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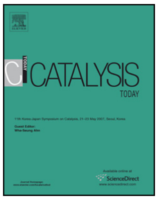

SCR and NO oxidation over Fe-ZSM-5 – The influence of the Fe content

Inga Ellmers[a], Roxana Pérez Vélez[b], Ursula Bentrup[b], Wilhelm Schwieger[c], Angelika Brückner[b], Wolfgang Grünert[a,*]

[a] Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany
[b] Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straße 29a, D-18059 Rostock, Germany
[c] Friedrich-Alexander-Universität Erlangen-Nürnberg, Lehrstuhl Chemische Reaktionstechnik, Egerlandstraße 3, 91058 Erlangen, Germany

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ABSTRACT

Fe-ZSM-5 catalysts (Si/Al in ZSM-5–14) were prepared by different routes and used for an investigation of relations between normalized reaction rates (rates per Fe atom present) and Fe content in reactions relevant for NO$_x$ abatement by selective catalytic reduction (SCR) with NH$_3$: standard SCR, fast SCR, and NO oxidation. Samples were characterized by XRD, ex situ UV–vis and EPR spectroscopy. In standard SCR, normalized reaction rates increased with Fe content to a maximum around 0.5 wt.% (Fe/Al ≈ 0.07) and decreased at further growing Fe loading. This suggests the existence of Fe sites of different activity, which we identify with isolated Fe^{3+} sites (on α and/or β cation positions, lower activity) and Fe^{3+} in small oligomeric structures (higher activity) on the basis of our characterization data and recent results from operando-EPR experiments (Pérez Vélez et al., 2014). The decay with further increasing Fe loading is assigned to Fe being included in more aggregated structures. Normalized reaction rates of NO oxidation to NO$_2$ decrease from very small Fe contents on, which indicates that NO oxidation is catalyzed by a small minority of Fe sites, most likely by a variety of isolated sites, in strong contrast to standard SCR. Normalized reaction rates for fast SCR are difficult to establish due to complexity and high rate of the reaction. The results suggest, however, that fast SCR proceeds on a small minority of Fe sites as well, in agreement with our recent *operando* EPR and Moessbauer studies (Pérez Vélez et al., 2014). Fast SCR proceeds also in absence of Fe, but rates are inferior and easily exceeded even by contributions arising from Fe impurities usually present in technical zeolites.

1. Introduction

The selective catalytic reduction of nitrogen oxides by ammonia (NH$_3$-SCR) has been a major topic in environmental catalysis over many years due to its importance for compliance with upcoming legislation on emissions from lean engines [1,2]. While nowadays SCR with ammonia supplied in the form of urea is being introduced for duty in vehicles of different types, a better understanding of the processes proceeding on the catalysts (Fe- or Cu-exchanged zeolites or V–W–TiO$_2$ depending on type of vehicle) is still important to achieve further improvement [2]. The present communication deals with Fe catalysts, where identification of active sites has been seriously hampered by the complexity of species formed during introduction of Fe ions into zeolites [1–11].

The most important reactions in this field are the so-called “standard SCR” (1), “fast SCR” (2), and NO oxidation (3), which are stoichiometrically coupled in a way that standard SCR is the sum of NO oxidation and fast SCR.

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

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \quad (2)$$

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

The widely accepted view that this describes also the reaction mechanism of standard SCR, with a rate-limiting NO$_2$ formation step (3) followed by facile fast SCR (2) [1,12–15] has been challenged recently by observations of different responses of reactions (2) and (3) to water in the feed [14–18], of inequality of reaction rates between reaction (1) and its rate-limiting step (3) in a wide range of catalysts and reaction conditions [6,15,19,20], and on conflicting trends of activities with variations of catalyst properties [20]. The discussion on active sites for these reactions has been summarized in [21]. Regarding standard SCR, most authors agree that it is catalyzed by isolated Fe sites [22–26], while some

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* Corresponding author at: Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, P.O. Box 102148, D-44780 Bochum, Germany. Tel.: +49 234 322 2088; fax: +49 234 321 4115.
E-mail address: w.gruenert@techem.rub.de (W. Grünert).

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groups consider oligomeric Fe-oxo structures as active sites as well [5,27,28]. Less attention has been paid to fast SCR, where our earlier work suggested that it is catalyzed by a small minority of isolated sites [6]. In a recent operando-spectroscopic study by EPR and UV–vis, supported by Moessbauer work [29], we identified these with Fe ions that remain bivalent under severe calcination in air, but are oxidized by NO_2. They are predominantly located on β cation exchange sites, their properties are likely determined by a particular stabilization by two nearby framework Al atoms [11,30]. Regarding NO oxidation, opinions in literature include Fe oxide particles [31] and binuclear Fe-oxo ions [32]. In earlier work, we found a strong activation of fresh Fe-ZSM-5 catalysts initially calcined in air by processes involving redox cycling [20]. Despite the sometimes drastic effects, no significant changes that could be correlated with the increase in NO oxidation activity were found in preliminary EPR and UV–vis experiments [20], which suggests that the number of sites involved in this reaction may be very small.

In this paper, we present a study of the relation between reaction rates and Fe content for the reactions mentioned above over Fe-ZSM-5 catalysts of different site structure, which were made via different preparation routes. The results confirm that NO_2 is formed on a small minority of sites only, which is clearly different from those participating in standard SCR. For fast SCR, a more realistic assessment of contributions arising from the acid-catalyzed and the Fe-catalyzed pathways is given, for standard SCR, a model of at least two different active sites, among them Fe in oligomeric clusters is confirmed.

2. Experimental

2.1. Catalyst preparation

The starting material NH_4-ZSM-5 (Si/Al = 14) for the preparation of Fe-ZSM-5 catalysts was provided by Tricat Zeolites Bitterfeld, now a Clariant company. H-ZSM-5 was obtained from it by calcination in synthetic air (20.5% O_2/N_2) at 773 K for 5 h. To identify the contributions of Fe impurities incommercial zeolites to catalytic activities, an iron free H-ZSM-5 (Si/Al = 15) was employed for catalytic reference measurements. The absence of Fe in this sample, which will be labeled “Fe-free MFI” was confirmed by ICP-OES and EPR analysis.

The exchange of Fe into the zeolite was done using different methods, e.g. Solid-State Ion Exchange (SSIE), Liquid Ion Exchange (LIE) and Improved Liquid Ion Exchange (ILIE). SSIE was made along a route described in [33]: $FeCl_3$ was first impregnated onto the dried parent NH_4-ZSM-5 from a solution of a specified amount of the chloride in acetyl acetone, which was followed by thermal treatment in vacuum (623 K, 3 h). For the samples prepared by LIE, the parent zeolite was exchanged in a 0.05 M aqueous $FeCl_2$ solution at 353 K for 5 h. The Fe content was changed by varying the pH value between 0 and 3 (see detailed description in [7]). ILIE is a preparation which involves an exchange of NH_4-ZSM-5 with Fe^{2+} generated in situ from iron powder in acidic medium (room temperature, 5 d). It was performed under inert gas atmosphere (see detailed description in [20]). All catalysts were finally washed and calcined in synthetic air at 873 K for 2 h.

For all preparation methods the iron content was confined to <0.7 wt.% to avoid the undesired formation of iron oxide particles. The samples will be labeled with the abbreviation of the preparation method followed by the introduced iron content. For our ZSM-5, a Fe content of 0.5 wt.% corresponds to a Fe/Al ratio of 0.07.

2.2. Catalytic measurements

Reaction rates of all test reactions, i.e. standard SCR, fast SCR, and NO oxidation were evaluated in a parallelized reactor setup using quartz microflow reactors (4.2 mm i.d.). Experiments were performed in the temperature range of 423–873 K for standard SCR and NO oxidation and 473–673 K for fast SCR. In standard SCR the feed consisted of 1000 ppm NO, 1000 ppm NH_3, and 2% O_2, balance He, for fast SCR, 500 ppm NO and 500 ppm NO_2 were dosed instead of 1000 ppm NO. NO oxidation was measured using 1000 ppm NO and 2% O_2, balance He, i.e., the standard SCR feed without NH_3. For all reactions, the same Gas Hourly Space Velocity (GHSV) of 750,000 h^{-1} was chosen by using 10 mg catalyst (250–355 μm particle size) and a total flow of 183.3 ml min^{-1} per reactor. Conversions were measured at steady state for each reactor before the furnace was heated up to the next reaction temperature ($\Delta T = 50$ K for standard SCR and NO oxidation, 25 K for fast SCR, heating rate – 5 K min^{-1}). The measurements of standard SCR and NO oxidation were combined in a way that for every temperature the reaction rate of standard SCR was measured prior to that of NO oxidation: after the steady state of standard SCR was reached, NH_3 was removed from the feed and the rate of NO oxidation was registered after the steady state of this reaction had been achieved (see detailed description in [20]).

The concentrations of NO, NH_3 and NO_2 were determined using non-dispersive IR photometry for NO and NH_3, and UV spectrometry for NO_2 (XStream X2 gas analyzer, Rosemount Analytical, Emerson). The formation of side products, especially N_2O, was checked by using a quadrupole mass spectrometer (Omnistar, Pfeiffer). No significant extent of N_2O formation could be observed in the experiments. In case of fast SCR measurements, a NH_3-trap was inserted prior to the XStream to avoid the formation of ammonium nitrate in the cuvettes. In this case, conversions of NH_3 were evaluated from the mass-spectrometric data. The N balance was checked in special standard SCR runs over the whole temperature range with different Fe-ZSM-5 samples, where it was found to close typically within ±5%.

The results of the catalytic measurements will be reported in terms of conversion of NO or of NO_x (sum of NO and NO_2). For standard SCR and NO oxidation, normalized reaction rates r_{Fe} were also evaluated (stoichiometric coefficient $\nu_{NO} = -4$ for standard SCR, −2 for NO oxidation, n_{Fe} – amount of Fe present):

$$r_{Fe} = \frac{1}{\nu_{NO} n_{Fe}} \frac{dn_{NO}}{dt} \tag{4a}$$

As the conversions were not limited to the differential range, a reaction order in NO of 1 was assumed, which converts Eq. (4a) into

$$r_{Fe} = \frac{1}{\nu_{NO} n_{Fe}} c_{NO_0} \dot{V} \ln(1 - X) \tag{4b}$$

Analogous measurements have been published recently for a set of samples including a few of those discussed here [20]. In this paper, it has been shown by reaction engineering assessments (e.g. Weisz module) that the rate measurements are not influenced either by internal or by film diffusion limitations.

2.3. Characterization

The Fe content was analyzed by atomic absorption spectroscopy (Spectra AA 220, Varian). For digestion of the sample, a melt of 20–30 mg catalyst and 400 mg $Na_2O_2/LiBO_2$ was produced, which was subsequently dissolved in diluted nitric acid.

XRD measurements were performed in reflection geometry with a Panalytical MPD theta-theta diffractometer, using Cu Kα radiation and a secondary graphite monochromator. The patterns were recorded at ambient conditions in the range of $2\theta = 2–60°$ (step width 0.035°).

UV–vis spectra of as-received samples were recorded at room temperature with a Cary 400 spectrophotometer (Varian) equipped with a diffuse reflection accessory (Praying mantis, Harrick). $BaSO_4$