

The NO-N₂O-SCR reaction: a catalytic and spectroscopic investigation

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Nitric acid is one of the most produced commodity chemicals worldwide. However, since its production is accompanied with the formation of nitrogen oxides (NO + NO₂) and N₂O, catalytic abatement of the flue gases is necessary. Irrespective of the exhaust after-treatment approach, NO_x abatement by means of the selective catalytic reduction (SCR) reaction takes place always in the presence of N₂O. Yet, while the individual abatement technologies of NO_x and N₂O received tremendous scientific attention, their concomitant abatement under SCR conditions was far less studied [1]. In order to bridge the gap, we started to investigate the effect of N₂O on the SCR reaction over a commercial Fe-FER catalyst by combining catalytic and transient spectroscopic experiments.

Under NO-N₂O-SCR conditions, the NO_x conversion was enhanced above 300 °C in presence of N₂O. In the complementary N₂O decomposition test, the onset of the N₂O effect appeared when also N₂O started being decomposed, thus suggesting the onset of its reactivity. Time-resolved XANES spectra recorded at the Fe K-edge, showed a shift of the absorption edge towards higher energy and an increase of the white line intensity upon N₂O introduction in NO-SCR feed. After phase sensitive detection (PSD) [2], the phase-resolved spectra showed an increased contribution of the pre-edge associated with Fe³⁺ species (7115 eV) at the expense of Fe²⁺ (7112 eV). These results indicate that in the presence of N₂O the oxidation state of the Fe sites moves towards a higher average oxidation state. Phase-resolved DRIFT spectra obtained in identical conditions revealed the formation of Fe³⁺-O sites and simultaneous consumption of NO adsorbed on Fe²⁺ during N₂O addition. Enhanced consumption of bulk-NH₃ adsorbed on Brønsted sites also occurred, but was delayed compared to the changes associated with the Fe²⁺-NO and Fe³⁺-O signals. MS revealed a transient NO conversion activity upon N₂O addition. Moreover, according to additional XANES and DRIFT tests, and previous investigations [3], we believe the presence of two different Fe²⁺ sites within the Fe-FER catalyst under investigation. The majority devoted to adsorption and reaction of NO. Differently, a minor fraction (Fe_{*}²⁺), dedicated to activation of N₂O and successive formation of Fe³⁺-O sites.

The combination of the catalytic activity data of the effect of N₂O on NO-SCR with spectroscopic data of the effect of N₂O on Fe oxidation state and of the nature of adsorbed species enables us to propose the following rationale. 1) N₂O adsorption on Fe_{*}²⁺ sites, 2) Fe_{*}³⁺-O formation coupled with N₂ production, 3) migration of the deposited O atom towards Fe²⁺-NO sites coupled with Fe_{*}³⁺/Fe_{*}²⁺ transition 3) NO oxidation towards an oxidized intermediate 4) NH₃ transfer from nearby Brønsted acid sites leading to N₂ and H₂O production and thus, enhanced NO_x conversion. Finally, this latter process is rate-limiting under stoichiometric NH₃ conditions and hinders higher NO_x conversion

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