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Dipole Coupling of CO (NO) Adsorbed on Iron Oxide Surface Centres: a Typical Feature of Surface Active Sites

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FTIR spectroscopy combined with TEM and kinetic measurements has been used to demonstrate that cluster defect centres exhibiting dipole coupling of adsorbed CO (NO) determine the iron oxide activity in CO oxidation.

IR spectroscopy of adsorbed molecules is known to be an invaluable tool for studying the local coordination of surface centres of powdered oxides and their spatial distribution,[1] though additional transmission electron microscopy (TEM) data on the morphology and defect structure are highly desirable. Thus, Zecchina, Scarano *et al.*[2,3] on combining IR and TEM data for oxides with the corundum structure (α–Fe_2O_3, α–Cr_2O_3) were able to assign the various carbonyl absorption bands to CO adsorbed on the basal and/or prismatic faces. In order to verify this assignment, we have investigated a number of iron oxide samples (α- and γ-Fe_2O_3) with various morphology and defect structures studied earlier,[4–7] whilst also bearing in mind the task of elucidating the nature of the active centres in CO oxidation.

The details of the preparation and some basic properties of the samples are given in Table 1. The IR spectra were recorded in a high vacuum cell designed by Infraspac[8] using an IFS–113v Bruker spectrometer with a MCT detector at 4 cm^{-1} resolution. In the spectra presented the background absorption was subtracted on the optical density scale. The kinetic experiments were carried out under differential conditions on a pulse/flow microcatalytic installation with a vibrofluidized bed reactor.[9] All the specimens were examined in a JEM–100 CX electron microscope (100 kv accelerating potential).

Table 1 Some properties of the samples investigated.

No.	Method of preparation	Phase composition	S_{sp} /m^2g^{-1}	Morphology[a]	Wafer density /g cm^{-2} [b]
1	Thermal decomposition of oxalate, 400 °C, air	α-Fe_2O_3	14	platelets, (0001)	0.018
2	Thermal decomposition of goethite (1),[c] 400 °C, air	"	64	needles, elongated platelets, (01$\bar{1}$0),(0001)	0.015
3	Thermal decomposition of ammonium oxalatoferriate, 500 °C, air	"	18	platelets, (0001)	0.017
4	Thermal decomposition of goethite (2),[c] 400 °C, air	"	90	needles, elongated platelets, (1$\bar{1}$00),(0001)	0.029
5	Reduction of the sample N2 by CO in He at 400 °C, reoxidation at 227 °C by O_2 in He	γ–Fe_2O_3	27	platelets, (100),(110)	0.024
6	Ageing of amorphous iron hydroxide at pH~3, washing, decomposition at 400 °C, air	α-Fe_2O_3	27	thin platelets, (0001)	0.039
7	Thermal decomposition of goethite (2),[c] 600 °C, air	"	20	elongated platelets, (1$\bar{1}$00),(0001)	0.024

[a] The most developed face of the crystallites (TEM). [b] In the IR cell. [c] Two different samples of goethite were used.

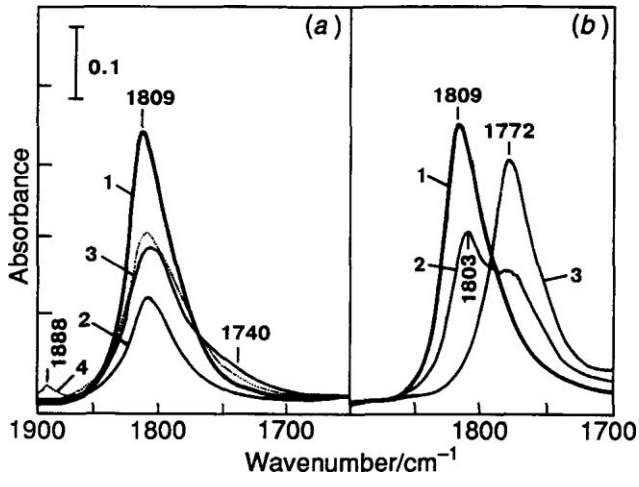

Fig. 1 IR spectra of NO adsorbed at 300 K on the sample N3 (spectra 1–3) and N2 (spectrum 4); P_{NO} = 1 Torr. (*a*) 1,4: after vacuum treatment at 673 K; 2: after treatment in oxygen at 673 K; 3: after vacuum treatment at 673 K, admission of CO at 300 K with subsequent vacuum pumping. (*b*) 1: ^{14}NO; 2: $^{14}NO + {}^{15}NO$ (1:1); 3: ^{15}NO, sample N3.

Adsorption of NO at 300 K on the sample N3 pre-treated in O_2 at 673 K leads to the appearance of absorption bands in the nitrosyl stretching region [Fig.1(*a*), spectrum 2, $\theta = \theta_{max}$]. The relative intensities and positions of these bands depend upon the nature of the samples [*cf.* spectra 1 and 4, Fig.1(*a*)]. A weak reducing treatment (673 K, 10^{-3} Torr) considerably enhances the intensity of the main absorption band at 1780–1810 cm^{-1}, thus demonstrating a reduced character of the adsorption centres (Fe^{2+}).[10] Slight isotope dilution [Fig.1(*b*)] revealed a pronounced low frequency shift even for ^{15}NO–^{14}NO (1:1) mixtures. This fact indicated the dynamic dipole–dipole interaction between the NO molecules adsorbed on these centres and, therefore, proved their location in the adjacent positions. A weak band at higher frequency, by analogy with ref. 10, could be tentatively assigned to NO complexes with $Fe^{(2+\delta)+}$ ions located in the vicinity of low-coordination Fe^{3+} ions. Indeed, a noticeable quantity of Fe ions in the defect positions (steps, tetrahedra, *etc.*) was detected in samples prepared from goethite.[5,6]

Fig. 2 shows the spectra of CO adsorbed at 80 K ($\theta = \theta_{max}$) on different Fe_2O_3 samples after treatment in a vacuum at 673 K. Several bands are clearly observed at ~2205–2195, 2195–2190, ~2180–2170, ~2166–2160, ~2150 cm^{-1}, the relative intensities being dependent upon the nature of the samples. In contrast to refs. 2 and 3, any simple relation between the type of the most developed faces and the intensities of absorption bands has not been found (*cf.* Table 1 and Fig. 2).

The absorption bands at ~2195–2170 cm^{-1} and at ~2166–2150 cm^{-1} have quite different properties: (i) On passing from $\theta = 0$ to $\theta = \theta_{max}$) the frequency of the maximum undergoes a pronounced red shift for the former [*cf.*, the spectra 1 and 2 in

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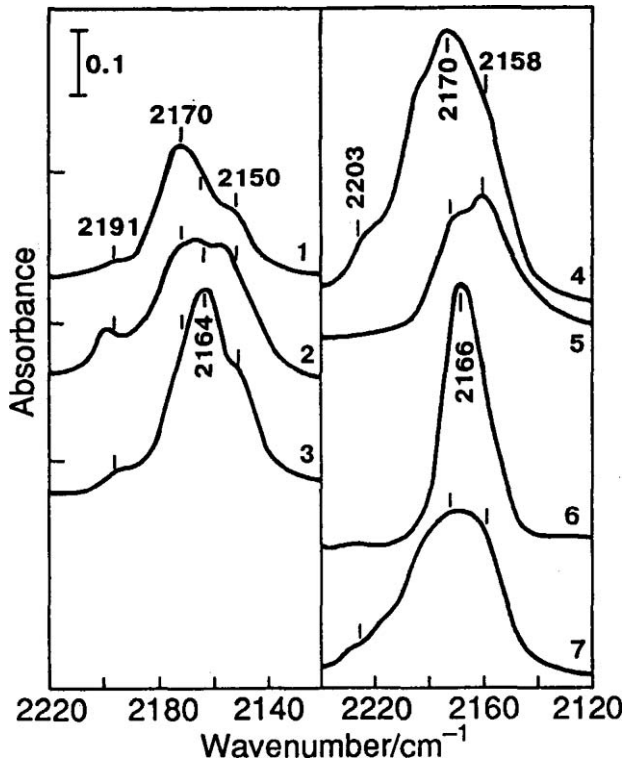

Fig. 2 IR spectra of CO adsorbed on different Fe_2O_3 samples at 80 K (P_{CO} = 0.5 Torr) (numbering as in Table 1).

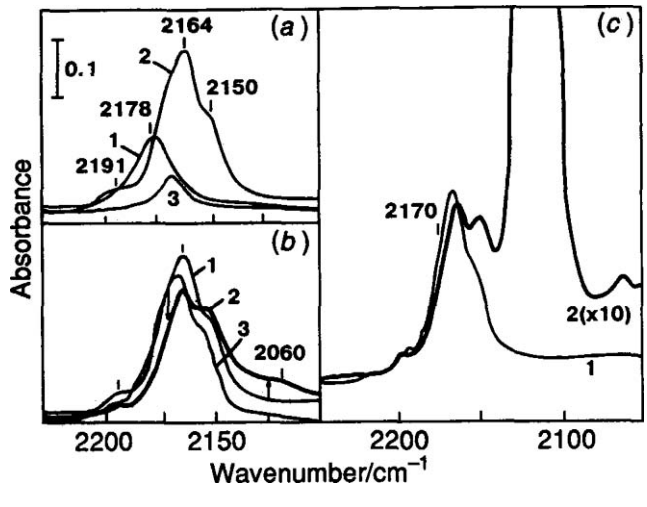

Fig. 3 IR spectra of CO adsorbed at 80 K on the sample N3 (vacuum pre-treatment at 673 K). (*a*) 1: P_{CO} ~ 0.01 Torr; 2: P_{CO} = 0.5 Torr; 3: P_{CO} ~ 0.01 Torr (after NO adsorption at 300 K). (*b*) P_{CO} = 0.5 Torr; 1: after vacuum pre-treatment; 2: after reduction by CO at 300 K and subsequent evacuation; 3: after admission of CO_2 at 300 K (P_{CO_2} ~ 0.01 Torr). (*c*) P_{CO} = 0.5 Torr; 1: ^{12}CO; 2: $^{12}CO + {}^{13}CO$ (1:7).

Fig. 3(*a*)], while it remains practically unchanged for the latter. This downward shift is caused by the superposition of the static (chemical) and dynamic shifts.[3,11]

(ii) Co-adsorption of CO and NO at 80 K has resulted in the almost complete disappearance of the adsorption band with $\nu_{CO} > 2170$ cm^{-1}, while low-frequency bands persist in CO pressure [*cf.*, Fig. 3(*a*), spectra 2 and 3]. Surface centres of the former type are blocked by NO due to rather high enthalpies of adsorption (~88–109 kJ mol^{-1} as estimated *via* the activation energy of desorption), while CO adsorption enthalpies are considerably lower (*ca.* 21 kJ mol^{-1}).

These points enabled the assignment of the absorption band with ν_{CO} ~ 2195–2170 cm^{-1} to CO complexes with coordinatively unsaturated Fe^{2+} ions,[12] while those bands with $\nu_{CO} < 2166$ cm^{-1} were assigned mainly to CO weakly interacting with coordinatively saturated centres (hydroxyl groups, CO physisorption, *etc.*).[13] The intensities of the absorption bands at ν_{CO} ~ 2205–2195 cm^{-1} correlate well with those of high frequency nitrosyls [ν_{NO} ~ 1888 cm^{-1}; *cf.* spectra N4,3 in Fig.2 and N1,3 in Fig.1(*a*)], thus enabling the assignment of high frequency carbonyls to complexes with $Fe^{(2+\delta)+}$ ions.[10]

The isotope dilution experiments at 80 K for ^{12}CO–^{13}CO (1:7) mixtures revealed a change in the shape of the complex band in the region 2200–2150 cm^{-1} and slight downward shift of the absorption band at 2164 cm^{-1} [Fig.3(*c*)]. One can see a pronounced decrease of the shoulder with ν_{CO} ~ 2180–2170 cm^{-1} [Fig. 3(*c*)]. The most adequate description of these variations is that the absorption band at ~2180 cm^{-1} shifts by 15–20 cm^{-1}, while that of band 2164 cm^{-1} only shifts by 1.5–2.0 cm^{-1}. As a result, these bands overlap. So, the existence of the dynamic shift for the former absorption band doubtless agrees with the results of NO dilution experiments (*vide supra*).

In contrast to NO adsorption, adsorption of carbon monoxide at 300 K is accompanied by a chemical reaction with the surface oxygen [Fig. 4 (*a*,*b*)]. A group of absorption bands in the carbonyl stretching region were detected: i, 2195–2180 cm^{-1} (*vide supra*); ii, 2140–2100 cm^{-1}, ΔH_{ads} ~ 76–84 kJ mol^{-1} (probably, $Fe^{1+}CO$); iii, 2060 cm^{-1}, $\Delta H_{ads} > 84$ kJ mol^{-1} (Fe^0CO); iv, ~2068, 2050 and 1990 cm^{-1}, ΔH_{adc} ~ 21 kJ mol^{-1} [sub-carbonyls $Fe^0_x(CO)_y$].[14] Carbonyl bands corresponding to reduced centres grow with exposure [Fig. 4(*a*)], thus monitoring the development of a surface reduction process occurring at room temperature; the same is true for the bands of carbonate-like species [Fig. 4(*b*)].

By examining the spectra of adsorbed CO (80 K) and NO (300 K) before and after room temperature reduction by carbon monoxide with subsequent outgassing at the same temperature, one concludes that only aggregated Fe^{2+} ions, whose typical feature is a dynamic coupling of the adsorbed molecules, are easily reduced up to $Fe^{1+(0)}$. Indeed, the intensities of the corresponding bands decline after the room temperature reduction, while the intensities of the bands associated with the reduced centres (ν_{NO} ~ 1740 cm^{-1}, ν_{CO} ~ 2140–1980 cm^{-1}) increase [*cf.* Fig. 1(*a*), spectra 1 and 3; Fig. 3(*b*), spectra 1 and 2].

The adsorption of CO_2 is also followed by the appearance of carbonates with the same spectral features as in the case of CO addition [Fig.4(*b*)]. A subsequent adsorption of CO at 80 K [Fig.3(*b*), spectra 3] reveals that some variations in the carbonyl stretching region are also caused by CO_2 pre-adsorption, but they are much weaker than in the case of the room temperature reduction. Hence, aggregated Fe^{2+} centres having high reactivity are spatially separated from the centres of location of the carbonates.

Estimates based upon the difference between the values of the pressure in the cell with a thick pellet and in the empty cell after admission of a known amount of CO have revealed that even at 80 K the saturation coverage of CO including the physisorbed forms (θ_{max}) is less than 15% of monolayer. Therefore, the density of aggregated centres should be substantially lower, and thus they can be termed as defect centres localized at the steps, outlets of extended defects and grain boundaries, *etc.*, revealed in these samples by TEM, X-ray powder diffraction and by other methods.[4–7]

The number of these centres was found to increase after high temperature treatment in a vacuum or in helium at ~700 K, this was accompanied by an increase in the unsteady-state catalytic activity in CO oxidation (up to one order of magnitude). Steady-state activities in this reaction (413 K, 1% CO + 1% O_2 in He) correlate well with specific densities of the readily-reduced aggregated centres estimated from the intensity of the band at ν_{CO} ~ 2110 cm^{-1} [see inset on Fig. 4(*a*)]. The hyperbolic character of the dependence of rate on density can be explained by an underestimate of the density of these centres for the most active samples due to a variation in the CO stretching frequency, and, therefore, its dynamic polarizability.

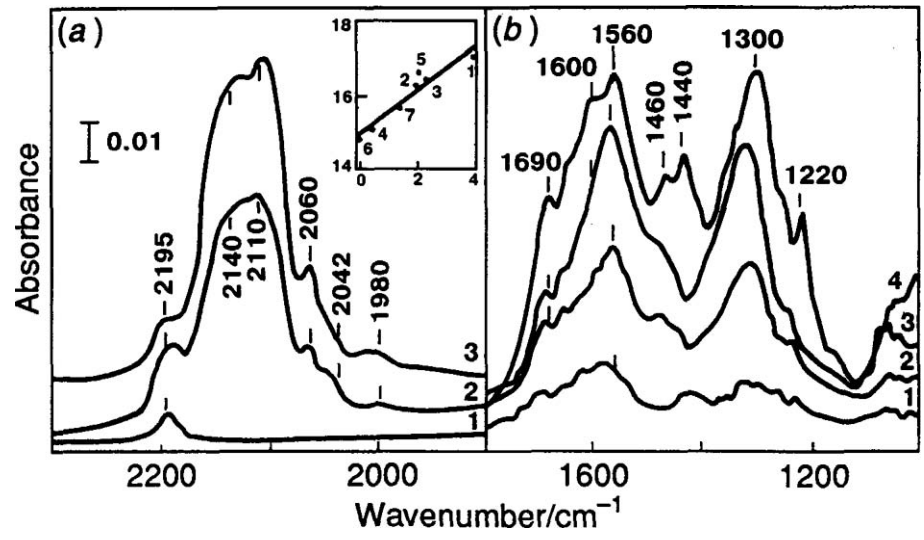

Fig. 4 IR spectra of CO and CO_2 adsorbed on the sample N3 at 300 K: (*a*) carbonyl region; (*b*) carbonate. 1: after 1 min exposure in CO (treatment in O_2 at 673 K); 2: after 1 min exposure in CO (vacuum treatment at 673 K); 3: after 30 min exposure in CO (vacuum treatment at 673K); 4: after 1 min exposure in CO_2. $P_{CO_2} \sim 0.01$ Torr (vacuum treatment at 673 K). Insert: lg *W versus* normalized intensity of absorption band at $\nu_{CO} \sim 2110$ cm^{-1} ($D/\rho S_{sp}$), where W is the velocity (molecules of CO per m^2 s^{-1}), D is the optical density, ρ is the wafer density (g cm^{-2}) and S_{sp} is the specific surface (m^2 g^{-1}).

Usually the interpretation of small values of dynamic shift due to the lateral interaction of CO and NO adsorbed on oxides are based upon the existence of large islands of adsorbed molecules. According to this view, these islands are to be compatible with the size of the most developed faces of the crystallites, but the interaction between adsorbed molecules on oxides are weak in comparison with metals. According to our results, the size of the islands of adsorbed CO and NO is not large. These small adsorbate islands exist due to the aggregation of coordinatively unsaturated cations occupying a small fraction of the Fe_2O_3 surface. We cannot exclude the existence of isolated coordinatively unsaturated ions, but it was found that Fe^{2+} centres on the surface of iron oxides exhibiting dipole coupling of adsorbed CO (NO) molecules are easily reduced and determine the catalytic activity in the CO oxidation reaction.

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