

NO oxidation on Fe- and Cu-zeolites mixed with BaO/Al₂O₃: relevance for the NH₃-SCR mechanism at low temperature.

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Highlights

- NO oxidation and Standard SCR mechanisms investigated by Chemical Trapping
- Relationship between NO oxidative activation and Standard SCR rate is studied
- Free oxidation regime allows to evaluate true intrinsic kinetic of NO oxidation
- NO₂ inhibition of NO oxidation complicates kinetic parameters estimation

1. Introduction

Fe- and Cu-promoted zeolites are excellent catalysts for the abatement of NO_x emissions from Diesel vehicles according to the NH₃/Urea-Selective Catalytic Reduction (SCR) technology. In particular, their cold start performance is crucial in order to comply with the current NO_x emission limits, but the catalytic mechanism governing the low-T SCR activity is still controversial.

There is now general consensus that oxidative activation of NO, i.e. the primary component of the NO_x mixture in the engine exhausts, is a key step in the low-T mechanism of Standard SCR [1-2]. However, a comprehensive and satisfactory account for the Standard SCR reaction mechanism is still lacking.

In the present work, we use chemical trapping techniques [3] to investigate the dynamics of NO oxidative activation at low-T on metal promoted zeolites + BaO/Al₂O₃ combined systems. Results reveal important differences between the steady-state NO oxidation rate and the initial rate of NO oxidative activation, which may be relevant both to estimate true intrinsic kinetic rates for NO oxidation and to improve our understanding of the Standard SCR catalytic mechanism. These findings may pave the way for the development of a chemically consistent kinetic scheme necessary to improve the mathematical simulation tools used for the optimization of commercial NH₃-SCR systems.

2. Methods

The dynamics of NO oxidative activation were investigated by chemical trapping experiments over metal promoted zeolites (Fe-ZSM-5 or Cu-CHA) + BaO/Al₂O₃ combined systems. In particular, the following spatial configurations have been tested: i) a physical mixture of Fe-ZSM-5 (22 mg) or Cu-CHA (16 mg) and BaO/Al₂O₃ (44 mg) powders with the two phases in loose contact; ii) a double-bed configuration with Fe-ZSM-5 (22 mg) upstream, followed by a BaO/Al₂O₃ (44 mg) layer; iii) the individual catalysts (Fe-ZSM-5 or Cu-CHA).

Two different types of transient experiments were performed at different temperatures (120°C-250°C): i) stepwise addition of 2% O₂ in a continuous flow of 500 ppm of NO on pre-reduced samples; ii) stepwise addition of 2% O₂ in a continuous flow of 500 ppm of NO on pre-reduced samples previously saturated with NH₃. All the tests were run under dry conditions, to avoid H₂O negative impact on the amount of NO_x trapped on BaO [3]. In all runs the product gas mixture was analyzed by a MS and a UV analyzer [3].

3. Results and discussion

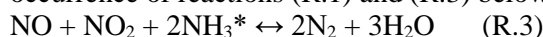
Figure 1 shows the effect of O₂ step feed during NO isothermal adsorption (150 °C) on three different catalytic systems. In the case of Fe-ZSM-5 alone (thin lines), as soon as O₂ is introduced, NO is consumed to produce NO₂, according to the well-known NO oxidation reaction (R1). The system rapidly reaches a steady-state situation in which about 50 ppm of NO₂ are formed. If a layer of BaO/Al₂O₃ is added after the Fe-zeolite layer (solid lines) in a double-bed segregated configuration, an apparently different behavior is

noticed: NO reaches a first steady state concentration which is exactly twice the NO consumption registered in the following steady state, i.e. the same of the Fe-zeolite only case. This is in line with nitrites storage on BaO/Al₂O₃ according to the reactions R1 and R2 below:



If Fe-ZSM-5 is combined with BaO/Al₂O₃ in a physical mixture (dotted lines), however, a peculiar transient is observed. Indeed, in this case, the NO concentration shows a dip of 200 ppm, i.e. significantly more pronounced than for steady state oxidation and in the double bed case. Apparently, by mixing the two phases, it is possible to trap NO₂ as soon as it is formed, promoting a “free oxidation” regime, wherein the oxidation activity is not kinetically hindered by the presence of its products or by other inhibition phenomena, as happens instead in the steady-state case.

If the same experiment is repeated over Fe-ZSM-5 after preadsorbing ammonia (dashed lines), the results are surprisingly in line with those recorded on the Fe-ZSM-5 + BaO/Al₂O₃ physical mixture configuration: the NO outlet concentration profile shows a significant dip, with a mirror evolution of N₂, in line with the occurrence of reactions (R.1) and (R.3) below:



Similar dynamics are observed also on Cu-CHA based combined systems (not shown). Thus, adsorbed NH₃ apparently plays exactly the same role of the BaO-based NO_x trap material in the physical mixture. Under SCR reaction conditions the products of the NO oxidative activation readily react with the adsorbed NH₃ to give N₂ and H₂O via ammonium nitrite decomposition: like in the chemical trapping runs, this prevents buildup of NO₂ in the gas phase and thus promotes an initially enhanced rate of NO oxidative activation. In principle, this indicates that, in the presence of NH₃, NO oxidation is significantly faster than normally measured in steady-state NO oxidation experiments, thus being potentially able to sustain the observed Standard SCR reaction rates.

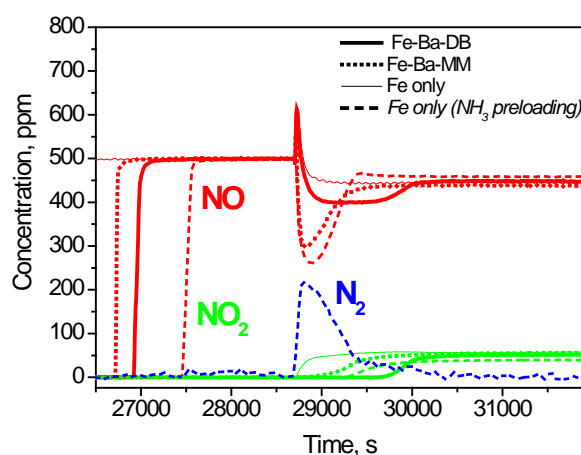


Figure 1. O₂ step feed during NO isothermal adsorption (T=150°C; NO=500 ppm; O₂=2%) on Fe-ZSM-5+BaO/Al₂O₃ double bed (solid lines); Fe-ZSM-5+BaO/Al₂O₃ mechanical mixture (dotted lines), on Fe-ZSM-5 only (thin lines) and on Fe-ZSM-5 only preloading NH₃ (dashed lines).

4. Conclusions

We have shown that in physical mixtures comprising a metal-promoted zeolite catalyst and a NO_x storage material (BaO/Al₂O₃), the low temperature oxidative activation of NO is greatly enhanced as long as BaO can efficiently remove the inhibiting NO oxidation products (such as NO₂) from the gas phase, storing them in the form of Ba nitrites. The very same behavior is observed when the NO_x storage phase (BaO/Al₂O₃) is replaced by ammonia preadsorbed on the metal zeolite: in this case the gaseous NO oxidation products are likewise effectively removed from the gas phase, being rapidly converted to dinitrogen. This suggests that in Standard SCR conditions the real NO oxidation activity of metal promoted zeolite catalysts can be much higher than expected from steady-state NO oxidation test. A kinetic analysis of these data allows therefore to estimate the true intrinsic rate of NO oxidation, as required for the development of chemically consistent kinetic models of NH₃-SCR systems.

References

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Keywords

“NH₃-SCR”, “Standard SCR”, “NO oxidation”, “NO₂ inhibition”