

Assessing quantitative kinetic insights from *operando*-UV-Vis spectroscopy: an application to NH₃-SCR on Cu-CHA

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Highlights

- Cu^{II}/Cu^I redox cycle in NH₃-SCR is kinetically monitored *via* UV-Vis *operando* spectroscopy
- Flow reactor data and *operando* spectroscopy provide holistic insights on Cu structure-activity relation
- The experimental redox behavior is successfully predicted by a gas-phase kinetic model

1. Introduction

The Selective Catalytic Reduction with ammonia (NH₃-SCR) is the state-of-the-art (SoA) technology to abate NO_x emissions from lean burn heavy-duty vehicles and passenger cars. Currently, Cu-exchanged chabazite zeolites (Cu-CHA) are the catalysts of choice, with good performances over a wide range of temperatures. Notwithstanding many in-depth studies about Cu speciation and reaction intermediates, 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] in the Reduction Half Cycle (RHC), that is, when Cu^{II} is reduced to Cu^I while releasing N₂ and H₂O, and in the Oxidation Half Cycle (OHC), when the cycle is closed by re-oxidizing Cu^I to Cu^{II}. In this work, UV-Vis *operando* spectroscopy has been applied to monitor the Cu^{II}/Cu^I redox dynamics, aiming at simultaneously extracting kinetic insights while acquiring relevant spectroscopic data. This approach allows for combined studies on 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.

2. Methods

The *operando* UV-Vis spectra were measured with an *ad hoc* setup developed in-house, coupling a packed bed powder reactor 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, loading the quartz reactor (148 mg, equal to 41.2 μmol Cu) with the 75 - 106 μm fraction. The temperature was controlled by a thermocouple placed in close contact with the catalytic bed. The outlet concentrations of NO, NO₂, NH₃ were monitored by means of an on-line ABB LIMAS analyser. Kinetic measurements were 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% H₂O) and the OHC (100 Ncc/min, 1-8% O₂ / He balanced and 2% H₂O) half cycles. The *operando* UV-Vis spectra are reported as relative reflectance (R%) defined as: $R\% = R_{\text{sample}}/R_{\text{reference}}$, using Teflon® powder as reference. The Cu^{II}/Cu^I redox dynamics were monitored by quantifying the relative amount of the two species *via* an in-house developed methodology [3].

3. Results and discussion

Using *operando* UV-Vis Diffuse Reflectance (DR) spectroscopy directly 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 with respect to the SoA for both kinetic and spectroscopic studies. Applying the developed experimental approach, we focused on monitoring *in operando* the redox dynamics and speciation of Cu active sites 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 reports the DR UV-Vis spectra measured during the RHC transient (from light to dark blue curves). The initial and the final spectrum can be assigned to dimeric Cu^{II}-oxo species (light blue curve, feature in the Ligand-to-Metal Charge Transfer (LMCT) region in the 25000-

35000 cm^{-1} range), and to mobile $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ moieties (dark blue curve), respectively. The reduction of dimeric Cu^{II} complexes results in $\sim 100\%$ of Cu^{I} , as highlighted by the quantification of the residual Cu^{II} fraction obtained by analyzing Cu spectral features in the *dd* region and in the LMCT region as shown in Fig.1-b.

In parallel, the evolution in Cu speciation is directly correlated with NO consumption monitored from the gas phase (Fig.1-c), the SoA approach in kinetic investigation to follow changes in Cu oxidation state. NO consumption monitored during RHC transients ($41.0 \mu\text{mol}$) confirms the 1:1 stoichiometry of the reduction between NO and Cu reduced, [1] and the complete oxidation of the Cu sites by O_2 alone, even at low temperatures. In addition, the observed dynamics were successfully compared with RHC kinetic model originally fitted to gas-phase data only [1] (solid line in Fig.1-b and -c). The model was able to predict the experimental behavior according to UV-Vis data, confirming the capability of our method to assess the reduction kinetic from UV-Vis spectra evolution. By evaluating the Cu^{II} fraction during RHC and OHC in different reaction conditions from UV-Vis spectra, we are able to reconcile the dynamics in the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox cycle obtained from the gas phase data, proving the sensitivity of this methodology to monitor and describe changes in the active site speciation and reactivity.

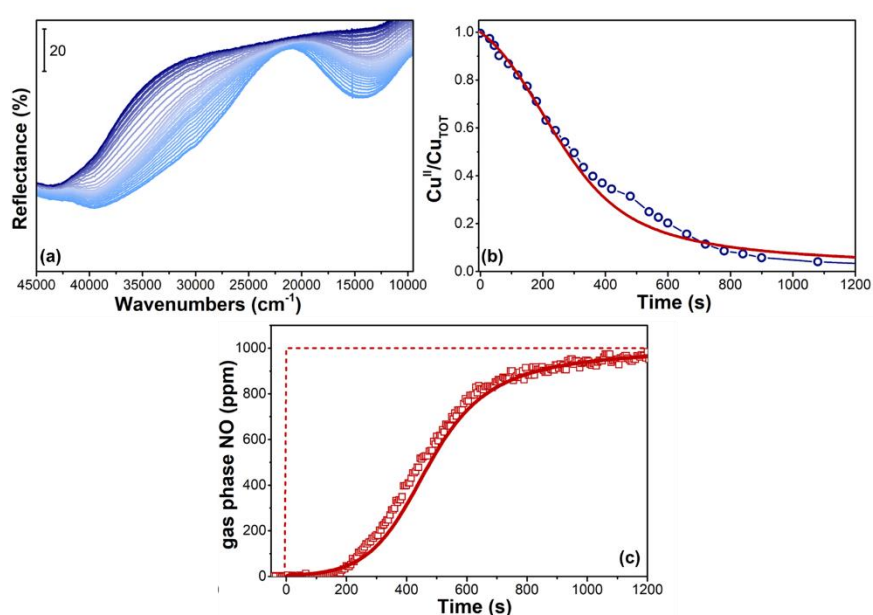


Figure 1. (a) *operando* UV-Vis DR spectra during a RHC transient at 175°C ; (b) Cu^{II} reduction dynamics from spectroscopic data (symbols) model predictions (solid line); (c) NO inlet (dashed line) gas phase NO (empty symbols) and model predictions (solid line)

4. Conclusions

This study highlights the accessibility of kinetically relevant data from spectroscopic studies. Specifically, here we show that the direct correlation between spectroscopy and gas phase behavior is pivotal to extract quantitative kinetic information from *operando* UV-Vis spectroscopy. Furthermore, the possibility to follow the dynamic changes of the Cu ions under reaction conditions enables a deeper understanding of the reactive routes during NH_3 -SCR over Cu-CHA catalysts.

References

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Keywords

NH_3 -SCR; *operando* UV-Vis spectroscopy, transient kinetic analysis; Cu redox cycle