

Irreversible dinitrogen adsorption on Cu-ZSM-5 catalysts and *in situ* IR identification of the NO decomposition sites

Sandro Recchia,^{*a} Carlo Dossi,^a Achille Fusi,^a Rinaldo Psaro,^b Renato Ugo^a and Giuliano Moretti^c

^a Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Milano, Via Venezian 21, 20133-Milano, Italy

^b Centro di Studio CNR 'SSCMTBSO', Università di Milano, Via Venezian 21, 20133-Milano, Italy

^c Centro di Studio CNR 'SACSO', Dipartimento di Chimica, Università 'La Sapienza', Piazzale Aldo Moro 5, 00185-Roma, Italy

Dinitrogen chemisorbs on two neighbouring copper atoms of Cu-ZSM-5 catalysts that are demonstrated to be the active sites for NO decomposition.

Dinitrogen chemisorption at room temperature on supported metal particles has been reported for rhodium on aluminium-rich zeolites and on titania.^{1,2} On Cu/mordenite (Cu/NaM)³⁻⁵ and Cu^I-ZSM-5⁶ systems, IR evidence supports a simple physisorption of N₂ while the presence of a small amount of strongly adsorbed N₂ on Cu sites is only claimed.

We now report adsorption data and direct IR evidence of N₂ chemisorption on different Cu/zeolites systems, with correlation to their catalytic activity for NO decomposition to N₂ + O₂.

NaY (Si/Al = 2.4) and H-ZSM-5 (Si/Al = 17) zeolites were ion-exchanged at room temp. with dilute solutions of copper acetate. Dinitrogen adsorption isotherms were determined by a conventional volumetric apparatus at 273 K in the range 0–100 Torr. Samples were pretreated at 10⁻⁵ Torr for (a) 1 h at 788 K before the first N₂ adsorption and (b) 0.5 h at 273 K before the second N₂ adsorption. The N₂ adsorptions were calculated from the intercepts at *P* = 0 Torr of the straight lines in the high-pressure range of the first and the second isotherm, respectively.

With NaY, H-ZSM-5 and Cu/NaY the same behaviour reported for NaM³⁻⁵ was observed: the intercepts of the straight lines are zero, corresponding only to N₂ physisorption. Moreover, the turnover frequency for NO decomposition on Cu/NaY is very low and quite insensitive of the copper loading.^{7,8} The Cu-ZSM-5 systems, catalytically very active, show instead an irreversible N₂ coverage [0.03, 0.04, 0.12 mol N₂ (mol Cu)⁻¹ at 25, 65, 117% Cu exchange, respectively]. The adsorption process was also investigated in a flow cell by diffuse reflectance infrared FT spectroscopy (DRIFTS), in order to retain the working conditions of the catalyst and to avoid the diffusional limitations often encountered when the sample is a self-supporting wafer.

DRIFTS measurements were carried out at room temperature on Cu-ZSM-5 (98% Cu exchange), activated in flowing Ar [Fig. 1(a)]. A weak band at 2130 cm⁻¹ [Fig. 1(b)] appears in N₂ flow and does not change its intensity even after 12 h of Ar purging at room temp. The observed stretching frequency is much lower than the ν_{N-N} vibrations at 2299 and at 2295 cm⁻¹ attributed to physisorbed N₂ on Cu/NaM (150% Cu exchange)³⁻⁵ and Cu^I-ZSM-5,⁶ respectively, or the vibrations at 2334 and 2352 cm⁻¹ due to physisorbed N₂ on Brønsted- and Lewis-acid sites of H-ZSM-5.⁹

According to the reported relationship between ν_{N-N} and the N–N bond lengths,¹⁰ the red shift of 201 cm⁻¹ with respect to the gaseous N₂ molecule (bond length = 1.098 Å) suggests a chemisorbed N₂ with a bond length of *ca.* 1.12 Å. Such a value is similar to those reported for the N–N bond distances in many N₂-dinuclear transition-metal complexes of [M–N≡N–M] type¹⁰ and is in accord with an 'end-on' bridging coordination with the nitrogen molecule bonded to two different copper centers. The arrangement of two copper ions bridged by extra

framework OH species was found by static atomistic simulation techniques to be particularly stable in ZSM-5 zeolite,¹¹ moreover, such binuclear species were independently proposed as the active sites for NO decomposition.^{12,13}

Information about the nature of the sites responsible for this kind of N₂ chemisorption was gained through competitive adsorption of N₂ and CO experiments.

The spectrum in Fig. 1(c), obtained after carbonylation, shows a strong band at 2154 cm⁻¹ with a shoulder at 2138 cm⁻¹ and a weak band at 2107 cm⁻¹, all being commonly assigned to linearly chemisorbed CO on different Cu⁺ intrazeolitic sites.¹⁴

Fig. 1(d) depicts the changes brought about by flowing N₂. The appearance of a new weak band at 2130 cm⁻¹ due to chemisorbed N₂ (partially overlapping the CO band at 2138 cm⁻¹), together with the marked decrease of the CO band at 2154 cm⁻¹, indicates an unexpected ability of N₂ to displace CO from that specific site. The driving force of this ligand-exchange reaction may be accounted for by the proposed bridging coordination of N₂ on two neighbouring copper sites.

Fig. 2 shows how the pattern of the 2154 cm⁻¹ carbonyl band intensity closely matches that of the catalytic activity at 773 K vs. % Cu exchange.⁷ A direct correlation between the number of NO decomposition sites and the intensity of the 2154 cm⁻¹ CO band emerges from the comparison of these two profiles; as a consequence of such a correlation, the adsorption of N₂ is proved to occur only on these catalytically active sites.

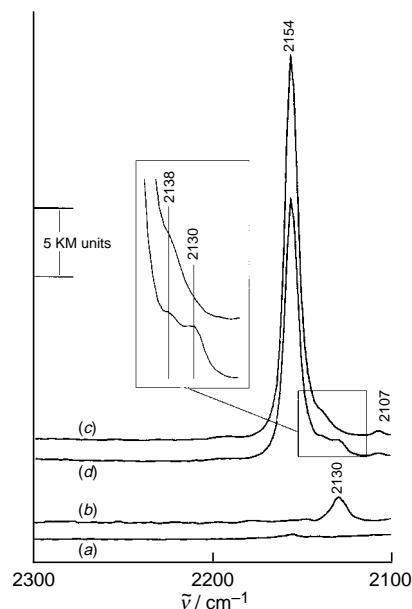


Fig. 1 DRIFT spectra recorded at 293 K of 98% Cu exchanged Cu-ZSM-5 system: (a) after activation in flowing Ar from 293 K to 703 K for 1 h (ramp 3 K min⁻¹), (b) (a) after 3 h in flowing N₂ at 293 K, (c) activation as in (a) followed by 12 h in flowing CO at 293 K and subsequent Ar degassing, (d) (c) after 3 h in flowing N₂ at 293 K

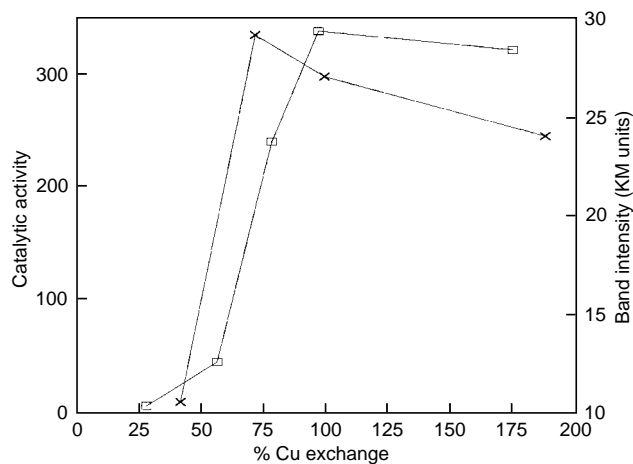


Fig. 2 (×) Intensity of the CO band at 2154 cm^{-1} of four Cu-ZSM-5 catalysts vs. % Cu exchange: spectra recorded in Ar after the same sequence reported in Fig. 1(c). (□) Catalytic activity at 773 K vs. % Cu exchange (ref. 6): the catalytic activity is expressed as $10^{-16} x$ (number of NO molecules converted to N_2) (g catalyst s) $^{-1}$.

The unique role of the ZSM-5 framework in the unusual catalytic activity of Cu-ZSM-5 systems can be therefore accounted for by its ability to provide the correct geometrical arrangement of dual copper sites for $\text{N}\equiv\text{N}$ bond formation from two NO molecules.

We thank the Ministry of University and Scientific and Technological Research (MURST) for financial support.

Footnote and References

* E-mail: sandy@csmto.mi.cnr.it

- 1 H. Miessner, *J. Chem. Soc., Chem. Commun.*, 1994, 927.
- 2 V. Vishwanathan, *J. Chem. Soc., Chem. Commun.*, 1989, 848.
- 3 Y. Kuroda, H. Maeda, Y. Yoshikawa, R. Kumashiro and M. Nagao, *J. Phys. Chem. B*, 1997, **101**, 1312.
- 4 Y. Kuroda, S. Konno, K. Morimoto and Y. Yoshikawa, *J. Chem. Soc., Chem. Commun.*, 1993, 18.
- 5 Y. Kuroda, Y. Yoshikawa, S. Konno, H. Hamano, H. Maeda, R. Kumashiro and M. Nagao, *J. Phys. Chem.*, 1995, **99**, 10 621.
- 6 C. Lamberti, S. Bordiga, M. Salvalaggio, G. Spoto, A. Zecchina, F. Geobaldo, G. Vlaic and M. Bellatreccia, *J. Phys. Chem. B*, 1997, **101**, 344.
- 7 M. C. Campa, V. Indovina, G. Minelli, G. Moretti, I. Pettiti, P. Porta and A. Riccio, *Catal. Lett.*, 1994, **23**, 141.
- 8 Y. Li and W. K. Hall, *J. Catal.*, 1991, **129**, 202.
- 9 F. Wakabayashi, J. N. Kondo, K. Domen and C. Hirose, *J. Phys. Chem.*, 1996, **100**, 4154.
- 10 J. D. Cohen, M. Mylvaganam, M. D. Fryzuk and T. M. Loehr, *J. Am. Chem. Soc.*, 1994, **116**, 9534.
- 11 D. C. Sayle, C. R. A. Catlow, J. D. Gale, M. A. Perrin and P. Nortier, *J. Phys. Chem. A*, 1997, **101**, 3331.
- 12 M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, *J. Phys. Chem.*, 1992, **96**, 9360.
- 13 G. Moretti, *Catal. Lett.*, 1994, **28**, 143.
- 14 K. I. Hadjiivanov, M. M. Kantcheva and D. G. Klissurski, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4595.

Received in Cambridge, UK, 16th June 1997; 7/04218C