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Oxidation and selective reduction of NO over Fe-ZSM-5 – How related are these reactions?

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ABSTRACT

Fe-ZSM-5 catalysts were prepared by different techniques, including some with additional inert cations such as Na^+ or Ca^{2+} blocking between 25% and 80% of the exchange capacity of the zeolite. Their catalytic behavior in NO oxidation, standard SCR, and fast SCR was studied, with their site structure in different catalyst states investigated by UV–vis and EPR spectroscopy. Their activity for oxidation of NO to NO_2 was greatly boosted by previous contact with a feed containing a reductant, e.g. NH_3, at elevated temperatures. Therefore, NO_2 formation rates measured after mere calcination of freshly prepared samples are irrelevant for mechanistic discussions related to NOx abatement reactions. The rates of NO_2 formation and standard SCR were demonstrated to be uncorrelated over a wide range of catalysts and reaction conditions. Depending on catalyst and reaction conditions, the rate of NO_2 formation exceeded, equaled or fell short of the rate of standard SCR. Our results strongly suggest that NO_2 formation is inhibited by NH_3 in the reaction environment of standard SCR. As a result, NO_2 formation is slower than standard SCR under many different reaction conditions, and therefore, it cannot be a part of the reaction mechanism of standard SCR. Our results favor earlier mechanistic concepts of standard SCR being initiated by oxidation of NO to nitrite, while oxidation to NO_2 seems to require specific sites.

1. Introduction

Iron zeolites have been a hot topic in environmental catalysis for many years because of their attractive potential as catalysts for reactions with nitrogen oxides [1–7], for instance, in their selective catalytic reduction (SCR) by NH_3. These materials are now considered for commercial application in the detoxification of lean automobile engine exhaust, which is based on the "fast" SCR reaction

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (1)$$

rather than on the "standard" SCR

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (2)$$

The question of which species are responsible for the various catalytic effects and which reaction mechanisms proceed on them has been subject to numerous studies. Unfortunately, iron forms a multitude of species when dispersed in the cavities of zeolites with the speciation depending strongly on the preparation procedure. A reliable and complete quantitative analysis of the site distribution is impossible with the characterization techniques routinely employed in catalytic laboratories (UV–vis, EPR, XAFS, Moessbauer on elementary level). Due to the problems in the structural analysis of coexisting Fe species, there is still a lot of disagreement as to their catalytic role in the different reactions.

More agreement has been achieved in the elucidation of reaction mechanisms with rather similar reaction schemes including the disproportionation of NO_2, the reduction of the resulting nitrate species (NH_4NO_3, HNO_3) by NO, and the final formation of nitrogen via NH_4NO_2 having been proposed by different groups [4,8]. Actually, recent computational studies favor a different pathway via the highly reactive nitrosamide [9,10]; however, spectroscopic evidence for the intermediate Fe amide species predicted, in particular in [10], is scant. For the SCR of NO by NH_3 (standard SCR), a consecutive scheme is widely accepted in which part of the NO is initially oxidized to NO_2 in the rate-determining step

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

which is followed by the very facile fast SCR (Eq. (1)) [4]. This idea has been supported by a correlation between rates in NO oxidation and standard SCR over different catalysts [11], by strong differences in the reactivity of surface NH_4^+ species with NO and with NO/NO_2 mixtures [12], by the observation of equal rates for both NO oxidation and standard SCR in differential kinetic studies [13] and by the

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strong accelerating effect observed when NO_2 is admixed to the feed of standard SCR [14]. This has very much pushed aside earlier views, e.g. a route via substitution of extra-lattice oxygen on Fe ions by NH_3 resulting in amide and subsequently nitrosamide species [15], or the oxidation of NO to the oxidation degree of 3+ followed by symproportionation with NH_3 [16]. As already mentioned, the Fe amide species has been predicted on the basis of DFT calculations in [10], where a mechanism of standard SCR proceeding via this species has also been proposed.

The concept of NO oxidation to NO_2 being rate limiting for standard SCR has been challenged by a number of experimental results. It has been found that the former reaction is slower than the latter [14,17,18], which prevents its participation in the reaction since a reaction step cannot be slower than the total reaction. To reconcile the consecutive mechanism with this observation, a rate-liming role of NO_2 desorption in the NO oxidation reaction was assumed. NO_2 might thus enter the fast SCR step (1) from the adsorbed state [4,14,17]. However, this would mean that highly reactive NO_2 molecules accumulate on Fe^{2+} sites during NO oxidation if the mechanistic concepts related to this assumption [4,14,17] are taken seriously. In addition, the different responses of NO oxidation and standard SCR to the water content in the feed, which has been repeatedly reported [13,14,19–21], are difficult to explain with a rate-limiting role of an NO_2 formation step in standard SCR.

In this paper, we report on the strong impact of the reaction atmosphere of standard SCR on the Fe sites in Fe-ZSM-5, which can cause a dramatic activation of the samples for NO oxidation. The proposed correlation between rates of NO oxidation and standard SCR was disproved with a series of catalysts containing Fe together with inert cations, which were introduced to force the iron to take different cation positions. The rate of NO_2 formation exceeded that of standard SCR in many cases, which excludes a rate-limiting role of NO_2 desorption, but the reverse relation was also found in a wide range of reaction conditions. As both NO oxidation to NO_2 and fast SCR cannot be faster than their stoichiometric sum (standard SCR) in a reaction system, one of these reactions has to be inhibited under standard SCR conditions, and it is apparently NO_2 formation, which is inhibited by NH_3. As a result, NO_2 formation will be slower than standard SCR in the presence of ammonia under a wide range of reaction conditions; therefore, it cannot be a mechanistic step of standard SCR.

2. Experimental

2.1. Catalyst preparation

The starting material NH_4-ZSM-5 (Si/Al = 14) was provided by Tricat Zeolites GmbH Bitterfeld, now a Clariant company. Fe-ZSM-5 was prepared through different routes, e.g. different versions of Solid-State Ion Exchange (SSIE) and Improved Liquid Ion Exchange (ILIE). A series of samples (“SSIE-I-Ca/Na”) were prepared by SSIE-I, i.e. by dry exchange of H-ZSM-5 with $FeCl_3{\cdot}6H_2O$ via thermal treatment in flowing N_2 (573 K, 1 h) as described in detail in [18]. In this series, the NH_4 form was previously doped with different quantities of Na^+ or Ca^{2+} ions in order to influence the site distribution of the iron subsequently introduced. Therefore, NH_4-ZSM-5 was initially exchanged in aqueous solutions of $NaNO_3$ or $CaCl_2$ of different concentrations, and the products were transferred into the H form by calcination in synthetic air (20.5% O_2/N_2) at 773 K for 5 h.

In another version of SSIE (SSIE-II), $FeCl_3$ was first impregnated onto dried NH_4-ZSM-5 from a solution in acetyl acetone, and the thermal treatment (here at 623 K for 3 h) was performed in vacuum [22]. ILIE is a preparation involving an exchange of NH_4-ZSM-5 with Fe^{2+} generated *in situ* from iron powder in acidic medium. It is performed under inert gas atmosphere (see description in [18]). All catalysts were finally washed under conditions which have been shown earlier [23] to ensure the thorough removal of chlorine (i.e., until no Cl^- in washing water). After preparation, all catalysts were calcined in synthetic air at 873 K for 2 h.

In Table 1, the samples are introduced together with their labels. In the SSIE-I-Ca/Na series, the Fe content introduced by SSIE-I is approximately constant at (0.26 ± 0.02) wt.%, which is approximately 4% of the exchange capacity estimated by assuming H: $(FeO)^+$ = 1. The Fe content of the remaining materials is included in their labels. In the labels of the SSIE-I-Ca/Na series, it is omitted and the modifying ion is given together with a qualitative indicator of its exchange degree. The Fe content has been kept low in all samples to avoid excessive complication of the Fe speciation. In the SSIE-I-Ca/Na series, the Ca content is much smaller than that of Na, but owing to the double charge on Ca, the exchange degrees of the samples are roughly equally spaced between 0 and 1. In Table 1, some textural data of the catalysts are also reported.

2.2. Catalytic measurements

Measurements of reaction rates (NO oxidation, standard SCR, and fast SCR) were carried out in a parallelized reactor setup containing six microflow quartz reactors (4.2 mm i.d.) in the temperature range of 423–873 K. In standard SCR, the feed consists of 1000 ppm NO, 1000 ppm NH_3, and 2% O_2 with He as balance; for fast SCR, 500 ppm NO was dosed with 500 ppm NO_2 instead of just 1000 ppm NO. NO oxidation was measured with 1000 ppm NO and 2% O_2, balance He. In a study of the influence of NO_2 on the NO oxidation rate, up to 150 ppm of NO_2 was added to this feed. For all reactions, the same Gas Hourly Space Velocity (GHSV) of 750,000 h^{-1} was achieved by using 10 mg catalyst (250–350 μm particle size) and a total flow of 183.3 ml min^{-1} per reactor. Conversions were measured at steady state for all six reactors of the parallelized scheme by directing the effluent to the analytical scheme described below. The sixth tube was left empty to allow for checking the analytical instruments. After the conversion measurements, the furnace was heated up to the next reaction temperature (temperature steps – 50 K, heating rate – 5 K min^{-1}).

Regarding NO oxidation, the data from this type of experiment will be designated as “initial.” In other experiments, measurements of NO oxidation and standard SCR were combined in such a way that NO oxidation was measured at every temperature step directly after a steady state of standard SCR was reached (after ca. 20 min), replacing the ammonia by an equivalent He flow. After reaching steady state of NO oxidation, the reaction gas was changed back to the standard SCR feed, and the temperature was raised. This catalyst state will be labeled “activated.” These switching experiments were meant to reflect the NO oxidation activity in the catalyst state which gave rise to the standard SCR conversion just measured.

NO and NH_3 conversions, and NO_2 formation were determined with an instrument using non-dispersive IR photometry for NO and NH_3, and UV spectrometry for NO_2 (XStream X2, Rosemount Analytical; Emerson). To monitor the formation of side products, in particular N_2O, and to check the NH_3 conversion, a quadrupole mass spectrometer (Omnistar, Pfeiffer Vacuum GmbH) was employed. Neither NO_2 nor N_2O occurred among the products of SCR in significant amounts. For fast SCR measurements, a NH_3-trap that is inert toward the nitrogen oxides (Bühler) was inserted prior to the XStream to avoid ammonium nitrate formation in the cuvettes. In this case, NH_3 conversion was evaluated from the mass spectrometric data. The quality of the analysis was checked in special experiments with mass spectrometric N_2 analysis. In these runs, the N balance was found to close within ±5%. In a test where five reactor tubes contained the same catalyst prepared via the ILIE