

DRIFT in-situ study of the NO oxidation and Standard SCR reactions on a Cu-CHA commercial catalyst

M. P. Ruggeri¹, I. Nova¹, E. Tronconi^{1*}

¹Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

J. A. Pihl², T. J. Toops², W. P. Partridge²

²Fuel, Engines and Environment Research Center, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 37831, USA

*corresponding author: enrico.tronconi@polimi.it

Introduction

NO_x emission regulations for diesel vehicles have driven the development of efficient aftertreatment techniques, such as NH₃ Selective Catalytic Reduction (SCR) technology. In this context, the elucidation of reaction mechanisms and related fundamental implications has gained crucial importance for the design of improved catalysts, as well as for the development of more reliable mathematical simulation tools, based on detailed microkinetic models. Furthermore, recent controversial debates on the Standard SCR reaction mechanism over metal exchanged zeolites have raised a great interest in dedicated mechanistic studies. In alternative to other mechanistic proposals, some of us recently suggested [1] a key role of nitrite-related species as common reaction intermediates for Standard SCR and NO oxidation. Direct evidence about the nature and role of such nitrite-like species was obtained on a Fe-zeolite catalyst by chemical trapping techniques [2]. In this respect, in-situ DRIFT studies can provide valuable information on surface species dynamics and reaction mechanism.

We herein present an in-situ DRIFT study on a Cu-CHA commercial catalyst, aimed at clarifying the mechanisms of both Standard SCR and NO oxidation to NO₂ and their relationships, with the aim of formulating coherent detailed mechanisms for both reactions.

Materials and Methods

DRIFT in-situ measurements were carried out on a slab cut from a commercial Cu-CHA washcoated monolith. NO_x adsorption experiments (w/ or w/o gaseous O₂) were run on pre-reduced/pre-oxidized catalyst samples, also with pre-adsorbed NH₃, focusing in the low temperature region (120-200 °C) due to the main interest in understanding the low temperature NH₃-SCR mechanism. Each DRIFT spectrum was collected by averaging 8 scans with a 2 cm⁻¹ resolution: this ensured a high temporal resolution when following the surface species dynamics, while maintaining a reasonable signal-to-noise ratio. In the case of runs with pre-adsorbed NH₃, DRIFT measurements were coupled with gas phase analysis using a mass spectrometer to monitor N₂ formation.

Results and Discussion

The results of NO/NO+O₂/NO₂ adsorption at 120 °C on a pre-oxidized catalyst evidenced the formation of NO⁺ and nitrates (bands at 2190-2135 cm⁻¹ and 1620-1590-1570 cm⁻¹ respectively in **Figure 1**) as dominant adspecies. However, different dynamic behaviors prevail depending on the species present in the gas phase (NO₂, NO + O₂, NO on a pre-oxidized catalyst). In particular, as shown in **Figure 1b**, during NO/NO + O₂ adsorption

nitrates (N oxidation state + 5) are formed subsequently to NO⁺ (N oxidation state +3), resulting from the interaction of NO with a Cu²⁺ ion to form an adsorbed NO⁺ species [3]. On the contrary, such species are formed simultaneously upon NO₂ adsorption. The red-ox nature of the oxidative activation of NO to NO⁺ and nitrates was also clearly demonstrated, since such species were not observed upon NO adsorption on the pre-reduced sample but were formed on the pre-oxidized one, implying that oxygen reacts directly from the catalyst.

Based on these results, a mechanistic proposal for NO oxidation to NO₂ and nitrates over Cu-CHA was formulated accounting for the observed initial formation of NO⁺ (see **Figure 1**) which, having an oxidation state of + 3 can be considered a nitrite-like species and is identified as the key intermediate in the NO oxidation reaction to NO₂ [1-3]. Concerning the Standard SCR mechanism, DRIFT experiments of NO + O₂ reactivity with pre-adsorbed NH₃ showed that as soon as NO + O₂ is fed to the catalyst, the stored NH₃ is depleted from the catalyst surface; concurrently, gas phase N₂ evolution is observed. Formation of nitrates was detected only once the pre-adsorbed NH₃ was totally removed from the catalyst. These and other observations point out that NO₂ (N oxidation state +4) is not necessarily an intermediate in the process of N₂ formation from NO via Standard SCR. Accordingly, a mechanistic proposal involving nitrite-related species as

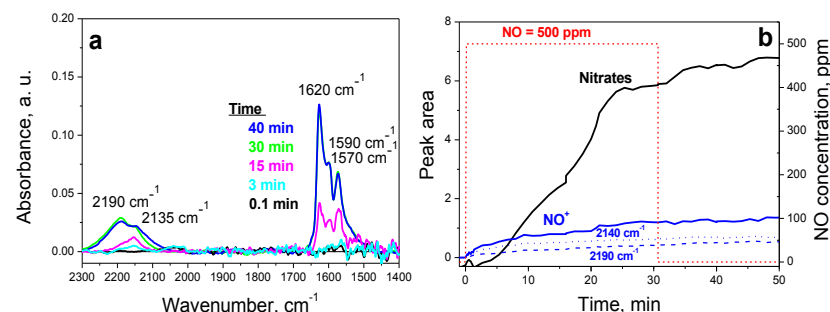


Figure 1. a) IR spectra during NO adsorption at 120°C on a pre-oxidized catalyst, no O₂ in the gas phase; b) Peak area dynamics.

reaction intermediates is formulated for this reaction, too.

Significance

A systematic in-situ DRIFT investigation of NO oxidation and Standard SCR on a commercial Cu-CHA catalyst reveals that the oxidative activation of NO to NO⁺, i.e. a nitrite-like adspecies, could be the common initial step in the mechanisms of both reactions at low T.

References

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