants ( $k_{\text{RHC}}$ ) are displayed in Figure 1C as Arrhenius plots. Remarkably, we reveal the RHC to be inhibited by the presence of water (in line with DFT calculations by Contaldo et al. [5]). Figure 1C suggests that, particularly under wet conditions, no alteration in the RHC mechanism occurs. Indeed, in contrast with dry conditions where two distinct regimes are clearly evident (above and below 200°C), both low and high temperature reduction constants well align along the same linear correlation, at least up to 300°C. Additionally, by replicating the same experiments on DG, MA and AG samples we also confirm the RHC to be unaffected by the catalyst aging level, in line with previous studies [3].



**Figure 1.** Example of NO and N<sub>2</sub> transients from RHC protocol over DG sample at **A)** 150°C and **B)** 300°C. Feed: H<sub>2</sub>O=O<sub>2</sub>=0% v/v, NO=NH<sub>3</sub>=500 ppm. Symbols: experimental data. Solid lines: model fit. **C)** Arrhenius plot of the estimated  $k_{\text{RHC}}$  values on a DG sample, T-range=150-350°C, H<sub>2</sub>O=0-2% v/v.

#### 4. Conclusions

In this work we investigate the reduction half-cycle (RHC) of Standard SCR reaction over a typical Cu-SSZ-13 catalyst. In particular, we assess the effects of hydrothermal aging, H<sub>2</sub>O content and temperature on the reaction chemistry. By testing three samples with different aging level (*i.e.*, DG, MA and AG samples), we confirm the RHC rate to be unaffected by HTA, in line with previous findings [3]. In addition, we experimentally and kinetically assess the inhibiting role of water on the RHC, as also observed in the literature and supported by DFT calculations [5]. Remarkably, under wet conditions and as long as enough NH<sub>3</sub> is stored on catalyst surface, we reveal for the first time the Cu<sup>II</sup> reduction mechanism to be unaffected by temperature. In view of the upcoming stricter environmental regulations, these results are an essential step to unveil the Standard RHC-SCR chemistry and give guidance to the automotive industry for the development of new generations of aftertreatment systems and catalysts.

#### References

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#### Keywords

NH<sub>3</sub>-SCR; Reduction half-cycle; Transient kinetic analysis; HTA and H<sub>2</sub>O effects