JOURNAL OF CATALYSIS 95, 558–566 (1985)

Surface Interactions of NO and CO with LaMO$_3$ Oxides

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Received December 31, 1984; revised June 3, 1985

The surface interactions of NO and CO with LaMO$_3$ perovskites (M = Cr, Mn, Fe, Co, Ni) have been studied by volumetric adsorption and infrared spectroscopy. NO adsorption at 200 mm Hg on LaNiO$_3$ was found to be constant over the temperature range 200–750 K. NO adsorption on LaMO$_3$ oxides at room temperature as a function of the atomic number of M showed maxima for LaMnO$_3$ and LaCoO$_3$ while CO adsorption exhibited one maximum for LaFeO$_3$. The inhibiting effect of NO preadsorption on the subsequent adsorption of CO was found to be larger than the inhibiting effect of CO on NO adsorption. NO is apparently more strongly adsorbed than CO on the surface of these oxides. Infrared spectra after simultaneous adsorption of NO + CO on LaFeO$_3$ contained bands between 1650 and 850 cm^{-1} due to species formed by the interaction of NO and CO with oxygen ions in the oxide surface, and a band at 2170 cm^{-1} assigned to isocyanate species. Spectra in the region 2300–1900 cm^{-1} after simultaneous adsorption of NO + CO on LaCoO$_3$ contained bands at 2175 and 2000 cm^{-1}, the latter being assigned to NO adsorbed via a donor-type or coordinative bond. The numbers of NO molecules adsorbed at monolayer coverage on the LaMO$_3$ oxides did not equal estimated numbers of transition metal ions exposed in the oxide surfaces. The observed constancy of NO adsorption on LaFeO$_3$ and LaNiO$_3$ over a wide range of temperatures could provide a method for oxide characterization. © 1985 Academic Press, Inc.

INTRODUCTION

LaMO$_3$ oxides (M, transition metal) have been used as such or as base oxides in multicomponent perovskites (having more than one metallic cation in each of the A and B positions of the structure) for NO reduction by CO (*1–6*). They have, also, been used for oxidation of CO and hydrocarbons and simultaneous reduction of NO$_x$ (*7*). In some cases the perovskite structure has been applied as a stabilizing matrix for NO reduction catalysts (*2*). The study of NO and CO interactions with the surface of these compounds should provide a better understanding of this catalytic reaction. The chemisorption of NO and CO directed to the characterization of oxide catalysts has been widely studied (*8–19*). One of the aims of this work is to obtain information on the potential applicability of NO and CO for the determination of metallic centers in oxides. The interactions of NO and CO with a series of LaMO$_3$ perovskites (M = Cr, Mn, Fe, Co, and Ni) have been studied by means of volumetric adsorption and infrared spectroscopy. CO interactions with these oxides have been already reported (*20, 21*).

EXPERIMENTAL

Materials. LaMO$_3$ oxides were prepared by cyanide decomposition (LaFeO$_3$) or by amorphous precursors decomposition (*22, 23*). The presence of a single perovskite phase was verified by X-ray diffraction (*24*). The BET specific surface areas of the samples (in m^2 g^{-1}) were as follows: LaCrO$_3$, 5.7; LaMnO$_3$, 12.1; LaFeO$_3$, 7.6; LaCoO$_3$, 8.5; LaNiO$_3$, 4.7. NO (99.0%) and CO (99.97%) were condensed at 77 K and distilled taking a middle fraction for use. He (99.995%) for volume calibration was passed through a trap at 77 K.

Equipment and methods. The adsorption work involved a volumetric apparatus in

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which a dynamic vacuum of 10^{-6} mm Hg (1 mm Hg = 133.3 N m^{-2}) could be maintained. Pressure measurements were made with a Schaewitz P-502-0004 absolute transducer for corrosive gases with a range of 0 to 300 mm Hg. Two sets of adsorption experiments were carried out. In the first, the adsorption of NO on $LaNiO_3$ was studied (Figs. 1 to 4). Temperatures of 113, 143, 195, and 273 K were maintained with external baths of solid–liquid isopentane and *n*-pentane, dry ice–acetone, and ice–water. Temperatures higher than room temperature (RT) were attained with a cylindrical furnace linked to a stabilized power supply. Prior to an experiment the sample was outgassed at 773 K for 15 h. After cooling to the desired temperature successive doses of NO were admitted to the adsorption cell. In the second set of experiments, the adsorption of NO and/or CO on LaMO$_3$ oxides at RT was measured. After evacuation (773 K, 15 h) and cooling to RT the sample was dosed with NO (isotherm for total adsorption of NO on a clean surface). After pumping (RT, 1h) a second isotherm (reversible adsorption) was determined. The sample was subsequently evacuated (RT, 1 h) and then dosed with CO (total adsorption of CO on a surface with preadsorbed NO). Finally, after evacuation (RT, 1 h) a second isotherm was measured (reversible adsorption). After outgassing at 773 K for 15 h, similar experiments were conducted in which CO was adsorbed before NO. Complete isotherms were effected with the extreme members of the series ($LaCrO_3$ and $LaNiO_3$). For other oxides only the part of the isotherms between 130 and 170 mm Hg (which allowed a proper calculation of the adsorption at 150 mm Hg) was recorded.

The infrared cell (NaCl windows) was connected to the high-vacuum line by means of a ground flat joint with a viton O-ring. Self-supporting disks were made by pressing 150 mg of dry powder to 8×10^7 N m^{-2} in a 25-mm-diameter die. Spectra were recorded with a Perkin–Elmer 682 spectrophotometer (the sample being at beam temperature) according to the following adsorption sequences:

(a) After contacting the sample with 10 mm Hg NO + 10 mm Hg CO for 1 h at each of the indicated temperatures (simultaneous adsorption of NO + CO).

(b) After contact with 20 mm Hg NO at RT for 1 h and pumping (RT, 15 min) (adsorption of NO). After subsequent contact with 20 mm Hg CO at RT for 1 h and pumping (RT, 15 min) (successive adsorption of NO + CO).

(c) After adsorbing CO first and then NO with the same conditions as in (b) (successive adsorption of CO + NO). The spectra after simultaneous adsorption were recorded in presence of the gaseous phase. Prior to each adsorption sequence the sample was outgassed at 773 K for 15 h. Representative spectra were obtained with samples that presented higher transmittance and lower scattering ($LaMnO_3$, $LaFeO_3$, and $LaCoO_3$).

RESULTS AND DISCUSSION

Adsorption of NO on $LaNiO_3$

NO adsorption isotherms between 0 and 200 mm Hg in the temperature zone 113–772 K are given in Figs. 1 and 2. The isotherm at 113 K belongs to type II of Brunauer's classification while those at 143 K and above are of type I. The adsorption at 113 and 143 K is fast while at 195 K and

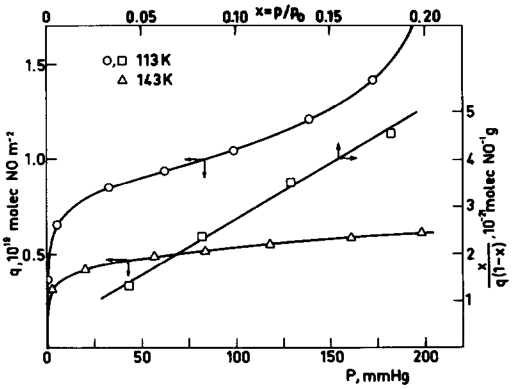

FIG. 1. Adsorption isotherms of NO on $LaNiO_3$ at 113 and 143 K and BET plot at 113 K.

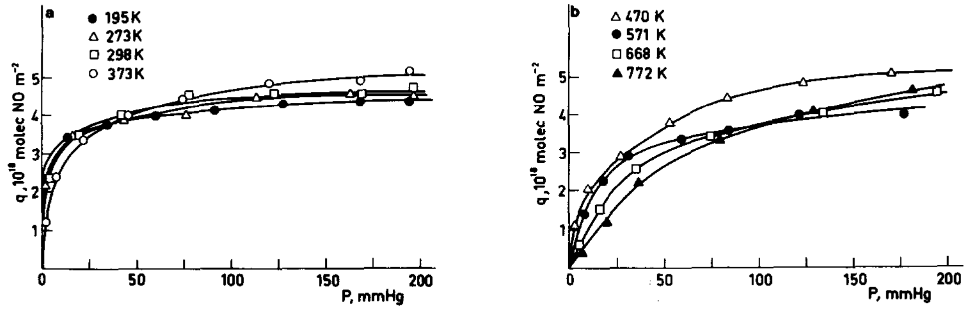

FIG. 2. Adsorption isotherms of NO on $LaNiO_3$ in the temperature ranges 195–373 K (a) and 470–772 K (b).

above is rather slow (about 70 h to complete an experiment). From the BET plot at 113 K (Fig. 1) a cross-sectional area for the NO molecule of 11.6 Å^2 (1 Å^2 = 10^{-2} nm^2) was calculated. The adsorption heat (calculated using the Clausius–Clapeyron equation) in the descending branch of the isobar (Fig. 3) decreases exponentially with coverage (Fig. 4). Thus, the adsorbent–adsorbate system should obey the Freundlich's model of adsorption as observed for simple oxides (*8–12*).

The adsorption at monolayer coverage ($q_{\mathrm{NO(m)}}$) (assuming this to correspond to the horizontal part of the isotherms) is practically constant and equal to $4.7 \pm 0.5 \times 10^{18}$ molec NO m^{-2} in the temperature interval 195–772 K (Fig. 3). The adsorption at $T <$ 195 K is larger because of a high participation of physical adsorption. The constancy of $q_{\mathrm{NO(m)}}$ suggests that the interactions between NO and $LaNiO_3$ involve surface sites which do not change substantially in character with temperature.

Adsorption of NO and Coadsorption of CO–NO

Isotherms for total and reversible adsorption of NO on a clean surface and on a surface with preadsorbed CO are shown in Fig. 5. As representative adsorbents $LaCrO_3$ (a) and $LaNiO_3$ (b) at RT have been chosen (in the text q_{NOtot} and q_{NOrev} denote, respectively, the total and reversible adsorption of NO on a clean surface and q'_{NOtot} and q'_{NOrev} the total and reversible adsorption of NO on a surface with preadsorbed CO. q_{COtot}, q_{COrev}, q'_{COtot}, and q'_{COrev} have similar meaning for CO). The curves are of Langmuir type and belong to type I of the Brunauer classification. Adsorption results obtained at 150 mm Hg for the series of LaMO$_3$ oxides are given in Fig. 6. The reversible adsorption represents less than one third of the total adsorption. Its small or negligible dependence on the state of the surface (clean or with preadsorbed CO) points to a mainly physisorption character.

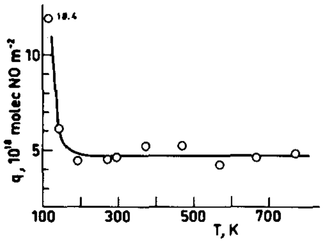

FIG. 3. Isobar for NO adsorption at 200 mm Hg on $LaNiO_3$.

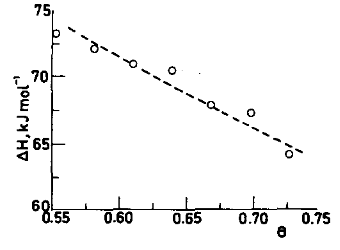

FIG. 4. Isoteric heats of NO adsorption on $LaNiO_3$ (113–195 K).

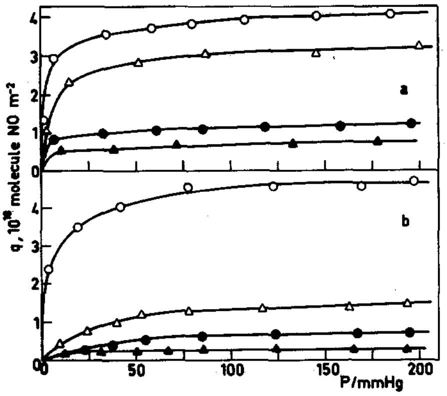

FIG. 5. Total (open symbols) and reversible (solid symbols) adsorption of NO on a clean surface (circles) of LaMO$_3$ and on a surface with preadsorbed CO (triangles). (a) LaCrO$_3$; (b) LaNiO$_3$.

The adsorption profile exhibits two maxima in q_{NOtot} for LaMnO$_3$ and LaCoO$_3$. Shelef *et al.* found similar maxima for manganese (*25*) and cobalt (*12*) oxides in NO adsorption at monolayer coverage on simple oxides of transition metals (Cr$_2$O$_3$, MnO, Fe$_2$O$_3$, Co$_3$O$_4$, and NiO). In previous work two maxima were also found (for LaMnO$_3$ and LaCoO$_3$) in O$_2$ adsorption and catalytic activity for total oxidation of CO, propylene, and isobutene on LaMO$_3$ oxides (*26*). These results were discussed within the framework of Dowden and Wells' ideas on the relationship between local symmetry of surface cations and adsorption (*27*). It would be of interest to test whether a similar parallelism between NO adsorption and catalytic activity for the reaction NO + CO to yield N$_2$ and CO$_2$ also holds for the LaMO$_3$ series of mixed oxides. The NO molecule is the oxidizing agent in the latter reaction as O$_2$ is in the former. To the authors knowledge there are no catalytic data available which would enable the test to be made.

Adsorption of CO and Coadsorption of NO–CO

Isotherms for CO adsorption and NO–CO coadsorption on LaCrO$_3$ (a) and LaNiO$_3$ (b) at RT are given in Fig. 7. Adsorption profiles for total and reversible adsorption of CO on clean surfaces and on surfaces with preadsorbed NO are given in Fig. 8. On all the oxides CO adsorption was found to be substantially lower than NO adsorption. A maximum for q_{COtot} was observed for LaFeO$_3$ resembling the maximum found for isobutene adsorption on LaMO$_3$ oxides (*26*). Ratios of the total adsorption of NO or CO on a clean surface (q_{NOtot}, q_{COtot}) to the total adsorption of these molecules on a surface with preadsorbed CO or NO (q'_{NOtot}, q'_{COtot}) are given in Table 1. q_{NOtot}/q'_{NOtot} increases from LaCrO$_3$ to LaNiO$_3$ while q_{COtot}/q'_{COtot} decreases in

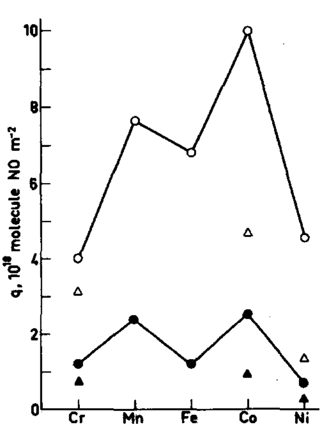

FIG. 6. Profile for NO adsorption on LaMO$_3$ oxides. Symbols as in Fig. 5.

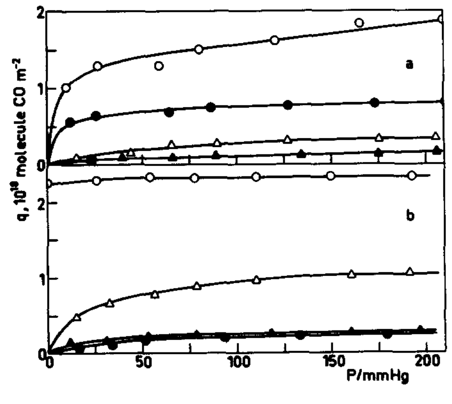

FIG. 7. Total (open symbols) and reversible (solid symbols) adsorption of CO on a clean surface (circles) of LaMO$_3$ and on a surface with preadsorbed NO (triangles). (a) LaCrO$_3$; (b) LaNiO$_3$.

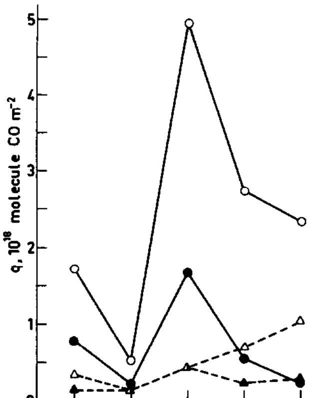

FIG. 8. Profile for CO adsorption on LaMO$_3$ oxides. Symbols as in Fig. 7.

the same direction (except for the anomalously high value found for LaFeO$_3$). The preadsorption of CO has an inhibiting effect on NO adsorption which is a maximum where the inhibiting effect of NO preadosrption on CO adsorption is a minimum (for LaNiO$_3$). These results indicate that NO and CO adsorption are partially competitive and that a fraction of these molecules adsorb on the same centers. The trends observed in q/q' ratios are probably related to different tendencies of LaMO$_3$ oxides to form surface species from interactions of metallic or oxide ions with NO and CO. Important differences were found previously between O^{2-} centers in the alumina surface with respect to the formation of surface nitrates and carbonates from the adsorption of NO and CO (*28*). The differences in reduction observed for LaMO$_3$ oxides may also play some role in the trends observed. More anion vacancies will be produced after the initial outgassing treatment at 773 K on the more easily reducible oxides, LaCoO$_3$ (*29*) and LaNiO$_3$ (*24*), than on LaCrO$_3$ and LaMnO$_3$ which are difficult to reduce (*24*).

TABLE 1

Ratios of Adsorbed NO (or CO) at 150 mm Hg on a Clean Surface of LaMO$_3$ Oxides at Room Temperature (q_{NOtot}, q_{COtot}) to Adsorbed NO (or CO) on a Surface with Preadsorbed CO (or NO) (q'_{NOtot}, q'_{COtot})

Oxide	LaCrO$_3$	LaMnO$_3$	LaFeO$_3$	LaCoO$_3$	LaNiO$_3$
$q_{\mathrm{NOtot}}/q'_{\mathrm{NOtot}}$	1.27	—	—	2.11	3.32
$q_{\mathrm{COtot}}/q'_{\mathrm{COtot}}$	5.27	3.32	12.21	3.91	2.28

The inhibiting effect of NO on CO adsorption (as measured by $q_{\mathrm{COtot}}/q'_{\mathrm{COtot}}$ ratios) is, in general, larger than the inhibiting effect of CO on NO adsorption (as measured by $q_{\mathrm{NO}}/q'_{\mathrm{NO}}$ ratios). These results suggest that NO is bound more strongly to the surface of LaMO$_3$ oxides than CO, in accordance with corresponding results of Alexeyev and Terenin for NiO (*30*), of Shelef *et al.* for NiO and Co$_3$O$_4$ (*10, 12*), and of Raskó and Solymosi for CrO$_3$ · Al$_2$O$_3$ (*31*).

Infrared Spectra after Simultaneous and Successive Adsorption of NO + CO on LaFeO$_3$

Infrared spectra recorded after simultaneous adsorption of NO + CO at increasing temperatures are shown in Fig. 9. Spectrum b (RT) contains bands at 1580, 1385, and 1210 cm^{-1}. After adsorption at 443 K (spectrum c) the band intensities increased and a new band appeared at 850 cm^{-1}. At 773 K (spectrum d) the bands at higher wavenumbers were greatly increased in intensity and shifted to lower $\bar{\nu}$ (1565 and 1355 cm^{-1}) and new bands appeared at 1130 and 1030 cm^{-1}.

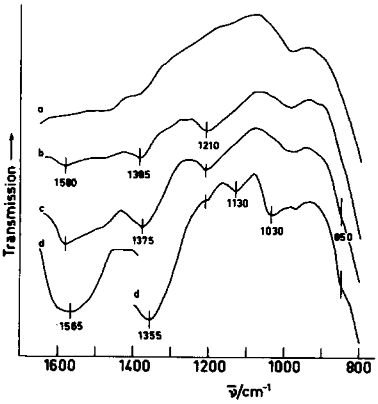

FIG. 9. Infrared spectra after simultaneous adsorption of NO + CO on LaFeO$_3$. (a) Background spectrum; (b) NO + CO at RT; (c) at 443 K; (d) at 773 K.

This increase in band intensities may be due, in part, to higher transmittance resulting from reduction of the sample by CO.

The spectrum recorded after adsorption of NO on LaFeO$_3$ (in the presence of the gas) contained bands at 1610, 1570, 1220, and 1030 cm^{-1} (ascribed to bridged or bidentate nitrates), at 1490 and 1150 cm^{-1} (monodentate nitrate), and at 1385 cm^{-1} assigned to a nitrate species associated with a La^{3+} ion (*32*). These assignments are consistent with those given for those species by Nakamoto (*33*), London and Bell (*34*), Davydov *et al.* (*35*), Rochester and Topham (*36*), Busca and Lorenzelli (*37*), and Lorenzelli *et al.* (*38*). Other bands at 1940 (assigned to a dinitrosyl), 1775 and 1725 cm^{-1} (mononitrosyls) were also observed (*32*). The interactions of CO with LaFeO$_3$ yielded bands at 1755 (bridged carbonate), 1640, 1615, 1580, 1285, and 1160 cm^{-1} (bidentate carbonates), 1495 and 1400 cm^{-1} (monodentate carbonate), and 840 cm^{-1} (typical of carbonates) (*21*). It follows that the broad bands at 1580–1565 and 1385–1355 cm^{-1} (Fig. 9) probably consist of overlapping bands due to different nitrate and carbonate species, while bands at 1210, 1030 (bidentate nitrates), and 1130 cm^{-1} (monodentate nitrates) are specific to the NO interaction with adsorbent. The band at 850 cm^{-1} is due to a carboante species.

Spectra obtained after successive adsorption of NO + CO at RT are given in Fig. 10 (only the spectral zone 1350–1150 cm^{-1} is included because of the overlap of bands at 1650–1350 cm^{-1}). NO adsorption (and pumping at RT) yielded a band at 1210 cm^{-1} (spectrum b) which was not modified after the subsequent adsorption of CO (and pumping, spectrum c). After outgassing the sample at 773 K (15 h), adsorption of CO (and pumping at RT), and then adsorption of NO (and pumping at RT) no bands were found (spectrum d). This indicates that the adsorption of NO (or CO) strongly inhibits the adsorption of the other molecule in accordance with the results of the adsorption experiments.

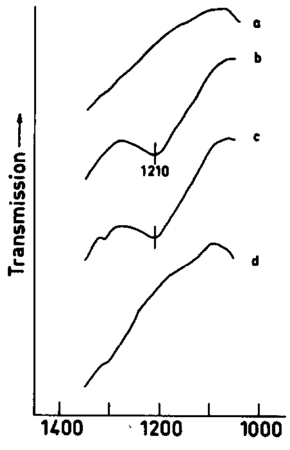

FIG. 10. Infrared spectra after successive adsorption of NO and CO on LaFeO$_3$ at RT. (a) Background spectrum; (b) NO; (c) NO + CO; (d) CO + NO.

Infrared Spectra after Simultaneous Adsorption of NO + CO on LaMO$_3$ Oxides

Infrared spectra in the region 2300–1900 cm^{-1} recorded after simultaneous adsorption of NO + CO on LaMnO$_3$ (a), LaFeO$_3$ (b), and LaCoO$_3$ (c) are given in Fig. 11. At 588 K bands at 2235 and 2210 cm^{-1} due to N$_2$O (spectra a$_1$, b$_1$, and c$_1$) were observed. These bands remained for LaMnO$_3$ at 773 K (spectrum a$_2$). However, they disappeared for LaFeO$_3$ and LaCoO$_3$ at this last temperature, giving place to a band at 2170 cm^{-1} (LaFeO$_3$, spectrum b$_2$) or bands at 2175 and 2000 cm^{-1} (LaCoO$_3$, spectrum c$_2$). These bands are probably not due to adsorbed CO as the spectra b$_2$ and c$_2$ are dissimilar to the spectra recorded for the systems CO/La FeO$_3$ and CO/LaCoO$_3$ (*21*). On the other hand, no bands were found for NO/LaFeO$_3$ or NO/LaCoO$_3$ in this spectral zone. The band at 2175 cm^{-1} may be assigned to an isocyanate group. This species exhibit bands at 2198 cm^{-1} of pseudoantisymmetric stretching and at 1330 cm^{-1} of pseudosymmetric stretching (*39*). This last band has not been observed probably because it is masked by the broad band centered at 1355 cm^{-1} (Fig. 9). Bands attributed to adsorbed

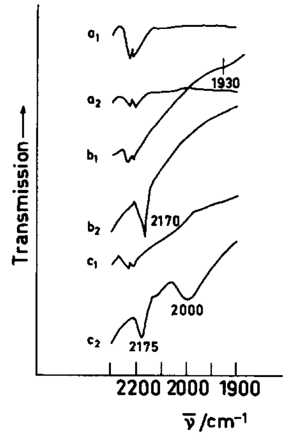

FIG. 11. Infrared spectra in the range 2300–1900 cm^{-1} after simultaneous adsorption of NO + CO on La*M*O$_3$ oxides. (a) LaMnO$_3$; (b) LaFeO$_3$; (c) LaCoO$_3$. (a$_1$, b$_1$, c$_1$) at 588 K; (a$_2$, b$_2$, c$_2$) at 773 K.

isocyanate have been observed at 2190 cm^{-1} for Co$_3$O$_4$ (*12*), at 2170 cm^{-1} for palladium (*40*), and at 2185 cm^{-1} for rhodium (*41*). Bands for the isocyanate complexes [Fe(NCO)$_4$]$^{2-}$, [Fe(NCO)$_4$]$^{1-}$, [Co(NCO)$_4$]$^{2-}$, and [Ni(NCO)$_4$]$^{2-}$ have been observed at $\bar{\nu}$ between 2171 and 2237 cm^{-1} (*42*). The wavenumber of bands of neutral isocyanate species are frequently higher ($\bar{\nu}$ > 2190 cm^{-1}) than wavenumbers of negatively charged species (*42*). The band at 2175–2170 cm^{-1} (spectra b$_2$ and c$_2$) should therefore be due to an isocyanate of the latter type. Taking account of the results in Table 1, the band at 2000 cm^{-1} should be due to adsorbed NO with a donor-type or coordinative bond (*31*). The La*M*O$_3$ perovskite oxides frequently exhibit higher transmittance of IR radiation in the reduced state. LaCoO$_3$ is the easiest oxide to reduce (*24, 29*) and this may explain why the 2000-cm^{-1} band has only been observed in spectrum c$_2$ (of NO + CO on LaCoO$_3$ at 773 K). A shoulder at 1930 cm^{-1} due to nitrosyls was clearly detectable only for LaFeO$_3$ (spectrum b$_1$). No bands were observed at 1650–1900 cm^{-1}.

Both N$_2$O and isocyanate species have been proposed at intermediates in the reduction of NO by CO on metallic oxides (*39, 43, 44*). N$_2$O decomposed only partially in contact with LaMnO$_3$ at 773 K as the bands at 2235 and 2210 cm^{-1} remained with lower intensity in spectrum a$_2$. However, the appearance of the isocyanate band in the spectra b$_2$ and c$_2$ was accompanied by the disappearance of the N$_2$O bands. This suggests some relationship between isocyanate formation and N$_2$O decomposition. Formation of both N$_2$O and isocyanate should take place by dissociative adsorption of NO and reaction of NO or CO with a N atom (*3, 39, 42*). The results in Fig. 11 seem to indicate that N$_2$O is formed in the presence of these oxides at 588 K. Nitrous oxide decomposes on LaFeO$_3$ and LaCoO$_3$ at 773 K yielding N atoms which react with CO producing isocyanate species.

Metallic Centers

NO has been used by Shelef *et al.* for estimating surface metal ions (M_s^{n+}) on simple oxides (Cr$_2$O$_3$, Fe$_2$O$_3$, Fe$_3$O$_4$, NiO, and CuO) (*8–11*). These authors found a ratio $q_{\mathrm{NO(m)}}/M_s^{n+} \simeq 1:1$ assuming a stable half populated (of cations and anions) surface layer. This correspondence was not found for the systems NO/La*M*O$_3$. For example, the number of surface Fe^{3+} ions in LaFeO$_3$ calculated from crystallographic data (assuming that the most frequently exposed planes are those of lower Miller's index {100}, {110}, and {111}) was found to be 2.56 × 10^{18} ions m^{-2}. This is appreciably lower than the number of adsorbed NO molecules at monolayer coverage (taking as monolayer the constant adsorption at 150 mm Hg of 6.82 × 10^{18} m^{-2}, Fig. 6). The number of metallic ions per square meter is similar for all the members of the La*M*O$_3$ series (the ionic radii range from 0.63 for Ni^{3+} to 0.69 Å for Cr^{3+}). If the ratio $q_{\mathrm{NO(m)}}/M_s^{3+} = 1:1$ at complete surface coverage, then the values of $q_{\mathrm{NO(m)}}$ for these oxides should all be similar. The profile given in Fig. 6 shows that $q_{\mathrm{NO(m)}}$ varies by more than a factor of 2. Irreversible adsorption of NO on a clean surface of La*M*O$_3$ oxides was also a function of the particular metal M in the perovskite structure (Figs. 5 and 6).

The substantial differences between the number of M_s^{3+} ions and $q_{NO(m)}$ for the different oxides may be rationalized as follows:

(a) The assumption that the {100}, {110}, and {111} planes are the most frequently exposed may not be correct. Furthermore, the proportion of each plane on the surface is, probably, a function of the preparation method.

(b) The NO molecule interacts not only with surface cations (yielding monitrosyls, dinitrosysls, dimers) but also with oxygen ions as shown by IR spectra of NO on simple (*30, 31, 34–38, 45–48*) and mixed (*32*) oxides.

(c) The surface of LaMO$_3$ oxides is not energetically homogeneous as shown by the observed decrease of the heat of adsorption with coverage (Fig. 4) (*32*). The metallic centers should exhibit different reactivities depending on their position on the surface.

The experimental results obtained for LaMO$_3$ perovskites together with data on simple oxides indicate that the adsorption of NO and the application of the stoichiometry $q_{NO(m)}/M_s^{n+} \simeq 1$ may not give a proper estimate of the number of surface transition metal ions because of the complexity of the interactions of this molecule with oxide catalysts. However, the NO molecule satisfies the desired requirement (*49*) of insensitivity of the adsorption with temperature. The observed constancy of $q_{NO(m)}$ over a wide range of temperatures on LaFeO$_3$ (from 200 to 600 K (*32*)), on LaNiO$_3$ (200–750 K), and also on simple oxides (at least in the temperature interval studied by Shelef *et al.* 273–423 K) (*8–12*) is probably the parameter which can best be applied to the estimation of metallic centers. By measuring the adsorption of this molecule on samples of unsupported oxide with different specific surface areas, it should be possible to determine a factor of adsorbed NO per surface unit. This factor could be applied (in the same way as this is done for O$_2$ adsorption at low temperatures) (*50–52*) for estimating the fraction of the support surface covered by the oxide. This molecule has the property of chemisorbing strongly on transition metal oxides but weakly on materials used as supports such as silica or alumina (*13*).

The differences in CO adsorption (total and irreversible) for the different members of the LaMO$_3$ series (of almost a factor of 10 for $q_{CO_{tot}}$) were found to be much more important (Figs. 7 and 8) than the differences in NO adsorption (Figs. 5 and 6). It has, also, been observed that CO adsorption is a strong function of temperature (*20*). Finally, the surface bond of CO on simple (*10, 12, 30, 31*) and mixed (Table 1) metal oxides seems to be weaker than that yielded by NO. This suggests that CO should be a less useful molecule than NO for oxide characterization.

ACKNOWLEDGMENTS

Thanks are due to Ministerio de Educación y Ciencia for a grant awarded to J. M. D. Tascón.

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