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XPS/FTIR Study of the Interaction between NO and $YBa_2Cu_3O_7$

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The combination of X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and simultaneous thermal analysis (STA) studies has shown that the interaction between NO and $YBa_2Cu_3O_7$ occurs at room temperature and above, resulting in the formation of the nitride, nitrate, nitrite (NO_2^-), and nitrito (–ONO) groups, as well as in the release of N_2, NO_2, and N_2O. The nitride species are observed at temperatures between 300 and 540 K but not at higher temperatures. The nitrate ion is the predominant nitrogen-containing species at temperatures below 540 K, and its concentration decays at elevated temperatures (>820 K). The nitrito group can be found at room temperature as well as elevated temperatures. The nitrite ion is observed with relatively low concentration at lower temperatures but becomes the predominant nitrogen-containing species at high temperatures. The maximum increase in the sample weight ($\sim$7%) as measured by thermogravimetry (TG) corresponds to a net uptake of a NO_2 group (or an NO molecule plus an O atom) per unit cell of $YBa_2Cu_3O_7$. The NO interaction also results in the oxidation of a small portion (<24%) of the lattice Cu(II) ions and, to a lesser extent, the oxidation of the lattice barium atoms. At 830–920 K the surface segregation of the barium atoms is evident and is thought to be indicative of the matrix degradation due to the formation of barium nitrite. A detailed mechanism of the interaction between $YBa_2Cu_3O_7$ and NO is postulated and applied to explain the high catalytic activity for the selective reduction of NO on $YBa_2Cu_3O_7$.

I. Introduction

NO decomposition and its selective catalytic reduction by CO or NH_3 have been increasingly investigated because of their great importance in air pollution control.[1–36] In addition to copper-exchanged zeolites,[21–29] $YBa_2Cu_3O_7$ and some other cuprates with perovskite-like structures have recently been regarded as potential catalysts for NO removal.[30–36] This is because they have been found to be even more active in catalyzing the reaction: $NO + CO \rightarrow N_2 + CO_2$ than CuO, which is one of the most active catalysts among the 40 metal oxides[37] and other non-perovskite cuprates. In view of this, it is therefore of significant importance to study the interactions of $YBa_2Cu_3O_7$ with NO and CO.

We have reported the study on the interaction between CO and $YBa_2Cu_3O_7$.[38] In this work we investigate the interaction between NO and a $YBa_2Cu_3O_7$ sample at different temperatures using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and simultaneous thermal analysis (STA). As will be shown in section III, the interaction is found to occur at room temperature and above, resulting in the formation of nitride, nitrate, nitrite, and nitrito complexes in the solid phase,

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as well as the release of N_2, N_2O, and NO_2 in the outlet gas. On the basis of these studies, a detailed mechanism of the interaction is postulated in the Discussion.

II. Experimental Section

The $YBa_2Cu_3O_7$ sample was prepared and characterized as previously described.[38] The X-ray diffraction spectrum of the sample was identical to that reported in the literature,[38,39] showing that the sample thus prepared was a single phase one and had the perovskite-type structure.[40,41] The samples resulting from the reactions with NO at a variety of temperatures were prepared from the STA apparatus as described below.

The simultaneous thermal analysis (STA) study of the NO interaction was performed on a Netzsch STA 409. Approximately 100–200 mg of the sample was placed in an open crucible, with the same amount of kaolin loaded into another identical and symmetrically located crucible as the reference. Two thermocouples attached to the crucibles measured the temperature difference (ΔT) between the sample and the reference material. NO was passed through the sample at a flow rate of 100 mL/min, and the samples were heated at a linear rate of 10 °C/min. The temperature difference (ΔT) was continuously recorded as a function of temperature, giving the differential thermal analysis (DTA) curve, while the weight of the sample was recorded, giving a thermogravimetry (TG) plot. The outlet of the STA 409 was directly connected to the gas cell of the Shimadzu FTIR-8101 in order to analyze the evolved gas by FTIR. Since N_2, which is one of the gaseous products resulting from the interaction, is homopolar and therefore infrared-inactive, the evolved gas was also analyzed by gas chromatography (GC) on a Perkin-Elmer Auto System using molecular sieve 5A and Porapak Q columns with helium as the carrier gas (30 mL/min).

The XPS experiments were made in a VG ESCALAB MKII spectrometer using a Mg Kα X-ray source (1253.6 eV, 120 W) at a constant analyzer pass energy of 20 eV. With an ultimate base pressure of $\sim 5 \times 10^{-10}$ mbar, the normal operating pressure in the analysis chamber was $< 2 \times 10^{-9}$ mbar during the course of the measurements.

The infrared spectra of the samples were recorded on the Shimadzu FTIR-8101 using the pellet technique, which involved mixing the finely ground sample and potassium bromide powder and pressing the mixture into an evacuable die at 8 ton of pressure to produce a transparent disk. Forty scans were taken for each spectrum to obtain a good signal-to-noise ratio.

III. Results and Analysis

1. DTA/TG Results. The differential thermal analysis (DTA) and thermogravimetry (TG) data in Figure 1 were obtained by heating the $YBa_2Cu_3O_7$ sample from room temperature to 1200 K in NO on the STA apparatus at a linear rate of 10 °C/min. Between 300 and 970 K, the TG curve shows a continuous NO uptake while the DTA profile exhibits two exothermic peaks. The increase in the sample weight reaches $\sim$4.5% of the total weight at 830–920 K. As will be shown by the XPS and FTIR data (vide infra), the predominant nitrogen-containing species in this temperature region are the nitrite, NO_2^-, and nitrito, –ONO, groups. Thus the 4.5% increase in the sample weight may correspond approximately to an NO molecule uptake for each unit cell of $YBa_2Cu_3O_7$. The maximum increase in weight is $\sim$7% and is reached at 970 K. At temperatures higher than 970 K, a weight loss accompanied by an endothermic effect is observed. The maximum weight loss ($\sim$7%) may correspond to the loss of an NO_2 group from each NO-saturated $YBa_2Cu_3O_7$. N_2, NO_2, and N_2O are detected from the evolved gas analysis whereas little O_2 is found.

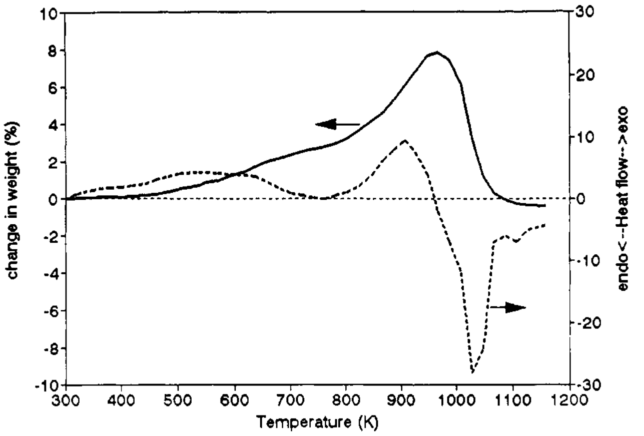

Figure 1. DTA/TG data for the $YBa_2Cu_3O_7$ sample in NO. Change in weight (%) is determined by the quotient of $\Delta W/W$. ΔW stands for the change in the sample weight due to the NO interaction, and W the initial sample weight. Heat flow is measured by the temperature difference between the sample and reference, ΔT, in mV/unit.

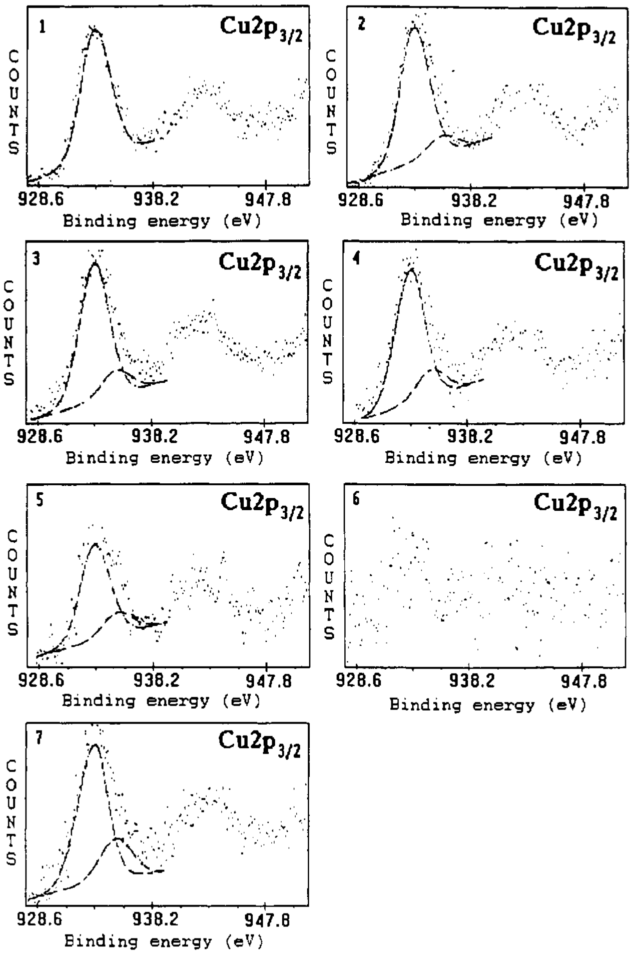

Figure 2. Comparison of $Cu2p_{3/2}$ X-ray photoelectron spectra: (1) the $YBa_2Cu_3O_7$ sample before the NO interaction; (2–7) the $YBa_2Cu_3O_7$ sample after the NO interaction at 300, 420, 540, 830, 920, and 1200 K, respectively. The charging shifts of the samples have been corrected by using the binding energy of C1s (284.6 eV) below the Fermi level as reference. The peaks of broken lines are produced by a peak-synthesis procedure that fixed the peak positions and widths and varied the heights to achieve a best fit of the experimental (dotted) spectra. For comparison all the spectra are plotted using the same scale for both the x and y axes.

2. XPS Results. Figure 2 shows the $Cu2p_{3/2}$ spectra for the $YBa_2Cu_3O_7$ samples before and after the interaction with NO at different temperatures. Spectrum 1 is for the pristine $YBa_2Cu_3O_7$ sample. The $Cu2p_{3/2}$ peak of spectrum 1 is located at the binding energy of 933.4 eV, with a strong satellite at 942.3 eV, which is characteristic of Cu(II) and indicates, in agreement with the literature,[40,41] that the Cu atoms in the $YBa_2Cu_3O_7$ sample exist mainly in the Cu(II) oxidation state. After

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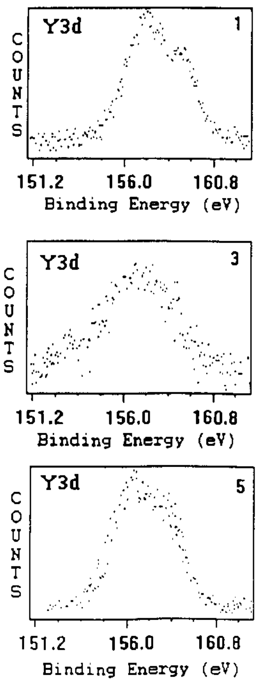

Figure 3. Comparison of Y3d X-ray photoelectron spectra: (1) the $YBa_2Cu_3O_7$ sample before the NO interaction; (2–5) the $YBa_2Cu_3O_7$ sample after the NO interaction at 300–540, 830, 920, and 1200 K, respectively.

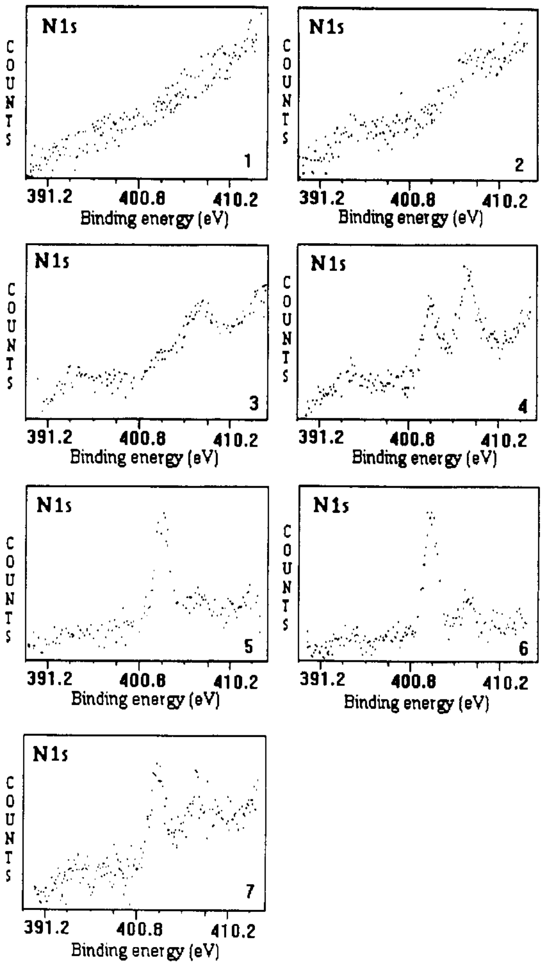

Figure 4. Comparison of N1s X-ray photoelectron spectra: (1) the $YBa_2Cu_3O_7$ sample before the NO interaction; (2–7) the $YBa_2Cu_3O_7$ sample after the NO interaction at 300, 420, 540, 830, 920, and 1200 K, respectively.

interaction with NO, the width of the main Cu2p$_{3/2}$ peak is shown to increase, with some intensity shifted to higher binding energy by 1.6 eV (see spectra 2–7 in Figure 2). The new copper species with high Cu2p binding energy may be assigned to Cu(III), which may be viewed as Cu(II) plus a hole on the oxygen ligand.[42] The intensity ratio $I_{Cu(III)}/I_{Cu(II)}$ seems to rise with increasing NO interaction temperature but is estimated to be less than 24% at all temperatures studied. This appears to mean that only a small fraction of the lattice copper atoms has been involved in and is oxidized by the NO interaction. It is very interesting to observe that the Cu2p peak decays at 830 K and becomes rather weak at 920 K (see spectra 5 and 6 in Figure 2). A notable drop in the peak intensity at 830 and 920 K is also found in the Y3d spectra (see Figure 3) but not in the Ba3d$_{5/2}$ spectra, which are not presented because little change in the spectral shape as well as the peak intensity is observed from the samples at different temperatures. Because XPS is a surface-sensitive technique, the significant decay in the Cu2p and Y3d intensities with respect to the Ba3d$_{5/2}$, intensity which remains high after the NO interaction at 830 and 920 K, may be attributed to the surface segregation of the Ba atoms as a result of the NO interaction. In fact, the decline in the intensity ratio of Cu2p/Ba3d with increasing NO reaction temperature has been observed even at temperatures between 300 and 820 K, although the significant decay in the Cu2p and Y3d intensities is not evident until the reaction temperatures reach 830 and 920 K. Although the Ba3d spectra do not evidently change their shapes as the result of the NO interaction, small chemical shifts may be observed at certain temperatures. For example, at 420–540 K the Ba3d peaks are found to shift to higher binding energy by ~0.6 eV. This chemical shift may be indicative of the partial oxidation of the Ba atoms and can therefore provide information on the mechanism of the NO interaction as will be discussed later. Figure 4 shows the N1s spectra for the samples before and after the interaction with NO at 300, 420, 540, 830, 920, and 1200 K, respectively. Three peaks can be observed in the N1s region as a result of the NO interaction at different temperatures. The peak at 395 eV is observed only at the temperatures between 300 and 540 K. Obviously, this peak can be attributed to the nitride species. Note that the value of 395 eV is lower than that normally reported for nitrides[43–45] and may be indicative of the presence of more positive ions near the nitride ion, as will be further discussed in section IV. The peak at 403.2 eV can be assigned to the nitrite, NO_2^-, or nitrito, –ONO, group according to the literature.[43,46] This peak is relatively weak at lower temperatures (<540 K) and becomes strong at high temperatures, indicating that the nitrite or nitrito group is the main nitrogen-containing species at high temperatures (>830 K). The peak at 407.4 eV may be assigned to the nitrate group.[43,46] It is relatively strong at lower temperatures (300–540 K) and rather weak at temperatures higher than 830 K. Consequently, the N1s data in Figure 4 appear to show that both dissociative and associative adsorption of NO may occur over the samples. The NO dissociation results in the formation of nitride, which exists mainly at lower temperatures (below 830 K), while the associatively adsorbed NO may exist as a nitrate or nitrite/nitrito group. The nitrate species appears to predominate in lower temperature regions (300–540 K) but decays at temperatures above 840 K; while the nitrito/nitrite species remain at high temperatures (above 830 K). The above information on

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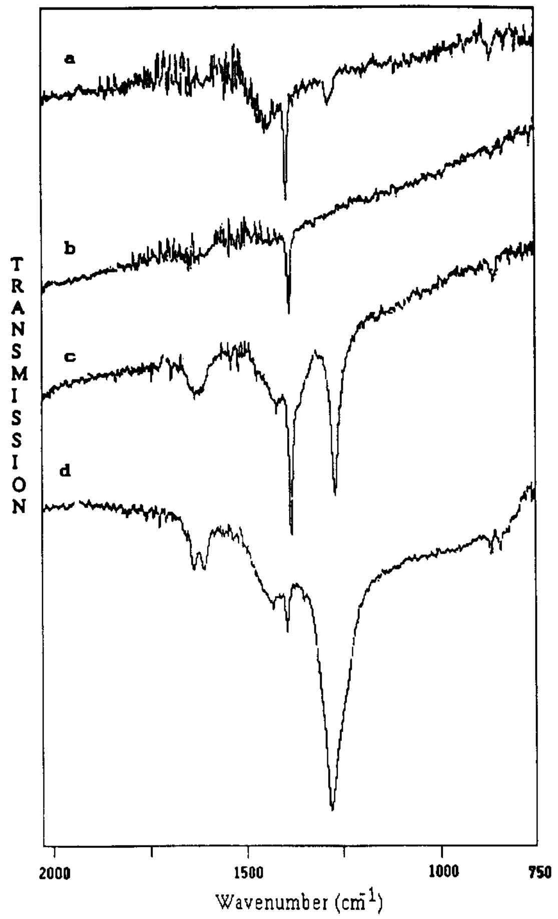

Figure 5. Comparison of FTIR spectra for the $YBa_2Cu_3O_7$ sample after the NO interaction at (a) 300, (b) 420, (c) 540, and (d) 830 K.

the nature of the nitrogen-containing species can be confirmed and supplemented by the infrared spectroscopic studies.

3. FTIR Results. Figure 5 gives the FTIR spectra for the samples after interaction with NO at 300, 420, 540, and 830 K. In spectrum a for the NO/$YBa_2Cu_3O_7$ sample at 300 K, three absorption bands are evident at 1420, 1380, and 1270 cm^{-1} in the region between 3000 and 1000 cm^{-1}, where no bands are observed for the pristine $YBa_2Cu_3O_7$ sample. Increasing the reaction temperature to 420 K results in the diminishment of the bands at 1420 and 1270 cm^{-1}, with the sharp peak at 1380 cm^{-1} remaining (see spectrum b). Obviously, the peak at 1380 cm^{-1} is produced by a nitrogen-containing species, which is different from those contributing to the bands at 1420 and 1270 cm^{-1}. For the sample prepared at 540 K (see spectrum c), in addition to the band at 1380 cm^{-1}, three absorption bands are observed at 1630, 1420, and 1270 cm^{-1}. In comparison with spectrum a, the band at 1420 cm^{-1} does not change greatly in intensity whereas the bands at 1630 and 1270 cm^{-1} grow significantly. Further increasing the reaction temperature causes the drop in the intensity of the peak at 1380 cm^{-1} while the intensities of the bands at 1630 and 1270 cm^{-1} are enhanced. It seems that the bands at 1630 and 1270 cm^{-1} are due to the same nitrogen-containing species since they change in intensity together. Figure 6 demonstrates the FTIR spectra obtained from $Cu(NO_3)_2$, $Ba(NO_3)_2$, $Y(NO_3)_3$, and $NaNO_2$. The 1380-cm^{-1} band is also observable from the nitrates listed above and can therefore be assigned to the free nitrate ion, NO_3^-, or covalently coordinated nitrato group, $-ONO_2$.[47] It is worthwhile to note that, among the four known nitrate and nitrite compounds in Figure 6, $Ba(NO_3)_2$ is the exceptional one which does not give the absorption band at 1630 cm^{-1}. This appears to mean that the sharp peak at 1380 cm^{-1} (with little absorption at 1630 cm^{-1}) in spectrum b of Figure 5 is due to barium nitrate. The decay of the absorption band at 1380 cm^{-1} at 830 K (spectrum d of Figure 5) thus indicates the relative decrease in the concentration of the nitrate ions, which is in good agreement with what is observed from the above XPS studies. The formation of the nitrides is not evidently observed from the infrared study because the vibrations of the nitrides would be located in the low-energy region around 400 cm^{-1} and may not be detected with a good signal/noise ratio. From a comparison with the spectrum of the known nitrite salt (see spectrum d in Figure 6), the bands at 1630 and 1270 cm^{-1} are attributed to the chelating NO_2^- ion,[47-50] which is bonded to a metal atom through the two oxygen atoms. It is well-known from the literature that the nitrito group, which is a ONO group coordinating to a metal atom through one of its oxygen atoms, normally exhibits a strong absorption band at 1400–1460 cm^{-1}.[50-53] Consequently, the band at 1420 cm^{-1} in Figure 5 is due to the nitrito group, –ONO. Both nitrite and nitrito nitrogens would give the N1s photoelectron at the same binding energy. Nevertheless, they could be distinguished by the infrared study as described above. FTIR can thus confirm and supplement the information obtained from XPS. From spectrum d of Figure 5, the increase in the intensity of the nitrite bands is obvious, which again agrees well with the XPS results.

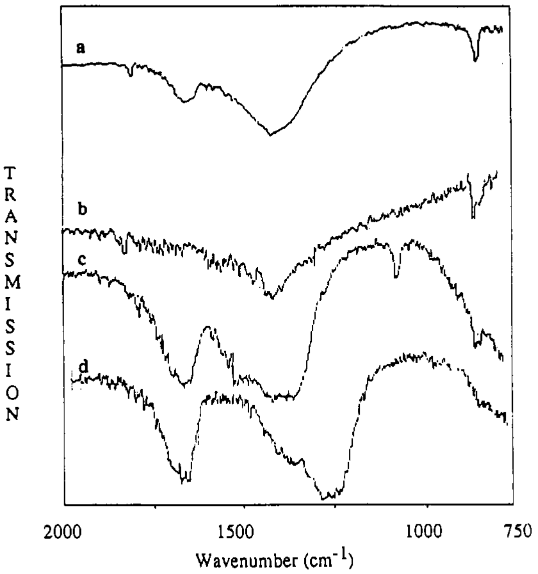

Figure 6. FTIR spectra: (a) $Cu(NO_3)_2{\cdot}5H_2O$; (b) $Ba(NO_3)_2$; (c) $Y(NO_3)_3{\cdot}5H_2O$; (d) $NaNO_2$.

IV. Discussion

In summary, the combination of XPS, FTIR, and DTA/TG/EGA studies has shown that the interaction between NO and $YBa_2Cu_3O_7$ occurs at room temperature and above, resulting in the formation of the nitride, nitrate, nitrite, and nitrito groups, as well as in the release of N_2, NO_2, and N_2O. The nitride species are observed at temperatures between 300 and 540 K but not at higher temperatures. The nitrate ion is the predominant nitrogen-containing species at temperatures below 540 K and decays at elevated temperatures (>820 K). The nitrito group can be found at room temperature as well as elevated temperatures. The nitrite

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ion is observed with relatively low concentration at lower temperatures but becomes the predominant nitrogen-containing species at high temperatures. The TG study has shown that the maximum increase in the sample weight as the net result of the NO interaction at temperatures is ~7%, which correspondes to a net uptake of an NO_2 group (or an NO molecule plus an O atom) per unit cell of $YBa_2Cu_3O_7$. As a result of the NO interaction, XPS has also shown that a small portion (<24%) of Cu(II) ions are oxidized to higher oxidation state. Partial oxidation of the lattice barium atoms by NO is also found to take place, in particular, at 420–540 K. Another important point of information provided by the XPS study is the decay in the Cu and Y core-level signals relative to that of Ba, as evidently observed at 830–920 K. Since the nitrite ion is the predominant nitrogen-containing species, as found from both the infrared and XPS studies, the abundance of Ba on the sample surface may appear to indicate that the surface segregation of the barium atoms may result from the formation of barium nitrite, rather than the copper and yttrium nitrites; i.e., the nitrite ions are bonded to the Ba rather than to the Cu or Y sites.

On the basis of the above experimental results and knowledge of the crystal structure of the $YBa_2Cu_3O_7$ sample, it is possible to discuss a detailed mechanism of the NO interaction. The crystal structure of the $YBa_2Cu_3O_7$ sample is known[38,40,41] to consist in each unit cell of two CuO_2, two BaO, one CuO, and one Y planes stacked in the sequence $-CuO/BaO/CuO_2/Y/CuO_2/BaO-$. The oxygen atoms in the cell assume perovskite-like anion positions, halfway between Cu atoms along the cube edges. Nevertheless, the anion positions in the CuO plane are only half-occupied and are totally vacant in the yttrium plane. Consequently, each Cu atom in the CuO planes has four near-neighbor oxygen atoms, with two in the same plane and two in the BaO planes. In other words, each Cu atom in the CuO plane has an oxygen vacancy which is also coordinated to the Ba atom in the BaO plane. Previous studies on the CO interaction[38] as well as on the halogen interaction with $YBa_2Cu_3O_7$[54] have suggested that the oxygen vacancies in the CuO plane may serve as the active centers for the CO or halogen intercalation. On the other hand, the NO decomposition was reported to require a coordination-unsaturated metal site.[4,20,49] These may suggest that, for the $NO/YBa_2Cu_3O_7$ system, the oxygen vacancy on the CuO plane, which may be expressed as $OBa\square CuO$, is the active center for the NO decomposition.[35,36] In the present study, the NO dissociation is observed to occur readily at room temperature and becomes more evident at higher temperatures. Meanwhile, a chemical shift is observed both from Cu2p and, to a lesser extent, from the Ba3d spectra at room temperature and becomes more evident with the increasing NO dissociation at 420–540 K (as shown by the N1s spectra in Figure 5). This may appear to confirm the above postulate that the NO dissociation may occur at the oxygen vacancy on the CuO plane, $OBa\square CuO$. The resultant nitride and oxide ions may most probably occupy the vacant site, leading to the chemical shifts of Cu2p and Ba3d:

$$OBa\square CuO + NO \rightarrow {}^{1}/_{2}OBaNCuO + {}^{1}/_{2}OBaOCuO \quad (1)$$

The nitride ion is bonded to both copper and barium ions and thus may withdraw more electron charge from the cations, resulting in a lower binding energy than that normally reported for the nitrides formed on metal surfaces (see section III-2.) The Cu ions in the CuO planes account for one-third of the total number of the lattice copper atoms. Therefore only less than 24% of the Cu2p intensity is observed to shift to higher binding energy. Note that the anion sites in the CuO plane, i.e. the vacancy site and the site of the oxygen ion in the CuO plane, are commensurate in the coordination to the Cu and Ba ions, that is $OBa\square CuO = OBaOCu\square$.

As shown by the infrared spectroscopic and XPS N1s spectroscopic studies, associative adsorption of NO is also observed, starting at room temperature. The adsorbed NO may appear to be bonded to the oxide ions, forming the nitrito group, –ONO, as observable from the infrared spectra. The nitrito complex thus formed may serve as a precursor which undergoes chemical transformation at elevated temperatures, leading to the formation of more thermodynamically stable products. Consequently, the associatively adsorbed NO may exist as the nitrite, NO_2^-, and nitrate, ONO_2^-, ions, which have large heats of formation. The heat of formation for the barium nitrite/nitrate are the largest (–25 for NO_2^-, –50 for NO_3^-, –72 for $Cu(NO_3)_2$, –184 for $Ba(NO_2)_2$, and –237 kcal/mol for $Ba(NO_3)_2$),[55] and accordingly, the probability to form barium nitrate species, –BaOONO, is the largest. This may be expressed as follows:

$$OBaNCuO + NO \rightarrow OBaNCuONO \quad (2)$$

$$OBaNCuONO \rightarrow ONOBaNCuO \quad (3)$$

$$ONOBaNCuO \rightarrow NOOBaNCuO \quad (4)$$

$$NOOBaNCuO \rightarrow ONOOBaNCu\square \quad (5)$$

The formation of the nitrate ion from the adsorbed NO may require an "extra" oxide ion as shown in reaction 5. Note that the nitrate ions are the predominant nitrogen-containing species only at 420–540 K when the NO dissociation is the most evident (see N1s spectra 3 and 4 in Figure 4). It may therefore be inferred that the dissociation of NO may provide the extra oxygen atom and favor the formation of nitrate ion.[56] At higher temperatures the reactions

$$N(ads) + N(ads) \rightarrow N_2(g) \quad (6)$$

$$N(ads) + NO(g) \rightarrow N_2O(g) \quad (7)$$

$$O(ads) + NO(g) \rightarrow NO_2(g) \quad (8)$$

may become more evident, resulting in the disappearance of the nitride ions and the deficiency of the adsorbed oxide ions. Consequently, the excess NOO groups must remain covalently bonded to the metal atoms, leading to the decay of the nitrate species and the predominance of the nitrite species (spectra 5 and 6 in Figure 4).

The barium nitrite and nitrate thus formed may appear to have lower surface energies and may segregate on the surface, which may explain the decay in the XPS signals of Cu2p and Y3d. The surface segregation of the barium atoms is evident at 830–920 K and is thought to be indicative of the matrix degradation due to the formation of barium nitrite. Barium nitrate and nitrite may decompose at high temperatures,[55] so that after the sample is heated to 1200 K, the Cu2p and Y3d photoelectrons can be observed with the intensity comparable to the Ba3d photoelectrons again.

On the basis of the above postulations, it is easy to understand why $YBa_2Cu_3O_7$ and some other cuperates with the perovskite-like structures can have higher activity than CuO and other non-perovskite cuprates. In catalyzing the reaction $NO + CO \rightarrow N_2 + CO_2$ at temperatures above 400 °C. The existence of Cu(II) ions has been found to be very essential for the NO selective reduction catalysis over Cu-exchanged zeolites,[51] CuO,[14,36,57] and many Cu-based mixed oxides.[34] As shown from this and previous[38]

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studies, $YBa_2Cu_3O_7$ is able to offer copper atoms in high oxidation states (mainly two) and therefore can serve as a good catalyst for the reaction. The barium ions in the $YBa_2Cu_3O_7$ sample may not be as good as Cu(II) in serving as the catalytic center for the NO decomposition since BaO was previously found to require higher temperature for the NO decomposition than CuO (850 versus 370°C).[37,58] Nevertheless, the Ba ions, which share coordinated oxygen atoms as well as oxygen vacancies with the copper atoms in the CuO plane, are nearest to the Cu ions and, thus, to the intercalated NO (<3 Å, according to the known structure). Therefore the Ba ions in the $YBa_2Cu_3O_7$ sample may play an important role in absorbing NO and retaining it in the form of a nitrite or nitrate, since the barium nitrate and nitrite are thermodynamically more stable than $Cu(NO_3)_2$ and $Cu(NO_2)_2$. The earlier studies have shown that the NO_2 or NO_3 radicals, which may be readily derived from nitrite or nitrate groups, may be the important intermediates responsible for the oxidation of NH_3,[51] and organic compounds.[59] The perovskite structure of the $YBa_2Cu_3O_7$ sample can thus provide both the active center for the NO adsorption and the stabilizer for the maintenance of the important reaction intermediates. Therefore it may show higher activity for NO decomposition or selective reduction than CuO or other non-perovskite cuprates.

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