Investigation of the standard SCR reaction mechanism at low T by chemical trapping techniques

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Introduction

The catalytic mechanism governing the low-T Standard SCR performances is still debated and different hypotheses about the nature of reaction intermediates have been suggested. While "adsorbed NO_2 " is favored by several authors [1-3], we have recently presented [4, 5] an alternative pathway wherein NO is first oxidized to HONO/nitrites which then decompose to NO_2 in the absence of NH_3 . Instead, when ammonia is present its reaction with nitrites leads to N_2 via formation/decomposition of unstable NH_4NO_2 .

In the present work we apply chemical trapping techniques, combined with both gas-phase transient response methods (TRM) and ex situ IR spectroscopy, to conclusively identify the products of the NO oxidative activation over Fe- and Cu-zeolites catalysts.

Materials and Methods

Transient NO+O₂ and NO₂ adsorption runs were performed at 120°C on a mechanical mixture of Fe- or Cu-zeolite (22 mg) + BaO/Al₂O₃ (44 mg) powders as well as on its individual components. In this way reaction intermediates resulting from NO activation over Fe or Cu and from NO₂ adsorption may be captured onto BaO, a well-known NOx trap. The trapped intermediates were then identified by i) analyzing their thermal decomposition products by TPD runs; ii) probing their reactivity with NH₃; iii) ex situ FTIR analysis of the BaO/Al₂O₃ phase unloaded and separated from the test reactor mixture.

Results and Discussion

In Figure 1A, TPD profiles obtained on the Fe-containing mixture (and related individual systems) after isothermal adsorption of NO_2 at 120°C are compared. Decomposition peaks are very different for the Fe zeolite and Ba components due to higher storage capacity and stability of nitrates species on the latter. Moreover, an interaction between the two components of the mechanical mixture is evident, resulting in an intermediate desorption peak temperature. This is in line with the assumption of gas phase equilibrium between adsorbed nitrates and nitric acid in gas phase; on increasing the temperature, the equilibrium between barium nitrates and HNO₃ is pushed towards the gas phase and the released nitric acid can then react on Fe, left empty by ferric nitrates decomposition that takes place at lower T.

TPD decomposition profiles after NO+O₂ adsorption at 120°C for mech. mixture (and related individual phases) have been collected as well. Since negligible storage is observed on the individual components, only the TPD profile for the mechanical mixture is displayed in Figure 1B. Notably,t NO and NO₂ are desorbed in equimolar amounts with a maximum at 200°C. Accordingly, our data suggest initial formation of nitrites (on Fe-sites) in equilibrium with gas-phase HONO, which leads then to the formation of more stable nitrites on BaO. Thermal decomposition of Ba(NO₂)₂ explains in fact the equimolar release of NO+NO₂ in the TPD of Figure 1B. Nitrites storage on the BaO phase was also confirmed by their reactivity with NH₃ at 120°C, a temperature at which nitrates are known to be not reactive, and by ex situ IR spectroscopy, which clearly showed the presence of Ba-nitrites along with some nitrates. Also,

the completely different decomposition profiles and the reactivity of the trapped nitrites with NH_3 to give Standard SCR products (N_2 and H_2O) at 120°C rule out "adsorbed NO_2 "/nitrates as intermediates in the oxidative activation of NO.



Figure 1. TPD decomposition profiles after adsorption at 120°C of A) NO₂ B) NO+O₂ on the Fe zeolite+BaO/Al₂O₃ mechanical mixture and individual components (only A). T=120-550 °C; heating rate=15K/min

In agreement with these and other findings we propose the following mechanism for NO oxidation to NO_2 on Fe zeolites:

$Fe^{3+}OH + NO \leftrightarrow Fe^{2+} + HONO$		R.1
$Fe^{3+}OH + HONO \leftrightarrow Fe^{3+}ONO + H_2O$		R.2
$Fe^{3+}ONO \rightarrow Fe^{2+} + NO_2$	rds	R.3
$2Fe^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe^{3+}OH$		R.4

The Standard SCR mechanism over Fe-zeolites shares the same initial step R.1 above. In the presence of NH₃, however, HONO is intercepted according to

 $HONO + Z - ONH_4 \rightarrow N_2 + 2H_2O + Z - OH$ R.5

and the reoxidation step R.4 becomes rate determining.

Similar results will be presented and discussed for a Cu-zeolite catalyst.

Significance

For the first time direct experimental evidence of HONO/nitrites (not NO_2) being the products of the NO oxidative activation over Fe- and Cu- zeolites is reported. Evidence of nitrites/HONO and of nitrates/HNO₃ equilibria is also revealed. Such results are highly relevant for the identification of the Standard SCR reaction mechanism at low temperatures. **References**

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