Well defined Cu\textsuperscript{I}(NO), Cu\textsuperscript{I}(NO)\textsubscript{2} and Cu\textsuperscript{II}(NO)\textsubscript{X} (X = O\textsuperscript{-} and/or NO\textsubscript{2}\textsuperscript{-}) complexes in Cu\textsuperscript{I}-ZSM5 prepared by interaction of H-ZSM5 with gaseous CuCl

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In this note an exchange procedure of the acidic protons of H-ZSM5 by Cu\textsuperscript{I} ions through reaction with CuCl in the gas phase is described. In the so obtained Cu\textsuperscript{I}-ZSM5 exchanged zeolite the Cu\textsuperscript{I} ions are in well defined configuration and form with NO mono and di-nitrosyl complexes of high structural and spectroscopic quality. The Cu\textsuperscript{I}(NO)\textsubscript{2} species are transformed at RT into Cu\textsuperscript{II}(NO)\textsubscript{X} (X = O\textsuperscript{-} and/or NO\textsubscript{2}\textsuperscript{-}) species which could represent an intermediate in NO decomposition.

Keywords: Zeolites; H-ZSM5; Cu-ZSM5; NO; Nitrosyl complexes; NO decomposition

1. Introduction

Zeolites represent a wide group of stable crystalline porous materials well permeable to gases. Special sites located in the channels and in the cavities confer to these solids interesting catalytic activity [1].

A good example is represented by H-ZSM5 (a zeolite of the pentasil family), whose structure is formed by tetrahedral [MO\textsubscript{4}] primary units linked through corners to form a three-dimensional framework characterized by two types of intersecting channels (straight and sinusoidal) with ≈ 5.7 Å diameter. Some tetrahedra (typically 6%) contain Al instead of Si. The charge difference between Al and Si is compensated by an equal number of protons located in the channels and at their intersection: these confer to the zeolite important catalytic properties. For instance, hydrocarbon molecules traveling along the channels are brought in contact with the protonic sites and so can undergo Brönsted acid transformation under space restrictions [2].

The protons at the \textgtr Si-(OH)-Al\textless sites can be exchanged with a variety of cations both monovalent (for example Na\textsuperscript{+}) and divalent (for example Cu\textsuperscript{2+}) with exchange procedures in solution or in the solid state [1,3].

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In this note we illustrate a very clean exchange method with monovalent Cu\textsuperscript{I} in the gas phase. In the so formed exchanged zeolite, the Cu\textsuperscript{I} ions are in a well defined configuration and form (with gaseous NO) mononitrosyllic and dinitrosyllic complexes of high structural and spectroscopic quality.

The dinitrosyllic Cu\textsuperscript{I} species undergo a transformation into mononitrosyl Cu\textsuperscript{II}(NO)\textsubscript{X} (X = O\textsuperscript{-} and/or NO\textsuperscript{y}) species which could be a key intermediate in NO decomposition into N\textsubscript{2} and O\textsubscript{2} observed at higher temperature [4,5].

2. Experimental

High external surface area H-ZSM5 (Si/Al = 90) has been prepared in the ENICHEM ANIC Laboratories. The zeolite particles have diameters in the 20–50 nm range and an external surface area of 70 m\textsuperscript{2} g\textsuperscript{-1}. The protonic form has been obtained from Na-ZSM5 by leaching in HCl (1 M).

The very high cristallinity of the samples has been checked through conventional X-rays and IR determinations. Electron microscopy under high resolution conditions adds further evidence on the cristallinity of the samples used in this investigation.

The Cu\textsuperscript{I}-exchanged zeolite has been prepared directly in the IR cell following the procedure described below.

A H-ZSM5 disk (~12 mg cm\textsuperscript{-2}) was evacuated under high vacuum (10\textsuperscript{-4} Torr) for 3 hrs at 623 K in order to remove adsorbed water and other impurities. After this treatment the disk was transferred under high vacuum in a chamber where pure CuCl (previously outgassed at 473 K to remove any trace of H\textsubscript{2}O impurities) is contained. The chamber containing the H-ZSM5 disk and the CuCl microcrystalline powder was then heated with an external furnace at 573 K. At this temperature CuCl vaporizes and penetrates the H-ZSM5 channels where reaction occurs with internal protons leading to elimination of gaseous HCl (monitored by pressure measurement and by the disappearance of the characteristic $\equiv\text{Al}-(\text{OH})-\text{Si}\equiv$ IR band at 3620 cm\textsuperscript{-1}) and fixations of Cu\textsuperscript{+} ions to the zeolite framework. After completion of the reaction, the disk was transferred (always under high vacuo) into an intermediate outgassing chamber where it was heated at 773 K for one hour in order to eliminate excess CuCl possibly entrapped in the channels. The small dimensions of the H-ZSM5 particles used in this experiment both favour the full reaction between the internal protonic sites and CuCl, and removal of excess CuCl. Finally, the disk was cooled to RT and transferred (always in high vacuo) into the optical part of the cell, which was placed in the sample compartment of a Bruker IFS48 FTIR spectrometer. The cell is designed to allow IR spectra to be taken in situ either at RT or at 77 K.

NO gas was dosed by means of a vacuum manifold permanently attached to the IR cell.