NO oxidation and reduction over Fe zeolites: Elucidating active sites and reaction mechanisms by operando spectroscopy and reactivity studies

Wolfgang Grünert[1*], Inga Ellmers[1], Roxana Pérez Vélez[2], Heming Huang[3], Ursula Bentrup[2], Volker Schünemann[3], Angelika Brückner[2*]

[1]*Lehrstuhl Technische Chemie, Ruhr-Universität Bochum, Bochum, Germany*

[2]*Leibniz-Institut für Katalyse e. V. at Rostock University, Rostock, Germany*

[3]*FB Physik, Technische Universität Kaiserslautern, Kaiserslautern, Germany*

* *corresponding authors: w.gruenert@techem.rub.de, angelika.brueckner@catalysis.de*

Introduction

Fe zeolites go on to attract major interest in environmental catalysis because of their potential for catalytic NOx abatement. Apart from N_2O decomposition and reduction, reactions relevant for this field are standard SCR (1), fast SCR (2), and NO oxidation (3), where (1) is the stoichiometric sum of (2) and (3).

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \quad (1)$$

$$NO + NO_2 + 2\,NH_3 \rightarrow 2\,N_2 + 3\,H_2O \quad (2)$$

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad (3)$$

Despite considerable effort there is still much debate on how to explain the catalytic properties of Fe zeolites. The multiplicity of sites usually resulting from post-synthetic introduction of Fe into zeolites is a challenge for any characterization effort, which has so far limited progress in the unanimous identification of active sites. Regarding reaction mechanisms, it has been widely accepted that standard SCR follows the sequence suggested by stoichiometry, with NO_2 formation being rate limiting [1], while routes via NH_4NO_2 and via nitrosamide (NH_2NO) are discussed for fast SCR [1-3]. We present here recent progress in the elucidation of active sites and mechanisms in this field obtained by combining ex-situ and operando spectroscopic studies with rate measurements on a variety of materials made by different preparation routes.

Materials and Methods

Fe-ZSM-5 catalysts of low Fe content were prepared by various techniques: liquid ion exchange (LIE) with aqueous solutions of Fe(II) precursors, improved liquid ion exchange (ILIE; Fe(0) + zeolite in dilute HCl), and two different versions of solid-state ion exchange (SSIE). In a particular series, 0.26 wt-% Fe were introduced by the dry SSIE method into ZSM-5 that had been previously exchanged with different amounts of inert cations (Na^+, Ca^{2+}) with the intention to force the Fe ions to take different intra-zeolite positions. Rates for reactions (1)… (3) were measured with 1000 ppm NO (or equimolar NO/NO_2), 1000 ppm NH_3 where required, and 2 % O_2, balance He, at a GHSV of 750,000 h^{-1}. Samples were characterized by UV-vis, EPR, and Moessbauer spectroscopy (the latter with ^{57}Fe enriched material), including operando work with UV-vis and EPR spectroscopy.

Results and Discussion

The catalytic studies provided ample evidence rejecting any role of NO_2 formation (3) for standard SCR (1). While the TOF of (3) decreased monotonously with Fe content, the TOF of (2) went through a maximum in the 0.4-0.5 wt-% Fe range. The effect of inert cations on reaction rates was different (Fig. 1) [4]: while NO_2 formation decreased with increasing Na/Ca content (similar to fast SCR rates, not shown), exchange of 50% of zeolite protons by Na had a reproducibly positive effect on standard SCR rate.

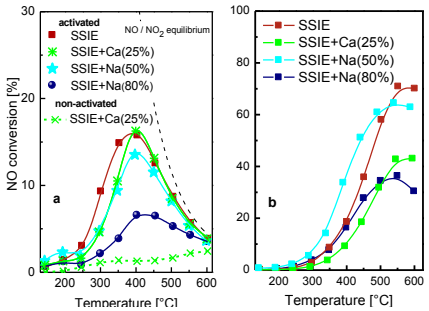

Figure 1. NO conversions in NO oxidation (a) and standard SCR (b) over Fe-ZSM-5 with different exchange degrees of inert cations. Fe content 0.26± 0.02 wt-%. Fig. 1a shows also activation effect in NO oxidation with SSIE-Ca(25%)

In Fig. 1a, a strong activation effect observed with NO oxidation is shown: while freshly calcined catalysts are usually very inactive, their contact with SCR feed or other conditions that cause redox cycling resulted in sometimes drastic boost in activity [4]. Rates for reactions (3) and (1) were uncorrelated, r(3) exceeding or falling short of r(1) depending on samples and reaction conditions. Beyond rejection of (3) as part of the standard SCR mechanism, this shows also that NO_2 formation is strongly inhibited in the SCR environment, probably by NH_3.

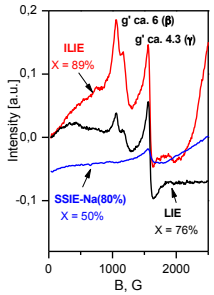

Figure 2. Operando EPR spectra during fast SCR and NOx conversions at 250 °C (in lab reactor). Fe contents: 0.46, 0.27, and 0.15 wt% in ILIE, SSIE, and LIE, resp.

Operando EPR measurements during standard SCR showed a significant part of the isolated sites (on β positions completely) reduced to Fe(II), which probably excludes them from participation in the reaction. These sites become oxidized in presence of NO_2 (fast SCR), with intensity growing with temperature. Moessbauer spectra confirmed the observation of Sobalik et al. [5] that Fe-ZSM-5 contains Fe(II) even after severe calcination. This Fe(II), mostly on β positions, is oxidized under fast SCR conditions, its spectroscopic intensity correlating with activity (Fig. 2) which shows them to be active sites for fast SCR [6]. Their stabilization by two close Al framework sites [5] might explain the high stability of Fe zeolites with respect just to this reaction.

Significance

We reject NO_2 formation as part of the standard SCR mechanism over Fe-ZSM-5 and propose oxidation of NO to a lower oxidation state (e.g. nitrite) as initial reaction step. We report a drastic activation effect in NO oxidation and identify active Fe sites for fast SCR.

References

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