In situ monitoring of DeNO$_x$-SCR on zeolite catalysts by means of simultaneous impedance and DRIFT spectroscopy

Peirong Chen$^a$, Simon Schönebaum$^a$, Thomas Simons$^a$, Dieter Rauch$^b$, Ralf Moos$^b$, Ulrich Simon$^a$*

$^a$Institute of Inorganic Chemistry and Center for Automotive Catalytic Systems Aachen, RWTH Aachen University, Aachen 52074, Germany
$^b$Department of Functional Materials, University of Bayreuth, Bayreuth 95440, Germany

Abstract

The development of more efficient zeolite catalyst for selective catalytic reduction of NO$_x$ (DeNO$_x$-SCR) requires the analysis of the real-time state of the catalyst (e.g. NH$_3$ storage level) and the reaction mechanism. Impedance spectroscopy (IS) allows to electrically sense the uptake of NH$_3$ into proton conducting catalysts. By means of IS we reveal that Cu-SAPO possesses higher response to NH$_3$ than Cu-ZSM-5 over a broad temperature range from 80 °C to 450 °C. IS can thus be used to determine the NH$_3$ storage and to monitor the SCR reaction in situ. Simultaneous IS and DRIFTS study under in situ conditions unveiled that the proton conductivity of Cu-SAPO is related to the ammonium nitrate intermediate, NH$_3$ species bounded to both Cu sites and Brønsted acid sites. However, the contribution of each species to the conductivity varied in different reaction conditions. This correlation of integral electrical response with molecular processes paves a new route for the in situ monitoring and mechanistic understanding of zeolite-catalyzed SCR reactions.

Keywords: DeNO$_x$-SCR; NH$_3$; Cu-ZSM-5; Cu-SAPO; impedance spectroscopy; DRIFTS

1. Introduction

Metal-promoted zeolites (with frameworks MFI, BEA, FAU, CHA, etc.) are widely explored as catalyst for the selective catalytic reduction of nitrogen oxides (DeNO$_x$-SCR), which is a key technology to control NO$_x$ emissions.

* Corresponding author. Tel.: +49-241-809-4644; fax: +49-241-809-9003.  
E-mail address: ulrich.simon@ac.rwth-aachen.de
from lean-burn diesel engines for road transport.[1,2] Although numerous investigations have been performed to clarify the reaction mechanism of DeNOx-SCR over well-established zeolite catalysts such as Cu-ZSM-5, Fe-ZSM-5, Cu-CHA,[1-4] the role of proton transport in DeNOx-SCR is rather unexplored.

As revealed in our previous studies by impedance spectroscopy (IS), the proton transport in H-ZSM-5 is supported by NH3 as a solvate molecule, which allows H-ZSM-5 zeolites to be used in NH3 sensing and in situ monitoring of SCR reactions.[5-7] It is of great academic and technological interest to know the proton transport properties of metal-containing zeolite catalysts under technically relevant conditions and the impact in SCR reactions, as well. In this study, we analyzed the proton conductivity of H-ZSM-5, Cu-ZSM-5, and Cu-SAPO upon exposure to NH3 by means of IS. As compared to Cu-ZSM-5, Cu-SAPO displayed a higher response to NH3 in terms of change in proton conductivity at temperatures from 80 °C to 450 °C. Simultaneous IS and DRIFTS (diffuse reflection infrared Fourier transform spectroscopy) measurements under in situ conditions allow us to correlate the electrical response with molecular processes on Cu-SAPO catalyst, thus providing important information about the mechanism of SCR reactions.

2. Materials and methods

Commercial H-ZSM-5 (SiO2/Al2O3 ratio of 27) and Cu-SAPO zeolites were supplied by Clariant AG and used without further treatment. Cu-ZSM-5 were prepared by aqueous ion exchange using H-ZSM-5 as starting material and Cu(NO3)2 as precursor. Briefly, 4 g of H-ZSM-5 powder and 600 mL of Cu(NO3)2 solution (0.0075 mol L^-1) were applied in a single preparation batch. After ion exchange for 24 h at room temperature, the mixture was filtered, thoroughly washed with distilled water (three times, 1 L water in total), and dried overnight at 100 °C. The procedure was repeated to ensure complete ion exchange. The obtained powders were calcined in air at 500 °C for 2 h resulting in the catalyst Cu-ZSM-5.

Details about the instrument, experimental procedure and data presentation of IS measurements are described elsewhere.[7] For improved electrical contact, the zeolite catalysts were deposited as a thick film by screen-printing on inter-digital electrodes (IDEs) comprising an alumina substrate with gold electrodes on the front side and integrated heater on the back side. IS measurements were performed at temperatures from 80 °C to 450 °C under dynamic gas conditions (pure N2 or with ppm-level NH3). The complex impedance Z of zeolite catalysts were measured at frequencies in the range of 0.1 Hz to 1 MHz. The NH3 response S was determined based on Z values at 10 kHz (close to the resonance frequencies of all the three zeolites in NH3) following Eq. 1, where |Z|N2 and |Z|NH3 are the absolute values of complex impedance Z recorded in N2 and NH3, respectively.

\[
S = \frac{|Z|\text{N2} - |Z|\text{NH3}}{|Z|\text{N2}}
\]  Eq. 1

Figure 1 Setup for simultaneous IS and DRIFTS measurements at the same catalyst film (A: Scheme of the chamber and measurement configuration; B: Photograph of open chamber; C: Photograph of chamber with dome).

In order to simultaneously monitor both, the proton conductivity of zeolites and the vibration modes of the molecules involved in the SCR reaction, a setup combining IS and DRIFTS was designed and constructed (Figure 1). A high temperature reaction chamber (HVC, Harrick Scientific Products, Inc.) was modified to allow introducing
the IDE sensor chips. A specially designed holder with electrical contacts was employed to keep the sensor chip inside the reaction chamber in a way that the zeolite film is in the focal point of the infrared beam of the DRIFTS mirror design. Simultaneous IS and DRIFTS measurements were conducted using the same catalyst film. In order to maximize time resolution, IS were measured at a single frequency (10 kHz) instead of a broad frequency range, and the admittance $Y^*$ was used for conductivity evaluation. For comparison, the recorded IS and DRIFTS signals were normalized to (0, 1) and denoted as $I_{IS}$ and $I_{DRIFTS}$, respectively.

3. Results and discussion

Figure 2 shows the NH$_3$ response of the three zeolite catalysts at temperatures from 80°C to 450 °C. Comparing H-ZSM-5 and Cu-ZSM-5, we notice that Cu-ion exchange led to significantly lower NH$_3$ responses at temperatures below 350 °C, most likely due to a decreased number of Brønsted acid site, which were found to be decisive for NH$_3$ sensing.[6] Above 350 °C, the NH$_3$ responses of both ZSM-5 samples decreased rapidly with temperature increase. At temperatures below 330 °C, the NH$_3$ response of Cu-SAPO is lower than H-ZSM-5 but significantly higher than Cu-ZSM-5. Surprisingly, at temperatures above 380 °C, a higher response to NH$_3$ was observed in case of Cu-SAPO (compared to H-ZSM-5).

![Figure 2 NH$_3$ response of H-ZSM-5, Cu-ZSM-5, and Cu-SAPO at different temperatures](image)

The promising NH$_3$ sensing performance at high temperatures allows the Cu-SAPO catalyst to be used as a sensor for *in situ* monitoring of SCR reaction, where NH$_3$ serves as reagent for the reduction of NO$_x$ to N$_2$ following

| Standard SCR | 4 NH$_3$ + 4 NO + O$_2$ → 4 N$_2$ + 6 H$_2$O | Eq. 2 |
| Fast SCR | 2 NH$_3$ + NO + NO$_2$ → 2 N$_2$ + 3 H$_2$O | Eq. 3 |
| NO$_2$ SCR | 8 NH$_3$ + 6 NO$_2$ → 7 N$_2$ + 12 H$_2$O | Eq. 4 |

Figure 3 shows simultaneously collected IS and DRIFTS signals ($I_{IS}$ and $I_{DRIFTS}$) at 250 °C in steady-state gas mixtures with varied concentrations of NH$_3$ and NO. It can be seen that exposure to NH$_3$ (II) led to enhanced conductivities due to the NH$_3$ supported proton transport.[5] Comparing the increasing trends of $I_{IS}$ and $I_{DRIFTS}$, we notice that NH$_3$ bound to Cu sites (at 1616 cm$^{-1}$) shows stronger influence than NH$_3$ bound to Brønsted acid sites on the conductivity of Cu-SAPO. The conductivity of Cu-SAPO increased further despite a lower amount of NH$_3$ is bound to Cu sites after exposing it to 70 ppm NH$_3$/20 ppm NO/10% O$_2$/N$_2$ mixture (III). This unexpected increase in conductivity is likely due to the formation of NH$_4$NO$_3$ intermediates resulting from reaction between NO and highly active NH$_3$ species on Cu sites in the presence of O$_2$.[8] As implied by an IS-DRIFTS measurement at a lower temperature of 100 °C, the NH$_4$NO$_3$ intermediates could serve as additional proton carriers, maintaining the conductivity of Cu-SAPO to a great extent. It has to be noted that NH$_4$NO$_3$ has characteristic vibration band close to that for NH$_3$ bound to Brønsted acid sites, which led to the increase of $I_{DRIFTS}$ at 1448 cm$^{-1}$ as well. Switching to the gas mixture (IV) with 45 ppm NH$_3$/45 ppm NO/10% O$_2$/N$_2$ led to the decrease of both $I_{IS}$ and $I_{DRIFTS}$ (at both 1448 cm$^{-1}$ and 1616 cm$^{-1}$) due to the consumption of surface-bound NH$_3$ species by the SCR reaction. A more significant decrease of $I_{DRIFTS}$ at 1616 cm$^{-1}$ than 1448 cm$^{-1}$ indicates a higher reactivity of NH$_3$ bound to Cu sites. While stable $I_{IS}$ and $I_{DRIFTS}$ values indicating reaction equilibrium can be reached in gas mixtures (III) and (IV), continuously
decreasing $I_S$ and $I_{DRIFTS}$ values were observed in 20 ppm NH$_3$/70 ppm NO/10% O$_2$/N$_2$ (V) pointing to the continuous consumption of NH$_3$ species on Cu-SAPO. No SCR reaction took place in NO/N$_2$ mixture (VI) as indicated by the stable $I_S$ and $I_{DRIFTS}$ values.

**Figure 3** Normalized IS and DRIFTS signals obtained at 250 °C in different gas mixtures. (I): pure N$_2$; (II): 100 ppm NH$_3$/N$_2$; (III): 70 ppm NH$_3$/20 ppm NO/10% O$_2$/N$_2$; (IV): 45 ppm NH$_3$/45 ppm NO/10% O$_2$/N$_2$; (V): 20 ppm NH$_3$/70 ppm NO/10% O$_2$/N$_2$; (VI): 100 ppm NO/N$_2$

4. Conclusions

As compared to Cu-ZSM-5, Cu-SAPO was found to have higher response to NH$_3$ in terms of change in proton conductivity over a broad temperatures range from 80 °C to 450 °C. Simultaneous IS and DRIFTS study under in situ conditions unveiled that the proton conductivity of Cu-SAPO is related to NH$_4$NO$_3$ intermediates, to NH$_3$ species bound to both Cu sites and to Bronsted acid sites. However, the contribution of each species to the conductivity varied in different reaction conditions. This correlation of integral electrical response with molecular processes thus paves a new route for the in situ monitoring and mechanistic understanding of zeolite-catalyzed SCR reactions.

Acknowledgements

This work was supported by the German Research Foundation (DFG) contracts Si609/14-1 and Mo1060/19-1, and by the Excellence Initiative of the German federal and state governments (Exploratory Research Space).

References

[1] U. Deka, I. Lezcano-Gonzalez, B.M. Weckhuysen, A.M. Beale, Local environment and nature of Cu active sites in zeolite-based catalysts for the selective catalytic reduction of NOx, ACS Catal. 3 (2013) 413-427.
[2] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, The state of the art in selective catalytic reduction of NOx by ammonia using metal-exchanged zeolite catalysts, Catal. Rev. 50 (2008) 492-531.
[3] R.Q. Long, R.T. Yang, Reaction mechanism of selective catalytic reduction of NO with NH$_3$ over Fe-ZSM-5 catalyst, J. Catal. 207 (2002) 224-231.
[4] F. Gao, J.H. Kwak, J. Szanyi, C.H.F. Peden, Current understanding of Cu-exchanged chabazite molecular sieves for use as commercial diesel engine DeNOx catalysts, Top. Catal. 56 (2013) 1441-1459.
[5] M.E. Franke, U. Simon, Solvate-supported proton transport in zeolites, ChemPhysChem 5 (2004) 465-472.
[6] M.E. Franke, U. Simon, R. Moos, A. Knezevic, R. Müller, C. Plog, Development and working principle of an ammonia gas sensor based on a refined model for solvate supported proton transport in zeolites, Phys. Chem. Chem. Phys. 5 (2003) 5195.
[7] T. Simons, U. Simon, Zeolites as nanoporous, gas-sensitive materials for in situ monitoring of DeNO(x)-SCR, Beilstein J. Nanotechnol., 3 (2012) 667-673.
[8] D. Wang, L. Zhang, K. Kamasamudram, W.S. Epling, In situ-DRIFTS study of selective catalytic reduction of NOx by NH$_3$ over Cu-exchanged SAPO-34, ACS Catal. 3 (2013) 871-881.