In-situ observation of nitrogen monoxide adsorption on perovskite-type $MTiO_3$ ($M = \text{Sr}, \text{Ba}$)

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Strontium titanate (SrTiO_3 ; STO) and barium titanate (BaTiO_3 ; BTO) powders were prepared using the solid-state reaction method. To study the tendency for nitrogen monoxide (NO) to adsorb on STO and BTO surfaces, we observed the morphology of the powders, calculated the specific surface areas, and made adsorption/desorption observations using scanning electron microscopy (SEM), nitrogen gas adsorption/desorption isotherms under 77 K, temperature programmed desorption (TPD), and diffuse reflectance fourier transformed spectroscopy (DRIFTS). The average STO and BTO powder particle size was 0.2 μm . The specific surface areas of the non-porous STO and BTO powders were 3 and 4 $\text{m}^2 \text{g}^{-1}$, respectively. TPD and DRIFTS measurements revealed the NO adsorption properties of the STO and BTO powders in the presence of oxygen gas. Additionally, it was considered that the adsorbed NO was formed as nitrates $[M(\text{NO}_3)_2, M = \text{Sr}, \text{Ba}]$ on surface of each powder.

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1. Introduction

Nitrogen oxides (NO_x ; NO and NO_2) are known air pollutants. A three-way catalyst,¹⁾ an intelligent catalyst²⁾ and a NO_x storage reduction catalyst³⁾ have been studied in the past for reducing automobile NO_x gas emissions.

Watanabe et al. reported that hollandite-type oxides had a capacity for NO selective catalytic reduction (NO-SCR).⁴⁾ The structure of hollandite-type compounds are tetragonal system and contain one-dimensional tunnels extending along a unique axis with a lattice period of about 0.3 nm. The hollandite structure framework consists of double chains of metal-oxygen octahedral edges that are adjacently shared. Some hollandite-type compounds include alkaline or alkaline-earth metal ions in the one-dimensional tunnels that provide a charge balance. After discovering the catalytic property, Fujimoto et al. predicted that the active point of NO gas adsorption was alkaline metal ions located at the end of the one-dimensional tunnels.⁵⁾ Recently, we also demonstrated the NO adsorption for lepidocrocite-type oxides which had layered structure with including alkaline metals in an interlayer. And, it was found that NO adsorption mechanism also corresponded exactly with a hollandite-type oxide.⁶⁾ Therefore, we focused on the ability of oxide-containing alkaline-earth metals to also adsorb NO gas.

In this study, we studied the presence of NO adsorption properties in strontium titanate (SrTiO_3 ; STO) and barium titanate (BaTiO_3 ; BTO) powders with perovskite-type structures. **Figure 1** shows crystal structures, and **Table 1** shows lattice

parameters of STO and BTO, respectively.^{7),8)} STO and BTO are known for their dielectric properties and are widely used as electronic component material for memory, sensor, and, energy devices.⁹⁾⁻¹¹⁾ Past studies demonstrated the catalytic property of Pt-loaded BaTiO_3 , but no mention has been made of direct NO_x adsorption/desorption on/from BaTiO_3 .

2. Experimental

STO and BTO powder were prepared by the solid-state reaction method. Strontium carbonate (SrCO_3 ; High Purity Chemicals Co. Ltd., 99.9%), barium carbonate (BaCO_3 ; Wako Pure Chemical Industry Ltd. special grade) and titanium dioxide (rutile-type TiO_2 ; High Purity Chemicals Co. Ltd., 99.9%) were used as starting materials. These starting materials were mixed with a stoichiometric composition. To obtain the STO and BTO powders, the mixtures were respectively heat-treated at 1000°C and 1100°C for 5 h each.

The obtained powders were identified using a powder X-ray diffractometer (XRD; Rigaku Corporation's Miniflex with $\text{Cu-K}\alpha$ radiation) and observed with a scanning electron microscope (SEM; JSM 5500 by JEOL Ltd.). The average particle sizes of the powders were calculated from 100 randomly selected particles in the SEM images. The specific surface areas were calculated from BET plots obtained by N_2 adsorption and desorption isotherms at 77K measured by a BELSORP-max instrument (MicrotracBEL Corp.). Each powder was then pretreated in a heating process at 150°C for 5 h.

Phase identification and particle property observation were followed by in-situ NO adsorption property observation with diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). The DRIFTS equipment comprised an FT-IR spectrometer (Cary 660 by Agilent Technologies) and a mounted furnace Environmental Chamber (Specac Ltd.) with ZnSe windows. After placing the STO or BTO powder in the Environmental Chamber, the powder was pretreated by heating at 650°C

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Fig. 1. Crystal structure of perovskite-type of SrTiO_3 (STO) and BaTiO_3 (BTO).

Table 1. STO and BTO crystal structure information

	SrTiO_3 ⁷⁾	BaTiO_3 ⁸⁾
Crystal system	Cubic	Tetragonal
Space group	$Pm\bar{3}m$	$P4mm$
Cell parameters	$a = 0.3905 \text{ nm}$	$a = 0.399 \text{ nm}$
	$\alpha = \beta = \gamma = 90^\circ$	$c = 0.404 \text{ nm}$
		$\alpha = \beta = \gamma = 90^\circ$

Table 2. STO and BTO lattice parameters

		Experimental	Ref.
SrTiO_3	a/nm	0.3885(3)	0.3905 ⁷⁾
BaTiO_3	a/nm	0.39994(8)	0.3994 ⁸⁾
	c/nm	0.4020(2)	0.4038 ⁸⁾

Fig. 2. Powder X-ray diffraction patterns of STO (a) and BTO (b) heat-treated at 1000 and 1100°C.

for 30 min to clean the sample surface. Single beam spectra of 650, 600, 500, 400, 300, 200, 100°C, and room temperature (RT) were measured as background data. The sample was then exposed to NO gas (c.a. 8000 ppm, Ar balanced) in the Environmental Chamber for 10 min followed by replacement of the atmosphere in the chamber with the carrier gas. DRIFT spectra of the NO-exposed powder were measured in-situ at RT, 100, 200, 300, 400, 500, 600 and 650°C by subtraction of the background data at each temperature. The carrier gases for this study were N_2 gas (99.9999%) and a mixture of N_2 and O_2 (99.5% or better) gas, adjusted to $(\text{N}_2)_{80\%}(\text{O}_2)_{20\%}$. The flow rates of the carrier gas and NO gas were controlled at 50 mL/min.

The behavior and amount of NO desorption from the STO and BTO powders were examined using a temperature programmed desorption apparatus (TPD; BELCAT-B by MicrotracBEL Corp.). Approximately 100 mg of powder was placed in a quartz glass tube and heated at 650°C for 30 min. The pretreated powder was cooled to room temperature and exposed to NO gas (c.a. 8000 ppm, He balanced) at 50 mL/min for 1 h at RT. The internal glass tube was purged by He gas with the same flow rate to remove the NO gas. The NO-absorbing sample was continuously heated at 5°C/min up to 700°C with a He gas flow. Desorption gases were analyzed by a quadrupole mass spectrometer (Q-mass). The signal intensity corresponding to NO and O_2 was measured respectively at 30 and 32 in m/z .

3. Results and discussions

Figures 2(a) and 2(b) show the X-ray diffraction patterns of the STO and BTO powders, respectively. These patterns were

identified as single-phase perovskite-type structures. Table 2 shows the lattice parameters calculated with the Appleman-Evans program.¹²⁾

Figure 3 is the morphology of the STO and BTO powders. Based on the SrTiO_3 and BaTiO_3 SEM images, the mean particle size for both powders were estimated to be 0.2 μm , respectively. Figures 4 and 5 are the N_2 gas adsorption and desorption isotherms under 77K and their calculated BET plots. The STO and BTO powders exhibit Type II isotherms characteristic of non-porous powders. The STO and BTO specific surface areas were approximately 3 and 4 $\text{m}^2 \text{g}^{-1}$, respectively.

Table 3 shows the particle sizes calculated from the specific surface areas and SEM images. We used the following equation to calculate the particle size from the specific surface area:

$$r = 3/(a_s \cdot \rho) \quad (1)$$

where r [m] is the radius of the particle, a_s [$\text{m}^2 \cdot \text{g}^{-1}$] is the specific surface area, and ρ [$\text{g} \cdot \text{cm}^{-3}$] is the density. In this study, we could not apply the Scherrer method because the average particle size was larger than 0.1 μm . Based on the morphology and calculated values, the produced particles were not agglomerates but primary particles.

Figure 6 is the DRIFT spectra for STO powder with adsorbed NO gas from R.T. to 650°C. Figures 6(a) and 6(b) are the respective results for the carrier gases N_2 and $(\text{N}_2)_{80\%}(\text{O}_2)_{20\%}$. After exposure to NO gas in the Environmental Chamber, the STO powder exhibited a distinguishable difference in absorption bands and desorption temperature. The absorption band near 1200 cm^{-1} in Fig. 6(a) is considered to be for physisorption of the NO gas

Fig. 3. Morphologies of STO and BTO powder [(a) STO and (b) BTO].

Fig. 4. N₂ gas adsorption and desorption isotherms under 77K [(a) STO and (b) BTO].

Fig. 5. BET plot of STO and BTO powder [(a) STO and (b) BTO].

Table 3. Comparison of specific surface areas (SSA), calculated particle sizes from SSA and density, and estimated sizes from SEM images

	Specific surface area /m ² ·g ⁻¹	Density /g·cm ⁻³	Particle size (Calc.) /μm	Particle size (SEM images) /μm
SrTiO ₃	2.98	5.12	0.197	0.224
BaTiO ₃	3.61	6.02	0.138	0.169

by the STO powder. And, in Fig. 6(b), the absorption bands of 1300–1400 and 1800 cm⁻¹ are likely from Sr(NO₃)₂ formed by chemisorption; the spectra are very similar to that of commercially available Sr(NO₃)₂ (Aldrich Chemical Co., 99.995%). The absorption bands of 1500–1700 cm⁻¹ in Fig. 6(b) are also believed to be from physisorption of NO.

Fig. 6. DRIFT spectra of STO powder with adsorbed NO gas from R.T. to 650°C [(a) Carrier gas; N₂, (b) (N₂)₈₀%(O₂)₂₀%].

Figure 7 is the DRIFT spectra of BTO powder with adsorbed NO gas from R.T. to 650°C. Figures 7(a) and 7(b) are the respective results for the carrier gases N_2 and $(\text{N}_2)_{80\%}(\text{O}_2)_{20\%}$. These spectra exhibited the same tendency as the STO powder. In Fig. 7(b), the absorption bands of 1300–1450 and 1780 cm^{-1} were attributed to $\text{Ba}(\text{NO}_3)_2$ based on the spectra of commercially available $\text{Ba}(\text{NO}_3)_2$ (Aldrich Chemical Co., 99.999%). The upper left corner in Figs. 6 and 7 showed absorption band of NO gas in the Environmental Chamber. Based on these results, it can be said that the presence of oxygen in the carrier gas plays a significant role in adsorption to form NO_3 on Sr or Ba-sites. In addition, these powders exhibit NO gas adsorption capability at 650°C in Figs. 6(b) and 7(b).

Fig. 7. DRIFT spectra of BTO powder with adsorbed NO gas from R.T. to 650°C [(a) Carrier gas; N_2 , (b) $(\text{N}_2)_{80\%}(\text{O}_2)_{20\%}$].

(a)

(b)

Fig. 8. TPD curves of STO and BTO powder.

(a)

(b)

Fig. 9. Wave deconvolutions of TPD curves.

Figure 8 shows the TPD curves for the STO and BTO powders. **Figure 9** shows the wave deconvolutions of the TPD curves. **Tables 4** and **5** show the amount of desorbed NO and O_2 from the surfaces of the STO and BTO powders. The TPD curves of $m/z = 30$ (NO) and $m/z = 32$ (O_2) can be separated into 5 peaks and their behavior corresponds closely to the DRIFT spectra. The amount of NO and O_2 desorption between 420 to 550°C

Table 4. Amount of desorption NO ($m/z = 30$) and O_2 ($m/z = 32$) from surface of STO powder

	Temperature range / °C	Desorption gas / $\mu\text{mol} \cdot \text{g}^{-1}$
$m/z = 30$	1 40–100°C	0.860
	2 30–370°C	8.88
	3 220–430°C	9.42
	4 370–430°C	4.80
	5 420–550°C	13.7
$m/z = 32$	420–550°C	12.7

Table 5. Amount of desorption NO ($m/z = 30$) and O_2 ($m/z = 32$) from surface of BTO powder

	Temperature range / °C	Desorption gas / $\mu\text{mol} \cdot \text{g}^{-1}$
$m/z = 30$	1 100–330°C	0.970
	2 160–330°C	1.83
	3 230–450°C	3.89
	4 400–560°C	1.62
	5 420–600°C	2.55
$m/z = 32$	420–600°C	2.54

Table 6. Amount of desorption NO per unit weight and area

	Specific surface area a_s /m ² ·g ⁻¹	Desorption gas /μmol·g ⁻¹	Desorption gas /μmol·m ⁻²
SrTiO ₃	2.98	13.7	4.60
BaTiO ₃	3.61	4.17	0.866

Table 7. Estimated number of exposed Sr²⁺ on STO surface and area per particle

Plane direction	Number of Sr ²⁺ on STO surface	Area per plane direction/m ²
(100), (010), (001), ($\bar{1}00$), ($\bar{0}10$), ($\bar{0}01$)	0	$6 \times (1.51 \times 10^{-19})$
(110), (101), (011), ($\bar{1}\bar{1}0$), ($\bar{1}0\bar{1}$), ($\bar{0}1\bar{1}$), ($\bar{1}10$), ($\bar{1}01$), ($\bar{0}11$), ($\bar{1}\bar{1}0$), ($\bar{1}0\bar{1}$), ($\bar{0}1\bar{1}$)	1×12	$12 \times (2.13 \times 10^{-19})$
(111), ($\bar{1}\bar{1}1$), ($\bar{1}1\bar{1}$), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}1$), ($\bar{1}1\bar{1}$), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}\bar{1}$)	1×8	$8 \times (1.31 \times 10^{-19})$
Total	0.77 (=N _{Sr})	1.73×10^{-19} (=S _t)

from the STO powder were respectively calculated to be 14 and 13 μmol·g⁻¹, which corresponds with the NO chemisorption. Similarly for BTO, the amount of NO and O₂ desorption from 400 to 600°C were respectively calculated to be 4.2 and 2.5 μmol·g⁻¹, which corresponds with the NO chemisorption. Therefore, we believe that the active point of NO adsorption on the STO and BTO surfaces was alkaline-earth metal ions and that the presence of oxygen in the carrier gas plays a significant role in NO adsorption. However, we wanted to know why the amounts of NO desorption from STO and BTO are different.

Table 6 shows the desorption amount of the chemically adsorbed NO molecule per unit weight and area. This result indicates that the amount of NO desorption from BaTiO₃ was less than that of SrTiO₃. It is considered that the difference in the amount of NO desorption is due to the difference in basicity strength.

For a quantitative analysis, we assumed NO molecules being adsorbed to all Sr²⁺ sites on the STO powder surface. And this adsorbed amount was treated as theoretical amount. Initially, we assumed the amount based on the exposed plane direction. We hypothesized that the following planes were exposed if one particle is a polyhedron. **Table 7** shows the number of exposed Sr²⁺ site on surface and area per unit cell which were calculated by the following equations:

$$(100), (010), (001), (\bar{1}00), (\bar{0}10), (\bar{0}01); 6 \times a^2 \quad (2)$$

$$(110), (101), (011), (\bar{1}\bar{1}0), (\bar{1}0\bar{1}), (\bar{0}1\bar{1}), (\bar{1}\bar{1}0), (\bar{1}0\bar{1}), (\bar{0}1\bar{1}); 12 \times \sqrt{2}a^2 \quad (3)$$

$$(111), (\bar{1}\bar{1}1), (\bar{1}1\bar{1}), (\bar{1}\bar{1}\bar{1}), (\bar{1}\bar{1}1), (\bar{1}1\bar{1}), (\bar{1}\bar{1}\bar{1}), (\bar{1}\bar{1}\bar{1}); 8 \times (\sqrt{3}a^2/2) \quad (4)$$

where a is the lattice parameter.

We can calculate the number of Sr²⁺ per unit area from multiplication of the hypothetical area and the number of Sr²⁺ on the STO surface. The theoretical amount of NO gas adsorption can be derived from Eq. (5):

$$NO_{ads} = \frac{a_s \cdot N_{Sr}}{S_t \cdot N_a} \quad (5)$$

where:

NO_{ads} [μmol·g⁻¹] is the amount of NO adsorption,

a_s [m²·g⁻¹] is the specific surface area,

N_{Sr} , S_t [m²] is the estimated number of exposed Sr²⁺ ions and the total area on one particle, and

N_a [mol⁻¹] is Avogadro's number.

N_{Sr} and S_t were calculated from the hypothesis that the one particle was accumulated 27 unit cells and formed by 26 direction planes as described in Eqs. (2)–(4) on the particle surface. Then, N_{Sr} was 0.77 because there was no Sr²⁺ on (100), (010), (001), ($\bar{1}00$), ($\bar{0}10$) and ($\bar{0}01$) planes.

From the above assumption, NO_{ads} was calculated to be 21.9 μmol·g⁻¹. Therefore, it was considered that 62.4% of the NO molecules desorbed from Sr²⁺ and 37.6% of the NO molecules remained on STO surface. The absorption bands at 650°C were attributed to the remaining NO molecules.

4. Conclusion

SrTiO₃ (STO) and BaTiO₃ (BTO) with perovskite-type structure were prepared by using the solid-state reaction method. The specific surface areas of STO and BTO were approximately 3 and 4 m²·g⁻¹, respectively. In-situ DRIFTS measurements and TPD curves indicated that NO gas adsorbed on surface alkaline-earth metal ions (Sr²⁺ and Ba²⁺) as Sr(NO₃)₂ and Ba(NO₃)₂. Moreover, the presence of oxygen gas promoted formation of nitrate with Sr²⁺ and Ba²⁺. It was considered that these powders can be using higher temperature than usually catalyst (The operating temperature: 300–400°C) because these spectra were able to exhibit NO gas adsorption capability at 650°C. NO desorption behavior in the TPD curve correlated well with the DRIFTS measurements. We therefore believe that the active point of NO adsorption on STO and BTO was alkaline-earth metal ions. The reason for the difference in the amount of NO desorption from STO and BTO is the different basicity between Sr²⁺ and Ba²⁺. Finally, STO and BTO are promising newly catalysts.

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