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Well defined $Cu^I(NO)$, $Cu^I(NO)_2$ and $Cu^{II}(NO)X$ ($X = O^-$ and/or NO_2^-) complexes in Cu^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^I ions through reaction with CuCl in the gas phase is described. In the so obtained Cu^I-ZSM5 exchanged zeolite the Cu^I ions are in well defined configuration and form with NO mono and di-nitrosyl complexes of high structural and spectroscopic quality. The $Cu^I(NO)_2$ species are transformed at RT into $Cu^{II}(NO)X$ ($X = O^-$ and/or NO_2^-) 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 $[MO_4]$ 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 $\geqslant$Si–(OH)–Al$\leqslant$ sites can be exchanged with a variety of cations both monovalent (for example Na^+) and divalent (for example Cu^{2+}) with exchange procedures in solution or in the solid state [1,3].

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

The dinitrosylic Cu^I species undergo a transformation into mononitrosyl $Cu^{II}(NO)X$ ($X = O^-$ and/or NO_2^-) species which could be a key intermediate in NO decomposition into N_2 and O_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^2 g^{-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^1-exchanged zeolite has been prepared directly in the IR cell following the procedure described below.

A H-ZSM5 disk (≈ 12 $mgcm^{-2}$) was evacuated under high vacuum (10^{-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_2O 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 $\geqslant$Al–(OH)–Si$\leqslant$ IR band at 3620 cm^{-1}) and fixations of Cu^+ 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.

3. Results and discussion

NO ADSORPTION AT 77 K

The results illustrated in fig. 1 are of straightforward interpretation. At the lowest dosages one main peak is observed, at 1812 cm^{-1}, which by comparison with the literature data [6] can be assigned to the stretching mode of $Cu^+(NO)$ mononitrosyl complexes. The formation of this species is irreversible at the measurement temperature.

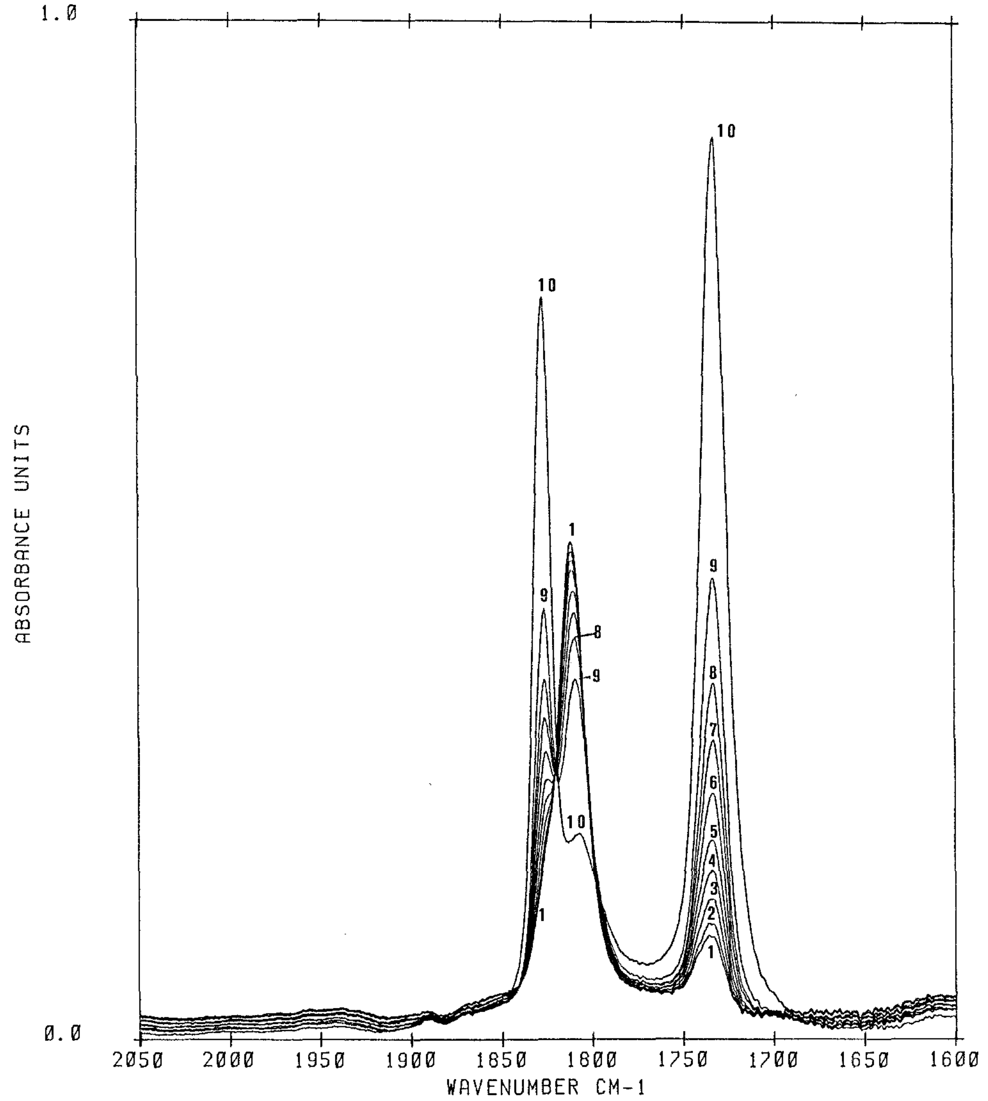


Fig. 1. IR spectra of NO adsorbed at 77 K on Cu^{I}-ZSM5. Effect of increasing the NO pressure (1–10); final pressure 0.7 Torr.

A gradual increase of the NO pressure from 0 to 0.7 Torr causes the transformation of the species responsible for the initial 1812 cm^{-1} peak into a new species characterized by two bands at 1827 and 1734 cm^{-1}. The clear isosbestic point at 1820 cm^{-1} indicates a well defined stoichiometric addition to form a dinitrosylic species following the scheme:

$$\underset{\text{I}}{Cu^{I}(NO)} \underset{-NO}{\overset{+NO}{\rightleftharpoons}} \underset{\text{II}}{Cu^{I}(NO)_2}.$$

This transformation is completely reversible at 77 K.

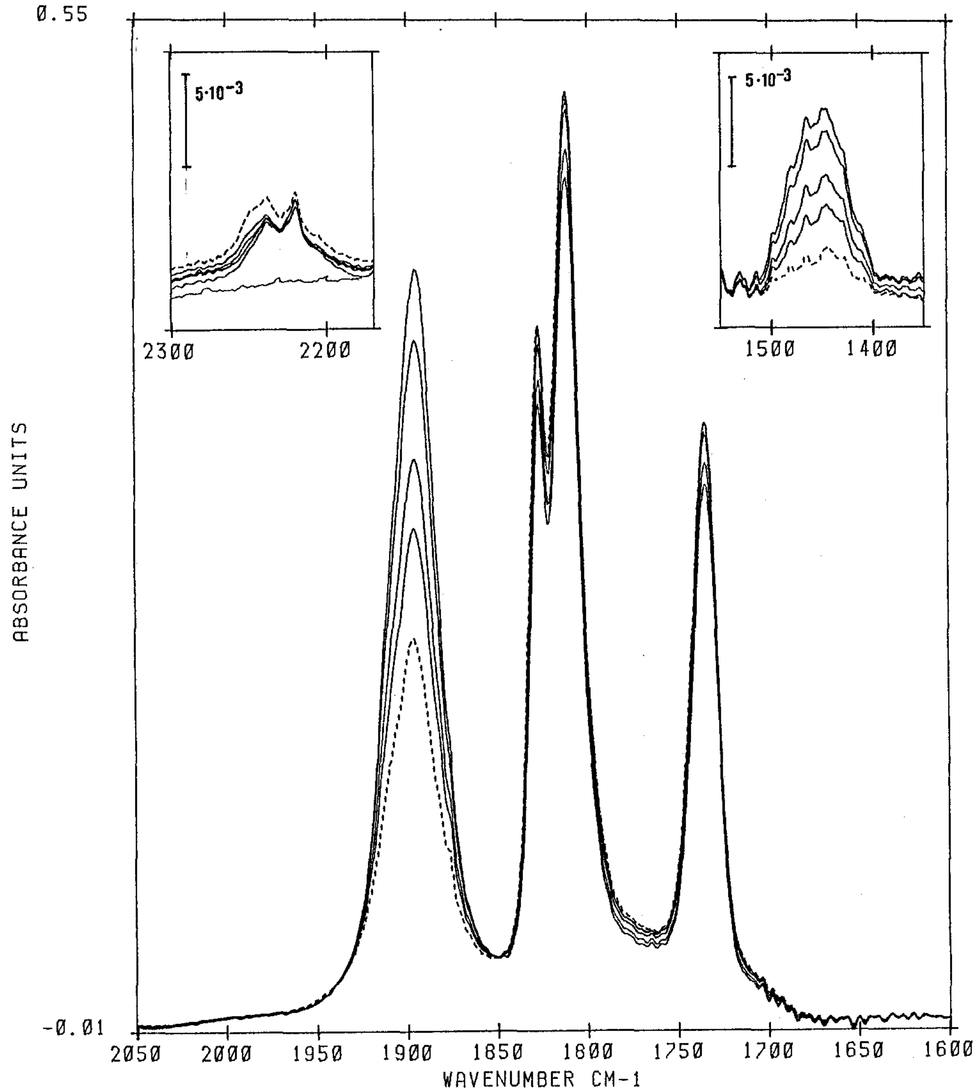


Fig. 2. IR spectra of NO adsorbed at RT on Cu^{I}-ZSM5. Broken line: immediately after NO admission (10 Torr). Full lines: evolution with time (last spectrum after 15 minutes contact).

From the intensity ratio of the two bands (symmetric, 1827 cm^{-1}, and antisymmetric, 1734 cm^{-1}, stretching) an angle between the two NO ligands of $\approx 102°$ is inferred [7]. The half width of the bands ($\Delta\bar{\nu}_{1/2} = 10$ and 17 cm^{-1}) is well comparable to that of nitrosylic complexes of known stoichiometry in solution: this is a further proof of their well defined structure within the zeolite.

NO ADSORPTION AT 300 K AND EVOLUTION WITH TIME

Upon adsorption of NO at 300 K ($p = 10$ Torr) the formation of the triplet associated with species I (1812 cm^{-1}) and II (1827 and 1734 cm^{-1}) is immediately observed (broken spectrum in fig. 2). From the intensity of the peaks it is inferred that at RT the two complexes are in 3 to 1 proportion. Beside these species, a new broad and strong nitrosylic absorption at 1895 cm^{-1}, together with very weak bands at 2220 and 2210 cm^{-1} and at 1448 cm^{-1}, is immediately formed.

Unlike the 77 K experiment, at 300 K the whole spectrum slowly evolves with time as follows (fig. 2):

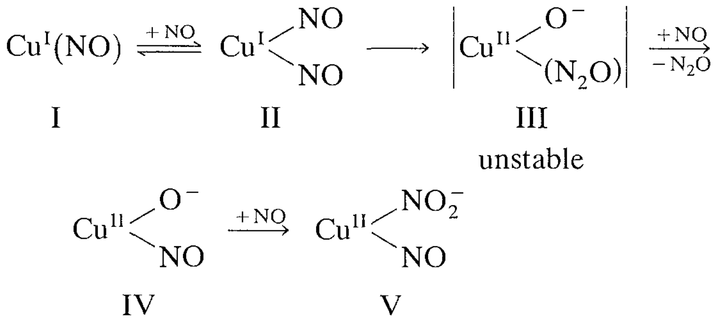
a) the intensity of the triplet due to complexes I and II decreases;

b) the broad band with maximum centered at 1895 cm^{-1} (and with a shoulder at 1910 cm^{-1}) gradually increases in a proportional way;

c) the bands at 2220–2210 cm^{-1} appear immediately after dosing NO and do not appreciably change with time. They disappear upon short evacuation at RT and so belong to physically adsorbed species. Blank experiments with N_2O directly dosed on the clean sample indicate that they are due to weakly adsorbed N_2O;

d) the band at 1448 cm^{-1} increases with time in the same way.

These findings indicate that a chemical transformation is slowly occurring at the surface sites. As the band at 1895 cm^{-1} can be undoubtedly associated with NO adsorbed on oxidized Cu^{II} sites, the following reaction scheme can be proposed (in presence of NO excess):



whereby the oxidation of Cu^{I} to Cu^{II} is associated with the decomposition of the dinitrosylic complex to give N_2O and O^-. In presence of NO excess, the N_2O

ligand is displaced to give mononitrosylic Cu^{II} species absorbing at 1895 cm^{-1} and physically adsorbed N_2O. The O^- species is then transformed into NO_2^-. Indeed, the weak band at 1448 cm^{-1} (which grows with time in a strictly parallel way) is indicative of the simultaneous formation of NO_2^- groups in monodentate form [8]. The presence of chelated NO_2^- species (which absorbs in the 1200–1000 cm^{-1}, i.e. where the skeletal vibrations of the zeolite are interfering) [8] cannot be excluded.

It is worth noticing that species V could further evolve to give N_2 and O_2 and so could represent the key intermediate in NO decomposition. In order to confirm this hypothesis further experimental work is needed.

Acknowledgment

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