JOURNAL OF CATALYSIS 25, 55–64 (1972)

An Infrared Study of Nitrous Oxide Adsorption on α-Chromia

A. ZECCHINA, L. CERRUTI, AND E. BORELLO

*Istituto di Chimica Fisica, Università di Torino, Corso Massimo d'Azeglio 48,
10125 Torino, Italy*

Received May 17, 1971

Room temperature adsorption of nitrous oxide on α-chromia has been studied by means of IR spectroscopy. Two different processes occur: (i) A rapid decomposition leading to a selective coverage of surface chromium sites with oxygen adsorbed through a quasi-double bond. (ii) A nondissociative adsorption on surface sites that are not covered with oxygen. Two types of N_2O_{ads} species are observed and discussed.

The heterogeneous decomposition of nitrous oxide has long been employed as a test reaction of reactivity of oxides (*1–3*). In our research program to characterize chromium oxide surface properties, we also have studied the N_2O/Cr_2O_3 system. As far as we know, there is no evidence of the existence of complexes with N_2O as a ligand, except as highly unstable reaction intermediates (*4*). Hence our interest in trying to characterize spectroscopically the adsorbed state of nitrous oxide. Already in the case of complexes containing molecular nitrogen and carbon monoxide coordinated through a basically σ bond, IR spectra of adsorbed species preceded the preparation of complexes (*5, 6*). We also recall that Burwell *et al.* (*7*) recently indicated that a surface on which coordinatively unsaturated sites have been created is particularly suitable for this kind of study. So far, the only infrared work on adsorbed N_2O was by Kozirovski and Folman (*8*), who studied physical adsorption on alkali halides at low temperatures. A reversible N_2O adsorption on Co^{II} ions in dehydrated $Co^{II}A$ zeolite has been observed by Klier (*9*) by reflectance spectroscopy.

Experimental Methods

Chromium oxide has been produced by thermal decomposition of ammonium dichromate, as described by Harbard and King (*10*). The bulky powder so obtained consists of amorphous chromia with an excess of oxygen. It was compressed at 100 kg/cm^2 into pellets that were 0.15–0.20 mm thick and contained 10 mg/cm^2. The preparation of a "reproducible" microcrystalline material, suitable for adsorption studies, consists of three phases.

Phase I. Samples are degassed for 16 hr at 400°C in a conventional vacuum line equipped with liquid nitrogen cold traps ($p \leqslant 10^{-5}$ Torr). After this treatment, the material is still amorphous and brown in color.

Phase II. Samples are kept 5–6 hr at 400°C under a static oxygen pressure of 10^{-2} Torr. Water is produced and is frozen in the cold trap. The sample turns green.

Phase III. Samples are now reduced with CO (40 Torr) at 400°C for 2 hr, and finally degassed at the same temperature for 2 hr.

The resulting material is stable to thermal and to redox treatments. During phase II, an exhaustive crystallization is promoted, as the characteristic X-ray pattern of α-chromia indicates. (Diffraction lines are just a little broader than usual due to small crystal size.) The color is green, the surface area is 60–70 m^2/g, and the *t*-plot (*11*) indicates that no micropores are present. Electron micrographs show crystals of linear dimension in the

300–600 Å range, shaped as very thin laminae of hexagonal or octagonal contour. The (001) face is definitely predominant (*12*).

Infrared spectra have been recorded on a Beckman IR 12 double beam spectrophotometer. Slit widths were 4–5 cm^{-1} at 1200 cm^{-1} and 12–14 cm^{-1} at 2200 cm^{-1}. A heavy scattering loss in the 850–2300 cm^{-1} interval was balanced by screening the reference beam. An arbitrary 90% transmission has been fixed at 1200 cm^{-1} for the 900–1400 cm^{-1} range and at 2100 cm^{-1} for the 2100–2250 cm^{-1} range by attenuating the reference beam with metal screens.

"Room temperature" operations actually refer to 36–38°C, for they have always been performed with the sample in the IR beam path. As far as the *in situ* cell is concerned, we recall our previous descriptions (*13*).

Ammonium dichromate was reagent grade (C. Erba, Milan). Carbon monoxide, used for reduction purposes, contained impurities amounting to 100 ppm (SIO, Milan) and has always been further purified by passing it through a liquid nitrogen cold trap to eliminate traces of $Ni(CO)_4$. Oxygen and N_2O contained impurities amounting to 100 ppm (Rivoira, Turin) and were not further purified.

RESULTS

Highly oxidized chromia (i.e., chromia that chemisorbed oxygen at 400°C) does not adsorb N_2O at room temperature and there are no differences in the IR spectrum before and after admission of N_2O.

Oxygen-free chromia (samples after phase III) when contacted with N_2O (54 Torr), exhibits absorption bands in three spectral regions (Fig. 1, solid line). In the 950–1050 cm^{-1} range, there are two bands of medium intensity: the first is rather broad and centered at 975 cm^{-1} and the second is sharper and centered at 1016 cm^{-1}. In the 1200–1400 cm^{-1} range, there are two bands: a medium one at 1237 cm^{-1} and a weak one at 1339 cm^{-1}. Between them, two wings with central minimum at 1285 cm^{-1} are due to the rotational contour of the ν_1 mode (*14*), the gaseous pressure being high enough for this mode to appear in spite of the small cell path (4–5 mm). In the 2100–2350 cm^{-1} range, basically two bands are present: a very strong one at

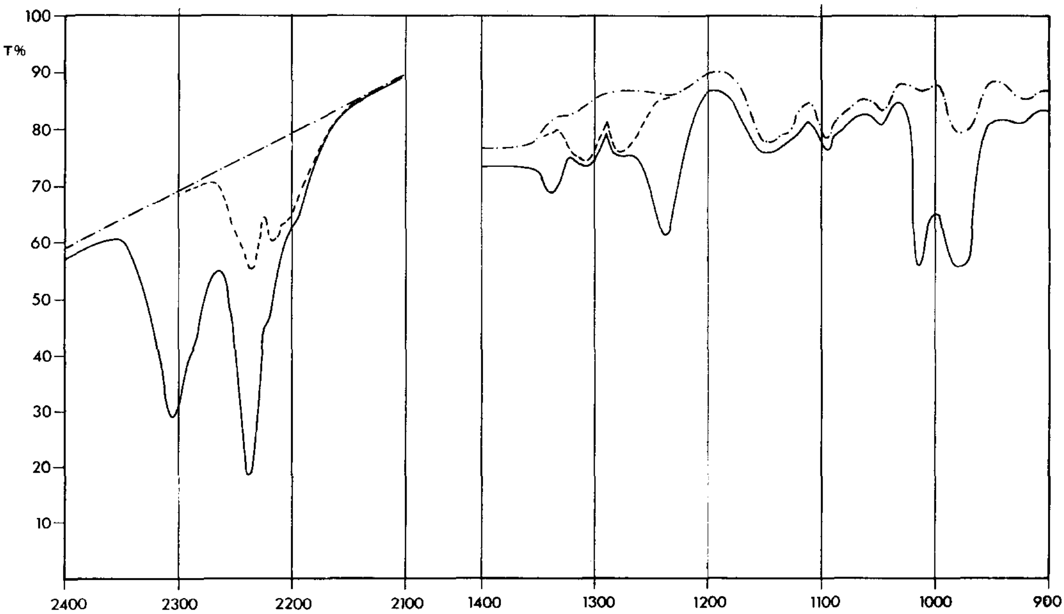


FIG. 1. IR spectrum of N_2O on α-Cr_2O_3: (— ·) background spectrum; (—) after admitting N_2O (54 Torr); (— —) spectral contribution of the gas phase.

2238 cm^{-1} with a broad tailing in the low frequency side, due to the gaseous phase, and a strong one at 2305 cm^{-1}. Curves of Fig. 2 correspond to different equilibrium pressure, as reported in the legend. With decreasing coverage, all the observed bands reveal a more and more asymmetric and complex nature. Meanwhile, the two bands at 2238 and 2305 cm^{-1} change their absorbance ratio (the contribution of the gas phase is obviously not included) from 1.5 to approximately 1. A similar behavior seems to be exhibited by the bands at 1237 and 1339 cm^{-1}, though the weakness of the latter makes the observations rather doubtful. When the residual N_2O pressure is lower than 5 × 10^{-3} Torr, absorption bands are no longer detectable in the high frequency range. Bands at 1016 and 975 cm^{-1} behave quite differently in that a prolonged evacuation at room temperature intensifies the former and shifts the latter to 995 cm^{-1} (see Fig. 3a, curve 2). Species responsible for these bands are not eliminated upon degassing, even at 400°C.

When molecular oxygen contacts at room temperature a bare surface (samples after phase III), several absorptions appear in the 1050–750 cm^{-1} range. Figure 3a, curve 3 shows the 1050–950 cm^{-1} range, where five peaks are visible at 1024, 1016, 995, 986, 980 cm^{-1}. A complete description and discussion of the whole 1050–750 cm^{-1} region is being published elsewhere (*15*). So a short discussion will suffice here. As in the case of bands produced in this region by N_2O adsorption, the above five bands cannot be eliminated upon degassing at temperatures up to 400°C but only by repeating the operations of phase III. A sample whose situation is as described by Fig. 3a, curve 2, when contacted with N_2O, gives back a spectrum like that of Fig. 3a, curve 1 and in the high wavenumber region, the

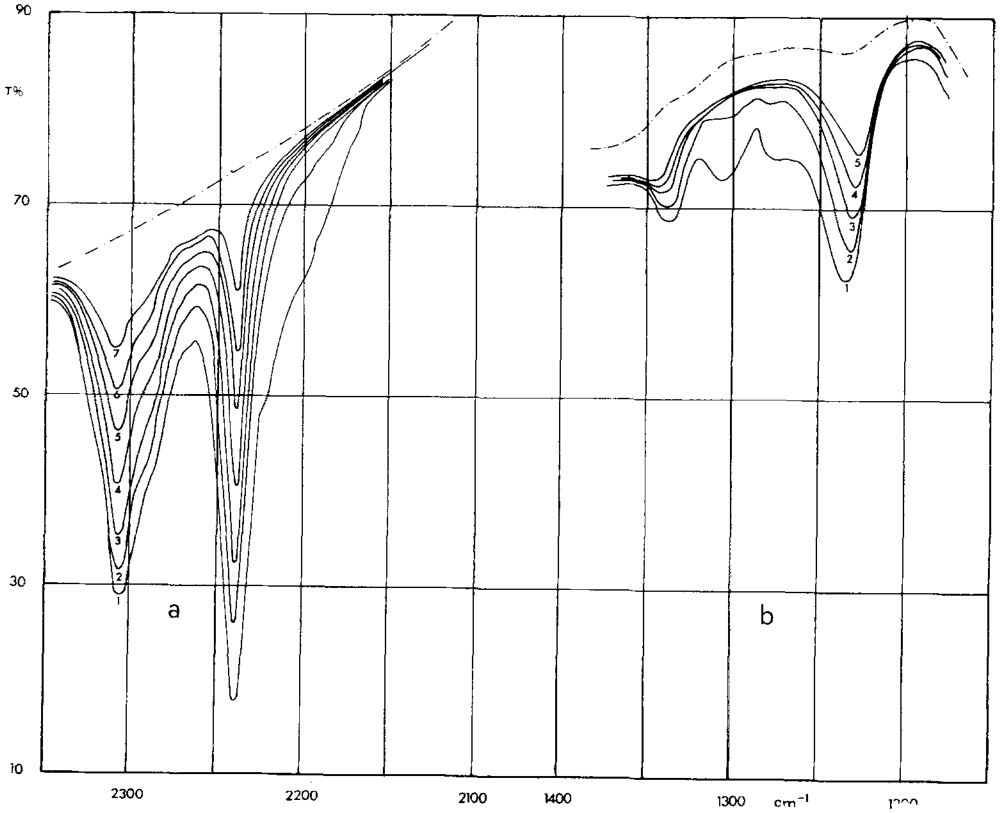


FIG. 2. IR spectrum of N_2O on α-Cr_2O_3: (— ·) background spectrum; Curves 1–7 correspond to various N_2O desorption stages, pressures (Torr): (1) 54; (2) 11; (3) 1; (4) 0.20; (5) 0.13; (6) 6 × 10^{-2}; (7) 3.3 × 10^{-2}.

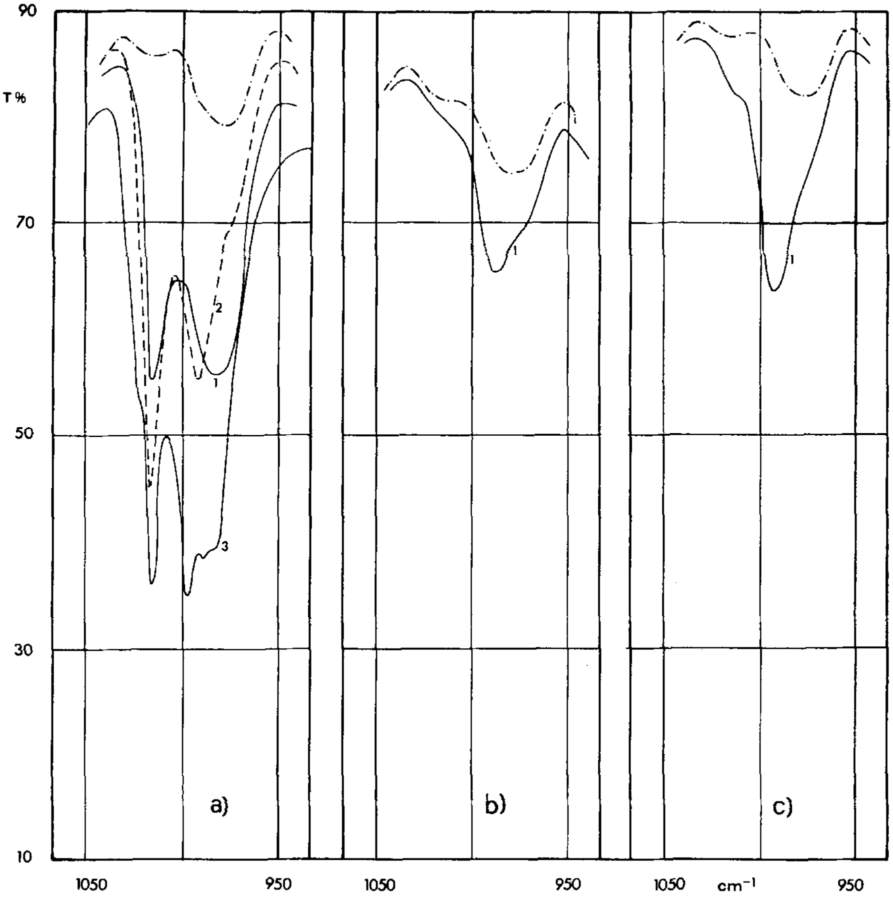


FIG. 3. IR spectrum of surface oxygen on α-Cr_2O_3: (— ·) background spectrum; (a) (1) α-Cr_2O_3 in equilibrium with 54 Torr of N_2O; (2) after evacuation of the gas phase; (3) IR spectrum of a bare α-Cr_2O_3 sample in equilibrium with oxygen (10 Torr) at room temperature. (b) (1) a rehydrated α-Cr_2O_3 sample has been dehydrated at 260°C, contacted with N_2O (52 Torr), and evacuated at room temperature; (c) (1) a rehydrated α-Cr_2O_3 sample has been dehydrated at 410°C, contacted with N_2O (54 Torr), and evacuated at room temperature.

peaks at 1237, 1339, 2238, 2305 cm^{-1}. Such adsorption–desorption cycles can be repeated indefinitely. No spectral modifications are observed even after a 48 hr contact with an excess of nitrous oxide.

In order to characterize the active sites and to correlate the bands at 2305 and 2238 cm^{-1} with those at 1339 and 1237 cm^{-1}, N_2O decomposition has been studied on variously hydrated samples. A sample after phase III is contacted with some 10 Torr of H_2O at 400°C for 1 hr. The overall result is a surface rehydration brought about by a dissociative chemisorption and by the adsorption of molecular water that is either coordinative to cationic sites or hydrogen bonded to surface hydroxyls. The rehydrated sample is dehydrated at a controlled temperature, by degassing for 1 hr, and the N_2O activity checked as described above. A phase III treatment followed by the rehydration process at 400° makes the sample ready for a further dehydration at a different temperature and for the catalytic activity test. Dehydration temperatures that have been used are: 25, 160, 260, 310, 360, 410°C.

No nitrous oxide is chemisorbed onto a

sample dehydrated at 25°C. A 160°C dehydration first promotes an N_2O activity: no bands are developed about 1000 cm^{-1}, and the other two regions only exhibit one band each, at 1245 and 2238 cm^{-1}, respectively (Fig. 4). The latter has an optical density of 0.1 (gas phase contribution is not included). At pressures below 2 Torr also the band at 2238 cm^{-1} is hardly detectable.

Dehydration at 260°C leads to rather different results: two complexes of bands are produced upon N_2O adsorption at 2305, 1339 cm^{-1} and at 2238, 1242 cm^{-1} respectively (Fig. 5a and b, curves 1), the intensities being lower than those of Fig. 1. In the 950–1050 cm^{-1} region, only one band is produced, whose maximum, after a room temperature evacuation, is at 986 cm^{-1} (Fig. 3b, curve 1).

Dehydration temperatures between 260 and 410°C do not cause the two pairs of bands due to reversible adsorbed species to vary appreciably, either in frequency or intensity. A higher intensity, reaching the situation of Fig. 3c, curve 1, is only observed in the 1000 cm^{-1} region when dehydration occurs at 410°C. In particular, a medium intensity absorption is visible at 995 cm^{-1} with a nonresolved shoulder at 1015 cm^{-1}.

DISCUSSION

Both for sake of clarity and to illustrate the dual nature of the information that can be derived from the above experiments, this discussion is divided into two parts. In the first one, whose aim is the characterization of surface complexes, we are mainly moving on a spectroscopic ground. In the second one, the N_2O-surface interaction is

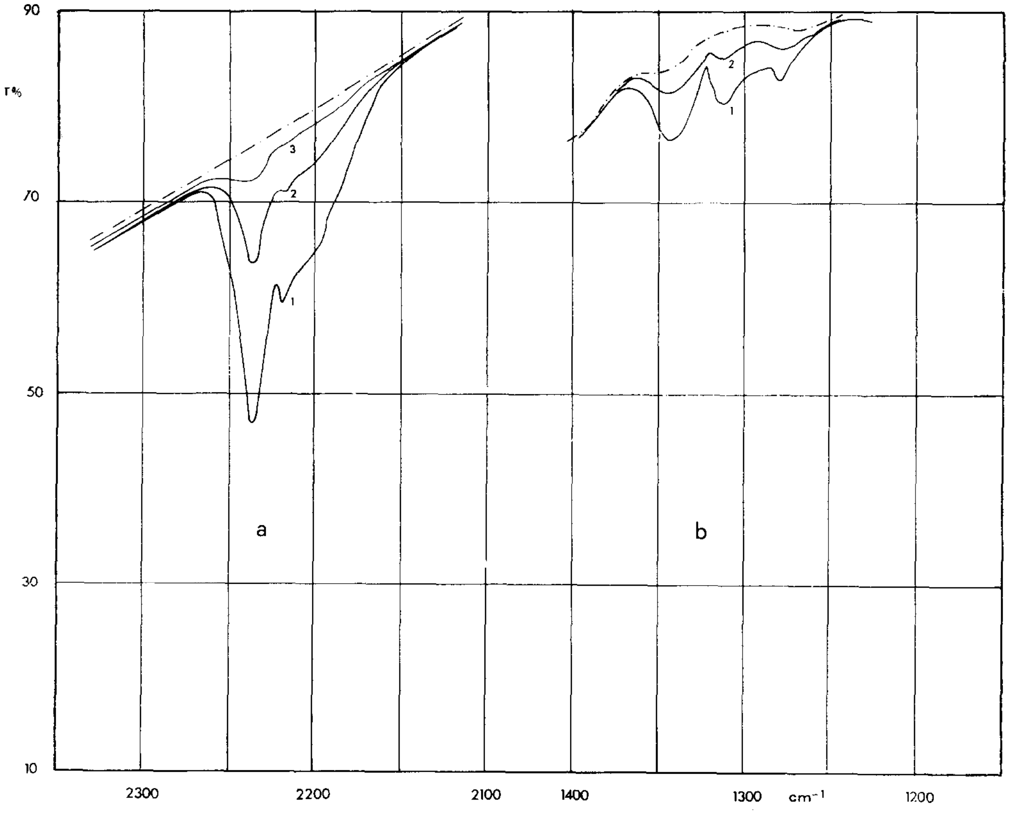


FIG. 4. IR spectrum of N_2O on rehydrated α-Cr_2O_3, dehydrated at 160°C: (1–3) N_2O equilibrium pressures (Torr): (1) 60; (2) 17; (3) 2.

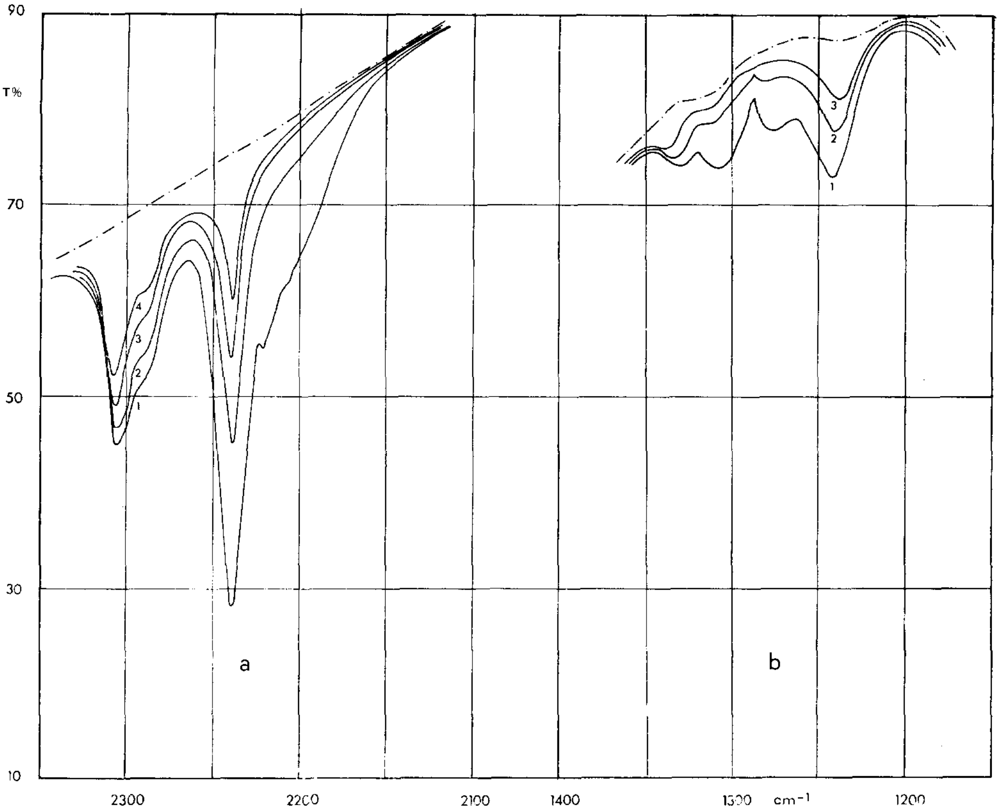


FIG. 5. IR spectrum of N_2O on rehydrated α-Cr_2O_3, dehydrated at 260°C: (1–4) N_2O equilibrium pressures (Torr): (1) 52; (2) 11; (3) 2; (4) 0.3.

described and the nature of sites that adsorb and decompose N_2O is investigated.

I. *Characterization of Surface Complexes*

a. Bands at 1016 and 995 cm^{-1}. The species responsible for these bands are definitely different from those absorbing at higher wavenumbers in that the former are nonreversible. They are only eliminated by reduction with CO at 400°C. In the same spectral region, bands are formed upon adsorption of O_2 which, though more complex, behave similarly. Bands at 1016 and 995 cm^{-1} are therefore assigned to chemisorbed oxygen that is probably released upon N_2O decomposition. The high frequency suggests surface Cr=O structures with bond index fairly close to two, as spectroscopic data of oxygenated chromium compounds tend to confirm (*16*a–g). Figure 3 shows that the two bands can have rather different absolute and relative intensities, the controlling factor being surface hydration. In particular, surface hydration plays a strong limiting role on the decomposing activity. A prolonged dehydration at temperature as high as 400°C does not restore the decomposing activity of α-Cr_2O_3 to the level that existed after phase III treatment, the sites responsible for the band at 1016 cm^{-1} being particularly sensitive.

An assignment of the various Cr=O surface groups has been proposed in another paper (*15*) so the discussion will not be reported again here. Some of these conclusions can be understood from Fig. 6, where two models for (001) face of α-Cr_2O_3 are drawn. Fig. 6a shows one of the many possible structures of an ideal, fully dehydrated face on which half the amount of oxide ions in a close-packed structure are left so as to maintain both overall and local electric neutrality. Chromium ions with

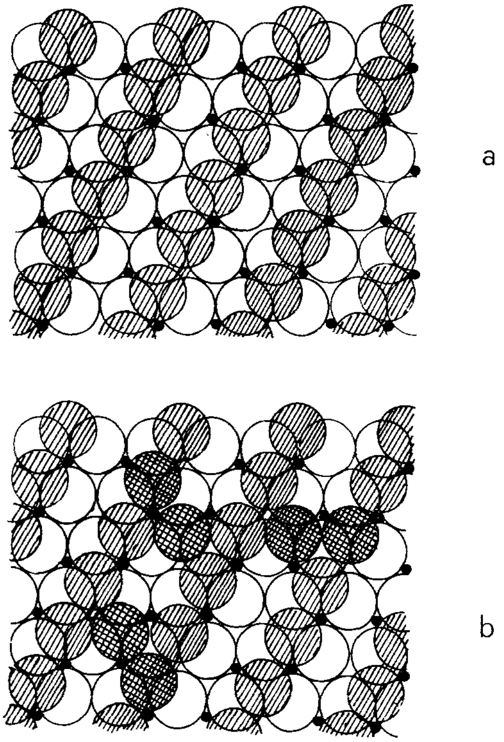
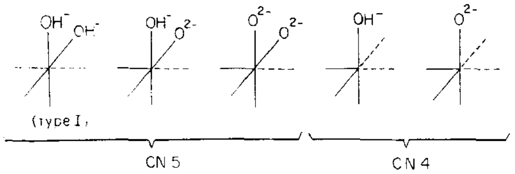


FIG. 6. (a) A possible model for a completely dehydrated (001) face: (○) O^{2-} ions of the underlying layer; (●) Cr^{3+} ions; (▨) O^{2-} ions of the upper layer. (b) A possible model of a partially hydrated (001) face: (▩) surface hydroxyls.

coordination number (CN) 4 and 5 are present in equal concentration. Such a model for a (001) face is fairly similar to that proposed by Stone (*17*) for faces perpendicular to (001). Real samples are never completely dehydrated and Cr^{3+} ions with CN 6 are also present. A possible situation is illustrated in Fig. 6b and has been obtained from the structure of Fig. 6a by supposing the dissociative chemisorption of few water molecules. As shown chromium ions with CN 4 and 5 can be arranged as in the scheme below:



We might observe: (a) *a coordination heterogeneity* that accounts for the difference between cations with coordination number 5 (*distorted* square pyramids) and cations with coordination number 4 (*distorted* tetrahedra). Ions with one coordinative unsaturation will be predominant at medium dehydration temperatures and ions with two vacancies will be appreciably formed upon degassing at higher temperatures; (b) a *ligand heterogeneity* accounting for the existence of three sites with CN 5 and of two sites with CN 4.

In our paper dealing with O_2 adsorption, the assignment was of the two bands above 1000 cm^{-1} (Fig. 3a, curve 3) to sites with CN 5. The present results seem to confirm the above assignment; in fact, the band at 1016 cm^{-1} is strong and clearly detectable only at high dehydration stages. Its intensity is lower when undissociated N_2O is present on the surface (Fig. 3, curve 1) and increases when N_2O is evacuated (Fig. 3, curve 2). This phenomenon can be indefinitely reproduced on admitting and evacuating the gas phase. The decrease in intensity of the 1016 cm^{-1} band is accompanied by the appearance of a large band at 982 cm^{-1}. We think that, in the presence of undissociated N_2O, a fraction of the Cr=O groups adsorbing at 1016 cm^{-1} is perturbed and their frequency shifted by 34 cm^{-1}. Thus N_2O might be thought to chemisorb on the second vacancy of the site influencing the bond order of the adjoining Cr=O group. Different coordinative situations have been observed to affect the frequency of the V=O group (*18*). The changes brought about by the presence of undissociated N_2O can be also caused by adsorbed pyridine (*19*). The band at 995 cm^{-1} is influenced by adsorbed N_2O as well and is shifted to 975 cm^{-1}. Such a smaller shift can be ascribed to lateral interactions or to collective electronic effects.

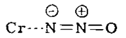
The intensity of the two bands produced by N_2O decomposition is much lower than that produced upon O_2 chemisorption on a bare surface, suggesting that not all of the surface sites that chemisorb oxygen can decompose nitrous oxide.

b. Pairs of bands at 2305, 1339, and at 2238, 1237 cm^{-1}. The species responsible for these bands are easily evacuated at room temperature, while some modifications are produced in the spectrum of adsorbed oxygen. Such changes are compensated if N_2O is admitted again to the surface. Our assignment is to molecular nitrous oxide reversibly chemisorbed.

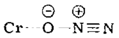
On a merely spectroscopic basis, neither species could possibly be the $N_2O^-_{ads}$ that has been suggested by several authors (*20*) as the intermediate of N_2O decomposition. Twenty-two electrons is a limiting number in triatomic systems above which both bonding character and geometry tend to vary (*21*). In particular, the lowest unoccupied orbital of N_2O (3π) is strongly N–N antibonding and weakly N–O antibonding (*22*) so that no active modes around 2200–2300 cm^{-1} would be expected for N_2O^-. A close parallelism is offered by nitrogen peroxide: NO_2^+ (linear and isoelectronic with N_2O) has two modes at 2375 and 1400 cm^{-1} and NO_2 (bent, 23 electrons) absorbs at 1621 and 1320 cm^{-1} (*23a*, *14*). On the other hand the IR spectrum of CO_2^- (isoelectronic with N_2O^-) (*23b*) completely supports our considerations. Nitrous oxide has been only studied in the gaseous and condensed phases, no data being available on N_2O complexes nor chemisorbed N_2O. Our discussion is limited to the stretching modes, the bending one falling in a spectral region where our α-Cr_2O_3 samples are completely opaque (<700 cm^{-1}). Gaseous N_2O has two strong bands centered at 2224 and 1286 cm^{-1} that are assigned to asymmetric (ν_3) and symmetric (ν_1) stretch, respectively. Solid N_2O has ν_3 at 2235 and ν_1 at 1293 cm^{-1} (*24*). Physically adsorbed N_2O on NaCl (*8*) shows one mode at 2240 cm^{-1} and a doublet at 1252–1265 cm^{-1}: the assignment was to N_2O held through the oxygen, normal to the surface, by Na^+ ions in two different coordinative situations.

Our N_2O species are readily adsorbed at $p/p_0 \cong 10^{-5}$, suggesting that they might involve the reversible chemisorption already observed on Cr_2O_3 and other oxides (*2*, *9*, *25*). Also, in this case, the similar behavior with the isoelectronic CO_2 adsorbed on various oxides might be mentioned (*26*).

The two species exhibit a similar resistance to desorption, while the spectral characteristics are rather different. One of the two has both ν_3 and ν_1 at frequencies considerably higher than the gas; but for the second species, ν_3 is above and ν_1 is below the corresponding modes of the gas. Our assignment is to highly polarized molecular structures, one being bonded through the oxygen and the other through the terminal nitrogen:

A: 
$\mathrm{Cr}\cdots\overset{\ominus}{\mathrm{N}}=\overset{\oplus}{\mathrm{N}}=\mathrm{O}$

bands at 2305 1339 cm^{-1}

B: 
$\mathrm{Cr}\cdots\overset{\ominus}{\mathrm{O}}-\overset{\oplus}{\mathrm{N}}\equiv\mathrm{N}$

bands at 2238 1237 cm^{-1}

Such a strong polarization would be induced by the coordinating cation and the resulting structures are fairly close to the canonical structures. N_2O is a molecule whose structure cannot be explained in terms of a single valence bond structure and Peyerimhoff and Buenker (*22*) indicated that one electronic configuration is not fully representative in the MO theory either. In particular, the canonical structure $N^-{=}N^+{=}O$ has been supposed (*27*, *28*) to have quite a remarkable importance.

The above assignment can be justified as follows: species A is rather similar to CO_2 whose ν_3 is IR active at 2349 cm^{-1} and ν_1 is Raman active at 1388 cm^{-1} (*14*). The weak intensity of the 1339 cm^{-1} band seems to confirm this assignment in that it would correspond to the IR forbidden mode of CO_2. In structure B the N–N and N–O bonds might be compared to $N{\equiv}N^+$ found by Eischens and Jacknow (*5*) at 2202 cm^{-1} and to N–O groups in N-oxides of nitriles, respectively. In fact the latter have a ν_{NO} in a rather long range about our frequency (*29*).

II. *The N_2O/α-Cr_2O_3 Interaction at Room Temperature*

As no nitrous oxide is adsorbed on a surface that carries either preadsorbed H_2O or pyridine, Cr^{3+} ions (*7*) are the most likely sites for N_2O adsorption. As far as polarizability is concerned N_2O is a highly anisotropic molecule: polarizability is 53.2×10^{-25} cm^3 in the bond direction and 18.3×10^{-25} cm^3 in the normal one (*30*).

It is therefore expected to be a very soft base (*31*) and its interaction with Cr^{3+} ions (hard acid) to lead to fairly weak complexes. Also, nitrous oxide is very sensitive to any surrounding variation, as confirmed by the unexpected raising of ν_3 in N_2O–CO_2 mixed crystals (*24*). A wide variability of the stretching modes is therefore expected owing to several coordinative situations probably existing on the (001) face of α-Cr_2O_3. On the other hand, surface heterogeneity of α-Cr_2O_3 cannot be studied too far by means of N_2O complexes in that a partial decomposition takes place. While O_{ads} coming from N_2O decomposition will give us some more information on the nature of active Cr^{3+} sites, it will also irreversibly modify the overall situation because coordinative and electronic properties have probably been changed.

Let us consider the experiment dealing with N_2O interaction with variously hydrated surfaces. Results in Fig. 4 indicate that a 160°C activation first induces a capacity of chemisorbing N_2O (only species B are formed), but not yet of decomposing it. In this case chromium ions with CN 5 (type I) are the only surface species and have been produced by elimination of coordinated water (*32*). A 260°C activation leads to a surface with a few sites capable of decomposing N_2O (chromium ions with CN 5) and of adsorbing it in both forms A and B. After this activation temperature, the amount of reversibly adsorbed N_2O does not vary, though more and more sites are likely to be created upon dehydration. This is due to the increasing amount of adsorbed oxygen with activation temperature which occupies more and more surface sites or possibly promotes more complex electronic phenomena that would inhibit a more abundant N_2O chemisorption. This situation cannot be varied just by increasing the dehydration temperature but only when α-Cr_2O_3 undergoes the treatments of phase II and phase III. In this way, the spectra go back to the situation of Fig. 1, confirming Burwell's hypothesis (*7*) that redox cycles promote a much more drastic dehydration than mere activation. The strong band at 1016 cm^{-1} due to O_{ads} also indicates that a high number of chromium ions with CN 4 and able to decompose N_2O are created.

N_2O decomposition at room temperature seems to be more selective than O_2 dissociation: the latter brings about the chemisorption onto all the five sites while the former only occurs on two, one with CN 4 and one with CN 5. This higher selectivity would also account for the lower O_{ads} coverage that is obtained by N_2O decomposition.

In the above discussion, two phenomena have not been dealt with that might be of some interest. (i) Bands due to adsorbed N_2O are quite complex, especially at low coverage. (ii) With decreasing coverage, band positions diverge more and more from the position they have in the N_2O-gas spectrum. The first observation might reveal a sensitivity of N_2O to surface heterogeneity. The second one might account for a lower importance of lateral interaction with decreasing coverage and for a diminishing contribution of molecules in different local situation to the overall absorption.

At present, a more detailed assignment of the various spectral components to different local structures is impossible. Experiments at temperatures where N_2O is not decomposed are now being carried out. In such a condition a more stable surface situation is obtained and more information on the band complexity will hopefully be derived.

In conclusion, IR spectroscopy has revealed for the first time that:

1. N_2O is readily decomposed at room temperature on the (001) face of α-Cr_2O_3, resulting in a partial, selective coverage of surface sites with O_{ads} through quasi-double bonds;
2. N_2O is reversibly adsorbed onto surface sites that have not been saturated by the decomposition process; the N_2O surface complexes so formed have no correspondence with complexes in the homogeneous phase;
3. spectral behavior and characteristics of adsorbed N_2O rule out the existence of N_2O^- species.

References

1. Hauffe, K., *in* "Advances in Catalysis and Related Subjects" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol. 7, p. 213. Academic Press, New York, 1955.
2. Winter, E. R. S., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky, and P. B. Weisz, eds.), Vol. 10, p. 196. Academic Press, New York, 1958.
3. Stone, F. S., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, P. W. Selwood, and P. B. Weisz, eds.), Vol. 13, p. 1. Academic Press, New York, 1962.
4. Banks, R. G. S., Henderson, R. J. and Pratt, J. M., *J. Chem. Soc. Ser. A*, **1968**, 2886.
5. Eischens, R. P., and Jacknow, J., *in* "Proceedings of the International Congress on Catalysis, 3rd, Amsterdam, 1964," Vol. 1, p. 627. North-Holland, Amsterdam, 1965.
6. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, London, 1966.
7. Burwell, R. L., Jr., Haller, G. L., Taylor, K. C., and Read, J. F., "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, eds.), Vol. 19, p. 62. Academic Press, New York, 1969.
8. Kozirovski, Y., and Folman, M., *Trans. Faraday Soc.* **65**, 244 (1969).
9. Klier, K., *J. Amer. Chem. Soc.* **91**, 5392 (1969).
10. Harbard, E. H., and King, A., *J. Chem. Soc., London* **1938**, 955.
11. Nicolaon, G. A., *J. Chim. Phys., Physicochim. Biol.* **66**, 1783 (1969).
12. Groth, P., "Chemische Krystallographie." Engelmann, Leipzig, 1906.
13. Borello, E., Zecchina, A., and Castelli, M., *Ann. Chim. (Rome)* **53**, 690 (1963).
14. Herzberg, G., "Molecular Spectra and Molecular Structure," Vol. 2. Van Nostrand, New York, 1945.
15. Zecchina, A., Coluccia, S., Cerruti, L., and Borello, E., *J. Phys. Chem.*, **75**, 2783 (1971).
16. (a) Barraclough, C. G., Lewis, J., and Nyholm, R. S., *J. Chem. Soc.*, **1959, 3525**; (b) Stammreich, H., Sala, D., and Kawai, K., *Spectrochim. Acta* **17**, 226 (1961); (c) Kon, H., *J. Inorg. Nucl. Chem.* **25**, 933 (1963); (d) Brown, D., *J. Chem. Soc., London* **1964**, 4944; (e) Griffith, W. P., *J. Chem. Soc., London* **1964**, 245; *J. Chem. Soc., Ser. A* **1969**, 211; *J. Chem. Soc., Ser. A* **1969**, 2270; (f) Beattie, I. R., and Gilson, T. R., *J. Chem. Soc., Ser. A* **1969**, 2322; (g) Campbell, J. A., *Spectrochim. Acta*, **21**, 1333 (1965); **21**, 851 (1965).
17. Stone, F. S., *Chimia* **23**, 490 (1969).
18. Ueno, K., and Martell, A. E., *J. Phys. Chem.* **60**, 934 (1956): Selbin, J., Holmes, L. H., Jr., and McGlynn, S. P., *J. Inorg. Nucl. Chem.* **25**, 1359 (1963); see also Ref. (*15*f).
19. Guglielminotti, E., unpublished data.
20. See, e.g., Ref. (*2*), and references therein.
21. Walsh, A. D., *J. Chem. Soc., London* **1953**, 2266.
22. Peyerimhoff, S. D., and Buenker, R. J., *J. Chem. Phys.* **49**, 2473 (1968).

23a. Teranishi, R., and Decius, J. C., *J. Chem. Phys.* **22**, 896 (1954).

23b. Hartmann, K. O., and Hisatsune, I. C., *J. Chem. Phys.*, **14**, 1913 (1966).

24. Yamada, H., and Person, W. B., *J. Chem. Phys.* **41**, 2478 (1964).
25. Cimino, A., Schiavello, M., and Stone, F. S., *Discuss. Faraday Soc.* **41**, 350 (1966).
26. Peri, J. B., *J. Phys. Chem.* **70**, 3168 (1966); Gregg, S. J., and Ramsay, J. D. F., *J. Phys. Chem.* **73**, 1243 (1969); Parkyns, N. D., *J. Phys. Chem.* **75**, 526 (1971).
27. Wagner, E. L., *J. Chem. Phys.* **43**, 2728 (1965).
28. McLean, A. D., and Yoshimine, M., *J. Chem. Phys.* **45**, 3676 (1966).
29. Colthup, N. B., Daly, L. H., and Wiberly, S. E., "Introduction to Infrared and Raman Spectroscopy," Academic Press, London, 1964.
30. Stuart, H. S., and Volkmann, H., *Z. Phys. Chem., Abt. B* **17**, 429 (1932).
31. Pearson, R. G., *J. Amer. Chem. Soc.* **85**, 3533 (1963).
32. Zecchina, A., Coluccia, S., Guglielminotti, E., and Ghiotti, G., *J. Phys. Chem.*, **75**, 2774 (1971).