

X-Ray Photoelectron Spectroscopy of Nitrogen Oxides Adsorbed on Iron Oxides

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Adsorption of N_2O , NO , and NO_2 on Fe_2O_3 and Fe_3O_4 was studied by means of X-ray photoelectron spectroscopy (XPS) using an AEI ES 100 spectrometer at temperatures from -100 to $+250^\circ C$. Adsorption isotherms and isobars of NO and NO_2 have been plotted for Fe_3O_4 and Fe_2O_3 . Isotherms are Langmuir curves, and the adsorption isobar of nitrogen dioxide adsorbed on Fe_2O_3 shows a maximum at room temperature. No adsorption of nitrogen monoxide is detected with Fe_2O_3 (the detection limit is about 0.1 monolayer). With adsorbed nitrous oxide a simple peak is recorded in contrast to what is observed in the vapor phase. The N 1s binding energy of adsorbed NO is lower than that of the gaseous species, suggesting that significant electron transfer from the iron oxides to the adsorbed nitrogen oxide occurs; however, this back donation is not observed with adsorbed nitrogen dioxide. Adsorption does not cause changes in the binding energies of Fe_2O_3 core electrons, but shifts the Fe 3p line of Fe_3O_4 toward the higher binding energies, suggesting that Fe_3O_4 is oxidized by the adsorption of nitrogen oxides.

INTRODUCTION

The understanding of catalytic reactions concerning nitrogen oxides is of great interest in studies related to the emission, transformation, and elimination of atmospheric pollutants (1-6). Numerous techniques have been used to study adsorption of N_2O , NO , and NO_2 (ir spectroscopy (1,7-12), temperature programmed desorption (13), electron paramagnetic resonance (14,15), X-ray photoelectron spectroscopy (XPS) (16-18)). The ir spectroscopic results demonstrate that adsorption is a complex process. In the case of NO , for example, Shelef and Kummer have listed seven adsorbate-adsorbent bond types (1). Moreover, for certain solids dissociative chemisorption (Ni) or a surface chemical reaction (lower oxides of transition metals) is observed (19). With Fe_2O_3 (2), Cr_2O_3 (20), NiO (21), and CuO (22), recent works suggest that each surface metal

atom chemisorbs an NO molecule with the formation of a $M-NO$ bond.

The mean free path of X-ray induced photoelectrons being 10-40 Å (23), XPS is a method particularly suitable for investigations of interactions occurring in adsorption. This technique has moreover given interesting results concerning NO adsorption on tungsten (16) and on nickel or cobalt oxides (17). For this reason, we have used it to study the adsorption of N_2O , NO , and NO_2 on Fe_2O_3 and Fe_3O_4 .

EXPERIMENTAL

High purity Fe_2O_3 and Fe_3O_4 were obtained from Merck and Prolabo, and nitrogen oxides from Air Liquide were used without further purification ($NO_2 = 99.5\% NO_2 + N_2O_4$; $NO = 99.9\% NO$, other oxides $< 0.1\%$; $N_2O = 99.99\% N_2O$, impurities < 50 vpm.).

Iron oxides were examined by electron

TABLE 1
SPECIFIC SURFACE AREA AND PARTICLE
DIAMETER OF IRON OXIDES

	Fe ₂ O ₃	Fe ₃ O ₄
d (μ)	0.5	1.5
S (m^2g^{-1})	2.3	0.8

microscopy and their textural properties are reported in Table 1.

Spectra were recorded on an AEI ES 100 spectrometer using Mg K α radiation. The carbon 1s line from oil contamination was used as an internal standard for calibrating the spectra. The binding energy of the C 1s electron was taken at 285 eV relative to the Fermi level and at 290 eV rel-

ative to the vacuum level (24,25). It has been reported in a previous paper that the C 1s line of the contamination layer is a suitable standard for the correction of the charging effect (26).

Oxide powders were compressed into a copper grid and cleaned by heating in a vacuum at 300°C. Nitrogen oxides were admitted through a stainless steel high vacuum valve; the adsorption pressure varied from 10⁻² to 10 Torr. The adsorption temperature was varied from -100 to +200°C, and the adsorbate was evacuated at the adsorption temperature until a pressure of 10⁻⁷ Torr was obtained so that the spectra were recorded following the removal of all reversibly adsorbed species. During the

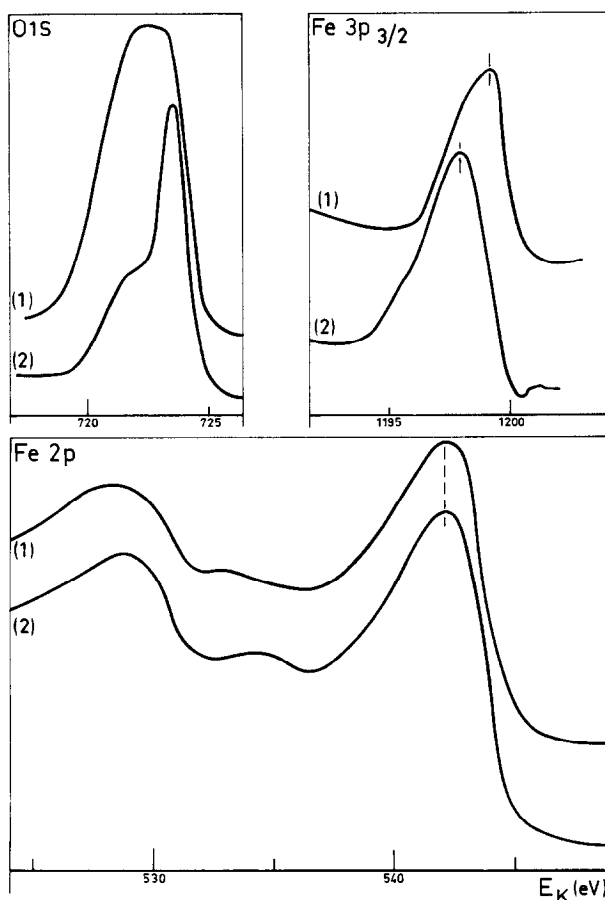


Fig. 1. XPS spectra of Fe₃O₄ (1) and Fe₂O₃ (2) free of adsorbate.

TABLE 2
BINDING ENERGIES (eV) RELATIVE TO THE FERMI LEVEL FOR Fe₂O₃

	Fe 2p _{3/2}	Fe 3p	O 1s	N 1s
Fe ₂ O ₃	711.0 ± 0.5	55.8 ± 0.3	530.1 ± 0.5 532.0 ± 0.2	
Fe ₂ O ₃ + NO ₂	710.8 ± 0.5	55.7 ± 0.3	530.3 ± 0.5 532.0 ± 0.2	(400 ± 0.5) 406.5 ± 0.5

recording, a pressure of $5 \cdot 10^{-7}$ Torr was maintained.

RESULTS

1. Fe₂O₃

Under our experimental conditions only NO₂ adsorption has been detected. The spectra of Fe₂O₃ and Fe₃O₄ before adsorption (Fig. 1) reveal a marked difference in the peak of oxygen 1s electrons; the 3p_{3/2} Fe peaks are slightly displaced relative to each other; on the other hand, there is no shift at the 2p level. The binding energies, relative to the Fermi level, are given in Table 2. No modification of the binding energies of electrons belonging to the elements of the solid is observed. The binding energies of the nitrogen 1s electrons of NO₂, adsorbed at 300°K and 1 Torr on Fe₂O₃ is very close to that of gaseous NO₂ and nitrate ion (Table 5). After NO₂ adsorption on Fe₂O₃, a second peak at 400 eV, is sometimes observed.

2. Fe₃O₄

The Fe 3p line of Fe₃O₄ recorded after adsorption of N₂O, NO, and NO₂ at

300°K and 1 Torr is given in Fig. 2. The binding energies are reported in Table 3.

The spectrum corresponding to adsorbed NO shows several peaks and indicates either the presence of several adsorbed species or the possibilities of surface chemical reactions leading to other nitrogen oxides. Such reactions are possible: They correspond to the superficial oxidation of Fe₃O₄ into Fe₂O₃ with the simultaneous reduction of the nitrogen oxides (Fig. 2) (19).

These reactions should be accompanied by an increase in the binding energies of the 2p and 3p iron electrons. However, only the binding energy of the 3p electrons is observed to shift ($\Delta E_B^F \approx + 1.1$ eV), the binding energy of the 2p electrons remaining identical in the two oxides. The 3p electrons are emitted from deeper layers of solid than the 2p electrons, since they have twice as much kinetic energy (23). It must therefore be supposed that the Fe₃O₄ is already superficially oxidized to Fe₂O₃ (to about 10–20 Å) so that the oxidation of Fe₃O₄ can only be detected for the 3p photoelectrons which come from a greater

TABLE 3
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	Fe 2p _{3/2}	Fe 3p	O 1s	N 1s
Fe ₃ O ₄	711.2 ± 0.5	54.9 ± 0.3	530.5 ± 0.5 532.5 ± 0.5	
Fe ₃ O ₄ + N ₂ O	711.3 ± 0.5	56.0 ± 0.3	530.6 ± 0.5 532.2 ± 0.5	399.2 ± 0.5
Fe ₃ O ₄ + NO	711.1 ± 0.5	56.0 ± 0.3	530.5 ± 0.5 532.4 ± 0.5	400.2 ± 0.5
Fe ₃ O ₄ + NO ₂	711.3 ± 0.5	56.1 ± 0.3	530.5 ± 0.5 532.4 ± 0.5	(400.5 ± 0.5) 406.5 ± 0.5

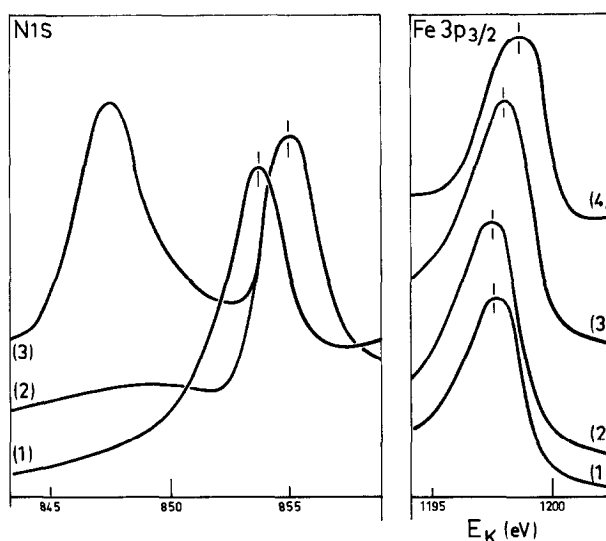


FIG. 2. Fe 3p and N 1s for Fe_3O_4 : (1) after NO adsorption (300°K, 1 Torr); (2) after N_2O adsorption; (3) after NO_2 adsorption; (4) free of adsorbate.

depth (20–40 Å). There is no shift in the binding energies of the O (1s) electrons.

3. Effect of the Adsorption Pressure and Temperature

The binding energy of the N (1s) electrons of adsorbed NO_2 is independent of the pressure. The binding energy decreases markedly when the temperature is lowered ($\Delta E_B^F \approx -3.5$ eV for Fe_2O_3 , $\Delta E_B^F \approx -2.5$ eV for Fe_3O_4).

It can be assumed that this decrease is related to the appearance of less strongly adsorbed species at low temperature (Table 4). In the case of NO, on the other

hand, the binding energies are independent of both temperature and pressure.

It seemed to us interesting to measure the intensity of the N (1s) peak as a function of the adsorption temperature and pressure. The isotherms and isobars obtained are given in Figs. 3 and 4: The area of the N (1s) peak, estimated by weighing, is plotted against the pressure and the temperature. In view of the weakness of the signal, the uncertainty on the adsorbed quantity is about 30%. These data are therefore only semiquantitative, but nevertheless classical isobar and isotherm profiles are obtained (27). From the plot of

TABLE 4
BINDING ENERGY OF THE N 1s ELECTRONS OF ADSORBED NO_2 : TEMPERATURE AND PRESSURE DEPENDENCE

$T(^{\circ}\text{K})$	E_B^F N 1s ± 0.5 eV		$P(\text{Torr})$	E_B^F N 1s ± 0.5 eV	
	Fe_2O_3	Fe_3O_4		Fe_2O_3	Fe_3O_4
175	402.6	403.5	0.1	406.0	406.5
225	406.1	405.1	0.5	406.5	406.5
300	406.0	406.1	1	407.0	406.5
375	406.2	406.0	5	406.5	406.5
475	No adsorption detected	No adsorption detected	10	407.0	406.0



FIG. 3. NO and NO₂ adsorption isobars (1 Torr) obtained with Fe₂O₃ and Fe₃O₄: (Δ) NO on Fe₃O₄; (○) NO₂ on Fe₃O₄; (●) NO₂ on Fe₂O₃.

the linear transform of the isotherm, it can be shown that it is a Langmuir isotherm (Fig. 4).

The adsorption isobar of NO₂ on Fe₂O₃ has a maximum in the vicinity of room temperature; there is no maximum in the curves for Fe₃O₄. The adsorption isotherm indicates that the detection limit is at about 0.1 monolayer. From the work of Shelef and Otto (2), it can be estimated that at 300°K and 1 Torr, Fe₃O₄ adsorbed about $5 \cdot 10^{-5}$ mole of NO per g, so that the detection limit will be reached for $5 \cdot 10^{-6}$, that is for 150 ppm.

DISCUSSION

It is interesting to compare the binding energies of N 1s electrons obtained by Siegbahn *et al.* (28,29) for N₂, N₂O, NO,

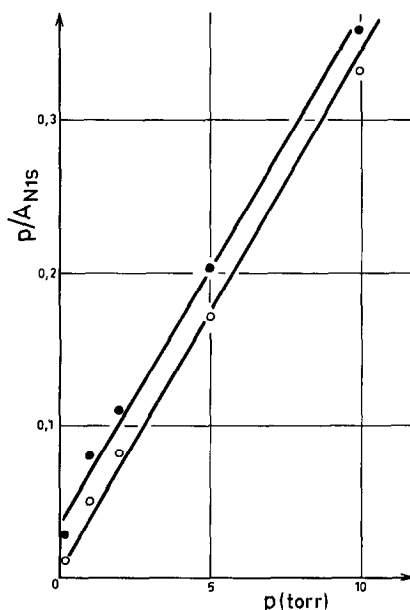


FIG. 4. Langmuir adsorption isotherm of NO₂ on Fe₂O₃ (●) and Fe₃O₄ (○).

and NO₂ in the gas phase and by other workers for adsorbed N₂ and NO with our results for adsorbed N₂O, NO, and NO₂ (Table 5). Our measurements on nitric oxide show that the N 1s binding energy of adsorbed NO is lower than that of the gaseous molecule and in good agreement with those of Yates *et al.* (16) for tungsten and of Dianis *et al.* (17) for NiO and Co₃O₄. An analogous interpretation can be advanced, that is to say, an electron transfer from the metal oxide to the π orbitals of the nitrogen atom of the adsorbed molecule occurs.

The adsorbed state would be comparable to that which can be observed in nitrosyl complexes (30).

For NO₂ and N₂O, no report concerning an XPS study of the adsorbed state has been published. In the case of NO₂ the binding energy is close to that found for the gaseous state and the nitrate ion. These results are in good agreement with those of Parkyns (12) who demonstrates that NO₃⁻ species are formed by adsorption of NO₂ on alumina. At low tempera-

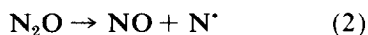
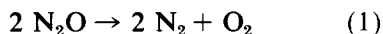
TABLE 5
 BINDING ENERGIES (eV) OF N 1s ELECTRONS OF GASEOUS AND ADSORBED NITROGEN OXIDES
 (RELATIVE TO THE VACUUM LEVEL)

Co_3O_4	E_B^V (This work)	E_B^V gaseous state (Ref. (29))	E_B^V (ads. on W) (Ref. (16))	E_B^V (ads. on NiO and Co_3O_4) (Ref. (17))
N_2		409.9	401.7–402.5	
N_2O	404.2 ± 0.5	408.5 413.0		
NO	405.2 ± 0.5	410	401.9–404.6	404–406
NO_2	411.5 ± 0.5	412.5		
NH_4NO_3	407.1 ± 0.2 412.6 ± 0.2			

ture the N 1s peak is slightly displaced toward low energies. This shift may indicate that the NO_3^- ions are no longer formed and that NO_2 is more weakly adsorbed.

The spectrum of adsorbed nitrous oxide is more difficult to interpret since only one peak is recorded; it corresponds to a binding energy very close to that of adsorbed nitric oxide. Two interpretations can be advanced: The first would imply electron transfer from the metal oxide to the adsorbed molecule with the formation of N_2O^- species, this electron transfer leading to a new charge distribution in the adsorbed molecule. The peaks corresponding to the two nitrogen atoms would then coincide. Similar surface species have been proposed by Hauffe (31), but they have been refuted by Borello *et al.* (10) who have detected by ir spectroscopy two distinct adsorbed species depending on whether the N_2O molecule is adsorbed by the terminal nitrogen atom or by the oxygen, but which does not correspond to the formation of an N_2O^- intermediate.

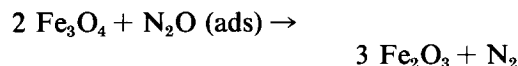
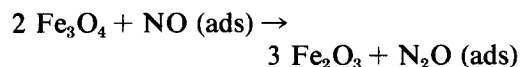
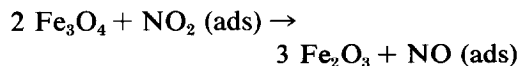
The second interpretation assumes that upon X-ray irradiation N_2O is likely to decompose:



According to Nicolle and Vodar (32)

reaction (2) would be produced by radiation of $\lambda < 235$ nm, and this reaction is the only one we can detect with XPS, because nitrogen produced in reaction (1) is removed from the surface of the iron oxides. Our results do not allow us to choose between these two possibilities; however, we think that the second interpretation would be the more plausible.

With Fe_3O_4 , the chemical shift recorded for the Fe(3p) peak after nitrogen oxide adsorption suggest that reactions such as:



could occur, as proposed by Sabatier and Senderens (19).

CONCLUSIONS

From our results, the following can be concluded. (1) Nitrogen dioxide adsorption is detected both on Fe_2O_3 and Fe_3O_4 . The N 1s binding energy of adsorbed NO_2 is close to those of NO_3^- and gaseous NO_2 . (2) Nitrogen monoxide adsorbed on Fe_3O_4 displays binding energies which are indicative of back donation from the solid. No adsorption is detected on Fe_2O_3 . (3) Nitrous oxide seems to be decomposed into

N_2 and NO under irradiation. (4) XPS makes possible a semiquantitative approach to adsorption. The detection limit is about 0.1 monolayer. (5) Chemisorption of nitrogen oxides induces surface oxidation of Fe_3O_4 into Fe_2O_3 .

X-ray photoelectron spectroscopy is thus a very interesting tool in studies of adsorbed species. Further work on nitrogen oxide adsorption by iron and oxidized iron is in progress and will be reported later.

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REFERENCES

1. Shelef, M., and Kummer, J. T., *Chem. Eng. Progr.* **67**, 74 (1971).
2. Shelef, M., and Otto, K., *J. Catal.* **18**, 184 (1970).
3. Shelef, M., and Otto, K., *J. Catal.* **10**, 408 (1968).
4. Shelef, M., Otto, K., and Gandhi, M., *J. Catal.* **12**, 361 (1968).
5. Contour, J. P., *Pollut. Atmos.* **1975**, 65.
6. Winter, E. R. S., *J. Catal.* **22**, 158 (1971).
7. Poling, G. W., and Eischens, R. P., *J. Electrochem. Soc.* **113**, 218 (1966).
8. Terenin, A., and Roev, L., *Spectrochim. Acta* **11**, 946 (1959).
9. Blyholder, G., and Allen, M. C., *J. Phys. Chem.* **70**, 352 (1966).
10. Borello, E., Cerutti, L., Ghiotti, G., and Guglielminotti, E., *Inorg. Chim. Acta* **6**, 45 (1972).
11. Borello, E., Cerutti, L., and Zecchina, A., *J. Catal.* **25**, 55 (1972).
12. Parkyns, N. D., in "Proc. Int. Congr. Catalysis," 5th (1972), p. 255, North-Holland, Amsterdam, 1973.
13. Yates, J. T., and Maddey, T. E., *J. Chem. Phys.* **45**, 1623 (1966).
14. Uehara, H., and Arimitsu, A., *Anal. Chem.* **45**, 1879 (1973).
15. Che, M., Naccache, C., and Vedrine, J., *Bull. Soc. Chim. Fr.* **1970**, 3307.
16. Maddey, T. E., Yates, J. T., and Erickson, N. E., *Surface Sci.* **43**, 526 (1974).
17. Dianis, W., and Lester, J. E., *Surface Sci.* **43**, 602 (1974).
18. Novakov, T., Mueller, P. K., Alcocer, A. E., and Otewos, J. W., *J. Colloid. Int. Sci.* **30**, 225 (1972).
19. Sabatier, P., and Senderens, J. B., *Ann. Chim. Phys.* **7**, 348 (1896).
20. Otto, K., and Shelef, M., *J. Catal.* **14**, 226 (1969).
21. Gandhi, H. S., and Shelef, M., *J. Catal.* **24**, 241 (1971).
22. Gandhi, H. S., and Shelef, M., *J. Catal.* **28**, 1 (1973).
23. Brundle, C. R., *J. Vac. Sci. Technol.* **11**, 212 (1974).
24. Johansson, G., Hedman, J., Berndtsson, A., Klasson, M., and Nilsson, R., *J. Electr. Spectrosc.* **2**, 295 (1973).
25. Jørgensen, C. K., *Mat. Fys. Medd. Danske Vidensk. Selskab* **38**, 51 (1972).
26. Contour, J. P., and Mouvier, G., *J. Electr. Spectrosc.* **7**, 85 (1975).
27. Germain, J. E., "Catalyse Hétérogène," Dunod, Paris.
28. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S., Lindgren, I., and Lindberg, B., ESCA: "Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy." Almquist and Wiksells, Uppsala, 1967.
29. Siegbahn, K., *J. Electr. Spectrosc.* **5**, 3 (1974).
30. Finn, P., and Jolly, W., *Inorg. Chem.* **11**, 893 (1972).
31. Hauffe, K., *Advan. Catal.* **7**, 213 (1955).
32. Nicolle, J., and Vodar, B., *C. R. Acad. Sci. C* **210**, 142 (1940).
33. Brundle, C. R., *J. Electr. Spectrosc.* **5**, 291 (1974).