Abstract
In this work a quantitative and qualitative investigation of the dynamic interaction between NO and Cu-ZSM-5 and the consequent formation of reaction intermediates in a range of temperature lower than the threshold of any steady-state reaction has been reported. The adsorption tests, followed by a TPD analysis, have been carried out by continuous monitoring the gaseous effluents starting from different initial oxidation state of copper, at different temperature of adsorption (25-225°C) and NO concentration (800-5000ppm), at variable exposure times in the presence and in the absence of O2. In situ FTIR experiments have also be performed under similar conditions.
On the basis of the results obtained under the different experimental conditions a quantitative analysis of nitrogen containing species and their evolutions with time on stream and a mechanism of N2, N2O and nitrate formation, have been proposed. Moreover, the adsorption properties of Cu-ZSM-5 towards nitrogen oxides have been evaluated to explore the interest about a novel periodic process of NOx abatement based on adsorption/decomposition cycles.

Introduction
The interest towards Cu-ZSM-5 is related to the possible application in several DeNOx reactions, ranging from the SCR of NO with hydrocarbons [1] to the decomposition of nitrous oxide [2, 3] but also to the classical SCR with ammonia or urea [4, 5] since Cu-ZSM-5 is able to activate this process at relatively low temperature. Cu-zeolites have been also recently proposed as alternative to the traditional V2O5-WO3/TiO2 catalysts for SCR applied to exhaust after-treatment from lean Diesel engines due to their higher thermal stability compared to titania based materials [6, 7]. However, the great interest towards Cu-ZSM-5 was mostly addressed to its unique properties in the direct decomposition of nitric oxide, which represents an ideal DeNOx process, since it does not need the use of a reductant [8, 9].
The formation of nitrate-like species over Cu sites is considered a key step in most of the reduction processes towards N2.
In this work the adsorption properties of Cu-ZSM-5 towards nitrogen oxides have been evaluated and the dynamic interaction between NO and Cu-ZSM-5 and the
consequent formation of reaction intermediates in a range of temperature lower than the threshold of any steady-state reaction has been investigated. A mechanism of the evolution of the adsorbed species with time on stream has been proposed in order to explore the possibility to develop a periodic process of NO adsorption/decomposition.

**Experimental**

The Cu-ZSM-5 was prepared by ion-exchange of a commercial H-ZSM-5 zeolite (Zeolyst CBU-5020, Si/Al = 25, BET surface area=350 m²/g) in aqueous solution of 20 mM copper(II) acetate monohydrate (Aldrich purity 99.8%) at 50°C for 2h. After calcinations the zeolite underwent a reducing pre-treatment under He flow (20 l h⁻¹) at 550°C (catalyst is “self-reduced” by spontaneously releasing molecular oxygen) or an oxidising pre-treatment under 20%vol. O₂/He at 550°C. NO adsorption experiment were carried out feeding 800-5000 ppm NO/He in the temperature range 80-225°C to a flow reactor containing an over-exchanged Cu-ZSM-5. The quantitative analysis was carried out by continuously monitoring the gas phase composition of the effluents from the catalytic reactor by means of specific analysers coupled with a micro-GC. After a controlled time, the NO/He flow was substituted by He flow carrying out a TPD by heating the reactor at 10°C/min up to 500°C. NO adsorption FTIR experiments were performed under the same conditions on the Cu-ZSM-5, pressed in a self-supporting disk, placed in an in-situ high temperature/high pressure IR cell connected to gas lines.

**Results and Discussion**

In all adsorption experiments, when NO passes through the zeolite, a nil NO concentration was measured for a time dependent on temperature, NO concentration and catalyst pre-treatment. Before NO concentration recovered the inlet value, N₂ and N₂O emission were detected only for pre-reduced Cu-ZSM-5. A further N₂O tail-like emission was detected even for longer time for both pre-reduced and pre-oxidized zeolite (Fig. 1/left). In the subsequent TPD tests (Fig. 1/right), in addition to the reversibly adsorbed NO (first peak at constant temperature), two NO peaks can be clearly detected, one in the range 180-220°C and another at about 400°C coupled to O₂ emission with 1:1 NO/O₂ ratio, associated to the thermal decomposition of nitrate species. Indeed, the intensity of bridged (1628cm⁻¹) and chelating (1575cm⁻¹) bands of nitrate species on Cu²⁺ increased with the exposure time to NO/He mixture in the FTIR spectra recorded under the same conditions of TPD tests.
The amount of NO adsorbed on the catalyst at the end of the adsorption test was evaluated by measuring the overall uptake of NO and the quantities of N2O, NO2, and N2 transiently produced. The quantitative analysis of all N-containing species adsorbed at 80°C and then desorbed in the following TPD is reported in Table 1 both for a pre-reduced and a pre-oxidized Cu-ZSM-5 in the absence or in the presence of O2 in the feed mixture. Large NOx amounts can be adsorbed over the Cu-ZSM-5, comparable or even higher than Pt/BaO systems used for the NOx storage/reduction process [10]. Moreover, although this amount is lower for the pre-oxidized catalyst a negligible emission of N2O takes place. In fact, the formation of N2O for the pre-reduced Cu-ZSM-5 was mainly attributed to the oxidation of Cu(I) by NO. Nitrous oxide desorbed in the gas phase, when contacts Cu+ sites not yet oxidized by NO, may be also reduced to N2. Although in the presence of O2 the NO uptake is reduced by the absence of physisorption, the NO saturation level of the catalyst is higher the formation of nitrates is greatly increased (Table 1). Moreover, when the catalyst is oxidized or oxygen is present in the feed mixture copper sites are preferentially oxidized by O2 thus inhibiting the formation of the undesired nitrous oxide. The quantitative analysis of TPD tests showed that the increase of nitrates concentration with increasing the time length of NO adsorption occurred even at constant amount of NO adsorbed, i.e. some adsorbed species turned into nitrates with time on stream. Formation of nitrates is also favoured by increased temperature and/or the presence of O2.
Table 1. Amounts of gaseous species evaluated by the integration of the signals during the adsorption at 80°C and the subsequent TPD over a pre-reduced Cu-ZSM-5 in the absence or in the presence of oxygen in the feed mixture.

<table>
<thead>
<tr>
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<th>Adsorption (μmol/g&lt;sub&gt;cat&lt;/sub&gt;)</th>
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<tr>
<td></td>
<td>pre-reduced</td>
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<tr>
<td></td>
<td>NO only</td>
</tr>
<tr>
<td>NO&lt;sub&gt;uptake&lt;/sub&gt;</td>
<td>404</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;prod&lt;/sub&gt;</td>
<td>107</td>
</tr>
<tr>
<td>N&lt;sub&gt;2,prod&lt;/sub&gt;</td>
<td>7</td>
</tr>
<tr>
<td>NO&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>176</td>
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<tr>
<td></td>
<td>Purging + TPD (μmol/g&lt;sub&gt;cat&lt;/sub&gt;)</td>
</tr>
<tr>
<td></td>
<td>NO&lt;sub&gt;des&lt;/sub&gt;</td>
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<tr>
<td></td>
<td>206</td>
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<tr>
<td>NO&lt;sub&gt;rev&lt;/sub&gt;</td>
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<td>57</td>
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<td>NO&lt;sub&gt;2HT&lt;/sub&gt;</td>
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<tr>
<td>NO&lt;sub&gt;HT/O&lt;sub&gt;2HT&lt;/sub&gt;&lt;/sub&gt;</td>
<td>0.8</td>
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In general, all the results confirm that after catalyst saturation with NO the interaction with copper sites results in the formation of new N-containing species, their relative amount being dependent on the starting oxidation state of the zeolite or the temperature.

The proposed reaction path leading to the formation of chelating nitrates starting from oxidized isolated copper ions is the following:

\[
\begin{align*}
\text{Cu}^{+2} - \text{O}^- + \text{NO} & \rightarrow \text{Cu}^{2+} \overset{\text{NO}}{\text{O}^-} \quad (1) \\
\text{Cu}^{+2} \overset{\text{NO}}{\text{O}^-} + \text{NO} & \rightarrow \text{Cu}^{+2} \overset{\text{NO}^-}{\text{NO}} \quad (2) \\
\text{Cu}^{+2} \overset{\text{NO}_2^-}{\text{NO}} + \text{NO} & \rightarrow \text{Cu}^{+} \overset{\text{O}}{\text{O}^-} \overset{\text{N=O} + \text{N}_2\text{O}}{\text{N=O} + \text{N}_2\text{O}} \quad (3)
\end{align*}
\]

However, a parallel reaction path was proposed since also bridging nitrates were spectroscopically observed which must be associated to the presence of copper pairs reasonably present in highly exchanged Cu-ZSM-5.
In conclusion, operating conditions as long exposure time, high adsorption temperature and presence of $O_2$ promote nitrates formation. The presence of these species is necessary for the activation of most of DeNOx reactions and, as a consequence, Cu-ZSM-5 can be considered an efficient NO sorbent. In addition, a subsequent DeNOx process can be potentially carried out on this catalyst to convert the adsorbed species into $N_2$.

**Conclusions**

The interaction of nitrogen oxides with Cu-ZSM-5 in a range of temperatures far from the activation of any steady-state reactions was studied. It was shown that Cu-ZSM-5 can adsorb large amounts of NO, comparable or even higher than Pt-BaO systems used for NOx storage/reduction. The main observed phenomena during the interaction between NO and the zeolite were: i) reduced Cu$^+$ sites are quickly re-oxidised by NO producing $N_2O$ ii) adsorbed NO slowly reacts with gaseous NO to give surface nitrates. Based on the results obtained under the different experimental conditions a network of gas-solid reactions occurring during the NO adsorption was proposed.

This study represents the basis to explore the possibility to carry out periodic process of NOx abatement based on adsorption/decomposition cycles.

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**References**


