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NO-Intercalation Properties of a Double-Layered Cuprate, $La_{2-x}Ba_xSrCu_2O_6$. Dissociative Desorption of Intercalated NO

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The desorption process of nitric monoxide intercalated into the double layered cuprate, $La_{1.4}Ba_{0.6}SrCu_2O_6$, was studied by temperature programmed desorption-mass spectrometry (TPD-MS). The desorption profile consisted of NO (<600 °C), O_2 (>600 °C) and N_2 (>800 °C) peaks, the latter two implying dissociative desorption of the intercalated NO. Qualitative relations between NO uptake and each desorption suggests the presence of two different NO sites in the layer structure. One is the site bound to Ba, where NO is converted to NO_2^- ions, and produces a reversible NO desorption on heating (<620 °C). Another site is ascribable to an anion vacancy in the CuO_5 pyramid layer, being occupied by NO strongly bonding to Cu. Instead of this NO ligand, lattice oxygens are eliminated as O_2 above 600 °C. A further increase of temperature results in cleavage of the N−O bond and subsequent elimination of N_2 while leaving the NO oxygen in the lattice. The dissociative NO desorption proceeds *via* the oxygen-exchange between the intercalated NO and the cuprate lattice.

Introduction

In previous publications,[1,2] we reported the NO-intercalation properties of the substituted double layered cuprate, $La_{2-x}Ba_xSrCu_2O_6$. This material shows rapid absorption of large quantities of gaseous nitric monoxide (ca. 1 mol/mol-Ba) at 250 °C. Although NO absorption was reported for several metal oxides containing Ba, i.e., Y-Ba-Cu-O[3−5] and Ba-Cu-O,[6−8] the present system is completely different from these conventional systems in the following two ways. First, the NO uptake is due to intercalation into the layer structure, whereas the other materials reported so far cause the precipitation of $Ba(NO_2)_2$ or $Ba(NO_3)_2$. Such characteristic reactivity to NO is associated with the superstructure including the ordering of Ba and oxygen vacancies.[1,2] Aging the cuprate in water vapor is also necessary to bring about the NO intercalation, because the formation of interlayer hydroxyls is effective in expanding the interlayer spacing.[2]

Another remarkable feature is concerned with the deintercalation process. From the thermal desorption profiles, we found that part of the NO incorporated into $La_{2-x}Ba_xSrCu_2O_6$ is liberated dissociatively as O_2 at >600 °C and N_2 at >800 °C.[9] This is in striking contrast to the other NO absorbents based on the formation of $Ba(NO_2)_2$ or $Ba(NO_3)_2$, from which absorbed NO is completely recovered as mixtures of NO/NO_2. Dissociative desorption is well-known for NO species adsorbed on noble metals or metal oxides.[10−13] On noble metals, such as Pt and Ru, the recombination of N from dissociatively adsorbed NO produces N_2 desorption, but the desorption of O_2 requires much higher temperatures because of its strong interaction with the surface.[10,11] The formation of N_2 from adsorbed NO was also observed over partially reduced metal oxides.[12,13] In most of these cases, however, the remaining O species are usually consumed to oxidize the metal oxides.[12] These previous studies cannot account for the dissociative desorption mechanism of the intercalated NO.

In the present study, the desorption behavior of intercalated NO was studied by means of TPD-MS. The major goal of this work was to gain insight into the desorption mechanism and to determine how the layered structure takes part in this process. The result was linked with parallel analyses of the crystal and chemical structure during desorption to elucidate the structure/reaction relationships in the present system.

Experimental Section

The double layered cuprate, $La_{1.6}Ba_{0.4}SrCu_2O_6$, was prepared by calcining powder mixtures of oxides and

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carbonates (La_2O_3, CuO, $BaCO_3$, and $SrCO_3$, 99.99%, Rare Metallic Co., Ltd.) in air at 1050 °C.[1,2] A dry sample thus prepared was treated with saturated water vapor (ca. 20 kPa) at 60 °C for 48 h to increase the NO absorbability. The average oxidation number of copper in the sample was determined by iodometric titration.[14] A sample was dissolved in dilute aqueous hydrochloric acid with an appropriate amount of potassium iodide. The amount of iodine formed was titrated with sodium thiosulfate solution. The crystal structure of the sample was determined by powder X-ray diffraction (XRD, Rigaku RINT-1400) using Cu Kα radiation (30kV, 20mA). The XPS measurement was performed on a PERKIN-ELMER PHI 5600ci spectrometer using monochromated Al Kα radiation (14kV, 350 W). For the analysis, sintered samples, prepared by heating powders pressed into a rectangular shape, were exposed to water vapor (60 °C) and subsequently to NO (250 °C). The sample was broken into two pieces in vacuo and the fracture surface thus formed was used for XPS analysis. The operating pressure in the analysis chamber was maintained less than 10^{-6} Pa during the course of the measurement. For the FT-IR analysis, a powder mixture of the cuprate sample and KBr pressed into a disc ($\phi 20$ mm) was placed in a temperature-controllable quartz cell with CaF_2 windows, which was connected to an evacuation system. The spectra were recorded on a JASCO FTIR-300 spectrometer after introducing NO (13 kPa) at 250 °C and after evacuation at elevated temperatures.

Temperature programmed desorption (TPD) measurements were performed in a conventional flow reactor, which was coupled to a volumetric vacuum system and to a differential evacuation system. The granular sample held in a quartz tube (8 mm i.d.) was exposed to various pressures of NO (99.9%) at 250 °C for 1 h. After evacuating at room temperature, the sample was heated in a He stream at 10 deg/min. The desorption gas was analyzed by a quadrupole mass spectrometer installed on the differential evacuation system. In this report, the NO uptake by the cuprate as well as amounts of each desorption species is expressed in terms of "mol/mol", which means "mol/formula unit of the cuprate".

To elucidate the desorption mechanism, nitric monoxide containing $N^{18}O$ ($N^{18}O$ 40%, $N^{16}O$ 60%) was used in the TPD measurement as a tracer molecule. The TPD of intercalated $N^{16}O$ was also performed on ^{18}O-exchanged $La_{1.4}Ba_{0.6}SrCu_2O_6$, which was prepared by isotopic equilibration with $^{18}O_2$ as follows. A pristine sample was evacuated at 950 °C to remove part of lattice oxygens. This was followed by the reaction with 98% $^{18}O_2$ (50 torr) for 2 h and subsequent cooling to room temperature at constant rate of 5 deg/min. The resultant isotopic fraction, $^{18}O/(^{18}O+^{16}O)$, in the cuprate was 0.04.

Results and Discussion

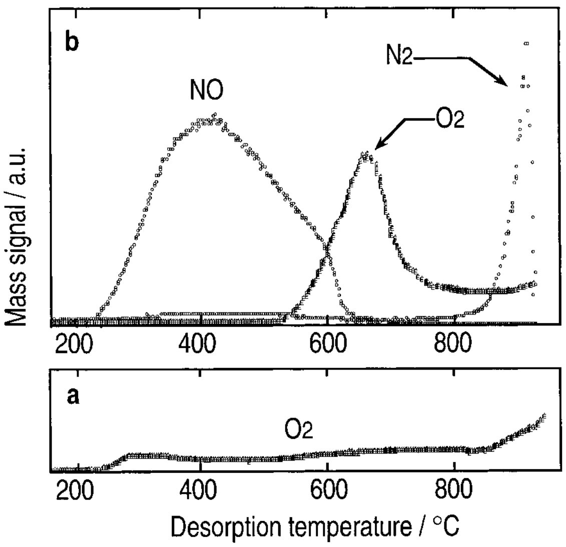

Figure 1. TPD profiles from $La_{1.6}Ba_{0.4}SrCu_2O_6$ after absorbing (a) 0.0 and (b) 0.5 mol/mol of NO at 250 °C. Heating rate, 10 °C/min; carrier gas, He.

Desorption Behavior of Intercalated NO. Figure 1 shows the TPD profiles of $La_{1.4}Ba_{0.6}SrCu_2O_6$ after water vapor treatment and subsequent intercalation of 0.5 mol/mol NO at 250 °C. The sample as treated with water vapor showed only broad O_2 desorption at 250–1000 °C (Figure 1a). The spontaneous oxygen evolution in this case is attributable to the desorption of lattice oxygens, being accompanied by the reduction of copper ions. The oxidation number of copper determined by iodometric titration decreased from 2.27 to 2.00 after the TPD measurement. The desorption profile was remarkably changed after the reaction with NO (Figure 1b). After 0.5 mol/mol of NO uptake, the termination of NO desorption (<620 °C) was followed by O_2 and N_2 desorption, with maxima at 650 and 920 °C, respectively. In the previous study,[9] we have already established the quantitative relationship between NO and N_2;

$$(\text{NO uptake}) = (\text{NOx desorption}) + (\text{N}_2\ \text{desorption}) \times 2 \quad (1)$$

and the following relationship concerning O_2 stoichiometry:

$$(\text{O}_2\ \text{desorption}) = (\text{O}_2\ \text{from cuprate}) + (\text{N}_2\ \text{desorption}) \quad (2)$$

The second relationship means that the whole oxygen evolution results from two sources, i.e., from dissociative NO desorption ($2NO \rightarrow N_2 + O_2$) and from the cuprate lattice ($La_{1.4}Ba_{0.6}SrCu^{2.27+}{}_2O_{5.97} \rightarrow La_{1.4}Ba_{0.6}SrCu^{2.00+}{}_2O_{5.70} + 0.135O_2$). The intensity of the O_2 peak increasing with the amount of NO uptake in parallel to that of the N_2 peak demonstrates that dissociative desorption of NO occurs on heating.

The desorption amounts of NO, O_2 and N_2 are plotted as a function of NO uptake in Figure 2, which gives us useful insights into how NO is being intercalated. The intercept with the ordinate for O_2 desorption represents the desorption of lattice oxygens from the cuprate (Figure 1a). For the desorption of NO, O_2 and N_2, each of the points fall on two straight lines with an intersection at ca. 0.1 mol/mol on the abscissa. Below this value, a large portion of the intercalated NO was desorbed dissociatively as N_2. Beyond the intersections, however, the N_2 desorption became almost constant, and thus

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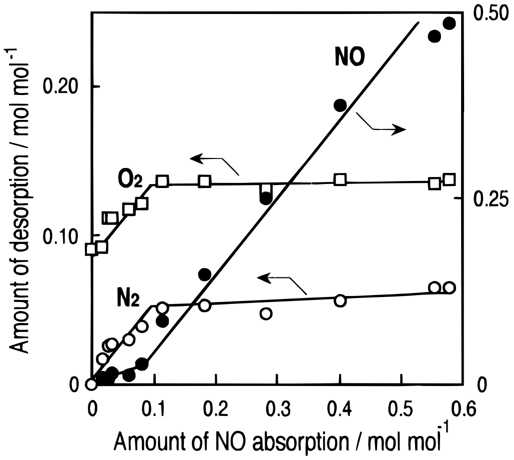

Figure 2. Amounts of desorption species as functions of NO uptake.

incremental NO uptake led only to desorption as NO_x (NO_2 fraction less than 5%). This result implies that the layered cuprate contains two different sites for the NO intercalation, i.e., a reversible site responsible for the NO desorption and an irreversible site responsible for the N_2 desorption. Since the NO intercalation is an equimolecular reaction between Ba and NO as revealed in our previous report,[2] the total NO site for $La_{1.4}Ba_{0.6}SrCu_2O_6$ is estimated to be 0.6 mol/mol. On the other hand, the irreversible site to bring about the N-O dissociation is less than 0.2 mol/mol. Figure 2 indicates that early NO intercalation proceeds until the irreversible site is fully occupied, and then further intercalation seems to occupy the reversible site.

Isotopic TPD Measurement. As is evident from Figure 1, the NO uptake into the layered cuprate gives rise to a new O_2 desorption peak at 650 °C. Here, we must examine two possible origins of the O_2 species, i.e., from the intercalated NO and/or from the cuprate lattice, to determine the mechanism of dissociative NO desorption. To clarify this point, the following TPD studies employed an oxygen isotope, ^{18}O, as a tracer. Figure 3a shows the desorption profile of oxygen from $La_{1.4}Ba_{0.6}SrCu_2O_6$ absorbing labeled NO (40% $N^{18}O$, 60% $N^{16}O$). On the assumption that the O_2 peak at ca. 650 °C is generated from NO, the desorbed oxygen must contain a substantial amount of ^{18}O. Actually, however, almost all of the O_2 desorption was composed of $^{16}O_2$ up to 950 °C, at which the N_2 desorption was terminated. The cumulative $^{16}O^{18}O$ desorption less than one-fiftieth of the $^{16}O_2$ desorption suggesting that no oxygens from intercalated NO were involved in the dissociative NO desorption.

As was described in our previous report,[2] the NO intercalated cuprates contain interlayer hydroxyls bonded to Ba. Heating the sample is postulated to produce successive elimination of H_2O from two hydroxyl groups residing on adjacent sites in the interlayer. When this process involves oxygen exchange between NO and OH, the resulting desorption profile should contain $H_2{}^{18}O$. Figure 4 shows the typical desorption profiles of water from $N^{16}O$ or $N^{18}O$-intercalated cuprates occurring over a broad temperature range above 200 °C. The maximum H_2O desorption rate was observed at around 650 °C, but the complete desorption required heating up to ca. 800 °C so that the hydroxyls seem to be tightly bound to the interlayer. While the $N^{16}O$-intercalated sample showed only $H_2{}^{16}O$ desorption, the desorption of $H_2{}^{18}O$ was detected from the $N^{18}O$ intercalated sample. However, the amount of $H_2{}^{18}O$ desorption was negligibly small (less than 3%) as compared to that of $N^{18}O$ intercalation.

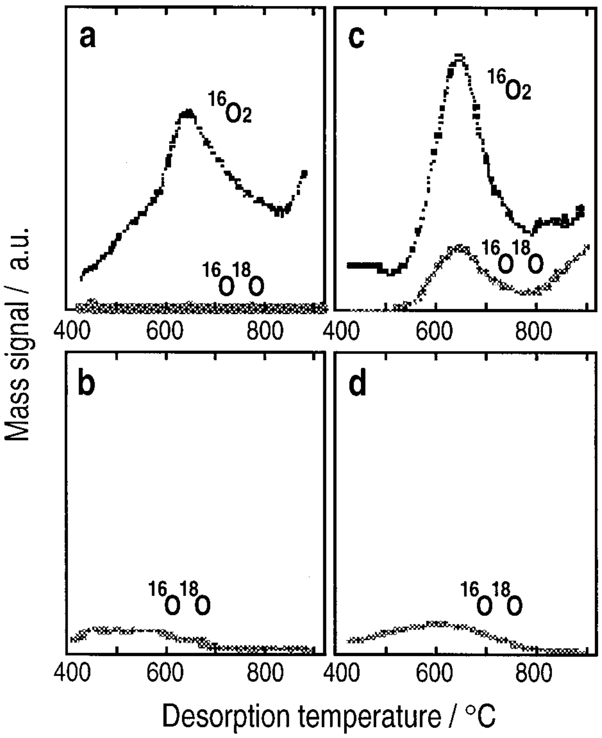

Figure 3. TPD profiles of oxygen after absorption of 40% $N^{18}O$ (60% $N^{16}O$) into $La_{1.6}Ba_{0.4}SrCu_2O_6$: (a) first run in He stream; (b) second run in 10% O_2/He stream, and after absorption of $N^{16}O$ into the ^{18}O-containing cuprate; (c) first run in He stream, (d) second run in 10% O_2/He stream. Each second run was took place after first run and subsequent cooling to room temperature in He stream. Heating rate, 10 °C/min.

Another possible route for the O_2-evolution should come from the cuprate lattice. After the first TPD measurement of the $N^{18}O$-intercalate (Figure 3a), the sample was cooled down to room temperature in a He stream and was subsequently submitted to a second run in a 20% $^{16}O_2$/He stream (Figure 3b). In this case, the profile clearly showed the formation of $^{18}O^{16}O$ as a result of isotopic exchanges between $^{16}O_2$ and the lattice ^{18}O. This means that NO oxygens remain in the cuprate lattice even at the end of the N_2 desorption in the first TPD run up to ca. 980 °C. Competitive experiments involving the $N^{16}O$ intercalation into a ^{18}O-containing cuprate were carried out in order to gain additional evidence concerning the reaction route. Although we do not know how ^{18}O was distributed at the various lattice sites, it is supposed to be situated randomly among the three different oxygen sites (see Figure 7) *via* a bulk diffusion process. The resultant TPD profile showed a large $^{18}O^{16}O$ desorption at 650 °C (Figure 3c). Note that the shape of the $^{18}O^{16}O$ desorption profile is characteristic of the NO-intercalated cuprate, but completely different from that of spontaneous desorption of lattice oxygens from a pristine sample (Figure 1a). Considerable ^{18}O desorption was also observed in a second run in a 20% O_2/He stream (Figure 3d) as a result of isotopic exchange reactions. These isotopic TPD experiments clearly indicate that the O_2 desorption from the NO-intercalate does not contain NO oxygens.

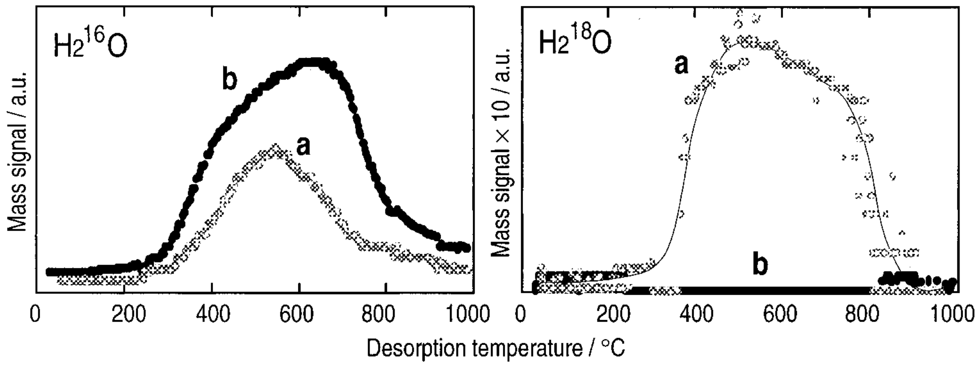

Figure 4. TPD profiles of water ($m/e = 18$ and 20) after absorption of (a) 40% $N^{18}O$ (60% $N^{16}O$) and (b) $N^{16}O$ at 250 °C. Heating rate, 10 °C/min; carrier gas, He.

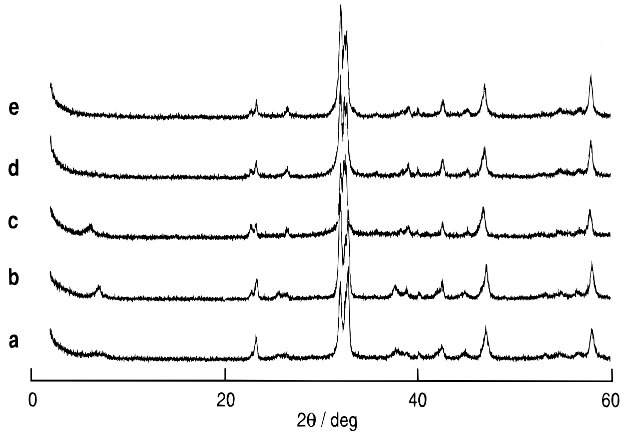

Figure 5. XRD patterns of $La_{1.6}Ba_{0.4}SrCu_2O_6$ after NO-intercalation and subsequent heating in a He flow: (a) pristine sample; (b) after exposing to water vapor (20 kPa, 60 °C), (c) after NO intercalation (0.5 mol/mol, at 250 °C), and (d) subsequent heating at 550 °C and (e) at 950 °C in a He flow.

Dissociative NO desorption proceeds *via* oxygen exchange reactions between intercalated NO and lattice oxygens.

Structural Changes during NO Intercalation and Desorption. In the preceding studies,[1,2,9] we demonstrated that the NO intercalation leads to a significant expansion of the interlayer spacing of the cuprate. As is shown in the XRD profiles in Figure 5, a two-stage lattice expansion along the c axis after reactions with water and subsequently with NO is evident from the appearance of the strong 002 reflection at $2\theta = 6.7°$. This characteristic reflection disappeared at the termination of the NO desorption in a He flow at 550 °C. The initial interlayer spacing was almost restored at 950 °C at the termination of N_2 desorption. Since the precipitation of any second phases was not detected during these processes, the dissociative NO desorption results from the deintercalation without destroying the layered structure. FT-IR spectra of the NO-intercalated cuprates showed two signals (1384 and 1270 cm^{-1}) ascribable to N-O stretching modes of NO_2^- ($\nu_{NO_2^-}$) surrounding Ba ions in the interlayer.[2] Evacuation at >300 °C reduced the intensity of these bands significantly in accord with the desorption of NO as shown in Figure 1b. However, other signals due to the irreversibly intercalated NO were not visible by FT-IR.

XPS measurement was performed to estimate the effect of NO intercalation on each element. A most drastic change was observed for the Ba3d peak, of which the binding energy at the peak maximum shifted from 780.2 to 781.1 eV (Figure 6). The latter binding energy, being close to that of barium nitrate/nitrite, is consistent with the formation of Ba-NO_2^- species in the interlayer as was detected by FT-IR. The chemical shifts due to the NO intercalation were also observed for the La3d and Cu2p spectra, but scarcely for the Sr3d spectrum. Barium must be more effective in bringing about the NO uptake, because the associated O^{2-} ions are more basic than those surrounding the La or Sr ions. Since La and Ba seem to occupy the same site in the intercalation layer,[2] the incorporated NO species consequently influence the La3d spectrum.

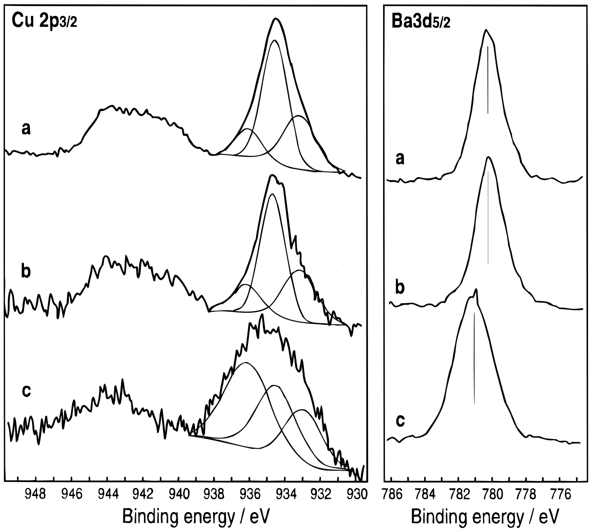

Figure 6. $Cu2p_{3/2}$ and $Ba3d_{5/2}$ XPS spectra of (a) pristine, (b) water-vapor treated, and (c) 0.6 mol/mol NO-intercalated samples ($x = 0.6$).

The $Cu2p_{3/2}$ spectrum of the pristine compound ($x = 0.6$) showed a broad anisotropic peak due to chemical inhomogeneity. One possible curve fitting of this peak is represented in Figure 6 by assuming 936.0, 934.4, and 933.1 eV as the peak maxima. Contrary to the second and third components, which correspond to Cu^{2+} and Cu^+, respectively, the first component may be attributed to a higher oxidation state. Actually, the average oxidation number of Cu, 2.27, as determined by iodometric titration showed the presence of an oxidation state higher than 2+. Neither $Cu2p_{3/2}$ spectrum or the average oxidation number of Cu were influenced by the water vapor treatment. However, the NO intercalation increased the highest binding energy fraction (936.0 eV), simultaneously decreasing the Cu^{2+} fraction (934.4 eV). This effect can be explained by a more electrophilic ligand, NO_2^-, than oxide ions, approaching the Cu

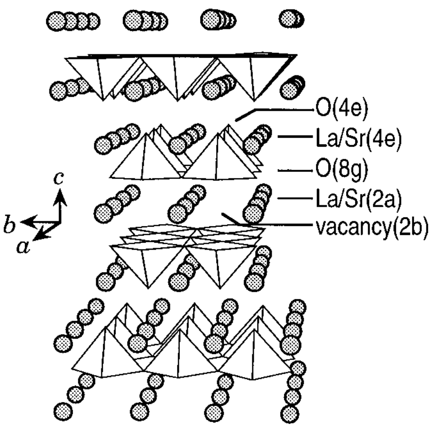

Figure 7. Ideal crystal structure of double layered cuprate, $La_2SrCu_2O_6$.

species which are exposed to the intercalation layer. The original Cu2p spectrum was restored when NO desorption was complete at 650 °C.

The Dissociative Desorption Mechanism. The ideal crystal structure of the double layered cuprate is composed of oxygen defect intergrowth between double pyramidal copper layers and rock salt type layers (Figure 7).[16–19] In the $La_{2-x}Ba_xSrCu_2O_6$ system, Ba and La are considered to be situated in the interlayer (2a site) between the basal planes of the CuO_5 sheets where the NO intercalation takes place.[2] The present study revealed that two different types of intercalation sites are provided in the interlayer. From one type of these sites, the intercalated NO is liberated at <650 °C similarly to that from the other Ba-containing cuprates.[3–8] Since NO uptake into these cuprates is based on the formation of barium nitrite or nitrate, the NO desorption is naturally complete at their decomposition temperatures, ca. 650 °C. Although the NO uptake into the present system does not produce the nitrite/nitrate phases, the intercalated NO should be also bound to Ba by a strong electrostatic force.[2] According to the *in situ* FT-IR measurement, the NO uptake was consistent with the intensity of IR absorption due to $\nu_{NO_2^-}$. The reversible site is therefore regarded as nitrite ions surrounding Ba in the interlayer. This idea is supported by the Ba3d spectra, (Figure 6) indicating that Ba ions are coordinated by anionic species (NO_2^-) after NO intercalation. The binding energy of N1s, 403.4eV, was also close to that of NO_2^- ions, e.g., 403 eV for $NaNO_2$.

Another intercalation site produces the dissociative desorption of NO. This is unlikely to be associated with the Ba-(NO_2^-) species because the desorption requires much higher temperature than for the decomposition of barium nitrate/nitrite. Although the nature of this type of active center has not been defined by the present work, it seems similar to that required for catalytic NO decomposition. It is well known that anion vacancies play a key role in NO decomposition over metal oxide catalysts.[12] In the case of a perovskite-related oxide, $SrFeO_{3-d}$, Shin et al.[13,15] proposed a reaction mechanism which involves occupation of oxygen vacancies by NO molecules followed by dissociation of the N-O bond and subsequent desorption of N_2 and O_2 thus regenerating the vacancy.

To understand the NO-anion vacancy interaction, the defect structure of $La_{2-x}Ba_xSrCu_2O_6$ is briefly summarized. There are various defect structures arising from oxygen nonstoichiometry and the ordering of cations involved in unsubstituted $La_2SrCu_2O_6$. A neutron diffraction study conducted by Caignaert et al.[20] revealed that a small amount of the corner oxygen site (8g in Figure 7) on the copper planes becomes deficient with simultaneous generation of an interlayer oxygen (2b) between copper planes. We have confirmed that the presence of the interlayer oxygen is reflected by the thermal desorption of lattice oxygens from $La_2SrCu_2O_6$ at low temperatures (>350 °C).[9] Such weakly bonding lattice oxygens are considered to react with the intercalated NO to produce NO_2^- species in $La_{2-x}Ba_xSrCu_2O_6$. As a result of charge compensation accompanied by the Ba^{2+}-substitution, additional oxygen vacancies should be introduced in CuO_5 pyramid sheets. Actually, an electron diffraction study in our previous report[2] indicated a $3a \times 3a$ superstructure due to the ordering of oxygen vacancies in $La_{1.5}Ba_{0.5}SrCu_2O_{6-d}$. As was proposed for catalytic NO decomposition, part of the intercalated NO may occupy such oxygen vacancies to form (NO)-Cu species. Because of this strong (NO)-Cu bond, the thermal reduction of the cuprate should be accomplished by elimination of the equivalent amount of lattice oxygens. This model is able to account for the isotopic TPD results, which suggest the exchange between the NO oxygen and the lattice oxygen, the latter being desorbed at >600 °C whereas former remains in the lattice even after N_2 desorption.

Taking these results into consideration, a possible reaction mechanism for the dissociative desorption of intercalated NO can be described as follows. The water vapor treated sample contains interlayer hydroxyl species, Ba-OH,[2] which are effective in expanding the interlayer spacing to accommodate NO molecules. However, the OH content in the expanded lattice does not influence the intercalation/deintercalation events. The absence of any NO-OH interactions was also confirmed by in situ FT-IR results. The NO intercalation is driven by an equimolecular interaction with Ba, and NO thus incorporated may react with the interlayer oxygen to produce NO_2^- species, which are reversibly eliminated at 300−650 °C. On the other hand, part of the NO thus incorporated occupies anion defects in Cu-O planes, yielding a strong (NO)-Cu bond as schematically illustrated in Figure 8(ii). The resultant highly oxidized Cu species become so unstable at elevated temperatures that lattice oxygens are eliminated above 600 °C (iii). At the end of this oxygen desorption, therefore, the lattice oxygen in CuO_5 is partially replaced by NO. A further increase in temperature finally leads to the thermal cleavage of the N-O bond and thus N_2 desorption above 800 °C (iv). Consequently, the whole reaction

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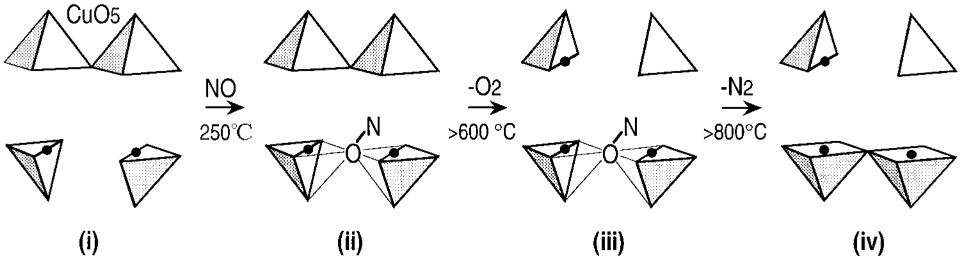

Figure 8. Reaction scheme of dissociative desorption of NO intercalated into the double layered cuprate.

can be regarded as an exchange between the intercalated NO and the lattice oxygen followed by the thermal dissociation of NO at elevated temperatures.

According to this reaction model, the layered cuprate lattice can be regenerated after N_2 desorption. As a matter of fact, the thermal desorption process also includes water desorption as a result of elimination of interlayer hydroxides (Figure 4), which are necessary to promote NO intercalation. However, a significant NO intercalation rate can be restored immediately if the reaction is carried out in the presence of water vapor (ca. 20 kPa). We also confirmed that the NO absorption/desorption process can be repeated by employing dynamic temperature cycles, the so-called thermal swing process. As compared to conventional catalytic reactions, absorption/desorption cycles may have possible advantages in separation and enrichment of dilute NO_x and its direct decomposition to N_2. Since NO uptake into other oxides containing Ba is always inhibited by CO_2, further work is in progress on the effects of coexisting gases as well as the long-term stability of the layered cuprate under various reaction conditions.

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