JOURNAL OF CATALYSIS 38, 238–244 (1975)

Infrared and Temperature Programmed Desorption Studies of Nitric Oxide Adsorbed on Cobalt–Silica Catalyst

HIROO NIIYAMA AND ETSURO ECHIGOYA

Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo, Japan

Received January 4, 1974; revised November 25, 1974

Infrared studies of adsorbed nitric oxide (NO) on cobalt–silica catalyst were carried out. Two species were found, with N–O stretching frequencies at 1790 and 1850 cm^{-1}, respectively. The former arose from strongly chemisorbed species and was the intermediate species in the reaction between NO and reduced surface.

Bases such as NH_3, NH_2CH_3, $NH(CH_3)_2$ and $N(CH_3)_3$ resulted in a lowering of the N–O stretching frequencies of preadsorbed NO, and thus a weakening of the N–O bond. On the other hand, HCl shifted the bands to higher frequencies and also facilitated desorption. These effects were explained on the basis of a change in the electron density of metal–N–O molecular orbitals when the second gases were admitted.

INTRODUCTION

There have been many investigations of the ir spectra of adsorbed NO (*1–6*). Two or more kinds of species have often been found on the surface of transition metals and their oxides. However, little attention has been paid to the relationship between adsorbed species and reaction. The present study was conducted to find out the adsorbed species which is the intermediate in the catalytic reduction of NO.

Recently special attention has been focused on the catalytic reduction of NO in exhaust gas with H_2, CO or NH_3. The system contains O_2 as well as NO and the reducing agent. Thus the behavior of adsorbed NO when these gases are admitted was worth investigating. In addition to this, the effects of these gases on preadsorbed NO provides useful information towards a better understanding of the bonding nature of adsorbed NO (*2*). The effects of acids or bases were also studied in this work, because of their ability to donate or accept electrons upon adsorption.

The effects of CO, H_2 or O_2 have already been studied by several authors (*1,4,7*), but not in a context where the electronic influence of these gases is of primary concern.

EXPERIMENTAL METHODS

The catalyst for ir studies was prepared by impregnating Aerosil with aqueous cobalt nitrate, followed by calcination at 650°C for 3 hr. The atomic ratio of Co/Si was 5/95. The catalyst for TPD studies was prepared by the same method except that silica was obtained from Snowtex O (colloidal silica, supplied from Nissan Chem. Co.).

Infrared studies were made using a conventional cell, attachable to an adequate vacuum and gas handling system. Standard pretreatment conditions were consisted of reduction with 400 mm Hg of hydrogen at 300°C for 1 hr, and evacuation under 10^{-5} mm Hg at 300°C for 1 hr. After these treatments, the system was cooled to room temperature and adsorption and ir measurements were made.

Temperature programmed desorption (TPD) studies were carried out as follows.

Weighed catalyst was placed in an adsorption vessel and was prereduced in stream of hydrogen at 300°C for 1 hr. Helium was then passed through the vessel at the same temperature for 1 hr to avoid traces of hydrogen. Adsorption of NO was carried out at room temperature for 14 hr. Helium was passed again for 1 hr to eliminate gaseous or physically adsorbed NO. Then the temperature of the vessel was raised at a rate of 7–8°C/min in stream of helium. Effluent gas was periodically sampled by gas chromatography. Helium used here was purified by passing through a column of molecular sieve 13X cooled with liquid nitrogen.

NO (Matheson Chem. Co.), H_2, O_2 (Suzuki Shokan) and CO (Takachiho Shoji) were obtained from commercial cylinders. NO and CO were introduced to the gas handling system through a KOH-packed column which was maintained at −76°C. NO was further purified by several freeze–pump–melt cycles before use. H_2 was introduced through a molecular sieve 13X-packed column cooled with liquid nitrogen. O_2 was used without further purification. The amount of impurities in the gases were beyond detection of gas chromatographic analysis. Amines, NH_3, and HCl were obtained from aqueous solution (Wako Junyaku, special grade). Water was eliminated by vacuum distillation.

RESULTS

1. NO Adsorption on Partially Reduced Catalyst

Infrared spectra of adsorbed NO were only found when the catalyst was prereduced. The development of bands is shown in Fig. 1. Two bands were found at 1790 cm^{-1} (band A) and 1850 cm^{-1} (band B) in addition to a band at 1876 cm^{-1} due to gaseous NO. The maxima shifted slightly to higher frequency as the adsorption proceeded. However, the shift is not too clear because of the strong background spectrum due to the catalyst. The band B quickly saturated within 5 min, while the band A developed very slowly for 5 days.

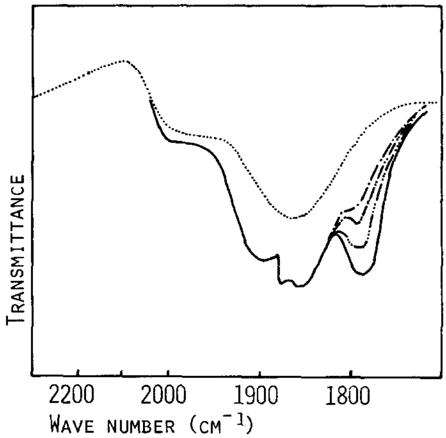


FIG. 1. Infrared spectra of adsorbed NO on Co–SiO_2. (····) Background spectrum; (—·) 10 min after the admission of NO, (—··) 1 hr after; (—···) 14 hr after; (—) 5 days after.

Figure 2 shows the effect of evacuation. Evacuation at room temperature produced little change in either band. Band B completely disappeared after pumping at 100°C, while Band A still remained. Thus the lower frequency band (band A) should be attributed to strongly chemisorbed species (species A).

A new band around 2200 cm^{-1} developed when the catalyst was heated at 300°C for several minutes in the presence of NO. The new band showed *R*- and *P*-

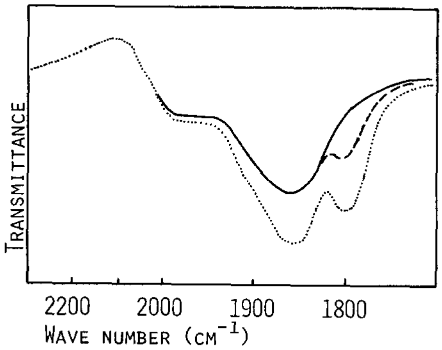


FIG. 2. Infrared spectra after evacuation. (—) Background spectrum and after pumping at 200°C for 1 hr; (····) after pumping at room temperature for 1 hr; (—) after pumping at 100°C for 1 hr.

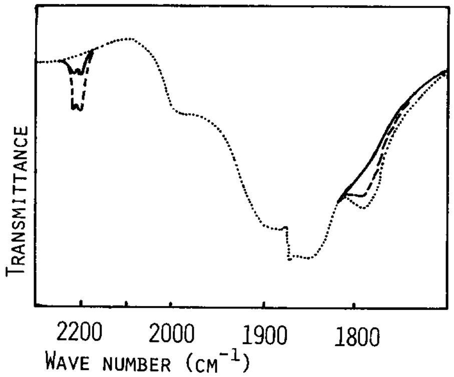


FIG. 3. Infrared spectra after heating at 300°C in NO atmosphere. (····) Before heating; (--) after heating; (—) after several heating–pumping cycles.

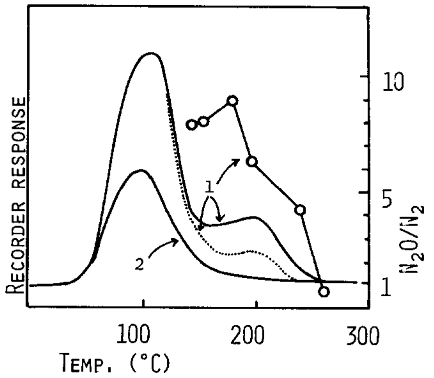


FIG. 4. TPD profiles of NO adsorbed on "fresh" (1) and "used" (2) catalyst. (—) Total recorder response; (····) contribution of NO to the total recorder response; (O—) ratio of N_2O/N_2 in the products.

branches and its position was completely the same as that of gaseous N_2O. These features are shown in Fig. 3. The formation of N_2O was also confirmed from gas chromatographic analysis. The formation of N_2 was also confirmed; however, O_2 was not found. The band disappeared after pumping for 1 min at room temperature. Thus the band around 2200 cm^{-1} was attributed to gaseous N_2O. It should be emphasized that N_2O was not adsorbed on the catalyst.

After several cycles of evacuation–NO admission–heating, the formation of N_2O was hardly found. Band A also disappeared while band B still remained after these cycles.

TPD profiles are given in Fig. 4. Two peaks around 100°C (peak B) and 200°C (peak A) were found. The desorbed gas was analyzed and the contribution of NO to the total recorder response is shown by the dotted line. Peak B mainly consisted of NO while N_2O and N_2 also contributed to peak A. The ratio of N_2O/N_2 was as high as 7.8 at 140°C and 6.4 at 200°C. The high selectivity for N_2O is a characteristic feature in the catalytic reduction of NO with hydrogen over Co–Al_2O_3 (*11*).

Only peak B was found in the TPD profile for the "used" catalyst, where "used" catalyst is the one heated at 300°C for 1 hr in the atmosphere of NO. Since neither N_2O nor N_2 was found in the effluent gas, the dotted line was superimposed on the solid line.

2. *The Effects of Basic and Acidic Substances on Preadsorbed NO*

A typical example of the effects of amines on preadsorbed NO is given in Fig. 5. A considerable shift to lower frequencies is observed, together with broadening of the bands. All the observed bands are attributable either to NO or to amines and evidence for direct bonding of

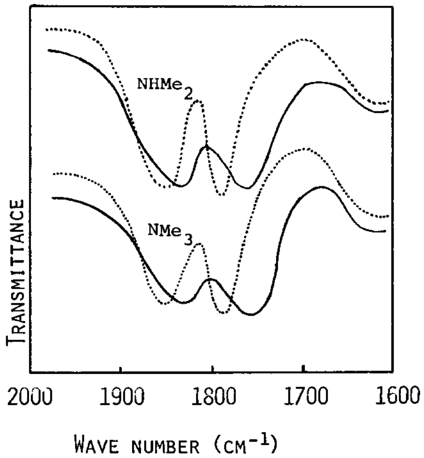


FIG. 5. The effects of added amines on adsorbed NO. (····) Before the admission of amine; (—) after the admission of amine.

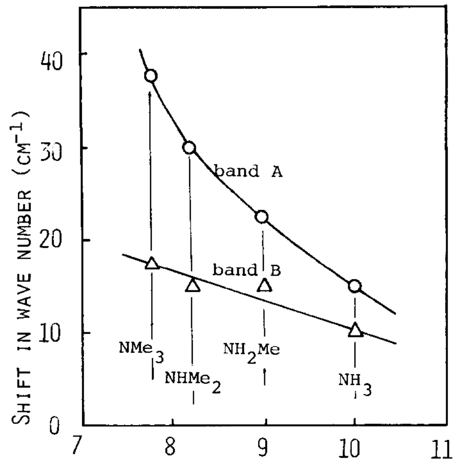


FIG. 6. The relation between the shift of N-O stretching bands and the ionization potential of added amines.

NO with amines is hardly found. The shift of band A was always larger than that of band B. The effects of other amines were more or less similar to that shown in Fig. 5.

The shift is plotted in Fig. 6 against the ionization potentials (IP) of the added amines (*8*), which is an index of electron donating ability. The shift was larger when amines having smaller IP and thus larger electron donating ability was admitted. It should be noted that no better correlation was observed when the shift was plotted against pK_b of the added amines (*9*) (4.2 for $N(CH_3)_3$, 3.23 for $NH(CH_3)_2$, 3.36 for $NH_2(CH_3)$ and 4.75 for NH_3). Since these values were measured in aqueous solution, not only the electronic factor but also solvation effects contribute to the pK_b value (*9*). Thus the pK_b is not the appropriate parameter in the gas phase reaction.

The effects of a typical Brønsted acid, HCl, on preadsorbed NO are given in Fig. 7. Contrary to the effects of amines, HCl brought a shift of the N-O stretching to higher frequency. The shift was $+15$ cm^{-1} for band A and 5-10 cm^{-1} for band B. Both bands gradually decreased on pumping at room temperature, in contrast to the behavior described above (Fig. 2) when no second gas was present. This indicates that the adsorbed acid facilitates desorption.

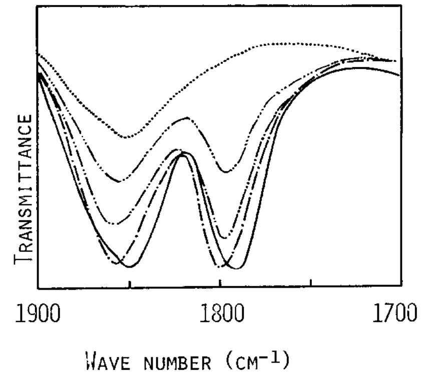


FIG. 7. The effects of added HCl on adsorbed NO. (····) Background spectrum; (—) after the adsorption of NO with subsequent pumping; (—·) in the presence of HCl (—··) after pumping for 1 hr at room temperature, (—···) after pumping for additional 4 hr.

The possibility that the admitted HCl reacts with the catalyst making irreversible changes, e.g., $2HCl + Co \rightarrow CoCl_2 + H_2$, should now be discussed. A very broad H-Cl stretching band was also found when HCl was admitted. The band disappeared after pumping at 100°C for 3 hr. Readsorption of NO gave spectra that were the same in their position but weaker in their intensities. The weakening indicated that some of the adsorbed NO reacted with the surface. The findings of the nondissociated H-Cl bond and the reproducibility of the position of the N-O stretching band showed that the admitted HCl was not the reactant but the adsorbent, because $CoCl_2$ is considered to be stable at 100°C.

A typical Lewis acid, BBr_3, also raised the frequency of the N-O band. However, Br_2 was liberated when BBr_3 was contacted with the catalyst. In this case, boron-containing species might be deposited on the catalyst and so the phenomena were too complicated to state definitely.

3. *NO Adsorption on an Amine-Preadsorbed Catalyst*

The ir spectra of NO adsorbed on amine preadsorbed catalyst are shown in Fig. 8. The largest shift was observed at the initial

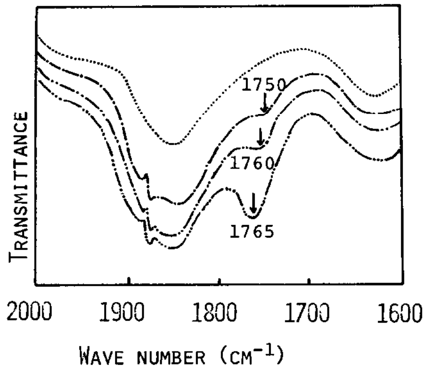


FIG. 8. The development of the bands for adsorbed NO on $NH(CH_3)_2$ preadsorbed catalyst. (····) Before the admission of NO; (—·) 10 min after the admission; (—··) 1 hr after; (—···) 15 hr after.

stage and then the shift decreased as the adsorption proceeded. This phenomenon was described suggestively in Sect. 1, where no amine-preadsorption was done. In that case the effect was ambiguous because of the strong background spectrum due to the catalyst. The effect was more pronounced on the amine preadsorbed catalyst.

4. *The Effects of Other Gases; H_2, CO and O_2*

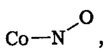
The effects of H_2, CO and O_2 adsorption on preadsorbed NO are summarized in Table 1, together with those of amines and HCl. The experimental conditions were slightly different one to another, e.g., the shift to lower frequency upon the admission of H_2 was found when the system was heated at 200°C. In spite of this, however, we can find a general tendency from Table 1. That is, H_2, CO and NH_3 which are commonly used as a reducing agent in NO_x conversion showed similar effects. On the contrary, the behavior of O_2 was quite different but similar to that of HCl.

DISCUSSION

1. *Mode of Adsorbed NO*

The sites available for the adsorption of NO are reduced (partially or completely) cobalt atoms because, (a) ir bands of adsorbed species were found only when the catalyst was prereduced with H_2, and (b) adsorbed CO which was commonly assigned to the "metal-bonded CO" was replaced by NO giving rise to the band A and B. Notwithstanding the interpretation of Poling and Eischens (*5*) the bonding of NO to surface oxygen atom would be insignificant in this case.

The possible modes of bonding to the surface cobalt atom are; (a) linear type through the nitrogen end, i.e., Co–N–O, (b) bent type through the nitrogen end, i.e.,



,

TABLE 1

THE EFFECTS OF SECOND GAS ADSORPTION ON IR SPECTRA AND DESORPTION PHENOMENA OF ADSORBED NO

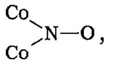
Gases	Shift of N–O stretch. freq.	Desorption phenomena of NO	Electron transfer
Bases (amines)	Lower wavenumber		Donate
Acids (HCl, BBr_3)	Higher wavenumber	Easily desorbed	Accept
H_2[a]	Lower wavenumber		Donate
O_2	—[b]	Very easily desorbed	Accept
CO	Lower wavenumber[c]		Donate (?)

[a] The shift was observed when the system was heated at 200°C.

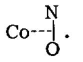
[b] Adsorbed NO was very easily replaced by O_2 and so the shift was hardly determined.

[c] Very small.

(c) bridge type through the nitrogen end, i.e.,



and (d) side-on type, i.e.,



The possibility of adsorption through the oxygen end is omitted, because it is highly improbable when the electronic structure of NO is taken into consideration.

As the bridge type bonding has been rarely reported in the inorganic chemistry of NO–metal complexes, little attention has been paid to this possibility (*4*). Recently bridge typed nitrosyl complexes were observed; however, N–O stretching for these complexes was found in a far lower region than in our observation (*10*).

The side-on adsorption is considered to take place through the donation of π^* electron to the metal. This brings the N–O stretching frequency to a higher value when adsorption take place. Terenin and coworkers assigned the band around 2000 cm^{-1} to species of this kind (*1–3*). Furthermore, the adsorption of this kind is weak enough that the gas is desorbed by pumping at room temperature (*1,2*). These features are not consistent with our findings.

The N–O stretching of the bent type is found in a lower frequency region than that of the linear type.

With this background in mind, it seems probable that the band A is due to bent NO and the band B to linear NO if the two bands correspond to two different modes of adsorption. However, as was pointed out by Blyholder and Allen (*4*), it is also probable that one mode of adsorption gives rise to two different bands. According to their view, band A is due to NO adsorbed on a corner or edge of a crystallite and band B is due to NO adsorbed on a plane. Their modes of adsorption may be the same. Further discussion is omitted because of lack of evidence. What we would like to emphasize here is that both bands arise from one molecule of NO bonded to one metal atom.

2. *Reactive Species in the Reduction of NO*

Several schemes have been proposed for the catalytic reduction of NO (*2,6,11–13*). These may be tentatively divided into two types. One is through redox cycles of catalysts, that is, the reduced surface is oxidized by NO to give N_2O and/or N_2 and then the oxidized surface is reduced again by H_2 or CO (*11,13*). The other is through direct interaction of NO with H_2 or CO on the surface (*6,12*). In the latter schemes, HNO or NCO are assumed as intermediate species.

As was shown in Fig. 3, NO gave N_2O at 300°C in the presence of reduced surface; however, no O_2 was found in the gas phase. This indicates that the reaction was not the catalytic one ($NO \rightarrow N_2 + O_2$, $NO \rightarrow N_2O + O_2$) but the stoichiometric one with the surface. The reduction of the oxidized surface also proceeded at 300°C in the presence of H_2. The redox cycle is thus completed and this scheme is the probable one for the catalytic reduction of NO. The reactive species herein discussed is the intermediate in the redox scheme. It should be emphasized, however, that this does not exclude the possibility of direct interaction schemes when NO and reducing agents coexist (*11*).

The results in Fig. 3 clearly showed that species A is the intermediate in the reaction of NO with the reduced surface and that species B plays a role of secondary importance. This is because the species A disappeared when the catalyst lost its activity to give N_2O while the species B still remained. TPD profiles for the "fresh" and "used" catalyst also support this view if it is reasonably supposed that the peaks A and B in TPD correspond to the bands A and B in ir spectra, respectively. Our observations are summarized by saying that the species having the lower N–O stretching frequency (smaller force constant for N–O bond) is the strongly chemisorbed species and is the reactive one.

3. *Molecular Orbital View of Adsorbed NO*

Since the similarity of adsorbed NO to adsorbed CO has been frequently stated, it is reasonable to refer to numerous studies devoted to CO chemisorption on metals, which were comprehensively reviewed by Little (*1*). MO calculations of adsorbed CO were done by Blyholder (*14*) and extended to adsorbed NO (*4*). The calculations were based on a simple Hückel approximation; however, the view satisfactory explained the behavior of adsorbed CO and NO. The MO of the lowest energy for the M–N–O system is bonding to both M–N and N–O. The MO of second lowest energy is bonding to M–N while antibonding to N–O. Since the second MO is the highest occupied orbital, it plays a significant role in adsorption and reaction. The finding that the strongly chemisorbed species is the reactive one is satisfactory explained on this view because, in the first approximation, the reactivity is related to the strength of the N–O bond and the adsorption phenomenon is related to the strength of the M–N bond.

When second gases are adsorbed, they increase or decrease the electron density of the catalyst according to their acidic or basic nature. Thus the electron density of the second MO is also strongly dependent on the nature of coexisting gases. The shifts of the ir bands and the change in the desorption phenomena when second gases were admitted are explained as follows. For instance, consider the effects of acid. Acid adsorption results in a decrease of electron density of the catalyst. The population of the second MO also decreases. Consequently the force constant of M–N decreases (the strength of adsorption decreases) and that of N–O increases (ir bands shift to higher frequency).

Electrons which have been present in the metallic bonds are localized in M–N–O molecular orbitals as the adsorption proceeds. The shift is largest in the initial stage and then gradually decreases (cf. Fig. 8).

Relation of this work with the catalytic removal of NO should be briefly discussed. It is considered that the reductive removal of NO promises more fruitful results than does oxidative removal, because reducing agents, e.g., H_2, CO and NH_3, promote adsorption and activation of NO while O_2 retards them. The addition of promoters of electron donating ability will improve the catalytic activity.

REFERENCES

1. Little, L. H., "Infrared Spectra of Adsorbed Species," p. 84. Academic Press, New York, 1966.
2. Shelef, M., and Kummer, J. T., *Chem. Eng. Progr., Symp. Ser.* **67,** n155, 74 (1971).
3. Terenin, A. N., and Roev, L. M., *Actes Congr. Int. Catal., 2nd, 1960* **2,** 2183 (1961).
4. Blyholder, G., and Allen, M. C., *J. Phys. Chem.* **69,** 3998 (1965).
5. Poling, G. W., and Eischens, R. P., *J. Electrochem. Soc.* **113,** 218 (1966).
6. Unland, M. L., *J. Phys. Chem.* **77,** 1952 (1973).
7. Roev, L. M., and Terenin, A. M., *Opt. Spektrosk.* **7,** 756 (1959).
8. Turner, D. W., *in* "Advances in Physical Organic Chemistry" (V. Gold, Ed.), Vol. 4, p. 47. Academic Press, London, 1966.
9. Sykes, P., "A Guidebook to Mechanism in Organic Chemistry," 3rd ed., Chap. 3. Longmans, Green, London, 1970.
10. Norton, J. R., Collman, J. P., Dolcetti, G., and Robinson, W. T., *Inorg. Chem.* **11,** 382 (1972).
11. Ebitani, A., Niiyama, H., and Echigoya, E., *Nippon Kagaku Kaishi* **1974,** 1185; **1974,** 222.
12. Kokes, R. J., *J. Phys. Chem.* **70,** 296 (1966).
13. London, J. W., and Bell, A. T., *J. Catal.* **31,** 32 (1973).
14. Blyholder, G., *J. Phys. Chem.* **68,** 2772 (1964).