JOURNAL OF CATALYSIS 65, 231–234 (1980)

Infrared Study of the Adsorption of Nitrous Oxide on η-Alumina

The major interest of N_2O as a probe molecule in the study of heterogeneous catalysts containing transition metals and transition metal ions consists in its easy decomposition, yielding information on the nature of active sites (*1–3*). N_2O can also coordinate without decomposition onto coordinatively unsaturated (cus) transition metal cations (*3*, and references therein), producing heterogeneous complexes that are almost unknown in homogeneous coordination chemistry.

Parkyns (*4*) reported that N_2O does not adsorb on Al_2O_3, but we have now found by ir spectroscopy that a little N_2O does adsorb at ambient temperature on activated transition aluminas and that it does so without appreciable decomposition. We suspect that the spectral features of adsorbed N_2O were not observed previously on account of the strong absorption of the gaseous phase.

For the present work we have mainly used an η-Al_2O_3 whose preparation and characteristics are thoroughly described in previous papers (*6–8*), but all transition aluminas were found to behave similarly. The spectra were run on a Beckman IR 12 double-beam spectrophotometer. The *in situ* cell was of conventional design, with a very small optical path (~2 mm) to reduce the absorption due to the N_2O gaseous phase.

Gaseous N_2O absorbs at 2224 (ν_1), 1286 (ν_3), and 589 cm^{-1} (ν_2), whereas in the solid state all modes are "blue-shifted" to 2238, 1293, and 591 cm^{-1}, respectively (*5*).[1] When adsorbed on η-Al_2O_3 (Fig. 1), N_2O exhibits bands due to the ν_1 and ν_3 modes, but the ν_2 mode is not observed as it falls below the alumina cutoff. The asymmetric stretching (ν_1) is weak and is superimposed at 2236 cm^{-1} on the R branch of the gas phase in the case of η-Al_2O_3 dehydrated at ambient temperature, but it strongly intensifies and moves up to 2244 cm^{-1} on more and more dehydrated samples. The band becomes broader after a 573 K dehydration, and definitely doubles (shoulder at ~2250 cm^{-1}) on the sample almost completely dehydrated at 973 K (*6*). A short evacuation at ambient temperature removes the ν_1 band entirely from samples dehydrated at temperatures as high as 573 K, whereas a sharp component remains at 2255 cm^{-1} in the case of samples dehydrated at $T \geq 573$ K. It increases with activation temperature, and is quickly eliminated at $T \geq 373$ K. In the ν_3 mode region the absorption due to the adsorbed phase is lower in frequency and almost not overlapped with that of the gas, but the actual spectral position is uncertain due to weakness and broadness of the band. There is a continuous downward shift of the peak from 1240 to 1225 cm^{-1} on increasing the activation temperature, and a component resistant to evacuation is clearly observed at a lower frequency (1195 cm^{-1}) on the 973 K activated sample.

The interaction of N_2O with other adsorbates, whose behavior is known from previous work, has been studied in order to identify the nature of the adsorbing sites. CO would normally be a favorite choice, but CO is not useful here as it interacts with adsorbed N_2O (and N_2O interacts with adsorbed CO as well) leading to CO oxidation and to the production of surface carbonates, typical of CO_2 chemisorption (*7*). We therefore examined interaction with pyridine. When N_2O is contacted with a highly dehydrated alumina sample on which preadsorbed pyridine (Py) is present, almost no

---

[1] Herzberg uses a reversed numbering for the two Σ^+ modes (ν_1 and ν_3), but the two notations are perfectly equivalent, in view of the non-centrosymmetric structure of N_2O. We adopted Nakamoto's notation, as his book is mostly used by inorganic and coordination chemists.

0021-9517/80/090231-04$02.00/0

N_2O bands are formed in the spectrum. If the preadsorbed Py is evacuated at 473 K, a further contact with N_2O produces in the ν_1 mode region a weak band at 2232 cm^{-1} in which only the low $\bar{\nu}$ component is present; its intensity and position are quite similar to those of the band produced on a bare alumina activated at ambient temperature (curve 1 of Fig. 1).

Figure 2 summarizes the interaction between N_2O and preadsorbed CO_2. In the high-frequency range N_2O adsorption yields the 2244-cm^{-1} band, whereas the band due to linearly held CO_2 (7) is almost entirely eliminated, a small band either remaining at or shifting to 2354 cm^{-1}. Meanwhile, organic carbonate species (7) absorbing in the 1750- to 1900-cm^{-1} range are intensified. Upon a short evacuation of the CO_2–N_2O-containing system, organic carbonate bands recover their original shape, some of the 2370 cm^{-1} band is reformed, and a part of the vacuum-resistant N_2O species remains at 2254 cm^{-1}. If the reversed experiment is carried out (CO_2 onto preadsorbed N_2O), a similar ligand

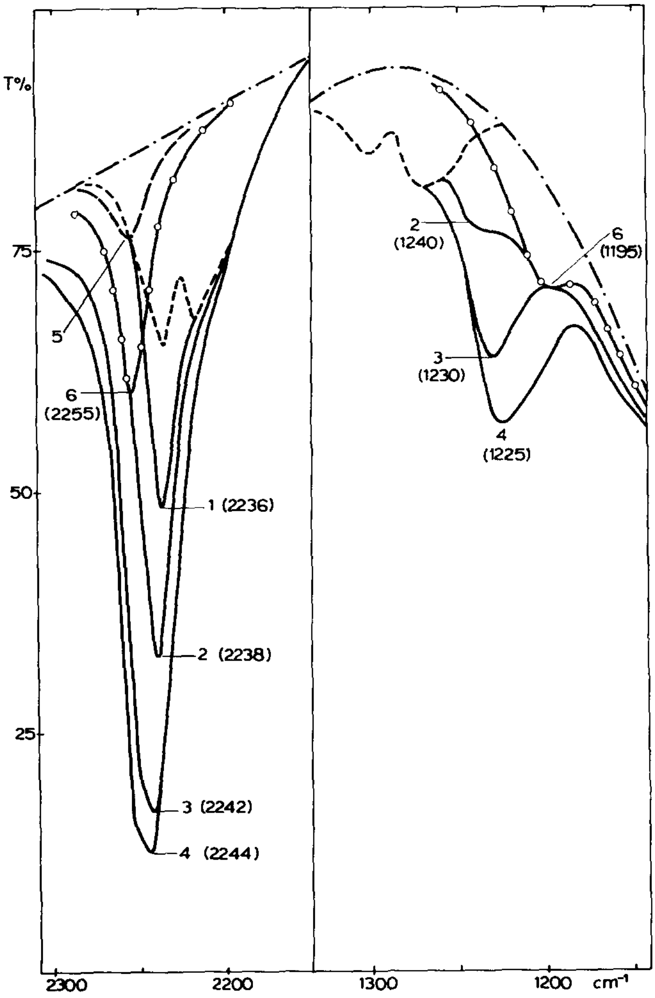

FIG. 1. Spectra due to the adsorption and desorption of N_2O on η-Al_2O_3. Dotted line: background; broken line: the spectral contribution of the gaseous phase to spectra 1–4. Curves 1–4: spectra after the contact of N_2O ($P = 5.3 \times 10^3$ N m^{-2}) with η-Al_2O_3 dehydrated at 298, 573, 773, 973 K, respectively. Curves 5–6: as for curves 3 and 4, after N_2O evacuation at 298 K for 1 min.

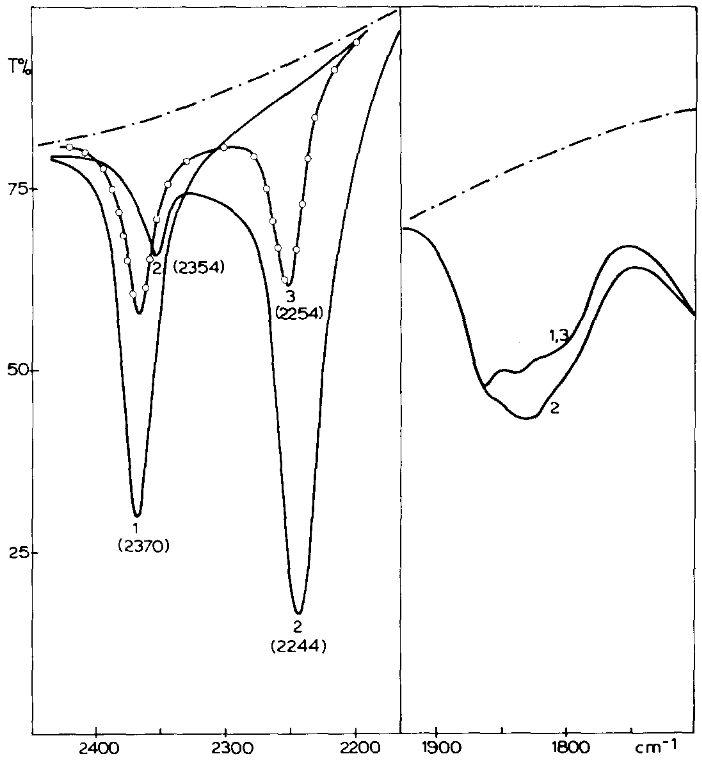

FIG. 2. The interaction of N_2O with adsorbed CO_2. Dotted line: background (η-Al_2O_3 dehydrated at 973 K). Curve 1: spectrum due to CO_2 adsorption at 298 K ($P = 267$ N m^{-2}). Curve 2: spectrum after the admission of N_2O ($P = 3 \times 10^3$ N m^{-2}) to preadsorbed CO_2. Curve 3: spectrum after evacuation at 298 K for 30 sec.

displacement occurs, but desorbed N_2O does not produce any alternative structure so that, upon further evacuation, no N_2O bands whatever are reformed.

The bands produced on N_2O contact with alumina cannot be ascribed to a plain physical adsorption on a BET-type model, as the N_2O vapor pressure is higher than 60 atm at beam temperature and P/P_0 is therefore extremely small. We think that the dependence of the intensity of the adsorbed N_2O bands on sample activation temperature clearly indicates that N_2O is weakly chemisorbed at sites produced by surface dehydration. These sites turn out to be of at least two types, those produced at higher dehydration stages being stronger and characterized by a larger splitting of the two stretching modes.

The fact that the regions in which the two observable modes absorb are the same as those of gaseous N_2O demonstrates that, upon adsorption, N_2O retains its linear shape. The frequency increase of the ν_1 mode and the frequency decrease of the ν_3 mode, observed for the chemisorption at both sites, indicate an enhanced importance of the canonical form A of Scheme I

$$\underset{A}{\overset{-}{O}-\overset{+}{N}\equiv N} \qquad \underset{B}{\overset{-}{N}=\overset{+}{N}=O} \qquad (I)$$

in which the triple-bond character of ν_1 and the single-bond character of ν_3 are higher (*8*). Structure A is thought to be compatible with a molecular species strongly polarized by a lone-pair σ donation from the oxygen to a coordinatively unsaturated surface cation, i.e., to a Lewis acid center. The inhibition of N_2O adsorption by pyridine preadsorption confirms the hypothesis of a Lewis coordination (*9*).

It is suggested that the most resistant N_2O species (bands at ~2250 and ~1190 cm^{-1}) is adsorbed at the sites that also chemisorb the most resistant Py species (8a mode at 1623–1629 cm^{-1}). In fact an evacuation of pyridine at 473 K eliminates Py species almost entirely, save for the most resistant one, whose concentration remains almost unaffected (*9*). Moreover, the strong N_2O species starts to be formed after alumina dehydration at 573–673 K, i.e., in the same temperature range in which the sites that chemisorb the strongest Py species start to be formed as well. It is thus deduced that the sites responsible for the strongest N_2O chemisorption belong to the family of tetrahedral Al ions carrying a coordinative vacancy (Al^{IV}_{cus}), i.e., to the sites that were previously shown to chemisorb CO (*10*).

As for the weaker N_2O species (bands at ~2238 and ~1230 cm^{-1}), this is formed again, though not completely, after the evacuation of preadsorbed Py at 473 K; thus adsorption at the sites which also adsorb the Py species whose 8a mode is at 1613–1622 cm^{-1} is strongly suggested (*9*).

The interaction with CO_2 indicates a strict correspondence between the sites which chemisorb N_2O and those which linearly adsorb CO_2, so that the assignment is consequently the same (*7*). In particular the sites responsible for the strong N_2O species are confirmed as belonging to the family of Al^{IV}_{cus} ions, as the ligand-displacement experiment of Fig. 2 is strictly analogous to one previously reported (*7*) in which CO was shown to chemisorb at the same sites which coordinate the strongest CO_2 species in the linear form. Also the reversible transformation of the strong linear CO_2 species into organic carbonates was observed to occur in that experiment as in the present one.

This work confirms that Al^{IV} ions, either carrying a coordinative vacancy or sharing it with an Al^{VI} ion, possess a field strong enough to coordinate N_2O through a σ donation, N_2O being a molecule that is known to be a "soft" Lewis base and not to yield homogeneous complexes very easily.

REFERENCES

1. Schiavello, M., Lo Jacono, M., Cimino, A., *J. Phys. Chem.* **75**, 1051 (1971).
2. Cimino, A., Schiavello, M., *J. Catal.* **20**, 202 (1971).
3. Zecchina, A., Cerruti, L., Borello, E., *J. Catal.* **25**, 55 (1972).
4. Parkyns, N. D., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 255. North-Holland, Amsterdam, 1973.
5. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," p. 87. Wiley-Interscience, New York, 1970.
6. Borello, E., Della Gatta, G., Fubini, B., Morterra, C., Venturello, G., *J. Catal.* **35**, 1 (1974).
7. Morterra, C., Zecchina, A., Coluccia, S., Chiorino, A., *J. Chem. Soc. Faraday Trans. I*, **73**, 1544 (1977).
8. Borello, E., Cerruti, L., Ghiotti, G., Guglielminotti, E., *Inorg. Chim. Acta* **6**, 45 (1972).
9. Morterra, C., Chiorino, A., Ghiotti, G., Garrone, E., *J. Chem. Soc. Faraday Trans. I* **75**, 271 (1979).
10. Della Gatta, G., Fubini, B., Ghiotti, G., Morterra, C., *J. Catal.* **43**, 90 (1976).

C. MORTERRA
F. BOCCUZZI
S. COLUCCIA
G. GHIOTTI

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

Received January 23, 1980; revised March 24, 1980