



The low-temperature interaction of $\text{NH}_3/\text{NO}/\text{NO}_2 + \text{O}_2$ with Fe-ZSM-5 + BaO/ Al_2O_3 and H-ZSM-5 + BaO/ Al_2O_3 : Influence of phase separation and relevance for the NH_3 -SCR chemistry



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ABSTRACT

In an effort to elucidate mechanism and intermediates of Standard SCR over metal-zeolite catalysts, we apply Transient Response Methods (TRM) to identify the mediating species in the low-temperature (120°C) interaction of $\text{NO}_2 + \text{O}_2$, $\text{NO} + \text{O}_2$ and $\text{NO} + \text{NO}_2 + \text{O}_2$ ($\text{NO}/\text{NO}_2 = 10/1$ v/v) with a composite Fe-ZSM-5 (Fe = 1% w/w) + BaO/ Al_2O_3 system in different configurations (physical mixture versus double-bed), corresponding to different degrees of separation of the two component phases. The results clearly indicate for the first time that the strong interaction between the two system components, already demonstrated in previous work, survives their complete segregation, proceeds via the gas phase, and is mediated by stable gaseous NOx species. The nature of the NOx species trapped on the BaO phase is identified by TPD experiments: in line with previous data, they include primarily nitrates for NO_2 adsorption, and nitrites for $\text{NO} + \text{O}_2$ adsorption at short exposure times. A new, striking finding is that formation of nitrites on BaO upon exposure of Fe-ZSM-5 + BaO/ Al_2O_3 to $\text{NO} + \text{O}_2$, which involves the oxidative activation of NO on Fe-sites, is fully equivalent to the formation of nitrites observed upon exposing only BaO/ Al_2O_3 to NO_2 in excess NO. This suggests that NO_2 (possibly in the form of N_2O_3) may play the role of mediating gas-phase species generated by the oxidative activation of NO on Fe centers. The reactivity with NH_3 of nitrites trapped on BaO is probed by Temperature Programmed Surface Reaction (NH_3 -TPSR) runs, which show rapid dinitrogen formation from low temperatures when Fe-ZSM-5 is not only mixed with, but also placed downstream from BaO/ Al_2O_3 , thus confirming the stability of the NOx intermediate formed on Fe-centers, and linking it to the Standard SCR reactivity. Finally, in order to study the role of the metal redox sites in the reactivity of nitrites stored on BaO with ammonia, we compare NH_3 -TPSR experiments over a Fe-ZSM-5 catalyst and over a parent H-ZSM-5 zeolite with a drastically reduced Fe content (Fe \cong 0.02% w/w). Results show that nitrites on BaO react with NH_3 to dinitrogen equally well on Fe- and on H-ZSM-5, which questions the role of the metal sites and therefore of the oxidative activation of NH_3 in such a step.

The present data emphasize the bifunctional (redox + acid) nature of the NH_3 -SCR catalytic chemistry at low temperatures, and should be considered in the development of comprehensive mechanisms for the Standard SCR reaction over Fe-zeolite catalysts.

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1. Introduction

Emissions regulations for both compression and spark-ignited internal combustion engines are becoming more stringent worldwide, as it is no longer possible to achieve the limits imposed by international legislation by just improving the combustion technology. For lean burn Diesel engines, in particular, the NH_3 /Urea-Selective Catalytic Reduction process (NH_3 /Urea-SCR)

has been successfully demonstrated at the commercial scale and currently represents the best available technology for NOx abatement. In NH_3 -SCR converters, excellent deNOx performances are attained over metal-promoted zeolite catalysts thanks to their high activity in two main reactions, namely the Standard SCR reaction ($\text{NO} + \text{O}_2 + \text{NH}_3$) and the Fast SCR reaction ($\text{NO} + \text{NO}_2 + \text{NH}_3$) [1].

The elucidation of the SCR catalytic mechanisms over state-of-the-art metal-exchanged zeolites has been a central research topic in recent years [1–16] but, particularly for what concerns the Standard SCR reaction, a comprehensive and satisfactory account is still lacking. In recent publications we have investigated the $\text{NO} + \text{O}_2$ adsorption on physical mixtures of metal (Fe and Cu) promoted zeo-

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lites and BaO/Al₂O₃ [12–14], with the aim of providing new insight in the catalytic chemistry of the low-temperature Standard SCR. In these works, we succeeded in trapping onto the BaO/Al₂O₃ phase unstable nitrites generated by the oxidative activation of NO on the metal-zeolite catalyst, and we speculated on the possible existence of a gas-phase pathway responsible for the observed interaction between the two physical mixture components. Nitrites storage on BaO was demonstrated in several ways, including: (i) their thermal decomposition to an equimolar mixture of NO and NO₂ during TPD, (ii) N₂ formation during their reaction with NH₃ at low temperature, (iii) ex-situ IR analysis of the BaO/Al₂O₃ phase after unloading and separation from the mechanical mixture.

In the present work, we further investigate the interaction of NO_x + O₂ with composite Fe-ZSM-5 + BaO/Al₂O₃ systems on the basis of a completely new set of data, with the dual goal of clarifying whether such an interaction proceeds indeed via gas phase, and of identifying the involved mediating species. To this purpose, herein we analyze the effect of phase segregation on the synergy between the two component phases. In particular, we have focused on the following configurations: (i) mechanical mixture with the two phases in loose contact; (ii) sequential segregated beds, where the two components (positioned in different orders) are separated by an inert quartz wool layer; (iii) single constituents of the mixture, individually tested.

The pathway leading to the trapping of nitrites on BaO is clearly relevant for the NO activation step in the Standard SCR chemistry, as discussed in the following paragraphs. To complete the analysis of the Standard SCR mechanism, herein we also investigate the subsequent reactivity of nitrites with NH₃, and perform dedicated experiments on H-ZSM-5 to clarify the role of redox Fe centers in this second stage of the mechanism.

Altogether, the present experimental results are significant for the elucidation of the Standard SCR reaction chemistry over Fe-promoted zeolites, provide new elements for the development of a comprehensive SCR mechanism, and may be useful to discriminate rival mechanistic proposals.

2. Experimental

In this study, different systems comprising a Fe-ZSM-5 zeolite (22 mg), an H-ZSM-5 zeolite (22 mg) and in-house prepared BaO/Al₂O₃ (44 mg), all in form of powders, were tested in different spatial arrangements. The Fe-ZSM-5 was a commercial catalyst manufactured by Zeolyst (CP 7117), with a SiO₂/Al₂O₃ ratio of 24, surface area of 300 m²/g and 1% w/w Fe content. The H-ZSM-5 sample was a commercial material manufactured by Zeolyst (CBV 2314), with a SiO₂/Al₂O₃ ratio of 23, surface area of 425 m²/g and 0.05% w/w Na₂O content. ICP-MS analysis revealed a residual Fe content of 0.0235% w/w, i.e. significantly lower (over 40 times) with respect to the Fe-exchanged catalyst. Both zeolite powders were dried at 120 °C for 1 h and sieved to 120–140 mesh (average particle size = 115 μm). The BaO/Al₂O₃ component (Ba content = 16% w/w) was prepared in-house by incipient wetness impregnation, using aqueous solutions of Ba(CH₃COO)₂ (Sigma Aldrich, 99% pure) to impregnate the γ-alumina support (Versal 250 from Eurosupport: surface area = 200 m²/g and pore volume = 1.2 cm³/g) calcined at 800 °C. After impregnation, the powder was dried at 80 °C overnight, calcined at 500 °C for 5 h, and sieved to 140–200 mesh (average particle size = 90 μm). Cordierite with 120–140 mesh size was added for dilution. In all runs, the powders were loaded in a quartz microflow reactor (ID = 7 mm). The following configurations have been tested: (i) a physical mixture of Fe-ZSM-5 and BaO/Al₂O₃ powders (identified in the following as Fe-Ba-MM) with the two phases in loose contact and a total dilution with cordierite up to 120 mg; (ii) a double-bed configuration with Fe-ZSM-5 first,

followed by a BaO/Al₂O₃ layer (identified in the following as Fe-Ba-DB); (iii) reverse double-bed configurations with BaO/Al₂O₃ first, followed by a layer of either Fe-ZSM-5 or H-ZSM-5 (identified in the following as Ba-Fe-DB or Ba-Z-DB, respectively). In the double-bed configurations, the two phases were completely separated by a quartz wool plug, and each layer was diluted with cordierite up to 60 mg. For completeness, the three components (Fe-ZSM-5, BaO/Al₂O₃ and H-ZSM-5) were also tested individually after dilution up to a total bed load of 120 mg.

Before running any test, each new sample was conditioned once for 5 h at 600 °C in a continuous flow of 10% v/v H₂O and 10% v/v O₂ in He. Moreover, prior to every experiment the powders were pre-treated feeding 8% v/v O₂ + He at 550 °C continuously for 1 h and then also during the cool-down transient to the test temperature (120 °C). For brevity, illustration of the pre-treatment process is omitted in the results shown here: the data acquisition started (t = 0) when the desired test temperature was reached. The feed mixture to the reactor was composed from calibrated NO + He, NO₂ + He, NH₃ + He, O₂ + He mixtures in gas bottles using several mass flow controllers (Brooks Instruments). In particular, NO and O₂ were fed to the reactor via independent lines and mixed just before the reactor inlet, in order to prevent formation of NO₂ upstream of the catalyst bed. The purity of the mixtures was checked by a UV analyzer during preliminary calibrations. The gas species concentrations at the reactor outlet were analyzed by a quadrupole mass spectrometer (Balzers QMS 200) and a UV analyzer (ABB LIMAS 11 HW) arranged in a parallel configuration or, in an upgraded alternative set-up, using a new quadrupole mass spectrometer (Hiden Analytical QGA), which granted significant reduction of the signal noise. Cross-check experiments gave however essentially identical results in the two rigs.

The experimental protocol herein adopted is similar to the one described and validated in our previous works [12–14]. In general, three different types of transient gas-phase experiments were performed: (i) isothermal adsorption of a mixture of NO + O₂, or NO₂ + O₂ or NO + NO₂ + O₂, followed by Temperature Programmed Desorption (TPD) in He; (ii) isothermal adsorption of the same gas mixtures followed by Temperature Programmed Surface Reaction (TPSR) with NH₃; (iii) isothermal adsorption of NH₃ followed by Temperature Programmed Surface Reaction (TPSR) with NO + NO₂. Unless otherwise indicated, all the tests were run with an overall volumetric flow rate of 120 cm³/min (STP) at an adsorption temperature of 120 °C under dry conditions. Our previous works, in fact, pointed out a strong negative impact of H₂O on the amount of NO_x trapped on BaO due to its inhibitory action both on the NO oxidation activity of Fe-ZSM-5 [4], as also well known in the literature, and on the nitrites storage on BaO, documented e.g. by a dedicated experiment in [13]. Additional details regarding the experimental set-up and procedures, as well as the preparation and the characterization of the tested samples, can be found in [12–14].

3. Results and discussion

3.1. NO₂ + O₂ adsorption/TPD tests

In the isothermal adsorption phases, not shown here for brevity, 500 ppm of NO₂, 8% O₂ and balance He were fed to the reactor until saturation at 120 °C. Fig. 1A shows the thermal decomposition (TPD) profiles of the NO_x species stored on the investigated composite systems, namely Fe-Ba-MM, Fe-Ba-DB, and Ba-Fe-DB. For comparison, the results obtained in previous work [13] on the individually tested component phases are also displayed in Fig. 1B.

For all the three combined systems, Fig. 1A shows that the adsorbed NO_x species decompose mainly to NO₂, as expected in the case of nitrates storage [13,14]. The formation of stable nitrates

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