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The chemistry of the NO/NO_2–NH_3 "fast" SCR reaction over Fe-ZSM5 investigated by transient reaction analysis

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ABSTRACT

We present a systematic study of the chemical steps in the NO/NO_2–NH_3 fast SCR reaction $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$ over a commercial Fe-ZSM5 catalyst. The study is based on transient reaction experiments at realistic conditions for removal of NO_x from mobile diesel exhausts. Its goal is to assess and critically evaluate the current ideas on the SCR mechanism, and also to establish to what extent the mechanistic pathways demonstrated for V-based catalysts also apply to Fe-promoted zeolites. Results show that the fast SCR reaction proceeds at low temperature via a global sequence involving NH_4NO_3 or related surface species as intermediates,

$$2NO_2 + 2NH_3 \rightarrow N_2 + NH_4NO_3 + H_2O,$$

$$NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O.$$

Such a sequential scheme is the same as that proposed previously for the fast SCR chemistry over V-based catalysts and other zeolite catalysts and thus is considered a general mechanism. It explains all of the available observations for stoichiometry (e.g., optimum NO/NO_2 unit molar ratio), selectivity (e.g., N_2O from NH_4NO_3 decomposition), and kinetics (e.g., rate of fast SCR = rate of nitrate reduction by NO). We further show that the redox reaction between NO and nitrates is the rate-controlling step and is inhibited by ammonia. Remarkably, the same strongly enhanced deNO$_x$ activity observed in the fast SCR reaction also was observed in the absence of gaseous NO_2 but in the presence of surface nitrates. We accordingly propose a general summary of the fast SCR chemistry over V-based and zeolite catalysts that emphasizes the key role of surface nitrates.

1. Introduction

In addition to the well-known "standard" SCR reaction,

$$2NH_3 + 2NO + \frac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O, \tag{1}$$

the so-called "fast" SCR reaction,

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O, \tag{2}$$

plays a critical role at 180–300 °C in boosting the denitrification (deNO$_x$) activity of new generation urea-SCR converters for diesel vehicles integrated with an upstream preoxidation catalyst that partially oxidizes NO to NO_2 [1].

Koebel and co-workers [1–4] first extensively investigated the fast SCR reaction over V_2O_5–WO_3/TiO_2 SCR catalysts. To explain the higher rate of the fast SCR reaction, they proposed a redox mechanism in close analogy with that of the standard SCR reaction, but with NO_2 serving as a more efficient oxidizing agent for the vanadium sites than oxygen [3]. Furthermore, for the NO–NO_2/NH_3 reacting system, they also reported the occurrence at low temperatures of two side reactions not observed in the presence of NO–NH_3 only—namely the formation of ammonium nitrate,

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O, \tag{3}$$

and the decomposition of ammonium nitrate by NO, described according to the following stoichiometry [4]:

$$NH_4NO_3 \leftrightarrow NH_3 + HNO_3, \tag{4}$$

$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O. \tag{5}$$

However, reactions (3)–(5) were considered to be side reactions occurring in parallel to fast SCR (1), not participating in its mechanism [4].

In our work aimed at developing a chemically consistent simulation model of SCR converters for automotive applications [5], we have addressed mechanistic aspects of the fast SCR chemistry

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over commercial vanadium-based catalysts by means of transient reaction analysis [6–10]. Our data have shown that the fast SCR chemistry proceeds over V_2O_5–WO_3/TiO_2 SCR catalysts at low temperature via a sequential scheme, which can be summarized as comprising two global reactions—ammonium nitrate formation [reaction (3)] and the following reaction between ammonium nitrate and NO—formally involving NH_4NO_3 as an intermediate:

$$NH_4NO_3 + NO \rightarrow NO_2 + N_2 + 2H_2O. \tag{6}$$

In fact, the sum of (3) and (6) yields the stoichiometry of the fast SCR reaction (2). Notably, reactions (3) and (6) are similar to those already reported by Koebel and co-workers, but here they are not just side reactions, but are intimately related to the fast SCR chemistry.

The mechanism of the first step in the fast SCR sequential scheme—ammonium nitrate formation [reaction (3)]—was clarified by Koebel's group [1–4] and implies NO_2 dimerization (7), disproportion (8), and successive reactions between nitrous and nitric acid and NH_3 (9), (10), with rapid decomposition of ammonium nitrite to nitrogen:

$$2NO_2 \leftrightarrow N_2O_4, \tag{7}$$

$$N_2O_4 + H_2O \leftrightarrow HONO + HNO_3, \tag{8}$$

$$NH_3 + HONO \leftrightarrow NH_4^+ + NO_2^- \leftrightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O, \tag{9}$$

$$NH_3 + HNO_3 \leftrightarrow NH_4^+ + NO_3^- \leftrightarrow NH_4NO_3. \tag{10}$$

Concerning the second step in the fast SCR sequential scheme—reaction (6) between NO and ammonium nitrate—we have demonstrated by dedicated transient experiments a mechanism based on: ammonium nitrate decomposition (10 reverse), successive oxidation of NO to NO_2 by nitric acid, which is thus reduced to nitrous acid (11), and reaction of the latter with NH_3 to form N_2 via ammonium nitrite decomposition (9) [6–10]:

$$NH_4NO_3 \leftrightarrow NH_3 + HNO_3, \tag*{(4) = (10 reverse)}$$

$$HNO_3 + NO \leftrightarrow NO_2 + HONO, \tag{11}$$

$$NH_3 + HONO \rightarrow N_2 + 2H_2O. \tag{9}$$

We further observed that the rate-limiting step (6) does not proceed over V-free WO_3/TiO_2 and thus is catalyzed by V_2O_5. The same results had been previously reported for reaction (5) [4]. According to a redox interpretation of the fast SCR chemistry over V-based catalysts, the key global reaction (6) actually is associated with a redox cycle involving the more effective reoxidation of reduced V-sites by surface nitrates [8,9]; the fast SCR activity of NO/NO_2–NH_3 is similar to the activity of $NH_3 + NO$ in the absence of gaseous NO_2 but in the presence of either NH_4NO_3 [6,7,10] or nitrates prestored onto the vanadium catalyst surface [8,9]. This rules out the possibility that the fast SCR reaction (2) can proceed in parallel or consecutively to the nitrate decomposition by NO [reaction (6)].

There is now a trend in the automobile industry to replace vanadium-based SCR catalysts with zeolite-based systems to expand the operating temperature window and address the problems associated with high-temperature deactivation of the anatase–rutile TiO_2 transition. Zeolites are the new class of automotive SCR catalysts. Various zeolites have been proposed for this purpose, including ZSM-5, mordenite, beta, ferrierite, and Y-zeolite [11]. In the most active systems, zeolites generally are promoted by transition metals, such as iron, copper, and silver. These catalysts reportedly are associated with good $deNO_x$ activity in the standard and especially the fast SCR reactions [11–17].

Concerning the mechanistic features of fast SCR over zeolites, Weitz et al. [18] proposed a fast SCR pathway over a BaNa–Y zeolite similar to that discussed above for V_2O_5–WO_3/TiO_2 catalysts, based on spectroscopic evidence and on steady-state reaction data. In addition, other authors have reported NO_2 disproportion [19–21] and ammonium nitrate formation [16,22] over promoted and unpromoted zeolites. Based on the analysis of their own data and of literature data, Kröcher et al. [23] recently proposed a common SCR reaction scheme for transition–metal zeolites and for vanadium-based catalysts that is in close agreement both with the chemistry over a V_2O_5–WO_3/TiO_2 catalyst reported in our previous work [6,7] and with the scheme proposed for the BaNa–Y zeolite [18].

Herein we present a dedicated investigation of the elementary steps of the fast SCR reaction at low temperature over the same commercial Fe-ZSM5 catalyst used in a previous SCR reactivity study [26]. Our goal is to assess and critically evaluate the current ideas on the SCR mechanism, and specifically to establish in a conclusive manner to what extent the same mechanistic pathways demonstrated for V-based catalysts also apply to Fe-promoted zeolite catalysts under fully representative conditions for automotive applications. For this purpose, we take the same experimental approach (transient reaction experiments) used in our previous mechanistic investigation over V_2O_5–WO_3/TiO_2, in order to establish a direct link to the results for V-based catalysts.

2. Experimental

The commercial catalyst used in this work was originally supplied by Daimler in the form of a cordierite honeycomb monolith (400 cpsi—6.5 mils) washcoated with Fe-ZSM5. For testing, the catalyst was crushed and sieved to 140–200 mesh, to avoid mass transfer limitations. Samples (160 mg of catalyst powder or 80 mg of catalyst powder diluted with 80 mg of quartz powder) were loaded into a flow-microreactor consisting of a quartz tube (6 mm i.d.) placed in an electric furnace. The reaction temperature was monitored and controlled by a K-type thermocouple immersed in the catalyst bed. Mass-flow controllers (Brooks Instruments) were used to dose He, Ar, NH_3, NO, NO_2, and O_2 in the gaseous feed stream, while water vapor was added via a saturator operated at controlled temperature. All of the lines before and after the reactor were heated to 200 °C to prevent H_2O condensation and NH_4NO_3 deposition. The species concentrations in the outlet stream were continuously monitored by a quadrupole mass spectrometer (Balzer QMS 200) and a UV analyzer (ABB-LIMAS 11 HV) in parallel. He was used as carrier gas to enable evaluation of N balances at steady state. More experimental details are available elsewhere [5,7,8,26].

Before the experiments, the catalyst was conditioned with a temperature ramp of 10 °C/min up to 600 °C in 2% O_2 v/v, then held at 600 °C for 1 h. Transient runs consisted of step-response experiments at 150–170–190 °C (transient response method [TRM]) and in temperature-programmed reaction (TPR) runs. In a typical TRM run, the reactor was kept at constant temperature under a flow of He + 1% H_2O, and step changes (e.g., $0 \rightarrow 1000 \rightarrow 0$ ppm or $0 \rightarrow 500 \rightarrow 0$ ppm) of feed NH_3 or NO or NO_2 concentrations were imposed. TRM tests were carried out over diluted catalyst beds at 72 or 140 cm^3/min (STP), corresponding to GHSV = 8600–23,000 h^{-1} if referred to a monolith catalyst. At the end, a temperature ramp (10 °C/min, $T_{end} = 550\,°C$) was run to clean up the catalyst surface. In the TPR runs, a stream containing NH_3 (1000 ppm) and NO_x (1000 ppm, with $NO/NO_x = 1$ or 0.5) with O_2 (0 or 2% v/v) and H_2O (1% v/v) in He was fed to the reactor initially at 150 °C, and then the reactor temperature was linearly increased up to 550 °C at a heating rate of 20 °C/min. Because the purpose of this work was to address the chemistry of the fast SCR reaction (2), many runs were performed in the absence of O_2 so as to eliminate contributions of the standard SCR reaction (1).