# Physicochemical Properties and Catalytic Performance of $Pr_{2-x}Sr_xCoO_{4\pm y}$ Mixed Oxides for NO Reduction by $CO^1$

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**Abstract**—Using the polyglycol gel method, a series of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  ( $0.2 \le x \le 1.0$ ) mixed oxides were prepared, and their catalytic activities were studied in the test reaction of NO reduction by CO. The solid-state physicochemical properties, including crystal structure, defect structure, IR spectrum, valence state of B-site ions, nonstoichiometry oxygen (*y*), oxygen species, and redox properties, were characterized by means of XRD, IR, TPD, TPR, XPS, and chemical analysis. The results show that all mixed oxides display a K<sub>2</sub>NiF<sub>4</sub> structure. When *x* = 0.2 and 1.0, the obtained samples still have little uncertain mixed oxides; however, the mixed oxides (*x* = 0.4, 0.6, 0.8) all represent a single A<sub>2</sub>BO<sub>4</sub> phase. With the increase of *x*, lattice parameters, unit-cell volume, and average crystalline size decrease gradually, whereas microstrain density, the concentration of Co<sup>3+</sup>, the amounts of lattice oxygen released and the concentration of oxygen vacancy increase. The catalytic activities of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts for NO reduction by CO are closely correlated with oxygen vacancy and the concentration of Co<sup>3+</sup>.

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# **INTRODUCTION**

Nitrogen oxides  $(NO_x)$  are major air pollutants that cause acid rain [1]. The removal of NO<sub>x</sub> is one of the key research topics in the protection of the environment. The method of  $NO_x$  reduction by  $NH_3$  has been used in practice, however, due to the cost and secondary pollution [2], it is urgent for us to search for effective but cheaper catalysts. The perovskite-type  $A_2BO_4$ mixed oxides of the K<sub>2</sub>NiF<sub>4</sub> structure, consisting of alternating layers of ABO<sub>3</sub> perovskite and AO rock salt, have recently been studied as new materials for their low cost, high catalytic activity, and high thermal stability [3]. Many studies have shown that the catalytic performance of A<sub>2</sub>BO<sub>4</sub> mixed oxides, to a greater extent, are associated with the A-site and B-site ions, their corresponding valences, and the crystal microstrain of these oxides as well [4]. It is noted that there has been much literature available, contributing to the investigations of  $LnSrCuO_4$  and  $LnSrNiO_4$  catalysts [5, 6]. Recently, CO and  $C_3H_8$  oxidation-catalyzing reactions of LnSrCoO<sub>4</sub> catalysts have been studied [7], but the studies involving the investigation of LnSrCoO<sub>4</sub> catalysts are considerably limited. Though the catalytic oxidation performance of LnSrCoO<sub>4</sub> catalysts is promising, almost no literature has been dedicated to the catalytic reduction performance in the removal of NO<sub>r</sub>. Therefore, further investigation is of great necessity.

In this paper, the Co-containing mixed oxides  $Pr_{2-x}Sr_xCoO_{4\pm y}$  (0.2  $\leq x \leq 1.0$ ) with K<sub>2</sub>NiF<sub>4</sub> structures

were prepared and characterized. The catalytic performances of all these catalysts were investigated in the test reaction of NO reduction by CO. In order to reveal the factors controlling the catalysts' performance, XRD, IR, XPS, TPD, and TPR were employed.

#### **EXPERIMENTAL**

## Catalyst Preparation

Praseodymium nitrate, strontium nitrate, cobalt nitrate, polyglycol-20000, and citric acid (all in AR grade purity) were supplied by the Shanghai Chemical Reagent Company (China), while nitric acid and hydrochloric acid were supplied by the Jiangxi Hongdu Chemical Reagent Company (China). A series of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  (x = 0.2, 0.4, 0.6, 0.8, 1.0) samples were prepared by the polyglycol gel method in a desired molar ratio, respectively. For example, the procedure was as follows for the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  (x = 0.2) sample:  $Pr(NO_3)_3$  (0.50 mol/l, 36 ml),  $Sr(NO_3)_2$ (0.50 mol/l, 4 ml), and 6.304 g (0.03 mol) citric acid were mixed with a solution of  $Co(NO_3)_3$  (0.50 mol/l, 20 ml). Polyglycol-20000 (20.0 g) was added after the solution was evaporated to 40 ml at 80°C with constant stirring until a viscous gel was formed. Then, the gel was evaporated to a completely dry state, and the obtained precursor was calcined at 600°C for 4 h, finally pelletized, and calcined again at 1100°C for 10 h. The sintered pellet was crushed and sieved to a fraction between  $\sim 0.25-0.18$  mm.

<sup>&</sup>lt;sup>1</sup> The text was submitted by the authors in English.

#### XRD Measurement

Phase analysis was performed by an X-ray diffractometer (D8/ADVNCE, Germany), with the operation conditions as 40 kV/10 mA,  $CuK_{\alpha}$  radiation, and nickel filter. For the evaluations of average crystal size and lattice distortion of  $Pr_{2-x}Sr_xCoO_{4\pm y}$ , the Scherrer equation [8]

$$L = 0.9\lambda/\beta\cos\theta \tag{1}$$

and equation

$$\beta^2 \cos^2 \theta = 4(\lambda/L)^2/\pi^2 + 32\varepsilon^2 \sin^2 \theta \qquad (2)$$

were used. Here, *L* is the average crystal size,  $\lambda$  is the wavelength of the X-ray used (0.154 nm),  $\beta$  is the effective line width of the X-ray reflection,  $\theta$  is the Bragg angle, and  $\epsilon^2$  is the microstrain density.

#### IR Spectra

The IR spectra were recorded by a Perkin-Elmer 683 spectrophotometer with KBr pressed pellets in the registration range of 1000–400 cm<sup>-1</sup>.

#### X-ray Photoelectron Spectra

The XPS analysis was carried out on a PHI 5000C ESCA X-ray photoelectron spectrometer using an Al $K_{\alpha}$ radiation source (hv = 1486.6 eV). A powdered sample was adpressed to the butt-end of a small stainless-steel cylinder and outgassed at 10<sup>-5</sup> Pa for 1 h before they were moved into the analysis chamber. The residual pressure in the ion-pumped analysis chamber was maintained below the vacuum of  $1.3 \times 10^{-7}$  Pa during data acquisition. Pretreatments in oxygen were carried out at 400°C. Energy regions of the photoelectrons were scanned at a pass energy of 20 eV. Each spectral region was scanned a number of times to obtain good signalto-noise ratios. Peak intensities were estimated by calculating the integral of each peak after subtraction of the S-shaped background and fitting to a curve mixed of Lorentzian and Gaussian lines of variable proportions. Although surface charging was observed for all the samples, accurate binding energies (BE) ( $\pm 0.2$  eV) could be determined by charge reference to the C1s peak at 285.00 eV.

### Analysis of the Valence State of Co

The total amount of Co was determined by using complexometric titration; the valence state of Co was measured by means of the oxidation state of iodine [9].

## SSA Characterization

The specific surface area (SSA) was calculated by the BET method from the nitrogen adsorption isotherms, recorded at a liquid nitrogen temperature on a Micromeritics apparatus model ST-2000, and taking a value of 0.16 nm<sup>2</sup> for the cross-sectional area of the  $N_2$  molecule adsorbed at  $-196^{\circ}$ C. Prior to the adsorption measurements, samples were outgassed at 130°C.

#### TPD and TPR Characterizations

Temperature-programmed desorption (TPD) experiments of catalysts were conducted on an automatic Micromeritics 3000 apparatus interfaced to a data station. Under  $O_2$  gas flow, catalyst samples (300 mg) were heated from ambient temperature to 950°C at a rate of 8 K/min, keeping this temperature for 1 h. When the system was cooled down to ambient temperature, He (carrier gas) was used to remove the  $O_2$  in the gas phase. Subsequently, with the ramp of 8 K/min, the curves of  $O_2$ -absorbed desorption were recorded by a TCD.

Temperature-programmed reduction (TPR) experiments were conducted on the same apparatus with TPD. Since water is produced during reduction, the gases out of the reactor were passed through a cold trap before entering the TCD. The samples (100 mg) were first heated to 950°C at a rate of 20 K/min in a flow of N<sub>2</sub> (99.9%) gas and then cooled to ambient temperature. After being 10%  $H_2/N_2$  purged for 1 h, with the ramp of 20 K/min, the curves of  $H_2$  reduction were recorded by the TCD.

#### Catalytic Activity Measurements

The catalytic activity tests (0.18–0.25 mm fraction, 250 mg catalyst) were conducted at atmospheric pressures in an automatic Micromeritics flow reactor with gaseous mixtures of 2.02% NO, 1.99% CO, and He balance, at GHSV 8000 h<sup>-1</sup>. The gas composition was analyzed before and after the reactor by an online gas chromatography with TCD and connected with a computer integrator system, using a TDX-01 column for N<sub>2</sub>, CO, and NO and a Porapak Q column for CO<sub>2</sub> and N<sub>2</sub>O. The ambient temperatures for the columns and the TCD are 50 and 75°C, respectively. The catalytic activity and the value of N<sub>2</sub> selectivity were calculated with the following respective equations:

Conversion of NO:  

$$([NO]_{in} - [NO]_{out})/[NO]_{in} \times 100\%,$$
(3)  
Selectivity of N<sub>o</sub>:

$$2[N_2]/([NO]_{in} - [NO]_{out}) \times 100\%,$$
(4)

where [NO]<sub>in</sub>, [NO]<sub>out</sub> are concentrations of NO before and after the reactor, respectively.

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**Fig. 1.** XRD patterns of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts. *T*, *T* phase; *T*\*, *T*\* phase; +, SrCO<sub>3</sub>; \*,  $Pr_2O_3$ .

# **RESULTS AND DISCUSSION**

# Crystal Structure of $Pr_{2-x}Sr_xCoO_{4\pm y}$ Catalysts

As is well-known, A2BO4 mixed oxides with a K<sub>2</sub>NiF<sub>4</sub> structure can be classified specially into two forms, i.e., a Fmmm orthorhombic phase and a I4/mmm tetragonal phase. Also, the I4/mmm tetragonal phase can be classified further into three phases  $(T, T^*, T')$ [10]. XRD patterns of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  mixed oxides are presented in Fig. 1. The results of phase analysis obtained by XRD clearly show that all  $Pr_{2-x}Sr_xCoO_{4\pm y}$ mixed oxides display K<sub>2</sub>NiF<sub>4</sub> structure under the appropriate condition. When x = 0.2 and 0.4,  $Pr_{2-x}Sr_xCoO_{4\pm y}$ mixed oxides display K<sub>2</sub>NiF<sub>4</sub> structure, which only consists of the T phase. When  $Pr^{3+}$  is substituted gradually by Sr<sup>2+</sup>, whose ionic radius ( $r_{Sr^{2+}} = 0.1310 \text{ nm}$ ) is larger than that of  $Pr^{3+}$  ( $r_{pr^{3+}} = 0.1109$  nm), the structure factor (cationic radius ratio  $r_A/r_B$ ,  $1.7 \le r_A/r_B \le 2.4$ ) increases, which leads to the structure change. In the range of  $0.6 \le x \le 1.0$ ,  $Pr_{2-x}Sr_xCoO_{4\pm y}$  display  $K_2NiF_4$ structure, which consists of the T phase and a smaller quantity of the  $T^*$  phase. However, for substitution degrees (x = 0.2 and 1.0), diffraction lines other than the K<sub>2</sub>NiF<sub>4</sub> structure are observed. These new lines of low intensity are indexed to Pr<sub>2</sub>O<sub>3</sub> or SrCO<sub>3</sub> phases, respectively.

By calculating and analyzing the correlations of lattice parameters, unit-cell volume, average crystal size, microstrain density, and x of  $Pr_{2-x}Sr_xCoO_{4\pm y}$ , as shown in Table 1, we find that the lattice parameters, the unitcell volume, and the average crystal size decrease with the increase of x; however, the microstrain density increases (Table 1).

# Infrared Spectra of $Pr_{2-x}Sr_xCoO_{4\pm y}$ Catalysts

Figure 2 depicts the observed IR spectra of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts. In the registration range of 1000–400 cm<sup>-1</sup>, all samples have the vibrational absorption band around 500 cm<sup>-1</sup>, which could be assigned to the characteristic absorption band of the K<sub>2</sub>NiF<sub>4</sub> structure of A<sub>2</sub>BO<sub>4</sub> [11], and the frequency of this band increases from sample x = 0.4 to sample x = 1.0. This result confirms that the series of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  all have the K<sub>2</sub>NiF<sub>4</sub> structure as well.

x	Structure	C	ell parameter, n	m	V nm <sup>3</sup>	<i>L</i> , nm (±0.3%)	$\epsilon^2 \times 10^3$ (±1%)
		а	b	С	<i>v</i> , IIII		
0.2	$T$ , $Pr_2O_3$	0.3815	0.3809	1.2425	0.1806	19.5	3.2
0.4	Т	0.3811	0.3805	1.2421	0.1801	18.0	3.4
0.6	<i>T</i> , <i>T</i> *	0.3802	0.3799	1.2418	0.1794	16.5	3.7
0.8	<i>T</i> , <i>T</i> *	0.3798	0.3795	1.2414	0.1789	16.2	3.8
1.0	$T, T^*, SrCO_3$	0.3791	0.3793	1.2411	0.1785	15.7	3.9

**Table 1.** Structure parameter of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts

Note: V, crystal cell volume; L, average crystalline size;  $\varepsilon^2$ , microstrain density.



**Fig. 2.** IR patterns of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts.

According to [11], the absorption band around 500 cm<sup>-1</sup> is attributed to the stretching vibration of A–O–B (i.e., Pr–O–Co) of  $A_2BO_4$  belonging to the  $A_{2u}$ vibration mode. The vibrational absorption band at 650-680 cm<sup>-1</sup> corresponds to the characteristic absorption band of the B–O (i.e., Co–O) bond in the  $K_2NiF_4$ structure. The frequency of this band increases from sample x = 0.4 to sample x = 1.0, indicating that Co–O bond distance becomes shorter and the band intensity becomes stronger. The IR spectra of this series of mixed oxides present weak absorption at 580-640 cm<sup>-1</sup>, which indicates the structure of  $Pr_{2-r}Sr_rCoO_{4+v}$ becomes deformed and the deformation of coordination polyhedra are different from x. A low intensity of deformation does not change their original structure. The absorption band appearing near 850 cm<sup>-1</sup> in the sample  $Pr_{2-x}Sr_xCoO_{4\pm y}$  (x = 1.0) could be attributed to the characteristic absorption band of SrCO<sub>3</sub> [12]. This is in accordance with the results of XRD.

# Defect Structure of $Pr_{2-x}Sr_xCoO_{4\pm y}$ Catalysts

The average valence of the Co ion and the concentration of  $\text{Co}^{3+}$  in  $\text{Pr}_{2-x}\text{Sr}_x\text{CoO}_{4\pm y}$  catalysts were determined by the titration of iodine. The nonstoichiometry oxygen (y) was calculated by using these data, and these calculations are listed in Table 2. According to the principle of electroneutrality [13], as the trivalent ion

Desorption rate, arb. units



**Fig. 3.** TPD patterns of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts.

 $(Pr^{3+})$  at the A-site is replaced by a lower valent cation  $(Sr^{2+})$ , the positive charge reduction can be balanced either by formation of a higher oxidation state ion at the B-site, i.e.,

$$\Pr_{2-x}Sr_{x}Co_{1-x}^{2+}Co_{x}^{3+}O_{4},$$

or by formation of oxygen vacancy (V<sub>0</sub>):

 $Pr_{2-x}Sr_{x}(V_{O})Co^{2+}O_{4-y},$  $Pr_{2-x}Sr_{x}(V_{O})Co^{2+}O_{4-y}.$ 

The results of the titration of iodine (Table 2) show that the two cases exist at the same time; therefore, the concentration of  $Co^{3+}$  and oxygen vacancy increase with the increase of *x*, and the charge of the mixed oxides is mainly balanced by the increasing of oxygen vacancy.

# Redox Properties of $Pr_{2-x}Sr_xCoO_{4\pm y}$ Catalysts

**TPD study.** The results of the O<sub>2</sub>-TPD investigation show that the adsorption/desorption behavior of oxygen in  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts varies with *x*. As shown in Fig. 3, peaks  $\alpha$  and  $\beta$  appear when x = 0.2 and 0.4; however, when x = 0.6-1.0, peak  $\alpha'$  can also be seen in addition to peaks  $\alpha$  and  $\beta$ . TPD profiles reveal a large oxygen peak at high temperature ( $\beta$ ) on the

**Table 2.** Nonstoichiometry oxygen (y), average valence of Co, concentration of  $\text{Co}^{n+}$ , BET areas, and composition of the  $\text{Pr}_{2-x}\text{Sr}_x\text{CoO}_{4\pm y}$  catalysts

x	Composition	Concentratio	n of Co <sup><i>n</i>+</sup> , %	Average valence		$\begin{array}{c}S_{\rm BET},{\rm m^2/g}\\(\pm2\%)\end{array}$	
		Co <sup>2+</sup> (±1%)	Co <sup>3+</sup> (±1%)	of Co	У		
0.2	Pr <sub>1.8</sub> Sr <sub>0.2</sub> CoO <sub>4.12</sub>	56	44	2.44	+0.12	2.7	
0.4	Pr <sub>1.6</sub> Sr <sub>0.4</sub> CoO <sub>4.03</sub>	53	47	2.47	+0.03	2.8	
0.6	Pr <sub>1.4</sub> Sr <sub>0.6</sub> CoO <sub>3.96</sub>	48	52	2.52	-0.04	2.9	
0.8	Pr <sub>1.2</sub> Sr <sub>0.8</sub> CoO <sub>3.91</sub>	38	62	2.62	-0.09	3.0	
1.0	PrSrCoO <sub>3.82</sub>	37	63	2.63	-0.18	3.2	

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 $Pr_{2-x}Sr_xCoO_{4+y}$  catalyst (x = 1.0) (corresponding to a desorption of  $2.3 \times 10^{-6}$  mol O<sub>2</sub>/m<sup>2</sup>) and a desorption decrease for the other four catalysts. The amount of oxygen removed in  $\beta$  peak corresponds to ~10% of the monolayer, so it can be assigned to oxygen bound with regular cobalt sites in the  $CoO_6$  octahedron, such as Co<sup>3+</sup> cations, including those in vicinity of anion vacancies. At lower temperature, the peak ( $\alpha$ ) (corresponding to  $3.4 \times 10^{-8}$  mol O<sub>2</sub>/m<sup>2</sup>) centered at about 180°C for the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalyst (x = 1.0) and at ~190–220°C for the other four catalysts is observed. The amount of  $\alpha$  form is nearly two orders of a magnitude smaller, so it certainly corresponds to oxygen bound with defect sites, such as those located at domain boundaries or associated with microstrains. Generally [14], the peak  $\beta$  may be due to the result of desorbing the chemically adsorbed oxygen  $(O_2, O_2^-)$  on the surface of the catalyst, while the peak  $\alpha'$  can be related to the chemically adsorbed oxygen (O<sup>-</sup>) in the oxygen vacancies of the catalyst. The release of vacancies oxygen can be due to the reduction of  $Co^{3+}$ :

$$2Co^{3+} + O^{2-} \longrightarrow 2Co^{2+} + 1/2O_2 + V_0.$$
 (I)

The peak  $\beta$  might be attributed to the release of oxygen  $(O^{2-})$  in the lattice of the catalyst. With the increase of x, the continuous oxygen desorption ( $\alpha$ ) at lower temperatures decreases gradually, whereas the continuous oxygen desorption ( $\beta$ ) at high temperatures increases. The results obtained by the titration of iodine show that the concentration of  $Co^{2+}$  of  $Pr_{2-x}Sr_xCoO_{4\pm y}$ catalysts decreases with the increase of x and the concentration of  $Co^{3+}$  increases. For  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts, when x = 0.2 and 0.4, the nonstoichiometry oxygen (y) is positive, indicating that there are no oxygen vacancies. However, when x = 0.6-1.0, the nonstoichiometry oxygen (y) is negative, indicating that there are oxygen vacancies, and the concentration of oxygen vacancies increases with the increase of x. This coincides with the results obtained from peak  $\alpha'$  of the TPD study.

**TPR study.** The TPR profiles of the catalyst provide useful information about the reducibility of  $Co^{n+}$  species in these  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts, since  $Pr^{3+}$  and  $Sr^{2+}$  of the A-site both are nonreducible under the con-

Hydrogen consumption, arb. units



**Fig. 4.** TPR patterns of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts.

dition of H<sub>2</sub>-TPR. As shown in Fig. 4, there are three peaks ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) for all catalysts, respectively, suggesting the occurrence of a multiple-step reduction. Conceivably, the partial substitution of Pr<sup>3+</sup> by Sr<sup>2+</sup> would result in an increase in the concentration of Co<sup>3+</sup> and oxygen vacancies due to the charge compensation accomplished by oxidation from  $Co^{2+}$  to  $Co^{3+}$  and by the formation of an oxygen-deficient perovskite-type  $A_2BO_4$ , which would lead to an increase in the reducibility. The amount of  $H_2$  related to the peak  $\beta$  ranges from 0.22 to 0.31 mol H<sub>2</sub>/mol M (M in substituted samples refers to the total amount of transition-metal cations), the maximum value being given by  $Pr_{2-x}Sr_xCoO_{4+y}$  catalyst (x = 1.0). However, the H<sub>2</sub> consumption of peak  $\alpha$  varies from 1.22 to 1.32 mol H<sub>2</sub>/mol M with the increase of x. Thus, the peak  $\alpha$  corresponds to reduction of the chemisorption oxygen. The peak  $\beta$ could be attributed to the partial reduction of  $Co^{3+}$ , i.e.,

$$2Co^{3+} + O^{2-} + H_2 \longrightarrow 2Co^{2+} + H_2O,$$
 (II)

and  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts still preserved in the perovskite-type phase structure as a whole. The peak  $\gamma$  most likely corresponded to the reduction of Co<sup>2+</sup> to Co<sup>0</sup>, which led to the breakdown of the perovskite-type phase and formation of the discrete phases Pr<sub>2</sub>O<sub>3</sub>, SrO, and Co.

**XPS study.** The binding energies  $(E_b)$  of various component elements in  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts obtained from XPS investigation are shown in Table 3.

x	$E_{\rm b}, {\rm eV}^*$					Surface catio	Co/(Pr+Sr),			
	Pr	3 <i>d</i>	Sr 3d 5/2	Co 2 <i>p</i> 3/2	0	1 <i>s</i>	Pr	Sr	Со	mol/mol
0.2	933.4	954.6	133.5	780.7	528.9	_	34	27	39	0.65
0.4	933.8	954.3	133.7	780.6	528.7	-	30	29	42	0.72
0.6	933.6	954.9	134.1	780.3	529.0	530.8	26	30	44	0.77
0.8	934.0	955.2	134.3	779.8	529.1	531.2	20	34	46	0.86
1.0	933.9	955.1	133.9	779.5	528.8	531.1	14	36	50	0.98

**Table 3.** XPS  $E_b$  and surface composition of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts

\* Calibrated internally by the carbon deposit C1s at 285.00 eV ( $E_{\rm b}$ ).





**Fig. 5.** XPS patterns of O1*s* of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts.



**Fig. 6.** Catalytic activity as a function of x in the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts for reduction of NO by CO: (1) 50% conversion and (2) 100% conversion.

**Fig. 7.** Influence of the substitution degree (*x*) on the intrinsic activity of the  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts for reduction NO by CO at reaction temperature (*1*) 220, (2) 250, and (*3*) 280°C.

The values of  $E_{\rm b}$  of these component elements are in good agreement with those reported in the literature [15, 16]. The results obtained from XPS investigation show that the measured  $E_{\rm b}$  for Co 2*p*3/2 deviates gradually from the value of Co<sup>2+</sup> ( $E_{\rm b}$  = 781.2 eV) with the

increase of x, which is in accord with the varieties of the surface concentration of Co2+ and Co3+ and the Co average valence in Table 2. The O1s spectra of Pr2- $_{x}$ Sr<sub>x</sub>CoO<sub>4±v</sub> catalysts are shown in Fig. 5. There are only peaks approaching the BE (529 eV) when x = 0.2and 0.4; however, the O1s spectra of  $Pr_{2-x}Sr_xCoO_{4\pm y}$ catalysts, when x = 0.6-1.0, included two peaks, and the peak areas approaching the BE (531 eV) increase with the increase of x. As commonly accepted [17], the peak of O1s spectra of  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts approaching the BE (529 eV) may be ascribed to the lattice oxygen species,  $O^{2-}$ (lattice), and the peak of O1scurves approaching the BE (531 eV) may originate from the adsorbed oxygen species such as  $O_{ads}^-$ , i.e., the oxygen chemically adsorbed on oxygen vacancies. According to Wagner et al. [18] for the Mg $K_{\alpha}$  source, the molar percentage of cations of the three kinds of component elements on the surface is estimated and also listed in Table 3. Table 3 shows that the Co/(Pr + Sr) surface ratios for the samples are much higher than expected, considering the nominal compositions, and increase gradually with the increase of x. These results suggest that enrichment of the Co cation on the surface occurred for all samples, and that the surface concentration of Co increased with the increase of x.

# Catalytic Activity of $Pr_{2-x}Sr_xCoO_{4\pm y}$ Catalysts

Figure 6 depicts the variations of 50 and 100% conversion for NO reduction by CO over  $Pr_{2-x}Sr_xCoO_{4\pm y}$ catalysts versus x. It can be seen that the activity of all samples increases monotonously with the increase of x. At the order of x = 0.2, 0.4, 0.6, 0.8, and 1.0, their N<sub>2</sub> selectivity values are 27, 30, 35, 42, 56% at 250°C and 58, 69, 74, 82, 91% at 300°C, respectively. The results of N<sub>2</sub> selectivity of these catalysts are similar to the results of catalytic activity. Since the BET area (Table 2) varies from sample to sample, activity is normalized to the BET area. Figure 7 shows the strong influence of the temperature and substitution degree on the intrinsic activity. The rate is calculated per unit surface area and increases with the increase of x, for which the oxygen vacancy increases with the increase of x. The reduction mechanism over  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts, a proposed mechanism of NO reduction by CO is presented as follows [19]:

$$Co^{3+}-O-Co^{3+}+CO \longrightarrow Co^{2+}-V_O-Co^{2+}+CO_2$$
, (III)

$$\text{Co}^{2+}-\text{V}_{\text{O}}-\text{Co}^{2+} + \text{NO} \longrightarrow \text{Co}^{3+}-\text{V}_{\text{O}}(\text{NO}^{-})-\text{Co}^{2+}, \text{ (IV)}$$

$$Co^{3+}-V_O(NO^{-})-Co^{2+} \longrightarrow Co^{3+}-O-Co^{3+}+N_{ads}, (V)$$

$$2N_{ads} \longrightarrow N_2.$$
 (VI)

It is found that the catalytic activity is closely correlated with oxygen vacancy for NO reduction by CO over  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts.

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### CONCLUSIONS

The perovskite-type  $Pr_{2-x}Sr_xCoO_{4\pm y}$  ( $0.2 \le x \le 1.0$ ) mixed oxides of  $K_2NiF_4$  structure have been prepared by the polyglycol gel method. All mixed oxides display  $K_2NiF_4$  structure; when x = 0.2 and 1.0, the obtained samples still have a trace of other mixed oxides; however, the mixed oxides with x = 0.4, 0.6, and 0.8 are the phase  $A_2BO_4$ . With the increase of x, lattice parameters, unit-cell volume, and average crystalline size decrease gradually; microstrain density, the concentration of  $Co^{3+}$ , the amounts of lattice oxygen released, and the concentration of oxygen vacancy increase gradually. The  $Pr_{2-x}Sr_xCoO_{4\pm y}$  catalysts possess different catalytic activities towards the NO reduction by CO, and their catalytic activities are closely correlated with oxygen vacancy and the concentration of  $Co^{3+}$ .

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