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Lithographically fabricated silicon microreactor for *operando* QEXAFS studies in exhaust gas catalysis during simulation of a standard driving cycle

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Abstract. Selective catalytic reduction of NO_x by ammonia over Cu-ZSM-5 was monitored by *operando* QEXAFS during simulation of the New European Driving Cycle. The required fast temperature transients were realized using a novel silicon microreactor, enabling simultaneous spectroscopic and kinetic analysis by X-ray absorption spectroscopy (XAS) and mass spectrometry (MS). Periods of high temperature were correlated to an increase in both N₂ production and change of coordination of Cu sites. This *operando* approach using Si microreactors can be applied to other heterogeneous catalytic systems involving fast temperature transients.

1. Introduction

The development of more efficient technologies for exhaust gas aftertreatment is a major driver for automotive catalysis research. In particular, increasingly strict legislation in Europe in recent years renders it important to proactively reduce vehicular pollution such as nitrogen oxide (NO_x) emissions. Selective Catalytic Reduction (SCR) of NO_x by ammonia (NH₃) over iron- or copper-based zeolite catalysts is currently one of the most efficient methods of NO_x abatement. However, the exact mechanism and structure of the active site is still the subject of strong discussion [1,2].

X-ray Absorption Spectroscopy (XAS) is a powerful tool for catalyst characterisation, as it can be applied to a range of realistic samples, allowing determination of metal oxidation state, coordination environment, phase and structural changes. To better understand catalyst performance and to further design future catalysts, it is crucial to perform spectroscopic analysis *in situ* or *operando*, and with high spatial- and time-resolution. However, laboratory conditions for catalytic test measurements are often over-simplified, limiting the validity of such measurements in describing realistic driving conditions. For testing exhaust gas catalysts under close to realistic conditions, so-called driving cycles [3] were developed which mimic conditions found on board a vehicle during driving. One such set of realistic model conditions is the New European Driving Cycle (NEDC), widely used to test exhaust aftertreatment systems in Europe. The cycle determines vehicle speed, which in turn defines the catalyst working conditions (temperature, concentration of exhaust gas components, space velocity). Due to abrupt speed changes (acceleration and braking) and high gas velocities, the catalyst temperature also changes rapidly. To successfully model temperature transients during NEDC and correlate it to the catalyst structure, it is necessary to use a system capable of high heating and cooling



rates, and to apply *operando* measurements with high time resolution. Until now only some special lab test benches designed for studies of monolithic catalysts were described [3] but none to our knowledge modelled driving cycles with powder catalysts while allowing simultaneous spectroscopic studies.

Recently our group described a novel silicon microreactor designed for *in situ* XAS measurements [4], allowing particularly rapid temperature transients (approx. 300 °C/s) in combination with product gas analysis by MS. The microreactors are constructed by anodic bonding of two channel-cut silicon (or silicon and glass) wafers, and are most suited for fluorescence measurements due to the presence of minor diffraction peaks observed in transmission, the latter as a consequence of the manufacturing process. The window between diffraction peaks is enough to measure quick XANES in transmission geometry. Here we demonstrate time-resolved *operando* Quick X-ray Absorption Spectroscopy (QEXAFS) measurements during fast temperature transients from an NEDC. As a first example we show structural changes of the active metal sites in zeolite catalysts during NH₃-SCR, while following the NEDC temperature profile.

2. Experimental Methods

Cu-ZSM-5 zeolite was prepared by aqueous ion-exchange of NH₄-ZSM-5 zeolite (Si/Al ratio = 11, Clariant). 5 g of zeolite was stirred in 250 ml of 0.05M Cu(II) acetate solution (Merck) for 24 h at 20 °C. The solid was then filtered, washed with 1 L of de-ionized water, dried overnight at 80 °C and calcined for 4 h at 500 °C in static air. Cu concentration in the final solid was estimated from X-ray absorption as ~2.9 wt.%. Sieve fraction of 100-200 μm was used for the measurements.

The newly designed *in situ* cell (Fig. 1) for catalytic testing is a lithographically etched Si-based microreactor [4] with U-shaped gas channel passing through a catalyst bed (500 μm width, 250 μm depth, approx. 4-5 mm length). Two types of microreactors are available with different composition: a “Si-Si type” and a “Si-Glass type”. The “Si-Glass” type can be used at temperatures up to 450-500 °C, allowing combination with light microscopy, UV-Vis and Raman techniques. Temperatures of at least 600 °C can be reached using “Si-Si” reactors which can be combined with IR spectroscopy. The microreactors are capable of performing fast temperature transients with simultaneous collection of catalytic data. A “Si-Si” microreactor was used in the current study. For temperature measurements a Pt100 resistance thermometer was glued below the catalyst channel and connected to a Eurotherm 2216 controller, an integrated Pt layer on the chip surface provided resistive heating.

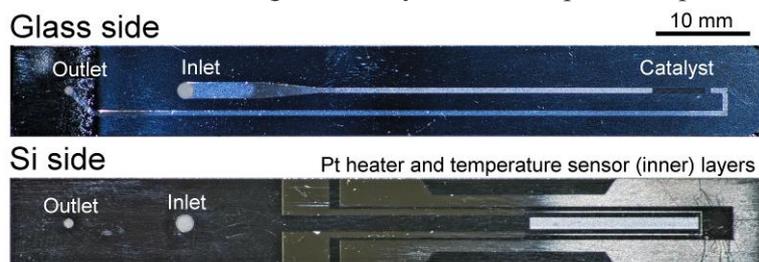


Figure 1. Exemplary photo of an Si-Glass type microreactor cell with a loaded catalyst. A sieved catalyst (grain size > 50 μm) is loaded via the inlet hole. A Si stopper holds the catalyst in place.

Operando XAS measurements were carried out at the Cu *K*-edge (8979 eV) at the SuperXAS beamline (Swiss Light Source, SLS) equipped with a Si(111) channel cut monochromator to allow data collection in QEXAFS mode at 10 Hz [5]. The storage ring was operated at 2.4 GeV in top-up mode with a ring current of around 400 mA. X-ray absorption spectra were collected in transmission mode using ionization chambers specially developed for quick data collection [6]. QEXAFS spectra were recorded at the beginning of the catalyst bed with a focused X-ray beam of about 100 x 100 μm. Spectra were averaged, normalized and Linear Combination Fitting (LCF) analysis was performed using JAQ 2 software (by O. Müller, P. Becker and R. Frahm). Spectra of the catalyst under SCR gas feed were recorded at 50 °C and 350 °C (Fig. 2, middle) and used as references for LCF. An example of the fitting procedure is shown in Fig. 2, right.

The gas feed contained 1000 ppm NO, 1000 ppm NH₃, 5% O₂ and approx. 2% H₂O in He (10 ml/min total flow and GHSV ~ 1,000,000 h⁻¹ respectively). N₂, NO, NO₂, N₂O and NH₃ signals were monitored using a Hiden Analytical QGA mass spectrometer. The applied temperature cycles for

mimicking NEDC temperature profiles were based on ref. [7]. Several repetitions of NEDC were conducted to ensure that the catalyst response was reproducible.

3. Results and discussion

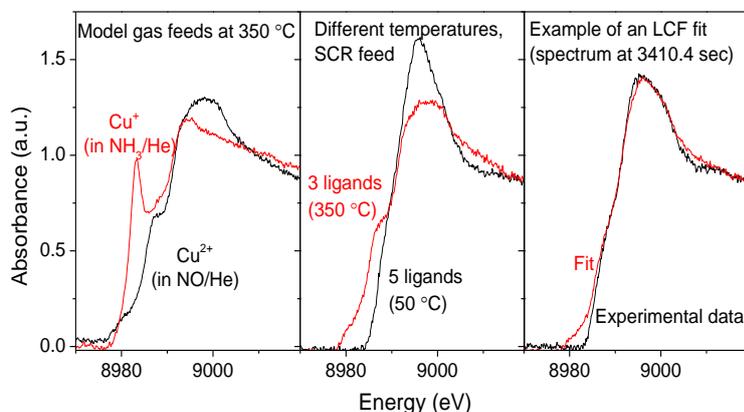


Figure 2. XANES spectra at Cu *K*-edge of Cu-ZSM-5 catalyst under: (left) model conditions typically used to determine Cu oxidation state; (middle) SCR feed at low and high temperatures; and (right) an exemplary LCF fit of a spectrum obtained during the NEDC test (at 3410.4 sec, Fig. 3).

First, spectra of Cu sites under steady-state conditions in pure NH_3/He and $\text{NO}+\text{O}_2/\text{He}$ were recorded (Fig. 2, left) to serve as model spectra with pure oxidized (e.g. Cu^{2+}) and reduced (e.g. Cu^+) species (cf. [2,8]). These differ significantly from spectra obtained in the full SCR feed at different temperatures (Fig. 2, middle; 350 °C with an SCR-active catalyst and 50 °C where no SCR activity is observed). Comparison of the experimental data in SCR feed gas atmosphere at different temperatures with literature [2,9] and also with our previous results obtained in a capillary reactor at steady state or “slow” transient conditions (5-10°C/min vs. $\sim 300^\circ\text{C}/\text{s}$) [8] shows that in this case changes in the coordination geometry of Cu sites were observed on heating/cooling, rather than changes in oxidation state. Although the catalytic activity varies as expected upon changing the temperature, the pre-edge peak ascribed to $\text{NH}_3\text{-Cu}^+$ [2,9] was observed in the *operando* spectra only during first heating of the catalyst but disappeared for the consequent heating / cooling cycles. This effect can be due to mass transfer limitations which result from the rather large sieve fraction and possible channeling effects [10]. Furthermore, at the low temperatures used in this study (<100°C) water adsorption could compete with NH_3 in the Cu coordination sphere [11] and also be retained in the microreactor, probably compacting the catalyst particles. In contrast, the adverse effects of high water concentration are also suggested by recent results obtained in our group for a $\text{Pt}/\text{Al}_2\text{O}_3$ diesel oxidation catalyst during NEDC cycling under dry conditions. In this case, typical variations of the “white line” in the Pt L_3 -edge spectra were observed together with conversion of CO, similarly to that shown in ref. [12].

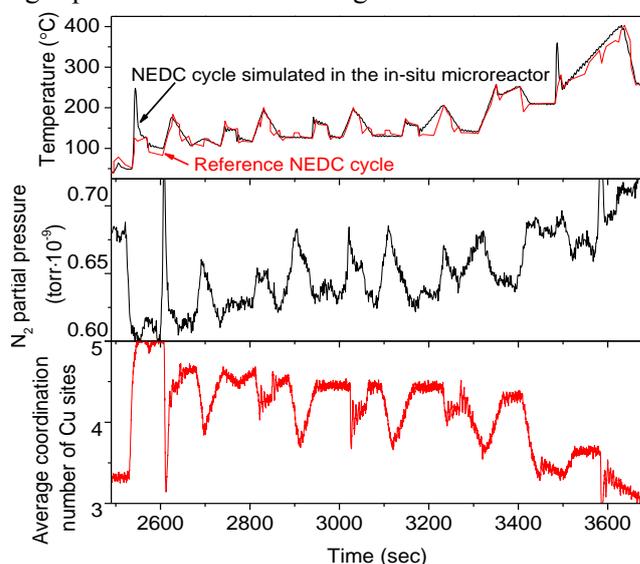


Figure 3. Temperature (top), amount of produced N_2 (middle), and (bottom) average coordination number of Cu sites in Cu-ZSM-5 catalyst during a simulated NEDC cycle (simulating inlet temperature of the first catalyst after the engine [7]). Conditions: 1000 ppm NO, 1000 ppm NH_3 , 5% O_2 , and approx. 2% H_2O in He, 10 ml/min total flow (GHSV $\sim 1,000,000 \text{ h}^{-1}$).

During application of rapid heating/cooling cycles for the Cu-ZSM-5 sample, LCF analysis was used to monitor changes in Cu coordination (Fig. 3, bottom). Fig. 3 (top) demonstrates how the simulated NEDC cycle can successfully mimic a real cycle, involving rapid temperature changes with sufficient accuracy. By comparing the temperature profiles (Fig. 3, top) to the catalytic (middle) and spectroscopic data (bottom) a direct correlation between the Cu catalyst performance, the operating temperature and Cu coordination can be observed. Heating of the catalyst led e.g. to an increase in N₂ production accompanied by a decreased number of ligands around Cu. A similar variation of the XAS spectra and thus of the coordination sphere was shown by other Cu-zeolite samples such as 1.2 wt.% Cu-SSZ-13 and 3.4wt.% Cu-SAPO-34.

4. Conclusions

A silicon based microreactor in combination with *operando* QEXAFS provides new opportunities for catalysis research as it opens up the possibility to understand the structure-activity relationship of heterogeneous catalysts during very fast temperature transients, i.e. under realistic driving conditions. Changes in the structure of SCR catalysts occurred simultaneously to the catalytic performance during fast temperature transients from the NEDC. Collecting catalytic and QEXAFS data on different Cu-zeolites with different pore sizes, sieve fractions and space velocities will help to determine whether differences in catalytic activity result from different diffusivity of gases and mobility of Cu ions or different intrinsic activity of the Cu sites. In addition, the versatility of the microreactor system will permit further studies on a range of exhaust gas aftertreatment processes.

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