



Investigation of NO₂ and NO interaction with an Fe-ZSM-5 catalyst by transient response methods and chemical trapping techniques



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ABSTRACT

We investigate the interaction of both NO₂ and NO with an Fe-ZSM-5 catalyst under oxidative conditions at low temperature. A combination of transient response methods, chemical trapping techniques, and ex situ IR spectroscopy is used to gain insight into the nature of the resulting surface intermediates, which are relevant to the mechanisms of NO oxidation to NO₂ and of the standard NH₃-SCR reactions. For this purpose, three different systems are comparatively studied in various transient runs: (i) a commercial Fe-ZSM-5 catalyst in powder form, (ii) a BaO/Al₂O₃ powder prepared in house, i.e., a well-known NO_x trap, and (iii) a physical mixture of the two compounds. Specifically, the BaO/Al₂O₃-Fe-ZSM-5 mixture is used in an attempt to trap and stabilize reactive and possibly elusive NO_x intermediates formed on Fe-ZSM-5, which might otherwise go undetected. Several important results are obtained, including (i) direct evidence of nitrite formation in the oxidative activation of NO over Fe-ZSM-5; (ii) exclusion of nitrates as primary reaction intermediates in the low-temperature standard SCR reaction; and (iii) evidence for the interaction between nitrites and nitrates adsorbed onto the two component phases of the physical mixture, possibly via the corresponding gas-phase species HONO and HNO₃. On this basis, a low-temperature redox mechanism for NO oxidation over Fe-zeolite catalysts, which fully accounts for the new experimental observations, is proposed and discussed.

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1. Introduction

Emissions regulations for compression- and spark-ignited internal combustion engines are becoming more and more stringent worldwide and, in many cases, it is no longer possible to achieve the limits imposed by international legislation by just improving combustion process technology. These considerations have led the automotive industry to promote intensive research work in order to develop effective after-treatment systems able to meet emission standards for all the main classes of pollutants. Nowadays a significant part of this effort is focused on the design and improvement of after-treatment systems for the control of NO_x emissions from diesel engines. In this area both lean NO_x traps (LNT) and NH₃/urea-selective catalytic reduction (NH₃/urea-SCR) have been successfully demonstrated at the commercial scale. In NH₃-SCR converters, excellent deNO_x performance is achieved over metal-promoted zeolite catalysts thanks to their activity in two main reactions, the standard SCR reaction (NO + O₂ + NH₃) and the fast SCR reaction (NO + NO₂ + NH₃) [1]. In recent years, several studies [1–11] have addressed the SCR catalytic mechanism over

state-of-the-art metal-exchanged zeolites, in order to determine the related intermediates and to conclusively identify the rate-determining step for both reactions. Attention has been focused mostly on the fast SCR mechanism, which is more efficient in the reduction of NO_x at low temperatures. In this case it is generally accepted that the rate-determining step at low temperature is associated with the reduction of surface nitrates to nitrites by NO [5,12].

For the standard SCR chemistry, on the other hand, the situation is more complex and still debated. Historically, a simple sequential scheme has been proposed, wherein NO is first oxidized to NO₂ in a slow rate-determining step; then NO₂ rapidly reacts with additional NO according to fast SCR stoichiometry. Recently, however, multiple experimental results showing inconsistencies between NO oxidation to NO₂ and the standard SCR mechanisms on Fe- and Cu-promoted zeolites have been reported in the literature [13–18]. In particular, it has been shown that under many circumstances there is hardly any correlation between the rate of NO oxidation to NO₂ and the rate of the standard SCR reaction [13,18]. Thus, although it is generally agreed that the standard SCR reaction mechanism is initiated at low temperature by the oxidative activation of NO, the nature of the reactive intermediate generated at this step is still a matter of discussion. At least three different types of

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intermediate have been proposed: nitrates (formal oxidation state $N = +5$) [11,19], nitrosonium ions (NO^+ , formal oxidation state $N = +3$) [10], and nitrites (formal oxidation state $N = +3$) [13]. While in situ FTIR evidence for the formation of both nitrates and NO^+ under SCR reaction conditions has been reported, this is not the case for nitrites. As a matter of fact, nitrites can hardly be detected on zeolites by IR spectroscopic techniques, since their characteristic bands, e.g., at 1260 cm^{-1} , fall into the same absorbance region of the zeolite framework (wavenumbers $< 1300\text{ cm}^{-1}$) [12,20]. Furthermore, nitrites are known to be highly reactive and unstable.

In a preliminary communication, we have recently reported that nitrites formed by NO oxidation at $120\text{ }^\circ\text{C}$ over Fe-ZSM-5 can indeed be detected by trapping them on $\text{BaO}/\text{Al}_2\text{O}_3$ [21]. In this paper we present a new, more extended set of experiments addressing comparatively the interaction of NO_2 and NO with the same Fe-zeolite catalyst in the presence of oxygen. In particular, three different systems are analyzed: (i) an Fe-ZSM-5 commercial catalyst, playing the role of active phase, (ii) a $\text{BaO}/\text{Al}_2\text{O}_3$ prepared in house, acting as a chemical NO_x trap in view of its well-known capability to store stable nitrites and nitrates [24], and (iii) a mechanical mixture of these two compounds. Depending on the system under study, different experiments are performed, including (i) NO_2 adsorption at $120\text{ }^\circ\text{C}$, followed by a temperature ramp (TPD) to analyze the decomposition of the adspecies stored during the isothermal adsorption phase; (ii) NO_2 adsorption at $120\text{ }^\circ\text{C}$, followed by a temperature ramp while feeding NO (TPSR in NO), in order to probe the reactivity of the adsorbed species with NO; (iii) adsorption of $\text{NO} + \text{O}_2$ at $120\text{ }^\circ\text{C}$, followed by TPD; (iv) $\text{NO} + \text{O}_2$ adsorption at $120\text{ }^\circ\text{C}$, followed by TPSR in NH_3 ; and (v) NH_3 adsorption at $120\text{ }^\circ\text{C}$, followed by TPSR in $\text{NO} + \text{O}_2$. In addition, ex situ IR spectroscopy is also applied to conclusively identify the intermediates captured onto both the BaO and the Fe-ZSM-5 phases.

The data collected provide new experimental evidence in favor of the hypothesis that the initial activation of NO proceeds at low temperatures via nitrite adspecies, NO_2^- , acting therefore as intermediates in both NO oxidation to NO_2 [22] and $\text{NO} + \text{NH}_3$ standard SCR reactions [23]. Moreover, they also show that surface nitrates, obtained by NO_2 disproportionation, are not the primary products of the oxidative activation of NO on Fe-promoted zeolite catalysts.

Finally, we propose a low-temperature mechanism of NO oxidation that is consistent with all the experimental results presented herein.

2. Experimental

Three different systems in powder form are analyzed in the present study: a commercial (Zeolyst) Fe-ZSM-5 catalyst (22 mg, Fe loading = 1% w/w, Si/Al = 12), an in-house prepared $\text{BaO}/\text{Al}_2\text{O}_3$ working as a NO_x trap (44 mg, Ba content = 16% w/w), and a mechanical mixture of these two compounds (22 mg + 44 mg). The relative amounts of the two components were selected to ensure a large excess of potential Ba storage sites with respect to the Fe sites. All the powders were diluted up to a total weight of 160 mg with cordierite and then loaded into a quartz flow microreactor.

Additional details regarding the experimental setup and the preparation and characterization of the tested samples can be found in [21].

When loaded into the microreactor, each new sample was conditioned once for 6 h at $600\text{ }^\circ\text{C}$ in a continuous flow of 10% v/v H_2O and 10% O_2 in He. In addition, prior to each run, the samples were pretreated by feeding 8% v/v $\text{O}_2 + \text{He}$ at $550\text{ }^\circ\text{C}$ continuously for 1 h and then also during the cooling-down transient to the test temperature (typically $120\text{ }^\circ\text{C}$). The pretreatment part has been

omitted in the reported results: the data acquisition started ($t = 0$) when the test temperature was reached.

Helium was used as the balance gas in all the microreactor runs. Gases from calibrated $\text{NO} + \text{He}$, $\text{NO}_2 + \text{He}$, $\text{O}_2 + \text{He}$ bottled mixtures were dosed using mass flow controllers (Brooks Instruments), while water vapor was added to the feed stream by means of a saturator operated at controlled temperature. NO and O_2 were fed into the reactor via independent lines and mixed just at the reactor inlet in order to prevent formation of any NO_2 upstream of the catalyst bed. The purity of the $\text{NO} + \text{He}$ mixture was checked by a UV analyzer during preliminary calibrations.

The gas phase experiments consisted of two separate stages involving first an isothermal adsorption, followed by a purge in inert gas (He) at the same temperature; the second stage was a linear temperature ramp up to $550\text{ }^\circ\text{C}$ at $15\text{ }^\circ\text{C}/\text{min}$ with or without the addition of a reagent. In a first set of runs, the adsorption of 500 ppm of NO_2 was performed in the presence of 8% v/v O_2 , followed by temperature-programmed desorption (TPD). In this way the nature of the species stored during NO_2 adsorption and their stability were investigated. In a second type of experiment, after the same NO_2 adsorption phase, the reactivity of the stored species with NO was tested in a temperature-programmed surface reaction (TPSR) run. In this phase 500 ppm of NO was fed into the reactor and, once the concentration profiles reached a stationary condition, the temperature was increased at $15\text{ }^\circ\text{C}/\text{min}$ up to $550\text{ }^\circ\text{C}$. In a third class of experiments, the adsorption of 500 ppm of NO at $120\text{ }^\circ\text{C}$ in the presence of 8% v/v O_2 was performed, followed by a TPD phase involving the release of the adspecies possibly trapped on the $\text{BaO}/\text{Al}_2\text{O}_3$. In a fourth set of experiments, the reactivity of the adspecies stored after 500 ppm $\text{NO} + 8\text{ }^\circ\text{v/v } \text{O}_2$ adsorption at $120\text{ }^\circ\text{C}$ was tested by feeding 500 ppm of NH_3 (TPSR). Finally, additional gas phase experiments were conducted by adsorbing 500 ppm of NH_3 at $120\text{ }^\circ\text{C}$ and observing its reactivity with 500 ppm of NO and 8% v/v O_2 during a TPSR test.

FTIR analysis was performed ex situ, unloading the powders from the microreactor after the isothermal adsorption of either NO_2 or $\text{NO} + \text{O}_2$. In particular, for the mechanical mixture, different particle sizes were used for its two components (90 μm for the Fe-ZSM-5 and 115 μm for the $\text{BaO}/\text{Al}_2\text{O}_3$) to enable their separation by sieving. Furthermore, no cordierite was added for dilution in these cases. The choice of the mesh sizes for the two components was the result of optimization of the sieving process. The separation efficiency of the sieving operation was eventually confirmed by the IR results: in fact, residual Fe-ZSM-5 powders in the $\text{BaO}/\text{Al}_2\text{O}_3$ samples, if present in significant amounts, would be easily recognized during the IR analysis by the typical T–O–T vibration features of the zeolite below 1000 cm^{-1} , which were not detected, however. Additional details on the ex situ FTIR measurements are provided in [21].

3. Results and discussion

3.1. Catalytic activity in standard SCR

Fig. 1 compares standard SCR steady-state activity runs over Fe-ZSM-5 and over the mechanical mixture of Fe-ZSM-5 and $\text{BaO}/\text{Al}_2\text{O}_3$. From Fig. 1 it is evident that the Fe-ZSM-5 sample exhibits the typical NH_3 SCR activity of Fe-zeolites [1,5], and that the presence of BaO did not affect the original catalytic performance of Fe-ZSM-5. This preliminary test therefore confirms the feasibility of running reactivity experiments over the mechanical mixture to gain insight into the interactions between NO or NO_2 and the Fe-zeolite catalysts under representative SCR conditions.

It may be worth pointing out also that the good standard SCR activity exhibited by both the Fe-ZSM-5-containing phases in

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