

Dinitrogen Irreversible Adsorption on Overexchanged Cu-ZSM-5

Sandro Recchia* and Carlo Dossi

Dipartimento di Scienze CC, FF, MM, Università degli Studi dell'Insubria,
Via Valleggio 11, 22100 Como, Italy

Rinaldo Psaro, Achille Fusi, and Renato Ugo

Istituto CNR "ISTM" and Dipartimento CIMA, Università degli Studi di Milano,
Via Venezian 21, 20133 Milano, Italy

Giuliano Moretti

Istituto CNR "IMIP", Dipartimento di Chimica, Università "La Sapienza",
P. le A. Moro 5, 00185 Roma, Italy

Received: June 24, 2002

Dinitrogen (N_2) adsorption on overexchanged Cu-ZSM-5 (Si/Al = 25, 104% ion exchange from copper acetate) was studied at 302 K by diffuse reflectance infrared spectroscopy (DRIFTS), N_2 -adsorption isotherms, and temperature-programmed N_2 desorption (TPD). We found that Cu-ZSM-5 adsorbs N_2 at least in two different modes. The weaker mode, evidenced by the appearance of an IR band at 2295 cm^{-1} , was already reported in the literature and assigned to N_2 coordinated *on-top* on Cu(I) sites. This kind of adsorption occurs only under N_2 atmosphere and is completely reversible at 302 K. The stronger mode, revealed by TPD and by the difference between total and reversible N_2 -adsorption isotherms, is completely irreversible at 302 K. The band at 2130 cm^{-1} , previously assigned by us to this kind of strong N_2 adsorption, is not observed if ultrapure gases are utilized. The introduction of controlled amounts of impurities, together with the utilization of $^{15}N_2$ and ^{13}CO shows that this band is instead related to hydrated Cu(I)–CO species formed by accumulation on the sample of traces of H_2O in the N_2 flow and from residual CO produced during activation. The coordination of N_2 onto Cu(I)···Cu(I) dimers is proposed as an adequate model to describe this IR-silent irreversible N_2 adsorption.

Introduction

After the pioneering work of Iwamoto, the interest in Cu-ZSM-5 catalysts in NO decomposition^{1,2} increased. Only overexchanged catalysts are very active, while Cu-ZSM-5 with an exchange level below 75–80% shows an activity 2 orders of magnitude lower.³

Because any potential utilization of these systems as an alternative to common three-way catalysts is limited by their easy deactivation by water,^{2,4} intensive studies were dedicated to characterize the role of copper in overexchanged Cu-ZSM-5 and to understand the mechanism of action.

Aspects such as the processes related to the achievement of Cu(II) overexchange levels and the redox chemistry of copper inside the cages are now well established.^{5–12} Nevertheless, there is still a lack of information about the nature of active sites and the elementary step in NO decomposition.

The unique structural properties of ZSM-5 zeolite are fundamental because it is not possible to reach comparable activities with other zeolites or mesoporous materials.^{3,13} This indicates that the geometrical arrangement of copper sites, as determined by the shape of the zeolite cages and by the distribution of aluminum atoms, is a key factor in the catalytic behavior. Low Si/Al ratios are required for high catalytic activity suggesting, as supported by other experimental evidences, that

the active sites are probably formed by two copper centers with a favorable geometric arrangement for the N–N bond formation.^{11,14–17} However, the Si/Al ratio must not be too low to avoid the presence of very stable Cu(II) lonely sites.¹⁴

Theoretical studies confirm that the structure of ZSM-5 is determining for the existence of neighboring copper centers and also of more complex structures such as neighboring copper atoms with bridging oxygens or hydroxo groups inside the cages.^{18–21}

From this picture of active sites, many studies on the mechanism of NO decomposition over Cu-ZSM-5 have been published (see refs 15, 22, 23, and 24, as examples), but direct experimental evidences of the dinitrogen formation elementary step are still lacking.

Joyner et al.²⁵ pointed out the importance to establish how and where the N–N bond forms, even if the N–N bond formation may not be the rate-determining step in the NO decomposition. Some information about this point came from the work of Kuroda's and Zecchina's groups who, almost independently, discovered that Cu(I) ions supported on ZSM-5 and mordenite adsorb N_2 at room temperature, as revealed by the appearance of an IR band at 2295 cm^{-1} and by N_2 -adsorption isotherms.^{26–28} More recently, this unique property was also used to gain indirect insights about the nature of the NO-decomposition active sites of Cu-ZSM-5 by means of a careful study of the N_2 adsorption in competition with the adsorption of CO.¹⁴

* To whom the correspondence should be addressed. E-mail: sandro.recchia@uninsubria.it. Fax: ++39 031 2386449.

However, the N_2 adsorption responsible for the 2295 cm^{-1} band is stable only under N_2 , while it is not strong enough to resist a vacuum treatment at room temperature. The constancy of the half-width of this band at various N_2 coverages has led Kuroda to suggest that only one kind of site is related to the N_2 adsorption process.

We reported in a preliminary communication that on overexchanged Cu-ZSM-5 catalysts N_2 adsorption occurs also in a stronger mode and that this kind adsorption is stable even without N_2 in the gas phase and under vacuum treatments.²⁹ This conclusion was based on the appearance of an infrared band at 2130 cm^{-1} upon treating under flowing N_2 an activated overexchanged Cu-ZSM-5 catalyst and on N_2 adsorption isotherms showing that a fraction of N_2 is irreversibly bound at room temperature. The infrared band was ascribed to dinitrogen irreversibly adsorbed on asymmetrical dual copper sites, probably in different oxidation states.

In that preliminary communication, the attention was mainly focused on DRIFTS data and the N_2 isotherms were used only to support the band assignment. However, even if the adsorption isotherms can be easily and accurately reproduced, we experienced a lot of difficulties while trying to replicate the 2130 cm^{-1} band. This latter point drove us to investigate more deeply, including the use of $^{15}\text{N}_2$, the nature of such a band, and its correlation with the N_2 -adsorption data. As we will show in this paper, we arrived at the conclusion that the results coming from the two techniques are not caused by the same phenomenon.

Experimental Section

Catalyst Preparation. The zeolite H-ZSM-5 ($\text{Si}/\text{Al} = 25$) was obtained from $\text{NH}_4\text{-ZSM-5}$ (PQ Corp. (CBV5020)) by a thermal treatment at 773 K in air for 5 h . This zeolite has a surface area of $396\text{ m}^2/\text{g}$ and a total pore volume of $0.18\text{ cm}^3/\text{g}$.³⁰ The Cu-ZSM-5 catalyst with Cu loading of $1.97\text{ wt } \%$ (104% exchange level) was prepared by ion exchange with a copper acetate solution according to the following procedure. H-ZSM-5 (2 g) was stirred with 250 mL of 0.1 M copper acetate solution. The temperature was increased in 30 min to 333 K and then kept constant for 90 min , always under stirring. The sample was filtered off, washed several times with deionized water, dried at 383 K in air for 2 h , and stored over a saturated solution of NH_4Cl at room temperature (79% relative humidity). Copper loading was determined by atomic absorption spectroscopy (Varian SpectraAA-30).

N_2 Adsorption Isotherms. N_2 adsorption isotherms were performed with a Micromeritics ASAP 2010 analyzer. Before adsorption, the solid was preheated under vacuum in three steps: 1 h at 423 K , 1 h at 523 K , and finally 4 h at 463 K . Before adsorption of N_2 , the catalyst was treated at 723 K in a vacuum (10^{-5} Torr) for 1 h .

Temperature-Programmed Desorptions (TPD). The TPDs of chemisorbed $^{14}\text{N}_2$ were carried out in a U-shaped glass reactor under flowing Ar ($5.6\text{ mL}/\text{min}$; SIAD, 5.8 nines purity grade). The temperature was raised from 302 to 723 K at $5\text{ K}/\text{min}$. The volatile decomposition products were detected downstream in the carrier gas as a function of temperature by an on-line quadrupole mass spectrometer (Leda Mass 0–130 amu, enclosed source quadrupole). Full instrumental details about this technique are reported elsewhere.³¹ Before adsorption of N_2 at room temperature, the catalyst was activated in flowing Ar from room temperature to 723 K for 1 h with a rate of $10\text{ K}/\text{min}$.

DRIFTS Investigations. In situ diffuse reflectance infrared spectra were recorded at 4 cm^{-1} resolution (200 scans collected

for each spectrum) on a FTS-40 Digilab FTIR spectrophotometer equipped with a Harrick Scientific DRA-3CO diffuse reflectance accessory. A high-pressure, high-temperature environmental chamber for DRIFT studies (Harrick Scientific model HVC-DR3) allowed spectra of powdered samples to be recorded both in flow conditions and under static atmosphere at controlled temperature and pressure. An evacuation step (10 min at 10^{-2} Torr) was always performed between every gas switching.

The purity level of every gas used was constantly monitored by means of an on-line mass spectrometer (Leda Mass 0–130 amu, enclosed source quadrupole). The presence of water traces was carefully avoided for all of the experiments with the only exceptions of the ones in which the effect of water has to be studied; in those cases, a glass saturator filled with ultrapure water ($10^{18}\text{ }\Omega/\text{cm}$) was maintained exactly at $292 \pm 0.1\text{ K}$ to have a constant water vapor pressure of 2.0 kPa (experimentally determined), which is in good agreement with the expected theoretical value (2.1978 kPa). All gas flows were controlled by mass flow controllers (Brooks 5850 TR series).

Ultrapure $^{14}\text{N}_2$ (SIAD, 6 nines purity level), $^{15}\text{N}_2$ (Aldrich, cat. no. 36,458-4, $98\text{ atom } \%^{15}\text{N}$), and O_2 (SIAD, 5 nines purity level) were used as purchased. The $^{15}\text{N}_2$ cylinder was directly connected to the gas manifold of the DRIFT cell. ^{13}CO (MSD, cat. no. MS-2162, $99\text{ atom } \%^{13}\text{C}$) was used as purchased and injected into the DRIFT cell using a $200\text{ }\mu\text{L}$ gastight syringe.

Results and Discussion

Catalyst Activation. It is known that during activation, the Cu(II) ionic species introduced by ion exchange into Na-ZSM-5 undergo the well-documented self-reduction pathway involving extra lattice oxygens;^{6,8} this process leads to the formation of low-coordinated intrazeolitic Cu(I) ions. More recently, it was shown that this reduction is almost quantitative.⁵ However, this is not the only process involved in the Cu(II) reduction. As we reported earlier,³⁰ also carbonaceous deposits originated from the organic templates could act as reducing agents because they are oxidized during the formation of Cu(I) species. Direct evidences of such an oxidation are given by the detection of the combustion species CO_2 and CO during the thermal activation. CO_2 is evolved at 573 K and detected downstream with an MS analyzer, while CO bonds to the forming Cu(I) sites, as revealed by the appearance of the well-known Cu(I)–CO carbonyl band at 2154 cm^{-1} ,^{32–34} which is actually the superimposition of two bands at 2159 and 2151 cm^{-1} .¹⁴

Because of the thermal stability of these Cu(I) carbonyl species, the evolution of CO occurs therefore at higher temperatures (673 K) with respect to CO_2 . This reduction pathway is quite general, as it was always observed, even with different Cu loadings³⁰ and on different supports.³⁵ It must be stressed that such a process can be observed only by following gas evolution and recording infrared spectra during the inert gas flow activation because, if the activation is done under vacuum, the 2154 cm^{-1} carbonyl band cannot be observed; in these conditions, Cu(I)–CO species are not stable at temperatures higher than 523 K .³⁶ Thus, if the activation is carried out under vacuum, only the extra lattice oxygen pathway can be assessed. In any case, the almost complete reduction of Cu(II) species was also checked in our samples by the complete removal of the 920 cm^{-1} band and by the appearance of the 980 cm^{-1} band, which are related to a $\nu_{\text{asym}}(\text{SiOAl})$ perturbed by Cu^{2+} and Cu^+ ions, respectively.⁵

Although under Ar flow the 2154 cm^{-1} carbonyl band is completely depleted at 700 K , it is necessary to maintain the sample at this temperature for 1 h to ensure the complete

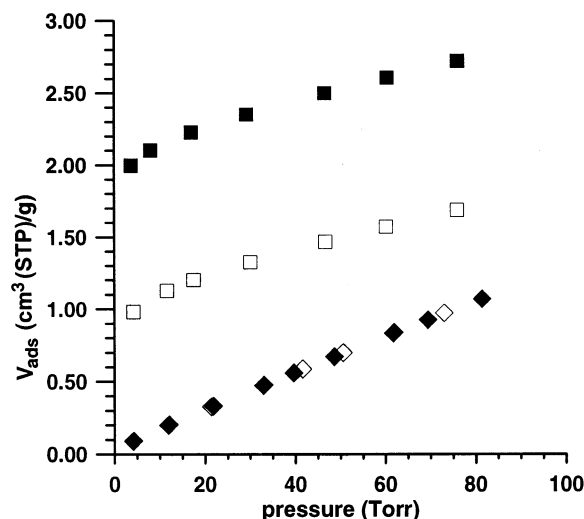


Figure 1. Adsorption isotherms of N_2 on Cu-ZSM-5 (104%) at 302 K (■) and on H-ZSM-5 at 273 K (◆): filled symbols = total N_2 adsorption; empty symbols = reversible N_2 adsorption (N_2 adsorption measured after evacuation at the adsorption temperature, 10^{-5} Torr for 30 min).

removal of CO from the DRIFT cell; otherwise, if the catalyst is cooled after few minutes at 700 K, the residual evolved CO binds back to the Cu(I) sites and the band due to Cu(I)–CO partially reappears, paralleled by a sharp drop of the downstream CO concentration.

While for N_2 -adsorption isotherms and TPD investigations only fully decarbonylated samples were obviously utilized, in the case of infrared studies, we decided to retain, after activation, a residual CO band at 2154 cm^{-1} (less than 5% of the total Cu(I), on the basis of the infrared band intensity) as an additional indicator of the actual chemical status of the system in the DRIFT cell. The reason for this choice will be clear later.

$^{14}N_2$ Adsorption on Cu/ZSM5. The N_2 adsorption isotherms on overexchanged Cu-ZSM-5 reported in the literature³⁶ clearly indicate that these systems are able to adsorb considerable amounts of N_2 at room temperature. It was also shown that this adsorption is strictly related to the presence of copper because Na-ZSM-5 does not adsorb N_2 ; the same behavior occurs with H-ZSM-5, which shows a Henry-type adsorption isotherm (Figure 1), clearly indicating that even this system does not adsorb N_2 at 273 K. The first N_2 adsorption isotherm of our overexchanged Cu-ZSM-5 shows instead that a considerable amount of N_2 ($2.1\text{ cm}^3\text{ STP/g}$) is adsorbed at 302 K onto this system. Again, these data agree with what was previously reported,³⁶ but in our experiment, we remarkably observed that this kind of adsorption is not totally reversible. In fact, if after the first isotherm the sample is evacuated and a second adsorption isotherm is performed (Figure 1), we can observe the adsorption of a substantially lower amount of N_2 ($1.1\text{ cm}^3\text{ STP/g}$). The difference between these two isotherms (about $1.0\text{ cm}^3\text{ STP/g}$) indicates the fraction of N_2 that is irreversibly adsorbed onto Cu-ZSM-5, which thus survives a vacuum treatment at 302 K.

To gain more information about the thermal stability of the irreversibly bound N_2 , TPD experiments were carried out on both Cu-ZSM-5 and H-ZSM-5 previously exposed to $^{14}N_2$, and then evacuated at 10^{-5} Torr for 30 min (Figure 2). In agreement with the adsorption isotherms, only Cu-ZSM-5 shows again a marked N_2 evolution: the decomposition starts at about 320 K and reaches its maximum near 380 K, as revealed by the $m/z = 28$ (N_2^+) and the $m/z = 14$ (N^+) channels. For both systems,

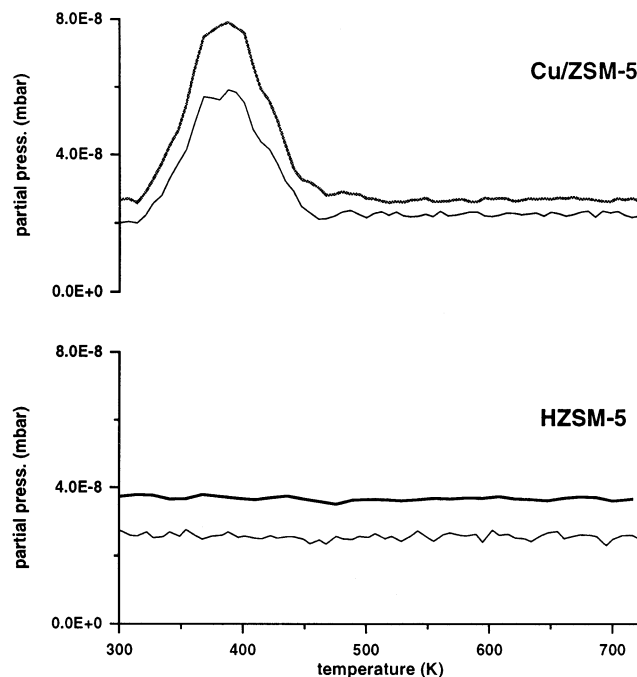


Figure 2. Temperature-programmed decomposition in Ar flow of Cu-ZSM-5 and H-ZSM-5. Before the TPD analysis, both samples were activated, exposed to $^{14}N_2$ (302 K, 30 min), and then evacuated at 10^{-5} Torr (302 K, 30 min). Thick lines represent $m/z = 28$; thin lines represent $m/z = 14$ ($\times 10$).

no other gaseous products (as revealed by the flat profiles recorded at $m/z = 12, 15, 16, 18, 30, 32$, and 44) were observed, making us confident that N_2 evolution is the only desorption process occurring in this temperature range.

The evidence of an irreversible N_2 adsorption, preliminarily outlined by us,²⁹ is thus confirmed. However, no similar evidences on copper-loaded zeolites from other research groups are reported in the literature. It must be underlined that the other research groups that have studied this phenomenon have commonly employed CuCl or $CuCl_2$ as copper precursor, while we have always used copper acetate to perform the ion exchange. This is a quite relevant difference because it was very recently shown³⁷ that the amount of adsorbed N_2 is almost doubled passing from $CuCl_2$ to $Cu(CH_3COO)_2$, thus leading to a more efficient Cu-ZSM-5 system for N_2 adsorption.

In Figure 3 are reported the DRIFT spectra of the activated catalyst (Figure 3a) in Ar atmosphere and after exposure to a flow of ultrapure $^{14}N_2$ (Figure 3b). While the intensity of the Cu(I)–CO band at 2154 cm^{-1} remains unchanged during this treatment, the band at 2295 cm^{-1} related to the formation of Cu(I)– N_2 species is now present. In agreement with the literature data,^{26,28} the latter band is observable only under N_2 atmosphere and completely disappears after an Ar purging (5 min) or a vacuum treatment at 302 K. This behavior is completely reversible, as confirmed by a further Ar– $^{14}N_2$ cycle (Figure 3c,d).

For the sake of clearness, this kind of N_2 adsorption, which is related to the 2295 cm^{-1} band, will be called “reversible”, while the stronger adsorption revealed only by adsorption isotherms and TPD studies will be called “irreversible”. This classification reflects the stability of these different species at room temperature.

The DRIFT results of Figure 3 are clearly different from what we preliminarily reported.²⁹ In that case, the exposure of $^{14}N_2$ (SIAD research-grade purity level) caused the appearance of a band at 2130 cm^{-1} that was assigned, on the basis of the

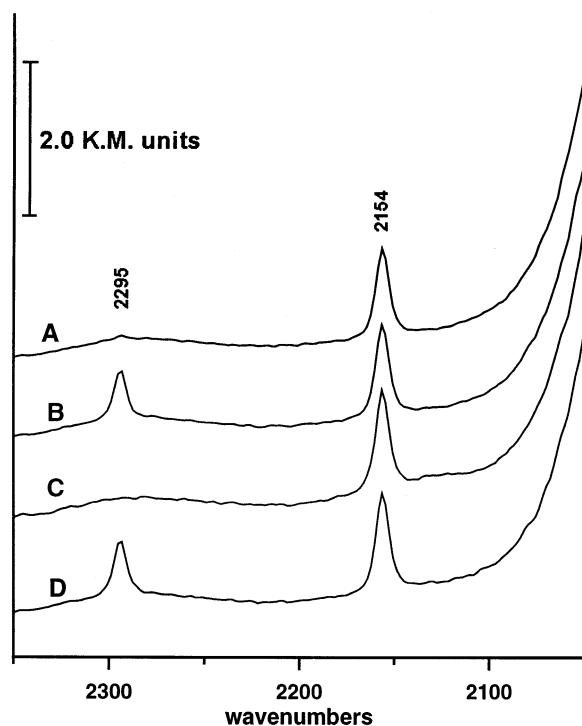


Figure 3. DRIFT spectra of Cu-ZSM-5 recorded at room temperature after activation: (A) in Ar flow; (B) switched from Ar flow to ultrapure $^{14}\text{N}_2$ flow; (C) switched from ultrapure $^{14}\text{N}_2$ flow to Ar flow; (D) switched from Ar flow to ultrapure $^{14}\text{N}_2$ flow.

stretching frequency,³⁸ to N_2 strongly adsorbed *end-on* onto dual copper sites. It must be noted that the main difference between the two experiments (the one here reported and the other previously published) relies on the purity level of the gases being used: in this study, a particular care was dedicated in trying to use and maintain a high purity level of the utilized gases because impurity accumulation may play a relevant role if we work in flow conditions. Because $^{14}\text{N}_2$ of a lower purity was used in our previous work, it is reasonable to think that the accumulation on the sample of trace gas impurities in the flowing N_2 could be responsible for these discrepancies.

Under this light, the assignment of the 2130 cm^{-1} band to N_2 adsorbed *end-on* needs thus to be reconsidered. It is possible that impurities themselves or impurity-induced transformations of the copper sites on the freshly activated catalyst (for example, a partial Cu(I) oxidation) could induce the appearance of this band.

Experiments carried out with NO plus O_2 at room temperature, and even at the working temperature of the catalyst,^{17,24,39,40} have shown that other bands are observable in the narrow spectral region between 2120 and 2135 cm^{-1} . These bands were assigned either to the formation of NO_2^+ species adsorbed on the acidic sites of the zeolite or to NO^+ adsorbed on Cu(I). However, we can exclude that the 2130 cm^{-1} band previously observed by us, can be related to the formation of these species, because it was also reported by the same authors that the interaction with NO causes the appearance of other bands at lower frequencies that were never detected in our experiments.

Because the major certified impurities of the N_2 used in the previous work published by us are O_2 and H_2O , the effect of both of these two gases on the DRIFT spectra of the sample were studied under controlled conditions. In Figure 4 are reported the spectra recorded under ultrapure $^{14}\text{N}_2$ flow after 5 and 35 min exposures to O_2 (Figure 4b,c). No sensible variation of the spectra could be detected. These observations fully agree

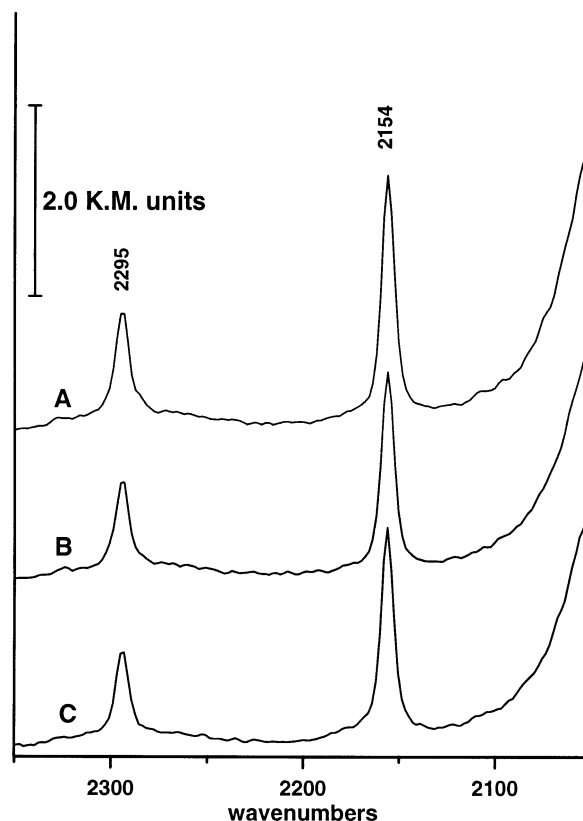


Figure 4. DRIFT spectra of Cu-ZSM-5 recorded at room temperature in ultrapure $^{14}\text{N}_2$ flow: (A) immediately after activation; (B) after 5 min exposure to O_2 ; (C) after additional 30 min exposure to O_2 .

with the report that O_2 is not able to oxidize Cu-ZSM-5 at room temperature.^{5,41}

To investigate the effect of water, an Ar flow (5.0 mL/min) presaturated with H_2O at 292 K was passed through the DRIFT cell containing the activated catalyst previously treated with ultrapure $^{14}\text{N}_2$. After 5 min of exposure, the band at 2295 cm^{-1} totally disappears while the band at 2130 cm^{-1} appears (Figure 5b). The great reproducibility of this experiment suggests that the 2130 cm^{-1} band, observed in our preliminary work, can be directly related to the presence of small traces of water impurities in the flow of $^{14}\text{N}_2$ (SIAD research-grade purity level).

Because water alone cannot cause the oxidation of Cu(I) sites, while it is known that the presence of water greatly enhances the rate of oxidation of Cu(I) sites by O_2 ,⁵ two possible explanations for the appearance of the band at 2130 cm^{-1} can be proposed: (a) Small traces of O_2 in the $\text{H}_2\text{O}/\text{Ar}$ stream cause the partial oxidation of neighboring Cu(I) sites to hydroxo-bridged Cu(I)–OH–Cu(II) where N_2 is now strongly adsorbed with an *end-on* geometry. The change of N_2 coordination from *on-top* to *end-on* moves the ν_{N_2} from 2295 to 2130 cm^{-1} . From a theoretical point of view, the hydroxo-bridged Cu(I)–OH–Cu(II) sites are expected to be the most abundant copper sites on overexchanged Cu-ZSM-5 systems.²⁰ (b) The disappearance of the 2295 cm^{-1} Cu(I)– N_2 band is simply related to the hydration of the low-coordinated Cu(I) sites where N_2 is weakly and reversibly adsorbed, while the formation of hydrated Cu(I)– $\text{CO}(\text{H}_2\text{O})_n$ species accounts for the appearance of a new ν_{CO} band at 2130 cm^{-1} .³²

$^{15}\text{N}_2$ Adsorption on Cu/ZSM5. To reach a definite attribution of the 2130 cm^{-1} band, $^{15}\text{N}_2$ was used to observe which bands undergo the typical isotopic red shift. Thus the same set of DRIFT experiments reported in the previous section was performed using $^{15}\text{N}_2$ instead of $^{14}\text{N}_2$. Our attention is focused

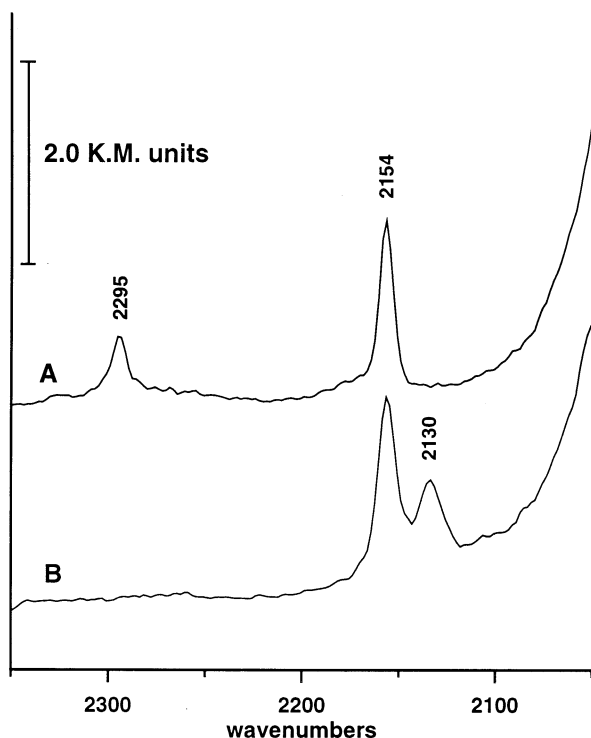


Figure 5. DRIFT spectra of Cu-ZSM-5 recorded at room temperature under ultrapure $^{14}\text{N}_2$ flow: (A) immediately after activation; (B) after 5 min exposure to an Ar flow saturated with H_2O at 298 K.

on the 2130 cm^{-1} band, which is expected to shift to 2057 cm^{-1} , because the isotopic shift of the 2295 cm^{-1} band was already reported.²⁶

Considering that the purity level of $^{15}\text{N}_2$ is far from being comparable to that of ultrapure $^{14}\text{N}_2$, preliminary experiments were carried out in flow conditions to make us confident about the comparability of spectra recorded with $^{15}\text{N}_2$ and $^{14}\text{N}_2$. We observed that the Cu(I) sites reversibly coordinating dinitrogen are not stable under a flux of rather impure $^{15}\text{N}_2$.

To avoid impurity accumulation and to partially compensate for the different purity level of these two gases, all $^{15}\text{N}_2$ spectra were thus recorded under static conditions. In these experimental conditions, $^{14}\text{N}_2$ and $^{15}\text{N}_2$ spectra are fully comparable.

In Figure 6 are shown the DRIFT spectra, recorded in $^{15}\text{N}_2$ atmosphere, prior (Figure 6a) and after (Figure 6b) 5 min exposure to a H_2O -saturated argon flow. The $^{15}\text{N}_2$ band at 2218 cm^{-1} , related to the 2295 cm^{-1} $^{14}\text{N}_2$ band, completely disappears after this treatment, while the band at 2130 cm^{-1} does not change its position. This clearly indicates that the 2130 cm^{-1} band is not associated with any N_2 adsorbed species and can be attributed instead to a water-induced transformation of Cu(I)–CO sites, according to the hypothesis b of the previous paragraph. However, to accept the assignment of the 2130 cm^{-1} band to hydrated Cu(I)–CO species, it was necessary to confirm that we are really dealing with a CO stretching.

Starting from an activated catalyst with only a residual CO band at 2154 cm^{-1} (Figure 7a), we admitted a small amount ($60\text{ }\mu\text{L}$) of ^{13}CO into the cell and recorded the DRIFT spectrum (Figure 7b). The Cu(I)–CO band at 2154 cm^{-1} shifts to 2108 cm^{-1} , but only after a 5 min exposure to a H_2O -saturated argon flow, a new band at 2082 cm^{-1} appears (Figure 7c). Because this shift exactly matches the expected ^{12}CO to ^{13}CO shift of the 2130 cm^{-1} band, this adsorption can be unambiguously assigned to Cu(I)–CO species derived from the original Cu(I)–CO species by hydration.

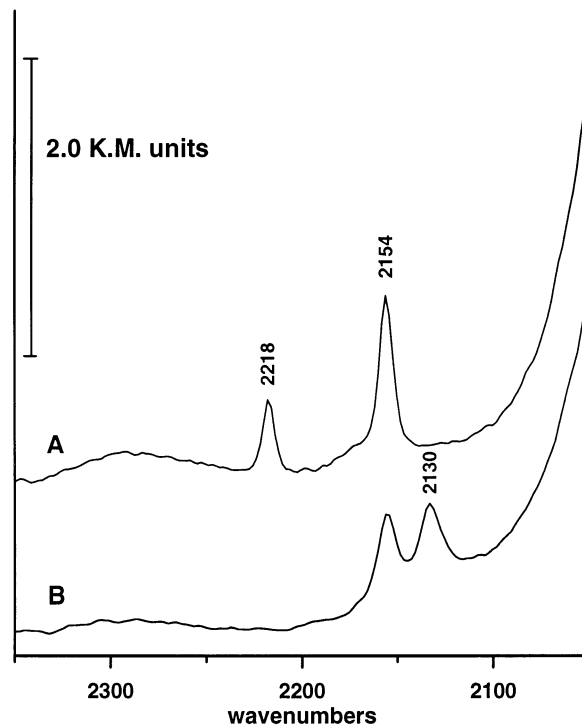


Figure 6. DRIFT spectra of Cu-ZSM-5 recorded at room temperature under $^{15}\text{N}_2$ atmosphere (120 KPa): (A) immediately after activation; (B) after 5 min exposure to an Ar flow saturated with H_2O at 298 K.

The whole body of the isotopic DRIFTS experiments discussed so far gives a complete picture of the behavior of Cu(I) sites of Cu-ZSM-5 in terms of infrared active vibrations. Cu(I) sites are almost stable toward O_2 exposure, but interaction with water causes the release of N_2 adsorbed on the low-coordinated Cu(I) sites. The hydration of the Cu(I)–CO sites is instead responsible of the appearance of a new carbonyl band at 2130 cm^{-1} .

Thus, the spectra reported in our preliminary communication can be easily explained assuming that hydrated Cu(I)–CO species are formed by accumulation of traces of H_2O in the N_2 flow and from residual CO produced during activation. If ultrapure gases are used, as in the present work, the 2130 cm^{-1} band cannot be observed.

On the Nature of the Irreversible N_2 Adsorption Sites.

We have shown that overexchanged Cu-ZSM-5 catalysts prepared from copper acetate adsorb N_2 in two different ways. The already reported^{26–28} reversible N_2 adsorption onto lonely Cu(I) sites is characterized by an IR band at 2295 cm^{-1} , while the irreversible N_2 adsorption is IR-silent.

If we look at the sites responsible for the irreversible N_2 adsorption as potential active sites for NO decomposition, infrared spectroscopy cannot give any information about their nature. Even in a recent study in which the direct decomposition of pulses of NO was followed at 673 K with an FTIR-MS apparatus, no direct evidence of the nature of the active sites emerges.²⁴

Although different hypotheses were formulated for the NO dissociation step,^{17,22,23,42} all of them are based on the suggestion that the dissociation mechanism must involve at least two neighboring copper centers and that the catalytic cycle probably requires a Cu(I)/Cu(II) redox process. These mechanistic suggestions were the basis of our preliminary assignment of the 2130 cm^{-1} band to N_2 strongly and asymmetrically *end-on* adsorbed on two copper atoms probably with different oxidation

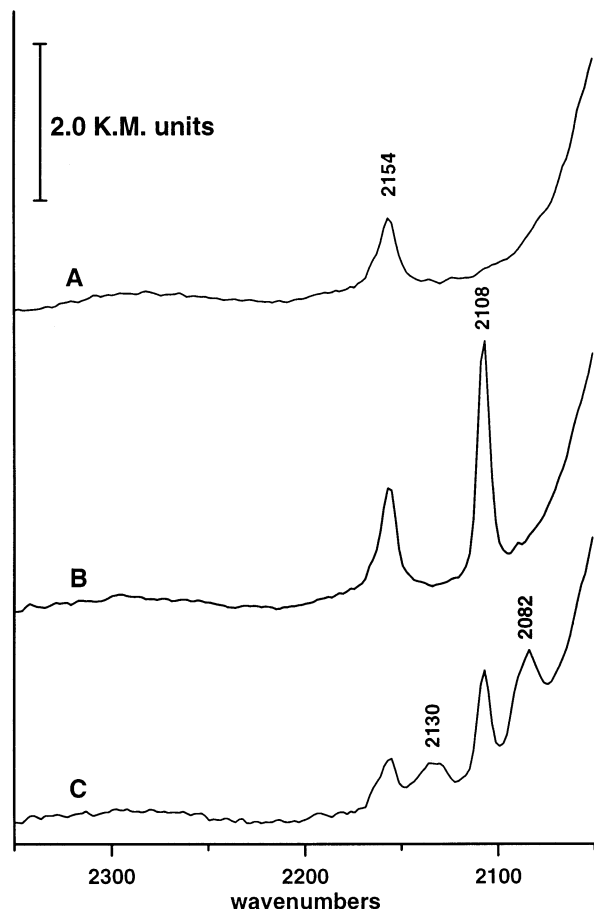


Figure 7. DRIFT spectra of Cu-ZSM-5 recorded at room temperature under pure Ar flow: (A) immediately after activation; (B) after a 60 μL injection of ^{13}CO into the DRIFT cell; (C) starting from trace B conditions, after 5 min exposure to an Ar flow saturated with H_2O at 298 K.

states. We have now evidence that this description is not correct and that irreversibly adsorbed N_2 is instead IR-silent.

It follows that (i) an IR-silent species requires a quite symmetric adsorption to copper sites with respect to the N–N bond, (ii) it can be excluded that Cu(II) sites are involved, in agreement with the recent findings that after activation almost all of the Cu(II) is reduced to Cu(I),⁵ and (iii) isolated Cu(I) sites can only adsorb N_2 in a reversible way with an *on-top* geometry. This latter point is also strengthened by the N_2 -adsorption isotherms recorded by us on a dilute 59%-exchanged Cu-ZSM-5 sample (prepared as for the 104% catalysts); while a marked reversible adsorption is still present, the irreversible adsorption is almost completely lacking ($0.03 \text{ cm}^3 \text{ STP/g}$).

Because the only relevant difference between under- and overexchanged samples relies on the presence of Cu(I)···Cu(I) dimers generated by the Al–O–Si–O–Al framework species, it should be concluded that the irreversibly adsorbed dinitrogen is coordinated to these sites. The Cu–Cu distances, calculated with different theoretical methods,^{20,43} are in any case lower than 3.8 Å. According to these distances, an *end-on* geometry should account for the irreversible N_2 adsorption only if a substantial distortion is invoked, while it is more appropriate to think of the coordination mode as belonging to a puckered (or a pure) *side-on* ($\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2$) geometry. A puckered *side-on* coordination was recently proposed by Goodman et al.⁴³ as the more stable coordination for $(\text{Cu}\cdots\text{O}_2\cdots\text{Cu})^{2+}$ inside overexchanged Cu-ZSM-5 with a low Si/Al ratio. Moreover, as in the case of dinuclear Zr– N_2 –Zr complexes,³⁸ the high local

symmetry of the *side-on* coordination also accounts for the observation that the dinitrogen stretching mode is IR-silent.

Although the N–N separation for a *side-on* coordination is considerably longer than that in N_2 ,⁴⁴ the occurrence of the N–N bond dissociation can be discounted considering that the final step of this process requires the cleavage of the dinitrogen molecule to form two nitrido (N^{3-}) ligands. To observe dissociation at room temperature, transition metal ion centers, such as Mo(III) of two Mo(III)(NRAr)₃ molecules where R is $\text{C}(\text{CD}_3)_2\text{CH}_3$ and Ar is 3,5- $\text{C}_6\text{H}_3(\text{CH}_3)_2$ ⁴⁵ with a marked electron donor capacity (formally six electrons per N_2 molecule), are thus necessary.

In the case of the Cu(I)···Cu(I) dimers, only two electrons are formally available, which are not sufficient to induce the N–N bond breaking. Therefore, the interaction between N_2 and Cu-ZSM-5 is correctly described as a strong adsorption.

If only the Cu(I)···Cu(I) dimers are involved in the irreversible adsorption of N_2 , we can use the adsorption isotherms to titrate such sites. The experimental concentration of Cu(I) dimers results in ca. 44 $\mu\text{mol/g}$, which corresponds to about 29% of the total copper present in our 104% exchanged Cu-ZSM-5. Because it is known that Cu-ZSM-5 catalysts start to become active toward NO decomposition above the 75–80% exchange level,³ this means that in a 104% exchanged Cu-ZSM-5 only about 30% of the total copper is really active. Thus, the very good match between the concentration of Cu active sites obtained from the catalytic behavior and adsorption isotherms would indicate that these rather symmetric Cu(I) dimers are not only responsible for the irreversible N_2 adsorption but may also be suggested as the most active sites in the process of NO decomposition to N_2 .

Conclusions

We have confirmed our previous findings that overexchanged Cu-ZSM-5, prepared from copper acetate, is able to adsorb N_2 in two different modes and revised our previous assignment of the 2130 cm^{-1} band, which is now attributed to hydrated Cu(I)–CO species. The irreversibly adsorbed N_2 is very stable at room temperature, and it is evolved from Cu-ZSM-5 above 320 K. A rather symmetric Cu(I)– N_2 –Cu(I) species is proposed as the more appropriate model for these IR-silent, irreversible N_2 adsorption sites.

The concentration of these symmetric Cu(I) sites, evaluated from the adsorption isotherms, is close to the copper threshold concentration required to shift from an unreactive low-exchanged catalyst to a very active overexchanged catalyst, thus suggesting that the catalytic activity in the process of NO decomposition could be linked to the presence of this kind of dimeric Cu(I) site.

Acknowledgment. MIUR (Roma) “Programmi di ricerca scientifica di rilevante interesse nazionale – 2000” is greatly acknowledged for financial support (scientific coordinator Prof. F. Trifirò). Thanks are due to Dr. G. Ferraris for his help in the adsorption measurements.

References and Notes

- (1) Iwamoto, M.; Furukawa, H.; Mine, Y.; Uemura, F.; Mikuriya, S.; Kagawa, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1272.
- (2) Iwamoto, M.; Yahiro, H.; Tanda, K.; Mizuno, N.; Mine, Y.; Kagawa, S. *J. Phys. Chem.* **1991**, 95, 3727.
- (3) Campa, M. C.; Indovina, V.; Minelli, G.; Moretti, G.; Pettiti, I.; Porta, P.; Riccio, A. *Catal. Lett.* **1994**, 23, 141.
- (4) Li, Y.; Hall, W. K. *J. Phys. Chem.* **1990**, 94, 6145.
- (5) Turnes Palomino, G.; Fiscaro, P.; Bordiga, S.; Zecchina, A.; Giamello, E.; Lamberti, C. *J. Phys. Chem. B* **2000**, 104, 4064.

- (6) Lo Jacono, M.; Fierro, G.; Dragone, R.; Feng, X.; d'Itri, J. L.; Hall, W. K. *J. Phys. Chem. B* **1997**, *101*, 1979.
- (7) Shertukde, P. V.; Marcelin, G.; Hall, W. K. *J. Catal.* **1993**, *139*, 468.
- (8) Jong, H. J.; Hall, W. K.; d'Itri, J. L. *J. Phys. Chem.* **1996**, *100*, 9416.
- (9) Pentuchi, J. O.; Marcelin, G.; Hall, W. K. *J. Phys. Chem.* **1992**, *96*, 9967.
- (10) Sarkany, J.; d'Itri, J. L.; Sachtler, W. M. H. *Catal. Lett.* **1992**, *16*, 241.
- (11) Lei, G. D.; Adelman, B. J.; Sarkany, J.; Sachtler, W. M. H. *Appl. Catal. B* **1995**, *5*, 245.
- (12) Beutel, T.; Sarkany, J.; Lei, G. D.; Yan, J. Y.; Sachtler, W. M. H. *J. Phys. Chem.* **1996**, *100*, 845.
- (13) Moretti, G.; Dossi, C.; Fusi, A.; Recchia, S.; Psaro, R. *Appl. Catal. B* **1999**, *20*, 67.
- (14) Kuroda, Y.; Kumashiro, R.; Yoshimoto, T.; Nagao, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 649.
- (15) Moretti, G. *Catal. Lett.* **1994**, *28*, 143.
- (16) Pirone, R.; Ciambelli, P.; Moretti, G.; Russo, G. *Appl. Catal. B* **1996**, *8*, 197.
- (17) Iwamoto, M.; Yahiro, H.; Mizuno, N.; Zhang, W.-X.; Mine, Y.; Furukawa, H.; Kagawa, S. *J. Phys. Chem.* **1992**, *96*, 9360.
- (18) Rice, M. J.; Chakraborty, A. K.; Bell, A. T. *J. Catal.* **2000**, *194*, 278.
- (19) Rice, M. J.; Chakraborty, A. K.; Bell, A. T. *J. Phys. Chem. B* **2000**, *104*, 9987.
- (20) Sayle, D. C.; Catlow, C. R. A.; Gale, J. D.; Perrin, M. A.; Nortier, P. *J. Phys. Chem. A* **1997**, *101*, 3331.
- (21) Sayle, D. C.; Catlow, C. R. A.; Perrin, M. A.; Nortier, P. *J. Mater. Chem.* **1997**, *7* (9), 1917.
- (22) Adelman, B. J.; Beutel, T.; Lei, G. D.; Sachtler, W. M. H. *J. Catal.* **1996**, *158*, 327.
- (23) Trout, B. L.; Chakraborty, A. K.; Bell, A. T. *J. Phys. Chem.* **1996**, *100*, 17582.
- (24) Konduru, M. V.; Chuang, S. S. C. *J. Catal.* **1999**, *187*, 436.
- (25) Hayes, N. W.; Joyner, R. W.; Shipiro, E. S. *Appl. Catal. B* **1996**, *8*, 343.
- (26) Spoto, G.; Bordiga, S.; Ricchiardi, G.; Scarano, D.; Zecchina, A.; Geobaldo, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91* (18), 3285.
- (27) Kuroda, Y.; Konno, S.; Morimoto, K.; Yoshikawa, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 18.
- (28) Kuroda, Y.; Konno, S.; Hamano, H.; Maeda, H.; Kumashiro, R.; Nagao, M. *J. Phys. Chem.* **1995**, *99*, 10621.
- (29) Recchia, S.; Dossi, C.; Fusi, A.; Psaro, R.; Ugo, R.; Moretti, G. *Chem. Commun.* **1997**, 1909.
- (30) Dossi, C.; Fusi, A.; Moretti, G.; Recchia, S.; Psaro, R. *Appl. Catal. A* **1999**, *188*, 107.
- (31) Dossi, C.; Fusi, A.; Psaro, R. *Thermochim. Acta* **1994**, *236*, 165.
- (32) Hadjiivanov, K. I.; Kantcheva, M. M.; Klissurski, D. G. *J. Chem. Soc., Faraday Trans.* **1996**, *92* (22), 4595.
- (33) Itho, Y.; Nishiyama, S.; Tsuruya, S.; Masai, M. *J. Phys. Chem.* **1994**, *98*, 960.
- (34) Hadjiivanov, K.; Knözinger, H. *J. Catal.* **2000**, *191*, 480.
- (35) Dossi, C.; Recchia, S.; Pozzi, A.; Fusi, A.; Dalsanto, V.; Moretti, G. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4515.
- (36) Kuroda, Y.; Yoshikawa, Y.; Emura, S.; Kumashiro, R.; Nagao, M. *J. Phys. Chem. B* **1999**, *103*, 2155.
- (37) Kuroda, Y.; Kumashiro, R.; Itadani, A.; Nagao, M.; Kobayashi, H. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1383.
- (38) Cohen, J. D.; Mylvaganam, M.; Fryzuk, M. D.; Loehr, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 9534.
- (39) Hoost, T. E.; Laframboise, K. A.; Otto, K. *Catal. Lett.* **1995**, *33*, 105.
- (40) Valyon, J.; Hall, W. K. *J. Phys. Chem.* **1993**, *97*, 1204.
- (41) Kasai, P. H.; Bishop, R. J. *J. Phys. Chem.* **1977**, *81*, 1527.
- (42) Hall, W. K.; Valyon, J. *Catal. Lett.* **1992**, *15*, 311.
- (43) Goodman, B. R.; Hass, K. C.; Schneider, W. F.; Adams, J. B. *J. Phys. Chem. B* **1999**, *103*, 10452.
- (44) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177.
- (45) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.