

A combined *operando* UV-vis and flow reactor study of the NH₃-SCR redox kinetics over Cu-CHA

<u>C. Negri</u>¹, N. Usberti¹, G. Contaldo¹, M. Bracconi¹, I. Nova¹, M. Maestri^{1*}, E. Tronconi^{1*} ¹Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, 20156 Milano (Italy)

*Corresponding authors: matteo.maestri@polimi.it; enrico.tronconi@polimi.it

Significance and Relevance

This study highlights the accessibility of extracting kinetically relevant data directly from spectroscopy. Specifically, we employ *operando* UV-Vis Diffuse Reflectance spectroscopy coupled with a packed bed flow reactor to extract quantitative kinetic information on Cu^{II}/Cu^I redox dynamics during the NH₃-Selective Catalytic Reduction (SCR) on Cu-CHA catalyst. We quantified the fraction of Cu^{II} by Multivariate Curve Resolution (MCR) while simultaneously monitoring the gas-phase evolution during the reaction. These data enabled the univocal estimation of apparent rate parameters, demonstrating that combined analysis of UV-Vis spectra and gas-phase dynamics provides kinetic insight able to shed new light on catalytic pathways.

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

Introduction and Motivations

A primary challenge in catalytic kinetics is to get direct insights on the catalytic cycle, that is crucial to derive mechanistic kinetic models and to optimize both catalysts and processes. In this context, simultaneously monitoring both gas phase species and the catalyst sites can provide an invaluable set of information. Herein we exemplify this concept in the case of the Selective Catalytic Reduction with ammonia (NH₃-SCR) redox chemistry over Cu-exchanged chabazite zeolites (Cu-CHA).

NH₃-SCR on Cu-CHA catalysts is the state-of-the-art technology to abate NO_x emissions from lean burn heavy-duty vehicles and passenger cars. The catalytic activity is associated with a Cu redox cycle. In the Reduction Half Cycle (RHC), Cu^{II} is reduced to Cu^{I} , releasing N₂ and H₂O, and in the Oxidation Half Cycle (OHC) Cu¹ is re-oxidized to Cu¹¹ with O_2 and H_2O . Notwithstanding many in-depth studies about Cu speciation and reaction intermediates during the two redox half-cycles, the NH₃-SCR mechanism over Cu-CHA is still lively debated in the literature. A crucial step regards the role played by binuclear Cu intermediates ¹⁻², with a longstanding debate in the literature regarding the RHC kinetic dependence on Cu^{II} (first versus second order rate).^{1,4} It appears clear that the direct and contemporary measure of the evolution of Cu oxidation state and of the gas phase composition would provide valuable data to discriminate these proposals. In this work, we employ UV-Vis operando spectroscopy to monitor the Cu^{II}/Cu^I redox dynamics during the NH₃-SCR RHC and OHC, while measuring in parallel the outlet NO and N_2 concentration transients to assess the gas-phase reaction kinetics. This approach aims at simultaneously extracting kinetic insights while acquiring relevant spectroscopic data. This approach allows for combined studies of heterogeneous catalysts, targeting a deeper understanding of the reaction mechanism and quantification of the kinetic, elucidating the nuclearity of the active sites and their evolution over time.

Materials and Methods

The operando UV-Vis spectra are measured with an *ad hoc* setup developed in-house specifically designed to extract kinetically relevant information, coupling a packed bed microreactor with a high temperature UV–Vis diffuse reflectance probe [3]. The Cu-CHA catalyst (Si/Al₂O₃ ratio = 25, Cu = 1.77 wt%) has been pelletized, chopped and sieved (75 - 106 μ m fraction), loading the quartz reactor with 64 mg of powders (total amount of Cu in the sample = 17.8 μ mol), diluted with 66 mg of cordierite. The temperature is controlled by a thermocouple placed in close contact with the catalytic bed. The outlet concentrations of NO, NO₂, NH₃ are continuously monitored by an on-line ABB LIMAS analyser.



Kinetic measurements are carried out under isothermal conditions in the low temperature range (150-220°C), with protocols addressing the RHC (100 Ncc/min, 1000 ppm NO, 1000 ppm NH₃ / He balanced and $2\%H_2O$) and the OHC (100 Ncc/min, $1-8\%O_2$ / He balanced and $2\%H_2O$) half cycles. The *operando* UV–Vis spectra are reported as relative reflectance (R%) defined as: R%=R_{sample}/R_{reference}, using Teflon[®] powder as reference. The UV-Vis spectra are analysed by using Multivariate Curve Resolution (MCR) to monitor the Cu^{II}/Cu^I redox dynamics and to quantify the relative amount of the two species.^{3, 4}

Results and Discussion

Using *operando* UV-Vis Diffuse Reflectance (DR) spectroscopy coupled with a packed bed reactor, we validated the possibility to extrapolate relevant kinetic information from spectroscopic data. To the best of our knowledge, this approach represents a novelty for both kinetic and spectroscopic studies. Applying the developed experimental approach, we focused on monitoring *in operando* the redox dynamics and Cu sites speciation in Cu-CHA as a function of the reactive gas feed (e.g., in presence or absence of H₂O) and of the temperature (e.g., at 150°C or 200°C), during the RHC and the OHC. Figure 1-a shows the DR UV-Vis spectra measured during the RHC transient (from grey to red curves).



Figure 1(a) operando UV-Vis DR spectra during a RHC transient at 175°C; (b) Cull reduction dynamics from spectroscopic data (symbols) model predictions (solid line); (c) NO inlet (dashed line) gas phase NO (empty symbols) and model predictions (solid line)

The initial and the final spectrum can be assigned to $[Cu_n(NH_3)_x(O_iH)_y]^{\parallel}$, with $n \le 2$ species (dashed grey curve), and to mobile $Cu^{I}(NH_{3})_{2}$ moieties (red curve), respectively.⁴ The $Cu^{II} \rightarrow Cu^{II}$ reduction is associated with the consumption of the Cu^{II} *d*-*d* feature in the visible range (broad signal centered at 14000 cm⁻¹) since Cu¹ has a d¹⁰ close-shell configuration. In parallel, the $Cu^{\parallel} \rightarrow Cu^{\perp}$ reduction is directly correlated with NO consumption monitored by gas phase analysis at the reactor outlet (Fig.1-b, red symbols). NO overall consumption monitored during RHC transients (16.0 µmol) confirms the stoichiometry of the reduction 1:1 between NO and Cu reduced,¹ and corresponds to an initial amount of Cu

present as Cu^{II} of about 90%. Accordingly, the fraction of oxidized Cu^{II} sites independently quantified by the MCR analysis of UV-Vis spectra (90% at the beginning of the RHC transient, Figure 1-c, grey symbols). In addition, the observed dynamics were successfully simulated by an RHC kinetic model originally fitted to gas-phase only ¹ (solid line in Fig.1-b and -c), assuming the Cu reduction rate to be 2nd order in Cu^{II} sites. The model nicely follows the dynamics of both Cu^{II} fraction and NO concentration, allowing for the estimation of a univocal apparent rate constant. These results provide clear evidence of the potential of the adopted approach in quantitatively describing redox catalysis. This can be applied to the study of metal-based catalysts, aiming at elucidating the active site structure–activity relation under kinetically relevant conditions.

References

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