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CO GAS SENSITIVITIES OF REDUCED PEROVSKITE OXIDE $LaCoO_{3-x}$

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The detection of CO gas was studied using $LaCoO_{3-x}$ as a sensing material which was obtained by reduction of $LaCoO_3$ in a hydrogen atmosphere at 500 °C. $LaCoO_{3-x}$ exhibits the change of the resistivity at low temperatures in the presence of hydrogen and has a sensitivity-temperature profile with a maximum at about 100 °C. CO adsorption causes a decrease in the resistivity of $LaCoO_{3-x}$ as in the case of O_2 adsorption although $LaCoO_{3-x}$ is a p-type semiconductor.

The detection of CO as a toxic gas is a matter of urgent public concern. Especially, the selectivity for CO gas sensing is an important factor for practical CO gas sensors. CO gas sensors have been studied in the following systems; Pt/Antimonic Acid/Pt,[1)] Au-TiO_2-Fe_2O_3,[2)] and $LaFeO_3$ and related perovskite oxides.[3)] Activities for CO gas detection is closely related with those for catalytic oxidation of CO on the semiconductors. On the contrary, the detection of CO on reduced perovskite oxides($LnCoO_{3-x}$) has been rarely studied, although CO gas adsorption on $LaCoO_3$ was reported.[4)] In this paper, the characteristics of CO gas sensing of $LaCoO_{3-x}$ which was obtained by reduction of $LaCoO_3$ in a hydrogen atmosphere at 500 °C are mainly presented.

A thin oxide film of $LaCoO_3$ for electrical measurements was prepared using a procedure similar to that reported previously.[5)] The thin film was set in a pyrex glass tube and a gaseous mixture(40 ml/min) of $N_2 + O_2$ or $N_2 + H_2$ was fed into the tube. 10 V was applied across the oxide thin film. Carbon monoxide(2.5×10^{-2} mmol; purity >99.99%) was introduced at an injection port, and the induced resistivity changes of the $LnCoO_3$ films were recorded as the variation of direct current. A temperature programmed desorption(TPD) apparatus used in this study was the same as that reported previously.[6)]

The addition of CO to the carrier gas(N_2) caused a change in the electrical resistance of the $LnCoO_3$(Ln = La-Eu) thin film. The temperature dependence of the sensitivity is shown in Fig. 1. Under the experimental conditions used $LaCoO_3$ did not show the activity for CO sensing. $NdCoO_3$, $SmCoO_3$, and $EuCoO_3$ have a sensitivity-temperature profile with a maximum at about 400 °C, 440 °C, and 450 °C, respectively. When the activity for CO sensing was given by the sensitivity at 400 °C, $NdCoO_3$ shows the highest activity. The sequence of the activity for CO sensing is different from that for methanol sensing.[5)] Rao et al. have pointed out that among rare earth cobaltites $NdCoO_3$ showed the highest catalytic activity for oxidation of CO to CO_2.[7] Since $LnCoO_3$ has p-type semiconductivities, chemisorption of CO must lead to an increase in the electrical resistance of the oxide, as observed.[5] The reaction product in the outlet gas was CO_2. The resistivity change caused by the injection of CO may be represented by Eq. 1.[5]

$$CO(g) + O^{2-}(s) \longrightarrow CO_2(s) + 2e^- . \quad (1)$$

where (s) denotes a surface species and (g) a gaseous species. An electron liberated upon CO adsorption causes a decrease in the conductivities of $LnCoO_3$ by reacting it with a free hole.

As Fig. 1 shows, $LaCoO_3$ did not exhibit any appreciable activities. In contrast, $LaCoO_{3-x}$ ($x = 0.77$), which was obtained by reduction of $LaCoO_3$ in a hydrogen atmosphere(10 H_2 + 90 N_2 ; 40 ml/min) at 500 °C, showed appreciable activities for CO sensing at relatively low temperatures in a dilute hydrogen atmosphere and a sensitivity-temperature profile exhibited a maximum at about 100 °C as shown in Fig. 2(a). In Fig. 2(b), typical response behaviors of $LaCoO_{3-x}$ are also included. The injection of CO caused an immediate decrease of the resistivity which was followed by restoration to the initial value. The resistivity change of $LaCoO_{3-x}$ in this case showed a reverse tendency to that of $LnCoO_3$ as described above and was similar to that observed on O_2 adsorption, although $LaCoO_{3-x}$ is a p-type semiconductor.[8] The product found in the outlet gases was only CO_2.

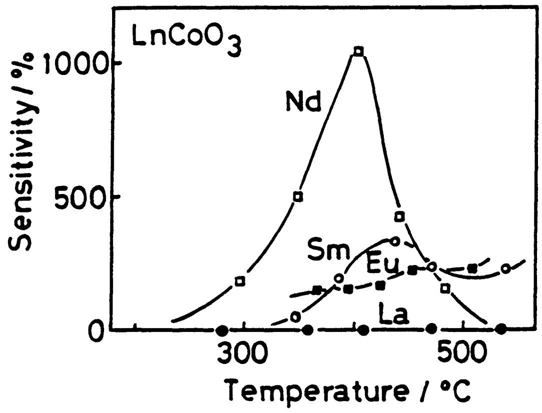

Fig. 1. Sensitivity as a function of temperature for CO adsorption. Carrier gas N_2(40 ml/min, contained $O_2 \simeq 50$ ppm). $\text{Sensitivity} = \left|\frac{R - R_o}{R_o}\right| \times 100(\%)$, R_o : the resistance in steady gas flow, R : the maximum resistance after CO adsorption.

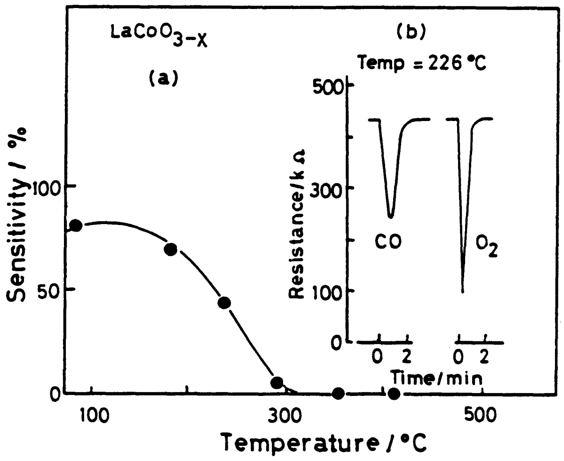

Fig. 2. Sensitivity as a function of temperature for CO adsorption in dilute hydrogen atmosphere. N_2(95 vol%) + H_2(5 vol%); 40 ml/min. The concentration of the injected O_2 was 2.5×10^{-2} mmol.

The production of CO_2 in the course of CO gas sensing of $LaCoO_{3-x}$ may be resulted either from a reaction of CO with lattice oxygens which did not react with hydrogen at 500 °C or from disproportionation of CO on the surface of the reduced oxide. It has been reported that disproportionation of CO occurs on several kinds of metal-supported catalysts.[9] Since the reduction of $LaCoO_3$ results in an oxy-

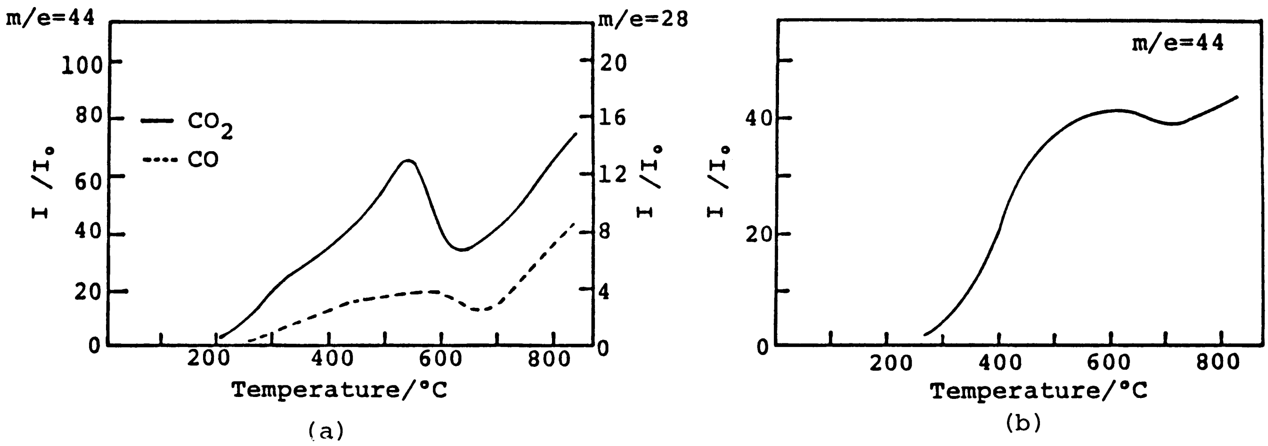

Fig. 3. TPD chromatograms given by relative sensitivity of the mass 28(CO) and 44(CO_2) to the mass 28 of $LaCoO_{3-x}$(x =0.77) after CO adsorption at 195 K. Before TPD experiments, the samples were reduced in H_2(1.33×10^4 Pa) for 1 h at 500 °C, evacuation($\simeq 10^{-4}$ Pa) for 15 min at 500 °C and cooling to 195 K in vacuo. (a) : exposed to CO(1.33×10^4 Pa) for 30 min and then degassing for 30 min. (b): coadsorption of H_2 (H_2/CO = 2/1, 3.33×10^4 Pa). Heating rate was 1.33 K/s.

gen-deficient perovskite oxide containing divalent cobalt ions and the produced oxide is not reduced by CO at low temperatures such as 100 °C,[10] the following disproportionation reaction of CO on $LaCoO_{3-x}$ seems likely to occur.

$$2(CO)_{ad} \longrightarrow C_{surf.} + (CO_2)_{ad} \qquad (2)$$

The chemisorption of CO on $LaCoO_{3-x}$ was investigated by means of the temperature programmed desorption method. Typical TPD chromatograms are shown in Fig. 3. It is suggested from the appearance of two TPD peaks with its maxima about 600 °C and >600 °C that there are at least two different states of adsorbed CO. Moreover, the CO_2 production was always accompanied by the desorption of CO. It seems then likely that desorbed CO_2 was resulted from the disproportionation reaction given by Eq. 2. The disproportionation reaction on $LaCoO_{3-x}$ was not disturbed by coadsorbed hydrogen(Fig. 3(b)). The produced CO_2, given by Eq. 2, changes into $CO_2{}^{\delta-}$ on the surface of the reduced oxide.

$$(CO_2)_{ad} + \delta e^- (\text{from the reduced sample}) \longrightarrow (CO_2)^{\delta-}_{ad} \qquad (3)$$

The decrease of the resistivity in Fig. 2(b) may be brought about by that a part of electrons which are consumed in the recombination with holes are utilized in the reaction given by Eq. 3. Since the product in outlet gases was only CO_2, the restoration of the resistivity in Fig. 2 must be due to desorption of CO_2. The utility of $LaCoO_{3-x}$ as a CO sensor may be limited oxygen-deficient atmospheres, however, because $LaCoO_{3-x}$ exhibits also appreciable activities to O_2 as shown in

Fig. 2(b). Further studies to investigate these interesting problems are in progress.

References

1) N. Miura, H. Kato, H. Kaneko, and N. Yamazoe, Nippon Kagaku Kaishi, in press.
2) T. Kobayashi, M. Haruta, H. Sano, and N. Nakane, private communication.
3) W.B. Li, H. Yoneyama, and H. Tamura, Nippon Kagaku Kaishi, 1982, 761.
4) J.M.D. Tascón and L.G. Tejuca, Z. Phys. Chem. Neue Folge, 121, 63(1980).
5) T. Arakawa, H. Kurachi, and J. Shiokawa, J. Mater. Sci., 20, 1207(1985).
6) T. Arakawa, M. Takakuwa, T. Takata, and J. Shiokawa, Mater. Res. Bull., 19, 429(1984).
7) Om Parkash, P. Ganguly, G. R. Rao, C.N.R. Rao, D.S. Rajoria, and V.G. Bhide, Mater. Res. Bull., 9, 1173(1974).
8) The Seebeck voltage was measured using a homemade apparatus. The temperature differences along the sample of 5 °C was used. The measurements were made in N_2 + H_2(5 vol%) for $LaCoO_{3-x}$. The Seebeck voltages in μV/K are : $LaCoO_{3-x}$(x = 0.77). -0.037(100 °C), -0.031(200 °C). Thus, it is suggested that mobile holes in $LaCoO_{3-x}$ are dominant carriers.
9) R.W. Joiner, and N.W. Roberts, J. Chem. Soc., Faraday Trans. 1, 70, 1919(1974); H. Yamasaki, Y. Kobori, S. Nito, T. Onishi, and K. Tamaru, ibid., 77, 2193(1981); S. Ichikawa, H. Poppa, and M. Boudart, J. Catal., 91, 1(1985).
10) T. Arakawa, N. Ohara, and J. Shiokawa, Chem. Lett., 1984, 467.

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