

IR SPECTROSCOPIC STUDY OF INTERACTION OF CO, NO AND NO + CO WITH $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ CATALYST : METAL OXIDE-SUPPORT INTERACTIONS

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SUMMARY: Infrared spectroscopy was used to study adsorption of CO and NO on alumina-supported iron oxide sample (containing 3 wt % Fe), oxidized or reduced at 723 K. It was clear that different sites for NO and CO adsorption were generated when $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst was conditioned under reducing or oxidizing atmosphere: (I) Fe^{2+} sites which were in a strong interaction with the support, (II) partially reduced Fe^{3+} ($\text{Fe}^{(3-b)+}$) and (III) Fe^{2+} located in octahedral environment of Fe_3O_4 formed by reduction of "free" iron oxide.

I. Introduction

Extensive research and development effort has been made to explain the process of the chemisorption of gases on catalysts, and several, make use of data obtained by infrared spectroscopy. This technique furnishes data indicating the creation of a bond between the reactant and the surface, the disappearance of bonds in the reactant, or the displacement of the frequencies of bonds within the reactant caused by its adsorption. The study by infrared spectroscopy of these new bonds or the displacement of existing bonds can give indirectly a picture of the solid surface and how it interacts with a chemisorbing gas.

Among the gaseous reactants, CO and NO have been commonly used to probe for the nature of surface transition metal ions by infrared spectroscopy. The extensive knowledge pertaining to the interaction of these molecules with metal atoms and ions makes their use attractive. Attempts have been made to use these molecules to deduce the charge, the degree of coordination unsaturation and the symmetry of the surface metal ions [1-11].

The low cost of iron and its use in ammonia process gave an impetus to its industrial applications [12] and to practical developments in the Fischer-Tropsch process [13]. However the nature of superficial sites existing particularly on the surface of supported iron oxide catalyst remains a subject of discussion. In fact the presence of dispersing medium such as alumina or silica induces almost two important modifications in iron oxide phase properties: (1) the reduction of iron

oxide is tempered by the presence of dispersing medium [14] whereas bulk iron oxide is reduced to the metallic state during this treatment and (2) iron oxide interacts strongly with the support [15] and this metal-support interaction leads even to the substitution of Fe^{3+} by support cations (i.e. Al^{3+} or Si^{4+}).

Previously [16] we have studied adsorption of carbon monoxide on different supported iron catalysts. We have concluded, in the case of aerosol catalysts, that the carbonyl species is adsorbed on an ionic iron site. Since NO adsorbs significantly more strongly than CO [17] on transition metal oxides, it may actually be a more sensitive adsorption probe of alumina supported iron oxide.

In the present work, we use infrared spectroscopy to study the surface species formed by the interaction of CO, NO and CO + NO with prereduced and preoxidised $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. An attempt is made to deduce the nature of active sites present at the surface of such catalyst.

II. Experimental

Materials: The catalyst $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ was prepared from vapor ferric chloride and aluminium chloride by reaction in an oxygen-hydrogen flame. The flame reactor has been described elsewhere [18]. The chloride vapor was carried by a stream of nitrogen into the central tube of the burner. After reaction (hydrolysis and/or oxidation) of corresponding chlorides vapor in the flame; the particles could be collected in an electrostatic precipitator. The size, morphology and crystalline quenching conditions, which, in turn,

were governed by the flame temperature, concentration and residence time of reactive species in the flame. The catalyst studied in the present work had been prepared in a flame at 300 K. The partial pressure of chloride (given by the molar flow rate of chloride divided by the molar flow rate of carrier gas) controlled the catalyst composition fixed at 3 wt % of metallic iron.

Methods: The catalyst $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ was characterised by its X-ray diffraction pattern. All the observed reflexions were attributed to Al_2O_3 . B E T (N_2) surface area was $20 \text{ m}^2 \cdot \text{g}^{-1}$.

The granulometric study of the sample had shown the monodispersion and the narrow size distribution of Fe_2O_3 (facetted grains) and Al_2O_3 (spheric grains) which mean sizes were almost the same (60 nm). High resolution microscopy and microdiffraction gave evidence for the monocrystallinity of Fe_2O_3 particles with occurrence of twins in the largest particles [19, 20]. The {111}, {100} and {110} faces were most common, generally in association; resulting in a rhombocuboctaedron. The {110} faces appeared often stepped by {111} planes.

Infrared spectra were recorded at beam temperature (b.t) with a Beckman 4230 I R double beam spectrometer. Two I R cells (sample and reference) were used with CaF_2 windows. A detailed description had been given elsewhere [21]. The experiments were conducted using sample pressed into tablets of 18 mm diameter and 15 mg/cm^2 thickness. The transmission at 4000 cm^{-1} was 40 and 15% respectively for the preoxidized and prereduced sample.

The products used were of commercial purity. They were further purified by adsorbing the impurities at low temperature using a molecular sieve.

III. Results

In order to define the differences in character of interaction of gases with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst in comparison with the individual oxides, and in order to establish the types of surface species and surface sites that were characteristic for CO; NO and CO + NO interactions, we had made use of data previously published on pure Fe_2O_3 as well as data obtained in the present work.

Interaction of CO with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$: In fig 1 (curve i) we showed the infrared spectra of carbon monoxide on a reduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ at 743 K and evacuated at this temperature. Maximum was observed at 2110 cm^{-1} having a lower frequency than $\nu_{\text{C}-\text{O}}$ for gaseous carbon monoxide (2143 cm^{-1}).

When carbon monoxide was admitted to the sample preoxidized a flow of oxygen at 743 K and evacua-

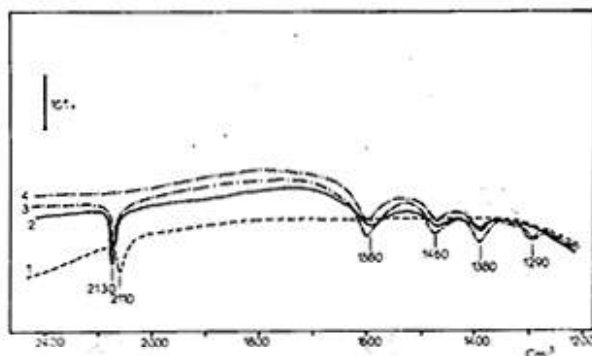


Fig. 1 : I.R. Spectra of CO adsorbed on prereduced and preoxidized surface of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$: 1) 10 torr on prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$; 2) 10 torr on preoxidized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$; 3) after 4 h of contact; 4) after evacuation at b.t.

ted at b.t, a sharp band immediately appeared at 2130 cm^{-1} (fig. 1 curve 2).

In addition to this, broad absorption occurred between 1300 and 1600 cm^{-1} . On standing for four hours the intensity of the 2130 cm^{-1} band remained unaltered while the 1300 - 1600 cm^{-1} absorptions increased and a weak band appeared at 1290 cm^{-1} (fig. 1 curve 3).

Evacuation at b.t for 10 minutes, entirely removed the species responsible for the 2130 cm^{-1} band, but the other bands were unaltered (fig. 1 curve 4). The addition of dry oxygen at b.t did not change the spectrum. After heating the sample in oxygen at 473 K for 2 hours and outgassing at 473 K for 1 hour, the spectrum was the same as that before the addition of carbon monoxide. Further addition of CO to the sample in this condition at b.t led to an identical sequence of spectra.

However, when the specimen was heated at 523 K for 30 minutes in the presence of gaseous carbon monoxide, a great increase in the intensity of the bands occurred. (fig. 2 curve 1). The absorption band at 2130 cm^{-1} was slightly shifted to lower frequencies ($\sim 2120 - 2125 \text{ cm}^{-1}$).

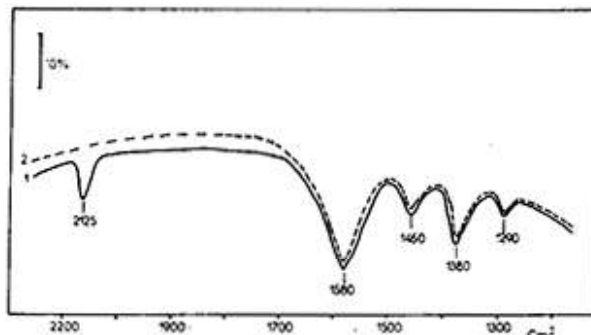


Fig. 2 : I.R. spectra of CO adsorbed on preoxidized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$: 1) after treatment, for 30 mn, in the presence of CO at 523 K; 2) after evacuation at b.t.

Evacuation at b.t for 10–15 minutes did not affect the low frequency bands but entirely removed the species responsible for the 2120–2115 cm^{-1} band (fig. 2 curve 2).

The ground state for CO is Σ^+ with the electronic configuration of $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$ [22]. Theoretical calculations indicate that the effective charge on carbon is positive and that on oxygen is negative [23, 24]. However using molecular beam electric resonance spectroscopy, Muentner [25] determined that CO has a polarity of $\text{C}^+ \text{O}^-$ and a very small dipole moment of 0.1222 D. This is due to the fact that the lone pair electrons in the 5σ orbital reside at the outside of the carbon atom.

On many oxides, infrared band is found at frequencies substantially higher than the gas-phase frequency of 2143 cm^{-1} [26–30]. Lokhov et al. [31] proposed that the frequency for M^{2+} (CO) is above 2170 cm^{-1} and M^0 (CO) below 2100 cm^{-1} (M: metal). They argued that for M^0 , dative and back bonding are present, and the importance of back π bonding is seen by the stretching frequency which is located below that of gas phase CO.

The absorption bands in the spectra of adsorbed CO lying below 2143 cm^{-1} were usually assigned to carbonyl compounds, in which the carbon-oxygen bond is weak in comparison with that of gaseous molecule. The weakening of C-O bond in the carbonyl structure was due to the formation of π -back-bond between the d-orbitals of the metal and the vacant antibonding π orbital of the carbon monoxide molecule.

Eischens and Pliskin [32] observed a band at 2125 cm^{-1} by the introduction of a trace of oxygen into the system CO/Fe/SiO₂ exhibiting already the band at 1960 cm^{-1} . In a recent work [33], we reported the presence of CO absorption band at 2130 cm^{-1} on pure Fe₂O₃. We also observed the same band on Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ [16]. Note that no bands were observed when CO was adsorbed on pure alumina.

The absorption of carbon monoxide on Fe₂O₃/Al₂O₃ catalyst to give a sharp band at 2110–2130 cm^{-1} according to whether the catalyst was prereduced or preoxidized, was extremely rapid at b.t and the activation energy for the process must be very small. The species was readily removed from the surface by evacuation at b.t for 10–20 minutes, adsorption was thus very weak. The proximity of this band to that of gaseous CO, would indicate a weak chemisorption process or adsorption by dipolar forces in which the essential carbon monoxide structure had been retained. The shift is in a direction normally produced by polar environments: in general it was found that the stretching frequencies of polar groups were dis-

placed to lower values when material was transferred from vapor to liquid [34]. In a recent work [35], we had determined isosteric heats for the interaction of carbon monoxide with a reduced Fe₂O₃/Al₂O₃ catalyst which showed by infrared study only the 2110–2120 cm^{-1} band. The weak obtained value (~ 5 kJ/mol) as well as entropy calculations, indicated that the surface species were extremely mobile, even at low coverages. This result suggested that the adsorbed species were in a gas-like-state on the surface of the adsorbent while the changes in vibrational frequency (~ 20 –30 cm^{-1}) indicated a significant perturbation in the molecule. In an attempt to explain this paradox, Gardner et al [36, 37] proposed that adsorbed species of CO were considered as charge entities with a non-integral number of valence electrons. The postulation of charged entities had been made without regard to the electron donor-acceptor properties of the adsorbent and Taylor and Amberg [38] had pointed out that CO adsorption on ZnO was inconsistent with an electron transfer-adsorption mechanism in the formation of positive adsorbed CO.

Hush and Williams [39] considered the effect of strong electronic fields on the equilibrium nuclear configuration, vibration frequency and vibrational transition intensity of CO and analysed existing results for the CO molecule in axial fields. For adsorption perpendicular to an ionic surface, it was concluded that a negative shift of CO stretching frequency was evidence for adsorption via carbon at an anionic site or via oxygen at a cationic site. Adsorption of a molecule parallel to the surface should result in only very small change in CO stretching frequency.

In spite of that, in the present study, the shift of CO stretching frequency is negative and is stronger for reduced ($\Delta \nu = -33$ cm^{-1}) than for oxidized ($\Delta \nu = -13$ cm^{-1}) specimen, it's difficult to put forward, from the only I.R. spectra, a proposal about species configuration (perpendicular or parallel to the surface). It's, therefore, careful to limit our assignment of the two bands at 2110 and 2130 cm^{-1} to carbonyl species weakly adsorbed on ionic sites partially (Fe^{3+}) and fully (Fe^{2+}) oxidized respectively. This assignment is supported by our recent results [33] obtained on pure Fe₂O₃. Note that there is no complete reduction of the cation to the state Fe⁰. This is indicated by i) the low weight loss (~ 8 %) due to the reduction compared to that necessary to complete reduction (30 %) [35] and ii) the absence of I.R. bands in the vicinity of 2000 cm^{-1} assignable to adsorbed CO on metallic iron sites.

Adsorption bands, which appeared below 1600 cm^{-1} in the spectrum of adsorbed carbon

monoxide on preoxidized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, will be considered in relation to the results already obtained for the carbonates [40, 41]. Table I summarizes the bands that had been observed in this spectral range, and their assignments.

Frequency	Vibration	Structure
1580	C = O stretch	
1290	Asym stretch	
1460	Asym stretch	
1380	sym stretch	

Table I : Adsorbed CO: Adsorption bands in the region 1600 - 1200 cm^{-1} .

The bands below 1600 cm^{-1} were compared to that of carbonates species. The 1580 and 1290 cm^{-1} bands were due to bidentate carbonate, however the 1460 and 1380 cm^{-1} bands were assigned to unidentate carbonate. The 1580 cm^{-1} band could not be due to the deformation mode of adsorbed water, since on exposing the sample completely to the atmosphere, a very intense band appeared at 1630 cm^{-1} which disappeared completely under vacuum at b.t., whereas the 1580 cm^{-1} band were unaltered after the same treatment.

The formation of carbonate groups on the preoxidized sample when such groups were not observed on the pre-reduced sample indicated that these groups might be formed by the interaction of CO with iron oxide, or by the interaction of catalytically formed carbon dioxide iron oxide. It was of interest to note that the formation of carbonate groups when carbon monoxide was admitted at b.t required the presence of activated oxygen at the surface. The bands observed when carbon dioxide was adsorbed on pure Fe_2O_3 [42] were attributed to uni and bidentate carbonate ligands. However the adsorption of carbon monoxide on the same adsorbent [33] at b.t did not show any band in the 2000-1000 cm^{-1} region. In this case carbonates were formed at high temperature adsorption of CO. It would be expected that carbon monoxide would form carbonates more readily on pure iron oxide than on supported iron oxide since the quantity of activated oxygen on pure Fe_2O_3 might be more important than that on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst (3 % Fe). In both cases the process of carbonates formation might be an activated one. The bands were:

intensified by heating carbon monoxide with pure Fe_2O_3 [33] or iron alumina sample. Yates et al [43] demonstrated that the formation of carbonate complexes on supported nickel oxide was deeply influenced by the support. Evidence for carbonate complexes was obtained for alumina supported nickel oxide, but not with titania or silica.

In order to understand the role of the support in the formation of carbonate groups, carbon monoxide was admitted on pure alumina (prepared with the same method as the catalyst studied in this work) preoxidized at 743 K and evacuated at b.t. No bands were observed at b.t. nor at higher temperature (473 K) in the presence of CO. It could be concluded that oxygen present at the surface of alumina was not mobile compared to that of pure Fe_2O_3 (at 473 K) [33] or $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst (at b.t). If we assume that no change had been produced in the alumina, which was the major portion of the surface in the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample (97%) by its preparation with iron oxide, it would be possible to conclude that the majority of carbonate species must be attached either to "free" iron oxide or coordinated to cations which were in strong interaction with alumina support (e.g present at the interface between iron oxide and alumina particles or as a surface iron aluminate phase). The absence of such carbonates on pure Fe_2O_3 at b.t [33] might exclude the possibility that these species were adsorbed on "free" iron oxide in the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. In addition the appearance of carbonate bands between 1300 and 1600 cm^{-1} did not alter the intensity nor the position of the 2130 cm^{-1} (which was assigned to carbon monoxide adsorbed on ionic iron site which pertained probably, to "free" iron oxide). Hence it was possible to assume in a first stage the existence of almost two types of iron sites on iron supported catalyst: the first one responsible for weak CO chemisorption (2130 cm^{-1}) and which belonged to "free" iron oxide, and the second one in a strong interaction with the support and was responsible for relatively strong chemisorption of carbonate species. The formation of carbonate complexes on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ at b.t was due to the presence of oxygen bonded to iron site (assumed as being in strong interaction with the support) which was more mobile than the oxygen of pure Fe_2O_3 or Al_2O_3 . This view was supported by the fact that the interaction of CO and pre-reduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst did not lead to the formation of carbonate structures but showed the presence of carbonyl structure (2110 cm^{-1}). No more information seemed to be available on the validity of this view concerning the interaction between alumina and the iron oxide which was obviously extremely difficult to establish.

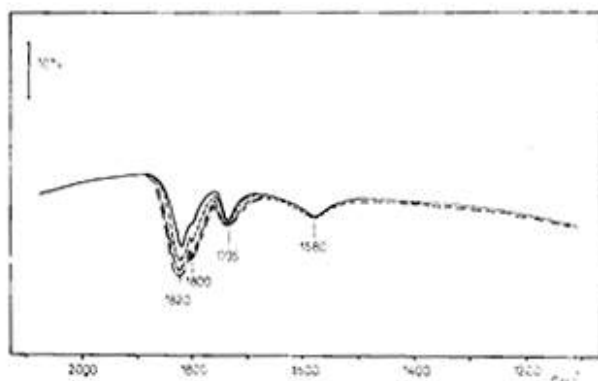


Fig. 3 : I.R. Spectra of NO adsorbed on prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. NO was added in doses of 2 torr.

Interaction of NO and CO/NO with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst: In fig. 3 we show spectra obtained by admittance of 10 torr of nitric oxide to the prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. At b.t., intense absorption were manifested in the 1900 - 1800 cm^{-1} region with maxima at 1820 (with a shoulder at 1800 cm^{-1}) and 1735 cm^{-1} . In addition, a very small band at 1580 cm^{-1} appeared. As nitric oxide was added to the sample in small doses, both bands at 1820 and 1735 cm^{-1} grew. The ratio of the intensities of the two bands was not constant. This condition should be expected if both bands were not due to the same adsorbed species. After several doses, the 1800 cm^{-1} shoulder appeared to reach maximum intensity and any growth with additional doses seemed to be due to broadening of the 1820 cm^{-1} band. After the cell was evacuated for 2 hours, the band at 1800 cm^{-1} almost disappeared while the bands at 1820 and 1735 cm^{-1} had been reduced in intensity (fig. 4 curve 1). The admittance of oxygen at b.t. led to the disappearance of 1735 cm^{-1} band and the shifting of that at 1820 cm^{-1} (fig. 4 curve 2).

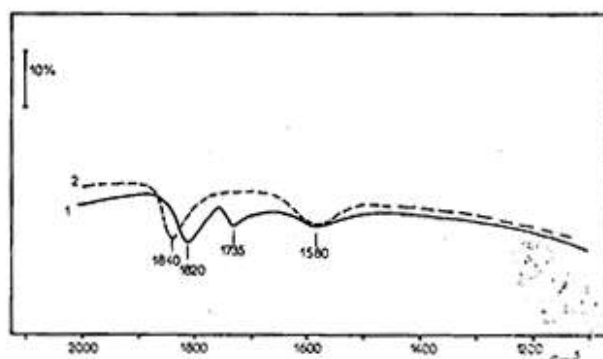


Fig. 4 : Spectra of NO adsorbed on prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$: 1) after evacuation at b.t. for 2h; 2) after admittance of 5 torr of oxygen.

The adsorption of the reacting gaz mixture with NO : CO molar ratio of 2 : 1 at b.t. on a prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ sample produced, after 10 minutes of

interaction, exactly the same spectra as that obtained with adsorbed NO (fig. 5 curve 1). When the gaz mixture was maintained for 12 hours in contact with the adsorbent, small band at 2110 cm^{-1} appeared when the band at 1820 cm^{-1} was reduced in intensity (fig. 5 curve 2).

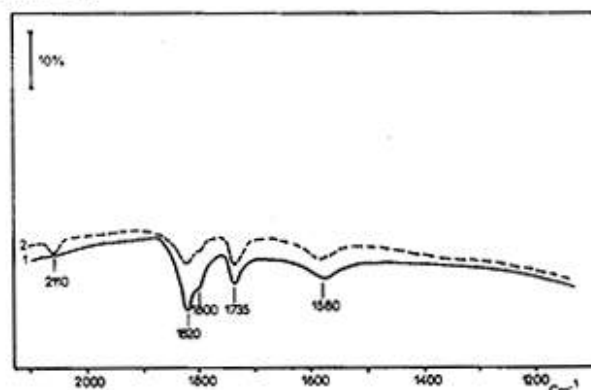


Fig. 5 : I.R. Spectra of NO + CO (NO : CO = 2 : 1) adsorbed on prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$: 1) after 10 mn of interaction at B.T.; 2) after 12h of interaction at b.t.

After exposure to the gaz mixture at 573 K, the infrared spectra were recorded (fig. 6). Absorption bands of different intensities were observed at 2320, 2240, 2110, 1820, 1800 and 1580 cm^{-1} . Two new bands at 2240 and 2320 cm^{-1} were not observed during the adsorption of the individual gases and which might be attributed to the formation of new surface complexes. Note that under the same conditions new bands at similar frequencies, 2240 - 2270 cm^{-1} , appeared on alumina supported noble metals [44 - 47].

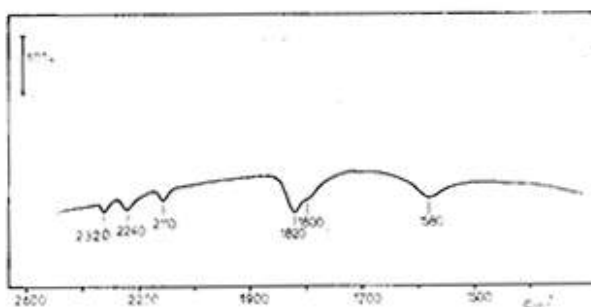


Fig. 6 : I.R. Spectra obtained by the interaction at 573 K of a mixture of NO + CO (NO : CO = 2 : 1) with prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$.

In order to determine the nature of the bands observed in the spectra produced by the interaction of prereduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst with NO and NO + CO and the effect of the oxidation state of iron sites on the formation of adsorbed species, we had carried out a study of the interaction of NO and NO + CO with the preoxidised catalyst and had analysed the changes in the spectra. Fig. 7 curve 1 represents the spectrum obtained after the adsorption of NO (10

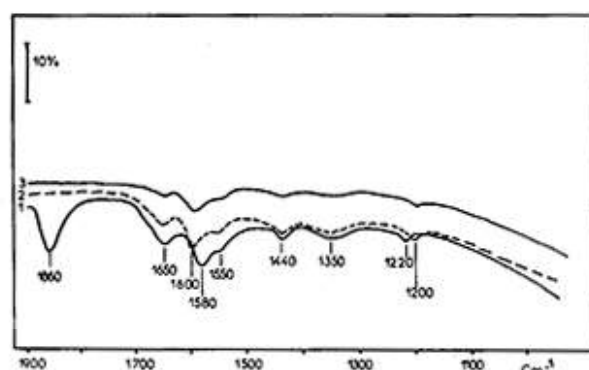


Fig. 7 : Spectra of NO adsorbed on preoxidized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$; 1) 10 torr on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$; 2) after evacuation at b.t.; 3) after evacuation at 473 K.

torr) at b.t. with preoxidized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. The spectrum shows absorption bands at 1220, 1440, 1550, 1580, 1650, 1860 cm^{-1} and broad absorption bands centred at 1350 cm^{-1} . The multiplicity of absorption bands in the 1600-1200 cm^{-1} region had been already obtained when NO was adsorbed on pure Fe_2O_3 [33] and might be related to the formation of nitrite-nitrate species.

After the cell was evacuated for 2 hours, the band at 1860 cm^{-1} disappeared and those at 1580 and 1220 cm^{-1} were shifted to 1600 and 1200 cm^{-1} respectively (fig. 7 curve 2). When the vacuum holding temperature was increased to 473 K (fig. 7 curve 3), the remained absorption bands decreased in intensity.

The adsorption of the reacting gas mixture with NO : CO ratio of 2 : 1 at b.t. on a preoxidized sample, produced absorption bands at 2130 and 1850 cm^{-1} (fig. 8 curve 1). In addition a great number of maxima appeared in the 1600-1200 cm^{-1} region. Under conditions of catalytic reaction at a temperature of 573 K, bands were observed at 2320, 2240, 2120, 1820, 1780 and 1770 cm^{-1} (fig. 8 curve 2). The addition of oxygen at b.t. following a brief period of evacuation to

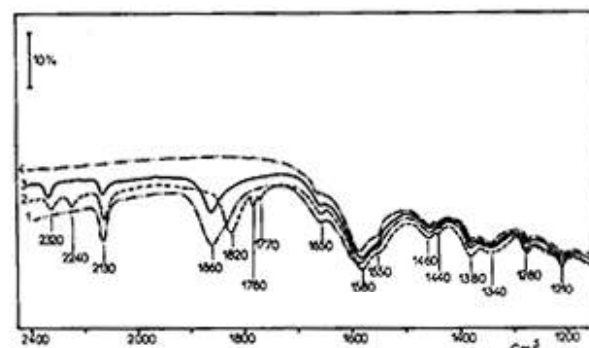


Fig. 8 : Spectra of NO + CO (NO : CO = 2 : 1) adsorbed on preoxidized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$; 1) NO + CO at b.t.; 2) after catalytic reaction at 573 K; 3) after the addition of 5 torr of oxygen at b.t.; 4) after evacuation at b.t.

remove gaseous NO + CO, led to disappearance of the 1790, 1770 and 2240 cm^{-1} and the shifting of the 1820 and 2120 cm^{-1} bands to 1860 and 2130 cm^{-1} respectively (fig. 8 curve 3). All these bands disappeared after the cell was evacuated (fig. 8 curve 4).

The adsorption of NO and NO + CO on pre-reduced or preoxidized catalyst leads to the appearance of spectral bands in the 1650-2400 cm^{-1} region characterizing various species adsorbed on different reduced or oxidized centers (table II).

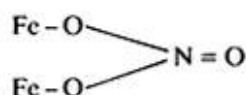
wave-number	reactant	assignment	Fig. n°
2320	NO : CO at 573 K	$-\text{CO}_2$	6-8
2240	NO : CO at 573 K	$-\text{NCO}$	6-8
2120-2130	NO : CO at b.t. or at 573 K	$\text{Fe}_{\text{II}}^{3+}(\text{CO})$	8
2110	NO : CO at b.t. or at 573 K	$\text{Fe}_{\text{II}}^{(3-\delta)+}(\text{CO})$	5-6
1860-1850	NO or NO : CO at b.t.	$\text{Fe}_{\text{II}}^{3+}(\text{NO})$	7-8
1820	NO at b.t. or NO : CO at 573 K	$\text{Fe}_{\text{II}}^{(3-\delta)+}(\text{NO})$	3-4-6-8
1800	NO : CO at 573 K	$\text{Fe}_{\text{III}}^{2+}(\text{NO})$	3-4-6
1780	NO : CO at 573 K	$\text{Fe}_{\text{I}}^{(2+\delta)+}(\text{NO})$	8
1735	NO or NO : CO at b.t.	$\text{Fe}_{\text{I}}^{2+}(\text{NO})$	3-4

Table II : Structure and spectral characteristics of surface compounds formed by adsorption of NO and NO + CO on pre-reduced and preoxidized catalyst.

The structure of the surface complexes found by adsorption of NO and NO + CO are listed in table II, a long with the frequencies characterizing these complexes. Assignment of the frequencies to the vibration of bonds of specific structures was made by a comparison of the band positions in the spectra of adsorbed NO and NO + CO (fig. 3-8) with a collection of frequencies characterizing complexes of adsorbed NO and NO + CO, [33, 45, 48-63], with due caution for the behavior of the bands when i) reactants were adsorbed on reduced or oxidized catalysts, ii) oxygen was admitted to the pre-reduced specimen and iii) catalyst was treated in vacuum or high temperature in the presence or absence of adsorbate.

It will be seen from table II, that adsorbed NO and CO in a nitrosyl and carbonyl structures give indirectly a picture of the catalyst surface on which several different types of surface sites (I, II, III) are distinguished. The nature and formation of these sites are discussed below.

The adsorption bands situated in the 1600 – 1200 cm^{-1} region and which are not mentioned in the table II, were already observed on pure Fe_2O_3 [33] and were assigned to nitrite-nitrate groups. Note that in the present case, only the adsorption band at 1580 cm^{-1} was observed when NO or NO + CO interacted with prereduced catalyst, indicating that even after reduced conditioning catalyst, some active anionic sites remained on the surface and reacted with NO to give a nitrate groups [33] of the type:



IV. Discussion

It was clear from infrared spectroscopy that different sites for NO and CO adsorption were generated when $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst was conditioned under reducing or oxidizing atmosphere. With respect to NO and CO, pretreatment affected the presence of surface oxygen or hydroxyl that caused reactions to occur after adsorption.

Infrared spectroscopy showed that a number of different adsorbed NO species were present on reduced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, suggesting that several different types of surface sites existed on the surface of this sample: (I) Fe^{2+} sites which were in a strong interaction with the support, (II) partially reduced Fe^{3+} ($\text{Fe}^{3.5+}$) and (III) Fe^{2+} located in octahedral environment of Fe_3O_4 formed by the reduction of "free" iron oxide. Note that sites of type (I) and (II) were not present when the specimen was in an oxidized state. So, to obtain information about the interaction between iron oxide and alumina, it was necessary to interpret more quantitatively the origin of sites (I) and (II). One possible explanation was that sites of type (I) were attributed to interface between iron oxide and alumina particules. These sites might form a superficial iron aluminate phase when the sample was severely reduced in a flow of hydrogen. However in a moderate reduced conditions (i.e. when NO + CO interacted with an oxidized sample at 573 K), these sites, in a strong interaction with the support, remained at the interface with perturbed environment. The infrared study showed that these sites were capable in adsorbing NO (1735, 1770 and 1790 cm^{-1}) and CO to give carbonates (1580, 1460, 1380, 1290 cm^{-1}) and were sensitive to the presence of oxygen.

The sites of type (II) and (III) were due to partially reduced Fe^{3+} (i.e. $\text{Fe}^{3.5+}$) and Fe^{2+} respectively) at the surface of "free" iron oxide particules. This would explain the conversion of $\text{Fe}^{3.5+}$ (NO) complex (1820 cm^{-1}) to Fe^{3+} (NO) complexe (1860–1850 cm^{-1})

when a small dose of oxygen was introduced in the cell at b.t. It might be questioned why the surface iron cations of the iron oxide particles could not be deeply reduced even at high temperature in a flow of hydrogen. For this reason it might be proposed that the degree of reduction of these "free" iron oxide particles was greatly influenced by the particle sizes. Smaller iron oxide particles were less reducible than were larger iron oxide particles. Furthermore the alumina carrier might have a dispersing effect on the active phase of iron oxide which was obtained in a more divided state and did not sinter, under reducing conditions, to the same extent as without the support [64]. It was therefore logical to attribute also the beneficial effect of the support on the protection of the partially oxidized state of iron. The sites of type (III) were formed when iron oxide Fe_2O_3 were reduced to Fe_3O_4 and were destroyed after the introduction of oxygen in the cell and fully oxidized iron cations (Fe^{3+}) were formed.

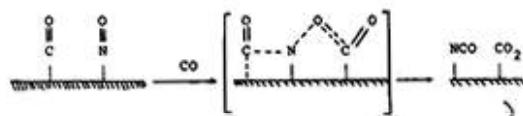
The inter conversion between Fe^{3+} and Fe^{2+} might explain the formation of Fe^{2+} (NO) complex (1800 cm^{-1}) where Fe^{2+} was octahedrally coordinated before interaction with NO.

It was also concluded in this study, that partially or fully oxidized iron cations adsorbed CO molecules to form weakly chemisorbed carbonyl complexes (2110–2130 cm^{-1}). The same complex was also formed on pure Fe_2O_3 (2130 cm^{-1}). Therefore it might be proposed that the sites of type (II) were responsible for the formation of such complexes. This proposal was in accord with the decrease in intensity of the 1820 cm^{-1} absorption band with the increase of the 2110 cm^{-1} absorption band when the gaz mixture NO + CO was introduced on a prereduced sample. In fact it was admitted and proved experimentally that NO adsorbed more strongly on Fe^{2+} than on Fe^{3+} [63, 65, 66]. Then it was conceivable that CO displaced slowly a small amount of NO adsorbed on $\text{Fe}^{3.5+}$ to form carbonyl complex.

The appearance of an absorption band at 1650 cm^{-1} assigned to the adsorption of NO on an oxygen site [33, 59, 60] shows that active anionic sites are also present at the surface of preoxidized catalyst. In addition some anionic sites remained on the surface even after reduced conditioning catalyst and are able to react with NO to give nitrite-nitrate groups. These anionic sites, probably strongly attached to particular cationic sites, resist to severe reducing conditions.

Note that the simultaneous appearance of 2240 and 2320 cm^{-1} bands under catalytic conditions (NO : CO at 573 K) and which are assigned to isocyanate and CO_2 species (table II) suggest a plausible mechanism which does not require the improbable presence of

adsorbed N-atoms [45, 54] and where a surface complex comprising one NO reacts with a CO molecule from gas phase to give CO₂. The resulted complex reacts simultaneously with an adsorbed CO molecule to give NCO:



In spite of the location of the NCO band (2240 cm⁻¹) is almost the same as for alumina-supported noble metals [53, 56-58] and in spite of there is a considerable amount of experimental data which suggest that, although NCO is formed on the noble metals, it subsequently migrates from the metal to the support, the active centers for the adsorption of NCO and CO₂ are not identified and remain in our case an open question.

soumis en février 1986
accepté en mai 1986

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