

Surface adsorption in the gas–solid reaction between NO and LaBaSrCu₂O_{6–δ}

F. Munakata,^{*a} Y. Akimune,^a Y. Shichi,^b M. Akutsu,^b H. Yamaguchi^b and Y. Inoue^b

^a Material Research Laboratory, Nissan Research Center, Nissan Motor Co. Ltd., 1 Natsushima-cho, Yokosuka 237, Japan

^b Research Department, Nissan ARC Ltd., 1 Natsushima-cho, Yokosuka 237, Japan

The chemical state of NO over LaBaSrCu₂O_{6–δ} investigated by X-ray photoelectron spectroscopic analysis suggests the surface adsorption of NO₂[–] corresponds to NO trapped by oxygen vacancies.

Since the discovery of high-*T_c* superconducting cuprates,¹ a number of studies have been made on layered cuprates. The physical and chemical properties of layered cuprates have drawn attention in relation to their superconducting properties. Some of these oxides have been studied in the applications of NO_x decomposition catalysis and gas sensors.^{2–8} The catalytic applications of cuprates have been studied by Misono and coworkers^{2–4} and by Shimada *et al.*⁵ for direct decomposition or reduction of nitric oxides. These studies suggested that the redox properties of copper ions and the resultant oxygen vacancies may play an important role in the catalytic conversion of NO. Also, Machida *et al.*^{9–11} have reported that rapid NO absorption by BaCuO_{2+δ} takes place through solid–gas reactions to produce barium nitrate and nitrite. By contrast, Misono and coworkers^{12,13} suggested the possibility of NO uptake *via* direct incorporation into bulk YBa₂Cu₃O_y. They indicated that the NO–CO reaction took place through absorption owing to the defective structure of the layered cuprate. Recently, Machida *et al.*¹⁴ reported the absorption–desorption properties of nitric oxide over the layered cuprate La_{2–x}Ba_xSrCu₂O₆ (0 ≤ *x* ≤ 1.0). These results suggest that the desorption process of NO contrasts to conventional NO absorption–desorption systems in the following ways: (a) NO absorption is not associated with the formation of nitrates or nitrites of barium and (b) the desorption temperature of N₂ is much higher than that of O₂. Therefore, it is worthwhile to study the adsorbed states of NO over La_{2–x}Ba_xSrCu₂O₆ in order to understand the absorption–desorption mechanism of NO over layered cuprates. Also, this mechanism indicates the existence of oxygen solubility in La_{2–x}Ba_xSrCu₂O₆. It is important to consider the oxygen non-stoichiometry effects for the adsorption–desorption properties of NO over La_{2–x}Ba_xSrCu₂O₆. However, the relation of the NO adsorption–desorption properties with the oxygen non-stoichiometry in La_{2–x}Ba_xSrCu₂O₆ has not been clearly defined.

In the present study, the surface adsorption of NO over LaBaSrCu₂O_{6–δ} was investigated by X-ray photoelectron spectroscopy (XPS) in order to understand the absorption–desorption process of NO over layered cuprate. We also discuss the chemical states of adsorbed nitric oxide near the surface of this compound and the effects of oxygen partial pressure on this surface reaction.

Powdered LaBaSrCu₂O_{6–δ} was prepared by coprecipitation of the citrates of the elements. After calcination at 1073 K for 5 h in air, the powder was ground and then heated at 1273 K for 10 h in air. The crystal phase of the powder was determined by powder X-ray diffraction (XRD) and the single-phase X-ray diffraction profiles are shown in ref. 14. The NO adsorbed samples were prepared by annealing at 627 K for 1 h upon introduction of 0.5 vol.% NO–5 vol.% O₂–94.5 vol.% N₂ or 0.5 vol.% NO–99.5 vol.% N₂. These powders were pressed into pellets, and analysed by X-ray photoelectron spectroscopy and powder X-ray diffraction. X-Ray photoelectron spectra (XPS) were measured using a commercial spectrometer (PHI ESCA-

5600) with a base pressure in the chamber of *ca.* 10^{–12} atm. The X-ray source was monochromated Al-Kα radiation (1486.6 eV) and the combined energy resolution was *ca.* 0.3 eV. Core-level binding energies were referenced to the C 1s peak at 284.5 eV to account for the surface charge-up, especially in the cases of samples that were poor electrical conductors.

The samples were prepared in a variety of process conditions as follows: (a) at 1273 K for 10 in air (sample A), (b) annealing sample A at 627 K for 1 h in the presence of 0.5 vol.% NO–99.5 vol.% N₂ (sample B), and (c) annealing sample A at 627 K for 1 h in the presence of 0.5 vol.% NO–5 vol.% O₂–94.5 vol.% N₂ (sample C). Fig. 1 shows N 1s XPS core-level spectra for these samples. The N 1s XPS peak was not detected for sample A. In Table 1, the binding energies of N 1s XPS core-level spectra are summarized for samples B and C, NaNO₂,¹⁵ Ba(NO₃)₂¹⁶ and Sr(NO₃)₂.¹⁶ The data in Table 1 suggest that the N 1s XPS spectra of nitrates occur in the range 407 < *E_b* < 408 eV, and those of nitrites at *E_b* ≈ 404 eV. The N 1s XPS peak for sample B is observed at 403.1 eV, similar to that for NaNO₂ (Na⁺NO₂[–]).¹⁵ It was considered that the N 1s XPS peak at *ca.* 404 eV indicated the surface adsorption of NO₂[–] corresponding

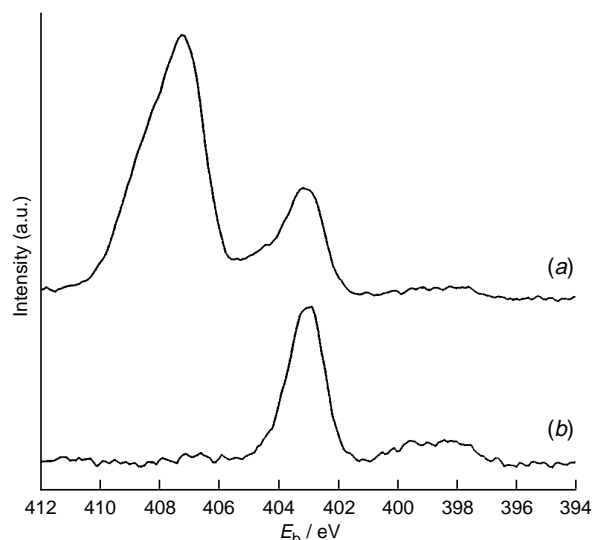
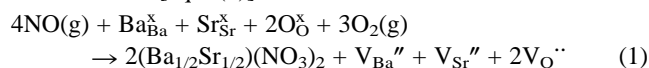


Fig. 1 N 1s XPS core-level spectra for samples after NO absorption: (a) annealing at 627 K for 1 h after introducing 0.5 vol.% NO–5 vol.% O₂–94.5 vol.% N₂ and (b) annealing at 627 K for 1 h after introducing 0.5 vol.% NO–99.5 vol.% N₂

Table 1 Binding energies of N 1s XPS core-level spectra

	<i>E_b</i> /eV
Sample B	403.1
Sample C	403.1, 407.3
NaNO ₂	403.9
NaNO ₃	407.4
Ba(NO ₃) ₂	407.5
Sr(NO ₃) ₂	408.1

to NO adsorption. Sample B showed an X-ray diffraction profile similar to $\text{LaBaSrCu}_2\text{O}_{6-\delta}$ and there were no additional reflections. The N 1s XPS peaks for sample C are observed at 407.3 and 403.1 eV, the former being similar to the N 1s XPS peak for NaNO_3 (Na^+NO_3^-).¹⁵ On the other hand, the X-ray diffraction profile of sample C showed additional reflections due to the formation of barium and/or strontium nitrate, $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{NO}_3)_2$.¹⁷ The occurrence of the N 1s XPS peak at *ca.* 407.3 eV showed the formation of nitrates of $(\text{Ba},\text{Sr})(\text{NO}_3)_2$ in sample C. This process may be represented using Kröger–Vink notation [eqn. (1)]



where V and g denote vacancy and gas, respectively. To simplify the discussion, the valences of Ba, Sr and O ions were assumed to be, respectively, +2, +2, and -2 on the lattice sites. The formation of nitrate is a consequence of the $\text{NO}-\text{O}_2$ atmosphere, according to eqn. (1). In the absence of O_2 , the formation of nitrates and nitrites of Ba, Sr and Cu was not observed.

In Table 2, the binding energies of Cu $2p_{3/2}$ XPS core-level spectra are summarized for samples A, B and C, CuO ¹⁸ and $\text{Cu}(\text{NO}_3)_2$.¹⁹ The XPS core-level spectra of samples A, B and C were similar to the spectrum of CuO in ref. 18. Also, the binding energy of the XPS core-level spectrum of Cu $2p_{3/2}$ in sample C is similar to that of $\text{Cu}(\text{NO}_3)_2$.¹⁹ The binding energy of the Cu $2p_{3/2}$ XPS core-level spectrum of sample B was different from 933.7 eV (the binding energy of Cu^{2+} ion in CuO) upon NO adsorption. As the formation of nitrates or nitrites was not observed in sample B, this result may reflect the intercalation of NO molecules into the layer structure.

Machida *et al.*¹⁴ reported that NO adsorption over $\text{La}_{2-x}\text{Ba}_x\text{SrCu}_2\text{O}_6$ was considered to proceed via intercalation of NO molecules into the layer structure. However, these compounds containing absorbed NO begin to desorb $\text{NO}-\text{NO}_2$ above 573 K.¹⁴ It is considered that the present results shown in Fig. 1 and Table 2 reflect the adsorption–desorption reaction of NO near the surface. Therefore, the N 1s XPS peak at *ca.* 404 eV suggests surface adsorption of NO_2^- resulting from NO adsorption. Thus, this NO adsorption (or intercalation) near the surface induces a change of the chemical state of the Cu ions. On the other hand, layered cuprates have a large number of oxygen vacancies in the lattice as reflected in the chemical formula $\text{LaBaSrCu}_2\text{O}_{6-\delta}$.¹⁴ Yasuda *et al.*²⁰ reported a mechanism in which the active sites for decomposition of NO over valency-controlled La_2CuO_4 -based mixed oxides where coordinatively unsaturated Cu^{2+} ions on the surface are easily oxidized to Cu^{3+} upon NO adsorption. Misono and coworkers^{2–4} and Shimada *et al.*⁵ suggested that the redox characteristics of copper ions and the resultant oxygen

vacancies should play an important role in the surface reaction of NO. Also, it is suggested that the chemical shift of Cu 2p XPS peak in Table 2 is related to the change of oxidation state of Cu ions which is caused by NO adsorption. Therefore, to explain the results of sample B, as shown in Fig. 1 and Table 2, we propose that NO gas is trapped by oxygen vacancies neighbouring the coordinatively unsaturated Cu ions on the surface of $\text{LaBaSrCu}_2\text{O}_{6-\delta}$.

In conclusion, the chemical state of NO over $\text{LaBaSrCu}_2\text{O}_{6-\delta}$ was investigated by X-ray photoelectron spectroscopy (XPS) and the results are interpreted as follows.

(i) The N 1s XPS peak was seen at a binding energy of *ca.* 404 eV for the sample annealed in 0.5 vol.% $\text{NO}-\text{N}_2$ and also seen at two binding energies of *ca.* 403.1 and 407.1 eV for the sample annealed in 0.5 vol.% $\text{NO}-5$ vol.% O_2-N_2 .

(ii) From the X-ray-diffraction profile of the sample annealed in 0.5 vol.% $\text{NO}-5$ vol.% O_2-N_2 , it is proposed that the N 1s XPS peak at 407.1 eV results from the formation of nitrates of Ba and/or Sr.

(iii) The N 1s XPS peak at *ca.* 403.1 eV suggests the surface adsorption of NO_2^- group corresponding to NO trapped by oxygen vacancies.

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Received, 29th September 1996; Com. 6/05258D

Table 2 Binding energies of Cu $2p_{3/2}$ XPS core-level spectra

	E_b/eV
Sample A	934.0
Sample B	933.1
Sample C	934.0
$\text{Cu}(\text{NO}_3)_2$	935.5
CuO	933.0