

Nature of the perovskites surface centers as studied by the Infrared spectroscopy of adsorbed NO test molecule

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Abstract

FTIR spectroscopy of adsorbed NO revealed a variety of types of coordinatively unsaturated surface cations for lanthanum cobaltites, manganites, and ferrites, some of which emerge due to room-temperature surface reduction by the test molecule. For the surface of LaFeO₃, clusters of coordinatively unsaturated Fe²⁺ cations associated with surface defects dominate. For the surface of LaCoO₃ and LaMnO₃, coordinatively unsaturated Me⁺³ cations are mainly revealed, being more coordinated by oxygen for the former system. These results could be used to analyze the catalytic properties of perovskites in the reaction of CO oxidation, provided the density of surface sites and reaction mechanism are taken into account. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to their high thermal stability, perovskites — mixed oxides of rare-earth, alkaline-earth and transition metals — have attracted a lot of attention in catalysis, including deep oxidation reactions [1]. By analogy with simple transition metal oxides, their active centers are thought to be transition metal cations. Their catalytic properties can be tuned by a partial substitution of lanthanum for alkaline-earth elements. This effect is usually described in terms of point defects generation. In particular, the introduction of such cation in the lan-

thanum sub-lattice is thought to be accompanied by an increase of the transition metal cation charge, by the formation of oxygen vacancies, or by two charge compensation mechanisms operating simultaneously.

Infra-red spectroscopy of adsorbed probe molecules is known to be among the most useful methods to investigate the nature of the surface centers. This method is based on the fact that the spectral features of the adsorbed molecules depend upon the oxidation and coordination states and on the degree of clustering of the adsorption centers [2].

The interaction of NO and CO with the surface of LaMeO₃ (Me = Cr, Mn, Fe, Co, Ni) perovskites synthesized from citrates has been already studied in detail [3,4]. The amount of adsorbed NO estimated from TPD data was

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found to depend upon the nature of the transition metal cation. In particular, it was found to be higher for manganites and cobaltites with respect to ferrites. Adsorption of NO can lead to both formation of nitrosyls (coordinated NO) and formation of NO oxidation products (nitrite–nitrate species) thus, evidencing a reduction of the surface. Compared with carbonyls, nitrosyls are usually the more strongly bound species. According to Shen and Weng [5], the amount of NO adsorbed at the surface of perovskites correlates with their catalytic activity for the NO + CO reaction. These results imply that NO, used as a probe molecule, can be successfully used to study the nature of the surface cationic centers of perovskites.

This work aims to elucidate the nature of the surface centers in $\text{La}_{1-x}\text{Me}_x\text{Me}^2\text{O}_3$ ($\text{Me}^1 = \text{Ca}, \text{Sr}; \text{Me}^2 = \text{Mn}, \text{Co}, \text{Fe}$) perovskites by means of IR spectroscopy of adsorbed NO. In order to assign absorption bands, the results obtained earlier for NO adsorbed at the surface of pure and mixture oxides as well as cation-exchanged zeolites (vide infra) were used.

2. Experimental

$\text{La}_{1-x}\text{Me}_x\text{Me}^2\text{O}_3$ perovskites were prepared by sintering a mixture of the corresponding pure oxides (chemical pure grade) at 1100°C for 100–150 h with multiple intermediate grinding. $\text{Ca}_2\text{Fe}_2\text{O}_5$ was synthesized by mixing the corresponding hydroxides (chemical pure grade) in the planetary ball mill EI, and subsequent annealing at $600\text{--}1100^\circ\text{C}$ [6]. For the samples prepared via the ceramic route, the specific surface area was found to be less than $1\text{ m}^2/\text{g}$. The specific surface area of calcium ferrite decreased from 13 to $1\text{ m}^2/\text{g}$ as the temperature of annealing increased from 600°C to 1100°C . According to the X-ray powder diffraction data, all samples studied here were monophasic perovskites.

NO (15 Torr) was adsorbed at room temperature. Before NO adsorption, the samples were

pretreated in vacuum at 500°C . IR spectra were recorded in the $1000\text{--}4000\text{ cm}^{-1}$ range in diffuse scattering mode using a Bruker IFS-113V spectrometer.

3. Results and discussion

According to the results shown in Fig. 1, NO adsorption on the surface of perovskites occurs with formation of various surface species. In the case of lanthanum manganite (spectrum 1), an intense band at 1600 cm^{-1} with a shoulder at 1670 cm^{-1} can be assigned to nitrite–nitrate species [2]. In agreement with previous data concerning the adsorption of NO on $\text{Mn}^{+2}\text{--ZSM-5}$ [7], the band at 1940 cm^{-1} can be assigned to $\text{Mn}^{+3}\text{--NO}$ complexes. The band at 2235 cm^{-1} is due to adsorbed nitrous oxide. The coupled bands at 1750 and 1835 cm^{-1} can be tentatively assigned to dinitrosyl complexes on highly coordinatively unsaturated Mn^{2+} [2,9]. Such bands are absent in the case of the $\text{Mn}^{2+}\text{--}$

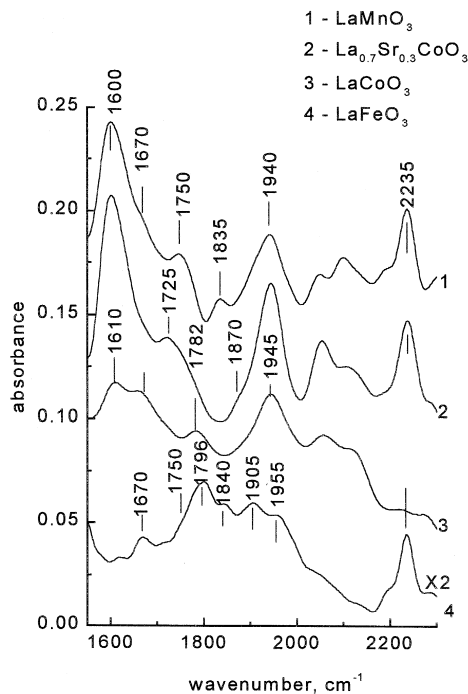
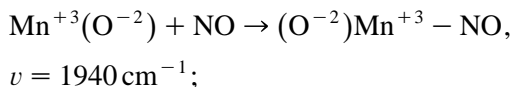


Fig. 1. Spectra of NO adsorbed on perovskites.

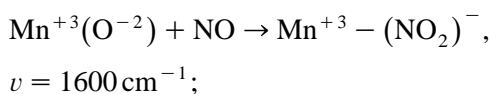
ZSM-5, where all Mn^{2+} cations are octa-coordinated, and hence, coordinatively saturated [7]. Because of the high coordinative state of Mn^{+2} , only weak bands due to nitrite–nitrate species and nitrous oxide were detected for NO adsorbed on Mn-exchanged zeolite. In the case of lanthanum manganite, extensive surface reduction takes place as indicated by the high intensity of the nitrite–nitrate bands (Fig. 1). As a result, low-coordinated manganese cations capable of forming dinitrosyl complexes emerge on the surface. However, it is worth mentioning that a pair of bands with similar positions (1877 and 1747 cm^{-1}) were detected after NO_2 adsorption on Na–ZSM-5 zeolite and assigned to adsorbed N_2O_3 and N_2O_5 , respectively [8]. The bands at 2050 and 2150 cm^{-1} are not assigned in this work due to existing controversy in their assignment.

Based on these results, the main steps of the NO interaction with the surface of the studied perovskites can be described by the following scheme, referred to the case of lanthanum manganite taken as a general example:

1. NO adsorption on the coordinatively unsaturated manganese cations having reactive oxygen in their vicinity, schematically- $\text{Mn}^{+3}(\text{O}^{-2})$



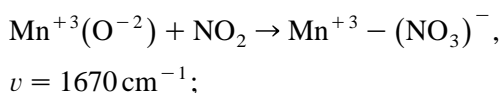
2. reaction between adsorbed NO and O^{-2} in the Mn^{+3} coordination sphere



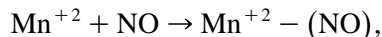
3. reduction of manganese cations



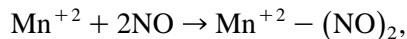
4. interaction of emerging NO_2 with the reactive oxygen species to form surface nitrate complexes



5. NO adsorption on reduced Mn cations

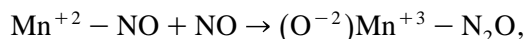


$$\nu = 1900\text{ cm}^{-1}(\text{shoulder}),$$



$$\nu = 1835, 1750\text{ cm}^{-1};$$

6. formation of nitrous oxide



$$\nu = 2235\text{ cm}^{-1}.$$

Hence, several types of coordinatively unsaturated Mn cations differing by their adsorption properties and reactivity appear to exist at the surface of lanthanum manganite.

For lanthanum cobaltite, the spectrum of adsorbed NO (Fig. 1, spectrum 3) differs from that recorded for lanthanum manganite (vide supra) and Co–ZSM-5 [10,11]. NO adsorption is accompanied by the appearance of the nitrite–nitrate species (1610 and 1670 cm^{-1} absorption bands) with decreased absorbances when compared to the same species on lanthanum manganite. In the nitrosyl region, a strong band at 1945 cm^{-1} and a weak one at 1782 cm^{-1} are observed, which can be assigned to mono and dinitrosyl complexes of Co^{+2} [11,12]. However, by analogy with the case of NO adsorption on lanthanum manganite, the former band can be assigned to $\text{Me}^{+3}-\text{NO}$ complexes. The second band can be assigned to $\text{Co}^{+2}-\text{NO}$. Next arguments support this assignment. First, on the surface of oxidic cobalt systems contacting with oxygen, cations of cobalt are usually in the $3+$ oxidation state, and cations with lower charges appear due to reduction. Meanwhile, a lower intensity of the nitrite–nitrate bands for lanthanum cobaltite as compared with those observed for lanthanum manganite suggests a smaller degree of the surface reduction by NO for the former system. Second, in our case, the ratio of bands at 1945 and 1782 cm^{-1} is reversed as compared with that observed by Aylor et al. [11]. By analogy with lanthanum manganite (vide supra), it implies a higher concentra-

tion of Co^{3+} cations on the surface of lanthanum cobaltite as compared with Co–ZSM-5. Third, in the case of NO and O_2 co-adsorption on Co–ZSM-5, only the intensity of 1782 cm^{-1} band was decreased, while that of the 1945 cm^{-1} band remained unchanged [11], thus suggesting their assignment to different species. At last, Aylor et al. [11] have not observed the band at $\sim 1850\text{ cm}^{-1}$, which is to be paired with the band at 1782 cm^{-1} in the case of dinitrosyl complexes. Our conclusion about the absence of low-coordinated Co^{2+} cations on the surface of lanthanum cobaltite agrees well with the fact that no bands, which can be assigned to adsorbed N_2O , were observed for this sample. Hence, for lanthanum cobaltite, low-coordinated surface cobalt cations do not seem to emerge during the course of NO adsorption. Such cations are expected to be generated by the partial substitution of lanthanum with the alkaline-earth cations provided oxygen vacancies appear. Indeed, for the case of NO adsorption on $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$, the spectrum is similar to that of lanthanum manganite (Fig. 1, spectrum 2); in addition to a strong band at 1945 cm^{-1} , a broad band at 1725 cm^{-1} and a shoulder at 1870 cm^{-1} (probably, dinitrosyl species) are observed, while the band at 2235 cm^{-1} indicates the appearance of adsorbed N_2O . These data are in favor of our assignment of bands emerged due to NO adsorption on the surface of lanthanum cobaltite. Hence, for the Sr-substituted sample, at least two surface cobalt cations differing by their coordination environment can be differentiated.

For lanthanum ferrite (spectrum 4), the band at 1670 cm^{-1} corresponding to nitrite–nitrate species is very weak, evidencing only slight surface reduction by NO. The most intense band at 1796 cm^{-1} can be assigned to NO adsorbed on Fe^{+2} clusters [13]. A weak band at 1840 cm^{-1} along with a shoulder at 1750 cm^{-1} may be due to Fe^{+2} dinitrosyls. The presence of isolated Fe^{2+} cations in a different coordination is inferred from the appearance of band at 1905 cm^{-1} . Coordinatively unsaturated Fe^{+3} cations

give rise to the band of adsorbed NO at 1955 cm^{-1} . The band at 2235 cm^{-1} corresponds to N_2O adsorbed on coordinatively unsaturated Fe^{+2} cations.

For ideal LaFeO_3 materials, surface iron cations are in the 3+ oxidation state, and as a result, the degree of surface reduction is low (vide supra), therefore Fe^{+2} cations detected can be associated with the surface defects, where oxygen bonding strength is decreased. As a result, such relatively weakly bound oxygen is removed either during vacuum pretreatment, or via interaction with NO molecules, forming nitrite–nitrate species [14]. Probably, both routes operate simultaneously. The results obtained here imply the existence of at least three types of centers on the surface of lanthanum ferrite: coordinatively unsaturated Fe^{3+} cations (near point defects); isolated coordinatively unsaturated Fe^{2+} cations capable of reacting with NO to form dinitrosyls (probably formed as a result of the reduction of coordinatively unsaturated Fe^{3+} cations); and centers easily reduced to clusters of Fe^{2+} cations (forming on the surface near extended defects).

Additional arguments in favor of assigning a pair of bands at 1750 and 1835 cm^{-1} to dinitrosyl complexes of low-coordinated Me^{+2} cations can be drawn from the data of NO adsorption on calcium ferrite synthesized via a mechanochemical activation route and annealed at different temperatures [15] (Fig. 2). For the sample annealed at 600°C , when oxygen vacancies are still not ordered, the spectrum of adsorbed NO resembles that of lanthanum ferrite (cf. Fig. 1, spectrum 4); the most intense bands are situated at 1790 – 1800 cm^{-1} due to NO adsorption on Fe^{+2} clusters. It is possible that there is dinitrosyl species on the sample calcined at 600°C (weak shoulders at 1850 and 1735 cm^{-1}) as well. At high annealing temperature (1100°C), oxygen vacancies are ordered, thus creating tetrahedral positions in which Fe cations are situated [16]. As a result, the density of cluster centers typical for low-temperature samples is decreased, and only other centers giving rise to

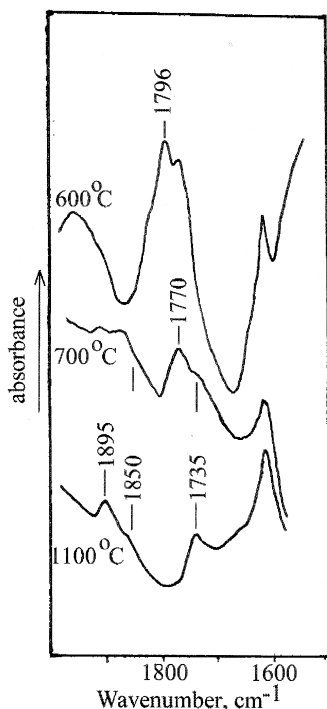


Fig. 2. Spectra of NO adsorbed on calcium ferrite samples annealed at different temperatures after mechanochemical pretreatment. Calcination temperatures are indicated in the picture.

bands of adsorbed NO at 1850 and 1735 cm^{-1} usually assigned to dinitrosyl complexes are observed. Hence, surface cations in low (tetrahedral) coordination indeed appear to be capable to stabilize the dinitrosyl complexes.

The ability of transition metal cations to be stabilized in the high-valence state is known to increase in the order $\text{LaFeO}_3 < \text{LaCoO}_3 < \text{LaMnO}_3$ [1]. This row correlates with the ability of the perovskite surface to be reduced by NO to form nitrite–nitrates. It is quite interesting that the predominant effective charge of the reduced transition metal cations probed by adsorbed NO (+2; +3; +2 and +3, vide supra) does not follow the same trend. Thus, the most reduced surface centers-clustered Fe^{2+} cations are obtained in the case of the least reducible lanthanum ferrite, and the least reduced centers- Co^{3+} cations predominate for lanthanum cobaltite. This feature can be tentatively explained by the ability of the Mn and Co cations

in the regular surface positions to be reduced by NO, while for lanthanum ferrite, only defect centers are reducible.

In the reaction of low-temperature CO oxidation, specific catalytic activity usually increases in the order $\text{LaFeO}_3 < \text{LaMnO}_3 < \text{LaCoO}_3$ [17]. We observed the same order as well. Hence, there is no correlation between the activity and the ability of the surface sites to be stabilized in the low-charge state. Similarly, no simple correlation is evident between the specific catalytic activity and event of reduction of the surface by NO. First of all, in the reaction of CO oxidation by oxygen, the degree of the surface reduction will certainly be different as compared with that after vacuum pretreatment or contact with NO at room temperature, hence any direct comparison could be too ambiguous. Secondly, the lower activity of lanthanum ferrite can be easily assigned to a low density of defect surface sites capable to coordinate the reactive oxygen, while for the other two systems, at least a part of the regular centers appear to be rather reactive. Finally, the highest activity of LaCoO_3 can be explained by the realization of more efficient Langmuir–Hinshelwood mechanism of CO oxidation typical for cobalt-containing oxide systems [18].

4. Conclusions

FTIR spectroscopy of adsorbed NO revealed a variety of different types of coordinatively unsaturated surface cations for lanthanum cobaltites, manganites, and ferrites, some of which emerge due to the room-temperature surface reduction by the test molecule. For the surface of LaFeO_3 , clusters of coordinatively unsaturated Fe^{2+} cations associated with the surface defects dominate. For the surface of LaCoO_3 and LaMnO_3 , coordinatively unsaturated Me^{+3} cations are mainly revealed, being more coordinated by oxygen for the former system. These results could be used to analyze the catalytic properties of perovskites in the

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Acknowledgements

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