



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

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ARTICLE INFO

Article history:

Received 4 August 2011

Received in revised form 27 October 2011

Accepted 31 October 2011

Available online 6 November 2011

Keywords:

Cu-ZSM-5

NO adsorption

TPD

Copper

Redox chemistry

Nitrogen oxides

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/O₂/He, N₂O/He and N₂/He) have been evaluated. In situ FTIR experiments have been also carried out under similar conditions.

The main observed phenomena are: (i) reduced Cu⁺ sites are quickly re-oxidized by NO producing large amounts of N₂O; (ii) adsorbed NO slowly reacts with gaseous NO to give surface nitrates and still N₂O 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 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 [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⁺ 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⁺ sites has been also reported [16,17].

On the other hand, in SCR processes over Cu-ZSM-5 the oxidation of NO to NO₂ is considered a key step [18]; this hypothesis is being further supported by the observation that SCR takes place

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