Contribution from the Istituto di Chimica Fisica, dell'Università di Torino, Turin, Italy

Surface Complexes of Nitrous Oxide Adsorbed on α-Cr_2O_3

E. Borello, L. Cerruti, G. Ghiotti, and E. Guglielminotti

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The nitrous oxide-α-chromia interaction at room temperature has been studied by infrared spectroscopy. Two surface complexes have been evidenced, each one being characterized by a pair of bands. The two modes of each pair are in the N_2O antisymmetric and symmetric stretching region respectively, suggesting that two molecular species are adsorbed onto coordinatively unsatured surface cations, either through the oxygen or the terminal nitrogen. Such surface complexes closely resemble the two resonant forms of nitrous oxide.

Introduction

A recent paper by Banks *et al.*[1] ascribes the apparent non reactivity of nitrous oxide more to a lack of any thorough investigation than to a real chemical stability. In fact, it is inconsistent with the positive free energy of formation (ΔG° +24.9 kcal mole^{-1}), with the potential oxidizing capacity and with the observation that N_2O is a normal product and substrate of bacterial metabolism. Therefore, the above Authors studied the reaction (at room temperature and 760 torr pressure) of nitrous oxide with several complexes of transition metals. They concluded that, at least in the case of Co^I complexes, there is quick oxidation of the metal and a release of molecular nitrogen. There is no evidence so far of the existence of complexes with N_2O as a ligand, except as highly unstable reaction intermediates. Also the interpretation of the reaction between gaseous nitrous oxide and solid metal amides (Wislicenus synthesis, one of the first known reactions of N_2O) admits an intermediate, containing molecular N_2O. According to Clusius and Schumacher[2] such heterogeneous reaction would occur through an initial physical adsorption on the amide surface, followed by a bulk diffusion and linking onto energetically favoured sites. They could be either metal ions or NH_2 ions depending on ionic radii ratio, in order to explain the formation of the two isotopic $^{15}NNNH$ and $N^{15}NNH$ species.

The existence of molecular N_2O physically adsorbed at low temperatures has been recently revealed by Kozirowski and Folman[3] on alkali halides and in our laboratory[4] on silica gel, by means of infrared spectroscopy.

As far as the chemisorption of nitrous oxide on solides is concerned, the formation of surface intermediates has been often suggested, to account for the decomposition of N_2O on semiconductors.[5] In fact N_2O decomposition and CO oxidation are the most commonly used reaction to check the catalytic activity of metal oxides. Proposed mechanisms for the decomposition are:

$$N_2O_{gas} \leftrightarrows N_2O_{ads} \qquad N_2O_{ads} \rightarrow N_2 + O^-{}_{ads} + p$$

or

$$N_2O_{gas} \leftrightarrows N_2O^-{}_{ads} + p \qquad N_2O^-{}_{ads} \rightarrow N_2 + O^-{}_{ads}$$

$$2O^-{}_{ads} + 2p \leftrightarrows O_2$$

Guilleux and Imelik[6] recently studied the N_2O decomposition on NiO by gravimetric and volumetric determinations at several temperatures and concluded that at 70°, together with the decomposition, chemisorption takes place with an initial activation energy of 8 kcal/mole. On the other hand the existence of N_2O reversibly chemisorbed on various oxides, including chromia, was already evidenced by Winter.[7] Recently, a reversible N_2O adsorption onto Co^{II} ions in dehydrated $Co^{II}A$ zeolites has been observed by K. Klier[8] by reflectance spectroscopy.

It can be concluded that N_2O reactions, both in homogeneous and heterogeneous phase, must involve intermediates containing molecular N_2O, and that these intermediates are only stable in very special conditions. The fact that on several oxides a chemisorption of molecular nitrous oxide occurs together with the decomposition[6-7] suggests that those very special conditions are more easily achieved on the surface of a semiconductor than with transition metals complexes. If it does so, infrared spectroscopy seems to be the most suitable technique to identify and characterize such species. In fact at least one of the N_2O normal modes, the antisymmetrical stretching, should be in a spectral region of good trasparency on oxides and must possess a high extinction coefficient. Besides, a good deal of references is available, the spectrum of N_2O being well known in several phases, including physical adsorption (see Table I).

On the other hand, this would not be the first time, that infrared spectroscopy allowed the identification of surface species containing molecules, only later

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(1) R.G.S. Bank, R.J. Henderson, and J.M. Pratt, *J. Chem. Soc.* (*A*), 2886 (1968).

(2) K. Clusius and H. Schumacher, *Helv.*, *41*, 972 (1958).

(3) Y. Kozirowski and M. Folman, *Trans Faraday Soc.*, *65*, 244 (1969).

(4) A. Zecchina, G. Ghiotti L. Cerruti, and C. Morterra, *J. Chim. phys* 68, 1479 (1971).

(5) K. Hauffe, *Advances in Catalysis*, *7*, 213 (1955).

(6) M.F. Guilleux and B. Imelik, *Bull. Soc. Chim.*, 1310 (1970).

(7) E.R.S. Winter, *Advances in Catalysis*, *10*, 196 1958).

(8) K. Klier, *J. Am. Chem. Soc.*, *91*, 5392 (1969).

Table I.

	(Asymm. stretching)		(Symm. stretching)
N_2O gas phase[a]	2224		1286
N_2O solid phase[b]	2235		1293
N_2O ads. on alkali halides[c]	2224 - 2250		1247 - 1274
N_2O ads. on Aerosil[d]	2230		—
N_2O ads. on α-Chromia	2305		1339
	2238		1237
CO_2 gas[a]	2349		1388 (Raman)
FCN gas[a]	2290		1077
NO_2^+[a]	2375		1400
NO_2 gas[a]	1621		1320
N_2gas[a]		2331 (Raman)	
N_2 phis. ads. on silica[e]		2330	
N_2^+ ads. on Ni/SiO_2[e]		2202	

[a] K. Nakamoto. Infrared Spectra of Inorganic and Coordination Compounds, Wiley - Interscience, New York, 1970[11]; [b] See Ref. (14); [c] Ref. (3); [d] Ref. (4); [e] Ref. (8).

studied as complex ligands. We remind the cases of molecular nitrogen, that Eischens and Jacknow[9] evidenced as $(N_2)^+$ group on silica supported nickel, and of carbon monoxide with an unusually high stretching frequency (about 2200 cm^{-1}) when chemisorbed without back-donation onto transition metal oxides.

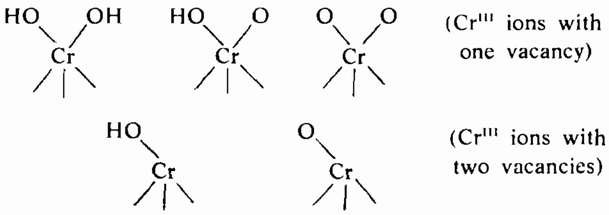
Other physical properties of nitrous oxide, that might be useful are reported here after. The dipole moment is small (0.16 D) and the quadrupolar moment quite large (4.4 10^{-26} e.s.u.). The polarizability is highly anisotropic, being 53.2 10^{-25} cm^3 along the molecular axis and 18.3 10^{-25} in the direction normal to it. The interatomic distances are 1.126 Å between the nitrogens and 1.191 Å between nitrogen and oxygen.[2,3]

The present paper deals with the I.R. detection and interpretation of nitrous oxide species adsorbed onto α-Chromia.

Results

Chromium^{III} oxide was obtained by thermal decomposition of ammonium dichromate. The preparative conditions and the treatments further needed to obtain samples of stable and reproducible surface properties are described elsewhere[10] We only remind that the surface area is between 60 and 70 m^2/gr and that the material is made of thin laminae of hexagonal or octogonal contour, whose linear dimension is in the 300-600 Å range. The (001) face is definitely predominant. In the above mentioned paper we described all the preliminary thermal treatments, that the sample is undergoing before its adsorbing capacities are investigated. They produce in the surface some active centers mainly constituted by chromium ions and oxide ions, that are coordinatively unsaturated (c.u.s. ions) according to Burwell's theory[11] Before the thermal treatments, all of surface metal ions are in a fully saturated octahedral coordination, that is achieved by water chemisorption (both dissociative and coordinative). The catalyst has therefore no chemisorptive capacity at all.

A thermal activation *in vacuo*, bringing about water elimination processes, develops the surface activity. A limited number at unsaturated configurations can thus be identified on the surface.



The relative concentrations of the above sites are somehow depending on dehydration temperature and time. Chemisorption processes might either occur on Cr^{3+} c.u.s. ions or on O^{2-} c.u.s. ions or on cationic-anionic pairs.

Nitrous oxide chemisorption at room temperature readily originates two pairs of I.R. absorption in the spectral regions 2350-2100 cm^{-1} and 1400-1200 cm^{-1}, the individual frequencies being: 2305, 2238, 1339, 1237 cm^{-1}.

We must first understand whether the chemisorption occurs onto cationic or anionic sites and whether the four bands belong to one species only or to more than one. The first question is quite easy to answer, because no N_2O chemisorption occurs on samples, that preadsorbed pyridine. As it is a hard base and gives strong surface complexes with unsaturated chromium ions,[12] the nature of the N_2O active sites is therefore evidenced. The second problem is also overcome if the spectral behaviour is considered as a function of decreasing gaseous pressure. Infrared spectroscopic study of the desorption process reveals that the four bands are two pairs, each of them being made up of a high frequency and a low frequency component. In fact they exhibit rather different desorption rates, the more easily removed pair being at 2238-1237 cm^{-1} and the other at 2305-1339 cm^{-1}. The spectral intensity ratios are schematically reported in Figure 1 for the two equilibrium pressures a = 40 torr and b = .1 torr

It is therefore concluded that we have two surface

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(9) R.P. Eischens and J. Jacknow, in *Proc. 3rd Intern. Congr. Catalysis*, Amsterdam, 1964, vol. 1, p. 627, North Holland Publ., Amsterdam, 1965.

(10) A. Zecchina, S. Coluccia, E. Guglielminotti, and G. Ghiotti, *J. Phys. Chem.*, *75*, 2774 1971).

(11) R. Burwell Jr., G.L. Haller, K.C. Taylor, and J.F. Read, *Advances in Catalysis*, *19*, 62 (1969).

(12) Unpublished data, this laboratory.

species that are independently chemisorbed and are rereversibly bonded with slightly different energies. Also, each pair has a component in the N_2O asymmetric stretching region and the other in the N_2O symmetric stretching region, leading to the conclusion that in both cases the chemisorption is non dissociative.

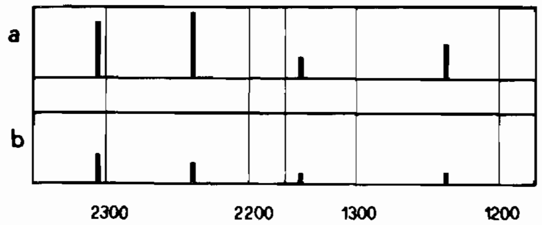

Figure 1.

As we are facing two species that are structurally similar, the question now arises, whether they differ in the nature of the adsorbing Cr_{cus} site or in the nature of the adsorbate-metal bond. In order to answer, a preliminary description of what is known about the structure of nitrous oxide seems to be of some importance. A detailed LCAO-MO SCF study has been carried out by Peyerimhoff and Bunker[13] leading to the conclusion that the 22 electrons are distribuited as follows:

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 6\sigma^2\ 1\pi^4\ 7\sigma^2\ 2\pi^4$$

The first six σ orbitals are almost entirely built up, by the 1s and 2s atomic orbitals of the three centers and might be disregarded. The 1 π orbital has a strong bonding character with high electronic density within the molecule and a maximum on the central atom. The 2 π orbital is weakly N–N bonding and N–O antibonding, with a higher density on the end atoms, particularly on the oxygen. The «end atom» character of 7 σ and 2 π orbitals in all AB_2 and ABC systems, accounts for the positive nature of the central atom and agrees with the resonant formes A and B usually adopted:

$$\text{A)}\quad \overset{-}{N}=\overset{+}{N}=O \qquad\qquad \text{B)}\quad N\equiv\overset{+}{N}-\overset{-}{O}$$

Similar conclusions are reached by Wagner,[14] through a simplified LCGO–MO study of the ABC molecule: the electronic structure is so described:

$$(\sigma AB)^2(\sigma BC)^2(\sigma A)^2(\sigma C)^2(w\pi)^4(u\pi)^4$$

and the N_2O diagram is:

$$\begin{array}{ccccc} -0.6246 & & 0.6607 & & -0.0362 \\ N & \equiv & N & \equiv & O \\ & 1.5113 & & 1.2652 & \end{array}$$

The first unoccupied orbital is the 3 π, which again exhibits a density maximum in the central atom with strong N–N antibonding character and weak N–O antibonding and is more stable in non linear systems. Therefore the occupation of such an orbital should favour a bent structure and lead to the dissociation of the linear molecule. Also, 22 electrons seems to be a limit, above which bent structures are favoured and this difference of electronic structure should clearly effect the infrared spectrum. An example is given by the NO_2^+–NO_2 systems. The ion is linear (isoelectronic with nitrous oxide) and exhibits two stretching frequencies at 2375 and 1400 cm^{-1}, while the molecule, that is bent (23 electrons) has the same modes at 1621-1320 cm^{-1} (Table I).

Dealing with the possibility of nitrous oxide to act as a ligand in coordination or surface compounds, linear perpendicular structures should be favoured through the formation of σ bonds by means of the lone pair on either terminal atoms. A back donation to the 3 π orbital would lead to dissociation or, at least, to bent structures with strong bond modifications, easily evidenceable in the infrared spectrum. Parallel structures seem quite unlikely, due to the previously mentiond « end atom » character of 7 σ and 2 π orbitals; on the other hand, they should be clearly recognizable in infrared.

In Table I the frequencies of nitrous oxide in various states and of a few isoelectronic species are reported. The frequencies of gaseous N_2O, if compared with those of solid and physically adsorbed N_2O, clearly indicate a remarcable state dependance, that is not easily understood. In particular in the solid state ν_3 and ν_1 are blue-shifted of 11 and 7 wavenumbers respectively, possibly due to repulsive forces between adjoining molecules in the lattice.[15] When physically adsorbed on alkali halides, ν_3 is blue-shifted up to as much as 26 cm^{-1} and ν_1 is red-shifted up to as much as 39 cm^{-1}, the observed rule being: the higher the upwards shift of ν_3, the higher the downward shift of ν_1. This might suggest that the observed spreading is due to a variable coupling of the two oscillator, owing to small changes of the force constants of N–N and N–O bonds.

In the present case of chemisorbed N_2O the shifts are much higher for one species ($\Delta\nu_3 = +14\ cm^{-1}$, $\Delta\nu_1 = -49\ cm^{-1}$) and for the other they do not even fit the above schema ($\Delta\nu_3 = +14 cm^{-1}$, $\Delta\nu_1 = -49\ cm^{-1}$). In other words, the surface bond energies as deduced from the desorption rate are pretty much the same in the two cases, but the spectral behaviour is quite different. It can be best explained in terms of the formation of the following species:

$$Cr\leftarrow\overset{-}{N}=\overset{+}{N}=O \qquad\qquad Cr\leftarrow\overset{-}{O}-\overset{+}{N}\equiv N$$

A B

They are molecular species strongly polarized by the surface cations and fairly close to the canonic forms. In fact species A exhibits a spectral behaviour similar to CO_2, whose ν_3 is I.R. active at 2349 cm^{-1} and ν_1 is Raman active at 1388 cm^{-1}. They would correspond to the 2305 and 1339 cm^{-1} bands, the latter being consistently very weak. In species B, the N–N

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(13) S.D. Peyerimhoff and R.J. Buenker, *J. Chem. Phys.*, *49*, 2473 (1968).

(14) E.L. Wagner, *J. Chem. Phys.*, *43*, 2728 (1965).

(15) H. Yamada and W.B. Person, *J. Chem. Phys.*, *41*, 2478 (1964).

bond can be compared with the $N \equiv N^+$ structure (2202 cm^{1-}), that Eischens observed with N_2 adsorbed onto silica supported Ni and N–O with the N–O bonds of nitrile N-oxides. In fact they have a typical absorption in a rather large range about our experimental frequency.[16] A N_2O^- surface species, that has been postulated by several Authors[5] as intermediate in catalytic decomposition of N_2O, must be rejected. In fact, according to the above discussion, it should be bent, as the isoelectronic NO_2 molecule, and its stretching frequencies should be definitely different (Table I). N_2O^- in gas phase decomposes with excess energy of only a fraction of an eV thus, $N_2O + e = N_2 + O^-$.[17]

N_2O must be a very soft base, in view of its high polarizability in the axial direction, and therefore its interaction with the hard Cr_{cus}^{3+} acid very weak. In fact the chemisorbed complexes are fully reversible at room temperature.

Already Kozirowsky and Folman[3] postulated N_2O to be adsorbable through the terminal nitrogen atom as well as through the oxygen, even if that possibility seemed to them rather unlikely. In fact their species was thought to be physically adsorbed through an electrostatic interaction between surface field and quadrupole moment with a weak contribution by the very small dipole moment. The high quadrupole moment is probably rather important also in our case, mainly in orienting the molecule with respect to the surface, according to the nature and charge of the ions next to the site. Needless to say, such an orientation is quite important in that it determines the formation of a σ bond either through the oxygen or the terminal nitrogen. The ligands attached to the Cr_{cus}^{3+} ion in the five reported configurations are therefore expected to be of some importance in the phase just before the formation of the bond, when the molecule is approaching the surface. On the other hand we cannot understand te effects of the « ligand heterogeneity » onto the chemisorption of nitrous oxide, until we do not know which of the five sites are responsible of either chemisorbed form and of the N_2O decomposition. Nitrous oxide chemisorption is now being studied at lower temperature both for that purpose and to check the oxidation kinetics by the two surface species.

In fact the N_2O/Cr_2O_3 system is extremely active, in the CO oxidation process, even at low temperatures, at which the N_2O_{gas}/CO_{gas} system is non reactive and the $Cr_2O_3/O_2/CO$ system is slightly active. The two N_2O surface species seem to exhibit different activity.

Finally, it is not surprising that it is much easier to reveal the coordination of N_2O in surface complexes than in homogeneous complexes. In fact in the former, the metal ions are rigidly confined to some crystal lattice positions and therefore the interaction between different coordinated molecules hardly occurs, especially at low surface coverages. Besides, the high cleanliness of adsorption experiments must be kept in mind, that almost completely eliminates the possibility of any other ligand to interact with N_2O_{ads}. We just recall that, if CO is allowed onto a surface covered by N_2O_{ads}, the two species immediately react to yield CO_{2ads} and N_2. This mutual reactivity of N_2O and CO on a α–Cr_2O_3 surface also leads support to Bank's viewpoint, that nitrous oxide must be thought as a non-reactive species only in that it has not been thoroughly investigated.

Note added in proof. While this paper was in press, it was noticed to us that complexes of nitrous oxide with Ru^{II} were isolated by J.N. Armor and H. Taube (Chem. Com. 287, 1971) and by A.A. Diamantis and G.J. Sparrow (Chem. Com. 819, 1970). However the structure of such complexes is not well known and their spectra are rather different from what we observe on our α—Cr_2O_3 surface.

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(16) N.B. Colthup, L.H. Dealy, and S.E. Wiberly, « Introduction to Infrared and Raman Spectroscopy », Acad. press, London - New York, 1964.

(17) R.K. Curran and R.E. Fox, *J. Chem. Phys*, *34*, 1590 (1961).