



## Nitrates and nitrous oxide formation during the interaction of nitrogen oxides with Cu-ZSM-5 at low temperature

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### ABSTRACT

The interaction of NO with Cu-ZSM-5 has been investigated in a temperature range (25–225 °C) in which no steady-state reactions occur. The study has been conducted by performing adsorption tests at variable exposure times and analysing the phenomena that occur by continuous monitoring of the gaseous effluents as well as by performing a subsequent TPD. The effect of temperature, catalyst pre-treatment and composition of the adsorbing mixture (NO/He, NO/O<sub>2</sub>/He, N<sub>2</sub>O/He and N<sub>2</sub>/He) have been evaluated. In situ FTIR experiments have been also carried out under similar conditions.

The main observed phenomena are: (i) reduced Cu<sup>+</sup> sites are quickly re-oxidized by NO producing large amounts of N<sub>2</sub>O; (ii) adsorbed NO slowly reacts with gaseous NO to give surface nitrates and still N<sub>2</sub>O in the gas phase regardless the copper oxidation state. A mechanism of copper re-oxidation and nitrates formation under the different conditions explored has been proposed on the basis of these findings.

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### 1. Introduction

Since the discovery by Iwamoto of the unique catalytic properties in DeNOx reactions [1–3], the copper exchanged ZSM-5 received a great attention by the scientific community, resulting in a huge number of papers published in international journals of several disciplines (catalysis, chemistry, physics and chemical and material engineering). The interest towards this material is related to the possible application in several DeNOx reactions, ranging from the SCR of NO with hydrocarbons [4] to the decomposition of nitrous oxide [5] but also to the classical SCR with ammonia or urea [6–8] since Cu-ZSM-5 is able to activate this process at relatively low temperature [9]. Actually, Cu-zeolites have been recently proposed as an alternative to the traditional V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> catalysts for SCR applied to exhaust after-treatment from lean diesel engines due to their higher thermal stability compared to titania based materials [10–12]. However, the great interest towards Cu-ZSM-5 was mostly addressed to the incomparable properties in the direct decomposition of nitric oxide, which has represented for a long time the most desirable DeNOx process. Cu-ZSM-5

basically represents the only catalyst effective for this reaction at a reasonable temperature range (400–500 °C), while no other similar formulation of catalyst (copper over other zeolites or mesoporous materials, or ZSM-5 exchanged with other transition metals) exhibits a detectable activity in NO decomposition [13,14].

Performances of the Cu-ZSM-5 in these processes are due to a series of peculiar properties of such a material joined with singular features in the interaction with nitrogen oxides.

One of the major characteristics of the system is the redox property of the exchanged copper that plays a very important role in the DeNOx reaction. It is accepted that Cu<sup>+</sup> is the active site for the decomposition of NO [14,15] even if some authors proposed different hypotheses too [13]; however, the formation of the reduced site in an oxidizing atmosphere is still a debated question. The copper “self-reduction” occurring at high temperature (>400 °C) has been often invoked, but this does not explain the unique behaviour of Cu-ZSM-5; this phenomenon has been observed also for other similar catalysts, that do not show the same DeNOx properties. More recently, the concept that copper reduction during the catalysis cycle occurs via nitrate species formation and subsequent decomposition with the formation of Cu<sup>+</sup> sites has been also reported [16,17].

On the other hand, in SCR processes over Cu-ZSM-5 the oxidation of NO to NO<sub>2</sub> is considered a key step [18]; this hypothesis is being further supported by the observation that SCR takes place

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much faster with an equimolar mixture of NO and NO<sub>2</sub> [6]. Generally speaking, the formation of nitrate-like species over Cu sites seems to be necessary in reduction processes towards N<sub>2</sub>.

Nitrates formation has also been observed in another singular phenomenon occurring on Cu-ZSM-5, namely the induction of a self-sustained and spontaneous N<sub>2</sub>O decomposition with oscillatory rate [5,20,21], whose nature is purely kinetic, namely attributable to the reaction mechanism. Fanson et al. [20] have proven that the concentration of nitrate species on the catalyst also follows an oscillatory pattern during oscillations of N<sub>2</sub>O conversion, so as to propose a mechanism that attributes a key role to nitrates formation and decomposition in the arising of oscillations.

Indeed, the formation of nitrate species during the interaction of NO with Cu-ZSM-5 has been demonstrated by several authors [2,15,22–24]. FTIR spectra [16,17] clearly show the presence of these species, both bidentate and chelating ones that are formed over copper sites with a ratio depending on the concentration of copper pairs. The interaction of bridged nitrates stabilized on copper cations with methane was demonstrated by Sadykov et al. [25], while Li and Guan [26] concluded that nitrate species are the main reaction intermediates in propane SCR. In addition, Solans-Monfort et al. [27] reported that the reduction of copper during the catalysis cycle of NO decomposition occurs via nitrate formation and subsequent decomposition with formation of Cu<sup>+</sup>. Concerning the direct decomposition of NO, further confirmations arrive from Konduru and Chuang [16], who determined the sequence of adsorbate formation during NO adsorption and asserted that Cu<sup>+</sup>(NO) initiates the reaction network that includes Cu<sup>2+</sup>(NO<sub>3</sub><sup>-</sup>) formation and decomposition (nitrates decomposition generates the active sites).

The mechanisms of formation and decomposition of such nitrate species are still under investigation. Olsson et al. [28] observed that a larger NO<sub>2</sub> adsorption takes place on Cu-ZSM-5 compared to NO adsorption and that nitrates formation occurs through NO<sub>2</sub> disproportionation producing nitrate and NO. They also showed that nitrates can be decomposed producing NO<sub>2</sub> if in the presence of gaseous NO or producing both NO<sub>2</sub> and oxygen when NO is absent. Torre-Abreu et al. [29] found the presence of mono-nitrosyl complexes on Cu<sup>2+</sup>, releasing NO at 120 °C, and of nitrate species associated to the simultaneous desorption of NO and O<sub>2</sub>.

Unfortunately, Cu-ZSM-5 could be not applied under practical conditions of interest for real processes, since it suffers at the least two challenging limitations: it strongly deactivates in the presence of water and cannot sustain the presence of sulphur compounds. Anyway, the Cu-exchanged ZSM-5 still represents a “model” catalyst, both in the view of searching new more resistant systems and explaining its singular features that makes it so active and interesting in DeNO<sub>x</sub> reactions.

In this work we report a quantitative and qualitative investigation of all N-containing species produced by the dynamic interaction between NO and Cu-ZSM-5 at different initial oxidation state of copper, temperature of adsorption and NO<sub>x</sub> concentration, in the presence and absence of O<sub>2</sub>. The effect of all these parameters on the formation and stability of all species has been analyzed and a mechanism of the evolution of these species with time on stream has been proposed. The qualitative and quantitative determination of all these species represents the basis for the definition of reaction patterns involving nitric oxide occurring on Cu-ZSM-5.

## 2. Materials and methods

### 2.1. Catalyst preparation

The Cu-ZSM-5 samples were prepared by ion-exchange of a commercial H-ZSM-5 zeolite (Zeolyst CBU-5020, Si/Al = 25, BET surface area = 350 m<sup>2</sup>/g) in aqueous solution of 20 mM copper(II)

acetate monohydrate (Aldrich purity 99.8%) at 50 °C for 2 h. Due to the high copper ion/zeolite amount ratio in all preparations, the pH variation during the exchange procedure was always lower than 10% of the initial value. After the exchange the sample was centrifuged, washed twice with bi-distilled water and dried at 120 °C overnight. Finally, the catalyst was calcined according to the following procedure: (a) 2 h at 550 °C (10 °C min<sup>-1</sup>) under helium flow; (b) cooling down at room temperature; (c) 2 h at 550 °C (10 °C min<sup>-1</sup>) under 1% O<sub>2</sub>/He mixture flow.

### 2.2. Catalyst characterisation

The copper content, determined by ICP-MS using an Agilent 7500 ICP-MS instrument after MW-assisted dissolution of copper in nitric acid solution, was 1.71 wt.%, corresponding to about 90% exchange.

FTIR experiments of NO adsorption were performed on a Perkin Elmer Spectrum GX spectrometer with a spectral resolution of 4 cm<sup>-1</sup> averaged over 50 scans. The Cu-ZSM-5 was pressed in a self-supporting disk and placed in an in situ high temperature/high pressure IR cell (Graseby Specac) equipped with a ZnSe window and connected to gas lines. Before the experiment the sample was treated under flowing Ar (100 cm<sup>3</sup> min<sup>-1</sup>) for 2 h at 550 °C or under a 20% O<sub>2</sub>/Ar mixture at 550 °C and then slowly cooled down to room temperature. NO was adsorbed by flowing an 800 ppm NO/Ar mixture at 80 °C for different times (0.5, 1.5 and 6 h).

Preliminary experiments collecting spectra in the presence of the NO/Ar mixture and after 0.75 h Ar purging at the same temperature showed that, excluding the band corresponding to gaseous NO (1875 cm<sup>-1</sup>), the signals are perfectly overlapped suggesting that they can be ascribed to irreversibly adsorbed species. As a consequence all spectra showed in this section have been collected after the Ar purging.

### 2.3. Adsorption and TPD tests

All adsorption tests were carried out after a catalyst pre-treatment (1 g of Cu-ZSM-5) as detailed below:

*Reducing pre-treatment:* The calcined catalyst was heated under high purity He flow (20 l h<sup>-1</sup>) from room temperature up to 550 °C (10 °C min<sup>-1</sup>) and maintained at this temperature for 2 h (catalyst is “self-reduced” by spontaneously releasing molecular oxygen), then cooled at 1 °C min<sup>-1</sup> down to the desired temperature under the same atmosphere (O<sub>2</sub> content < 1 ppm).

*Oxidizing pre-treatment:* The catalyst was heated under 20 vol.% O<sub>2</sub>/He mixture from room temperature up to 550 °C (10 °C min<sup>-1</sup>) and maintained at this temperature for 1 h, then cooled at 1 °C min<sup>-1</sup> down to the desired temperature under the same atmosphere.

Adsorption of NO and subsequent TPD tests were carried out according to two phases: (i) saturation and (ii) desorption.

In the saturation step an 800 or 5000 ppm NO/He mixture (20 l h<sup>-1</sup>) was fed to a flow reactor containing 1 g Cu-ZSM-5 in the temperature range 80–225 °C. The composition of the effluent stream was continuously monitored for the whole length of the experiment (transient and steady-state) until all concentrations of the different gas species exiting the reactor (NO, NO<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O and O<sub>2</sub>) were stable. A specific analyser (Hartmann & Braun URAS 10E) was used to measure NO, NO<sub>2</sub> and N<sub>2</sub>O concentration whereas a Varian CP4900 N<sub>2</sub> micro-GC was used for the analysis of N<sub>2</sub> and O<sub>2</sub> (with a 1 min<sup>-1</sup> frequency).

After reaching stable concentrations the NO/He flow was substituted by a He flow (15 l h<sup>-1</sup>) and the desorption phase started. The sample was initially purged at the adsorption temperature in

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