

Operando spatially- and time-resolved XAS and valence-to-core XES to study the mechanism of the NH₃-SCR over Fe- and Cu-zeolites

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Introduction

Fe and Cu ion exchanged zeolites are widely used for the selective catalytic reduction of NO_x with ammonia (NH₃-SCR) as relevant alternatives to the conventional vanadia-based catalysts [1]. Further improvement of the activity and hydrothermal stability requires detailed understanding and tuning of the structural parameters leading to high performance. Furthermore, knowledge about the reaction mechanism is essential in modeling and efficient planning of the exhaust aftertreatment control algorithms.

Among the different characterization methods, X-ray absorption spectroscopy (XAS) is one of the few techniques which can be applied under realistic reaction conditions without altering the process dynamics. Important information such as oxidation state, coordination geometry, type and number of nearest neighbors or structural changes due to interaction with reactants, can be derived by monitoring the changes occurring in the pre-edge, edge and extended X-ray absorption fine structure (EXAFS) of an XAS spectrum [2, 3]. However, the so far reported XAS studies on Fe- and Cu-based SCR catalysts have neglected that concentration or temperature gradients which may appear along a packed catalyst bed and often integral averaged data on the catalyst bed evolution was reported.

Here we report results of a spatially- and time-resolved *operando* XAS study of Fe-ZSM-5, Fe-BEA and Cu-SAPO-34 catalysts during the NH₃-SCR of NO_x. The obtained data significantly extend the understanding of the SCR reaction mechanism over zeolites.

Materials and Methods

0.5 - 2wt.%Fe-BEA, 1.3 wt.%Fe-ZSM-5 and 3.5 wt.% Cu-SAPO-34 were obtained either by preparation in our laboratories (incipient-wetness impregnation or liquid ion-exchange) or as commercial samples. XRD, BET surface area, AAS and UV-Vis were employed for material characterization. An appropriate in situ quartz capillary (20 µm walls) microreactor which allows on-line measurements of the catalytic performance was used for the QEXAFS measurements at the Fe and Cu K-edge at the SuperXAS beamline of the SLS (Swiss Light Source). The catalyst bed (10 mm length, sieve fraction 100-200 µm) was heated by a hot gas blower (FMB Oxford) between 185 – 550 °C while dosing a gas stream of 130 000 h⁻¹ - 360 000 h⁻¹ containing 0 – 1000 ppm NO, 0 – 1200 ppm NH₃, 5% O₂, ~1.5% H₂O in He. QEXAFS spectra were acquired at 5 different positions referred to as 1 to 5 (Fig. 1b), which correspond to 1-beginning, 3 – middle, 5 – end and 2,4 - in-between zones of the catalyst bed. The catalytic performance was compared to that obtained using conventional quartz plug-flow reactors.

Results and Discussion

Strong gradients of Fe and Cu oxidation state have been observed for the processes involving NH₃ (SCR and NH₃ oxidation) whereas the state of copper and iron in the NO and O₂

containing feed resembles that of catalyst in air. For temperatures higher than 185 °C a partial reduction and decrease of coordination number have been observed in the reaction zone when NO and NH₃ are present together. Figure 1 demonstrates this behavior on the example of XANES spectra of Cu-SAPO-34 under conditions of NO_x SCR. The absorption gradient at 8.983 keV (Figure 1a) along the reactor is caused by decreasing concentration of Cu⁺ species relative to Cu²⁺ sites, as supported also by the linear combination fit analysis (LCF) in Fig. 1b. The more pronounced reduction occurring during the SCR process as compared to the NH₃ oxidation conditions suggests a reaction of NO_x and NH₃ adsorbed on Fe³⁺ (Cu²⁺) leaving Fe²⁺ (Cu⁺) sites with a lower coordination number.

This hypothesis has been additionally verified by time-resolved transient NH₃-supply QEXAFS experiments and by X-ray emission spectroscopy [4] confirming ammonia coordination at the iron sites in the presence of water and NO_x under SCR conditions. Reoxidation of Fe²⁺ (Cu⁺) by oxygen is suggested to be the rate-limiting step of the NH₃-SCR above 250°C. This is also further demonstrated by X-ray emission spectroscopy (XES) recently measured in-situ in the valence-to-core transition region.

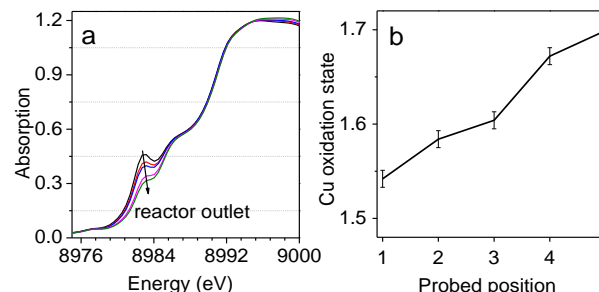


Figure 1. (a) X-ray absorption near edge structure (XANES) and (b) Cu oxidation state depending on the probed part of the reactor as resulted from the LCF for the spectra recorded at Cu K-edge during SCR at 255 °C. Conditions: 1000 ppm NO, 1000 ppm NH₃, 5% O₂, ~1.5% H₂O, He balance; GHSV = 360 000 h⁻¹, DeNO_x = 95%.

Significance

The results demonstrate that the structure of the catalytic active site should be interpreted only in a direct connection to the reaction rate and reactant concentration gradients present in catalytic reactors. Spatially resolved XAS was able to uncover the structure of the catalyst under *operando* conditions in a spatially- and time - resolved manner and could, therefore, give important input for the mechanistic understanding, i.e. ammonia inhibition and determination of Fe²⁺ reoxidation as the rate limiting step.

References

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