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CO_2 Sensing Mechanism of La_2O_3-loaded SnO_2

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The title mechanism was investigated by temperature programmed desorption (TPD). The TPD profile from La_2O_3-loaded SnO_2 consisted of two CO_2 peaks (450 K (α) and 650 K (β)) and one O_2 ascent. From the correlations among the amounts of β-CO_2 and O_2 desorbed, the amount of La_2O_3 loaded, and the sensitivity to CO_2, it was suggested that the decrease in the resistance of the sensor results from the adsorption of β-CO_2 and the desorption of O^- or O^{2-} to generate oxygen molecules and free electrons.

Various materials including the solid electrolyte,[1-3] mixed oxide capacitor,[4] K_2CO_3-polyethylene glycol solution supported on porous ceramics,[6] hydroxyapatite,[7] and n-type semiconductors[8-10] have been reported as the candidates for the CO_2 gas sensor. Recently, Tamaki et al. and we have reported that the oxides such as SnO_2,[8] La_2O_3-loaded SnO_2,[9] and CaO-loaded In_2O_3,[10] have a possibility to provide a simpler and more feasible CO_2 sensor system. Although the two reports[8,9] concern the SnO_2-based semiconductors, it should be noted that the electric resistance of the SnO_2 sensor increased on the introduction of CO_2-containing air at 373 - 438 K[8] while that of the La_2O_3-loaded SnO_2 element decreased at 673 K.[9] Therefore the elucidation of the CO_2 sensing mechanism is of great importance to develop the more effective sensors. Here we have studied the CO_2 sensing mechanism of La_2O_3-loaded SnO_2 element mainly by a temperature programmed desorption (TPD) technique.

SnO_2 powder was obtained from the Catalysis Society of Japan. The La_2O_3-loaded SnO_2 sensor element was prepared by the impregnation of the parent oxide element by coating aqueous solution of La nitrate with a brush unless otherwise noted.[9] Sample gas contains 2080 ppm CO_2 and dry air was used as balance. Hereafter the amount of lanthanum loaded is calculated and expressed by assuming the composition of La_2O_3. Prior to resistance measurements, each element was exposed to dry air (60 $cm^3 \cdot min^{-1}$) at 773 K for 1 h. The resistance was measured at 573 - 773 K. The sensitivity to CO_2 was defined as the ratio of resistance of an element in air containing no CO_2 to that in a diluent CO_2 gas, R_{air}/R_{CO_2}. The TPD experiments of oxygen and CO_2 were carried out on a powder sample shaved off from the element. After being mounted in the TPD cell, the sample was treated in dry air at 773 K for 1 h followed by the cooling to room temperature in the same atmosphere. Then the sample was kept in the dry air stream for 1 h in the case of TPD of O_2 alone, or in the dry air + CO_2 (2080 ppm) stream for 1 h in the TPD of CO_2 and O_2. The TPD profile was obtained at a heating rate of 10 $K \cdot min^{-1}$ in a He stream (60 $cm^3 \cdot min^{-1}$). Small portions of the gases desorbed were led into a stainless steal sampler at regular intervals and analyzed with a gas chromatograph using Porapack Q and Molecular Sieve

5A columns.

Figure 1 shows the TPD profiles from La_2O_3(4.1 wt%)-SnO_2 exposed to a CO_2 + dry air stream at room temperature. The profile consisted of two desorption peaks of CO_2 around 450 K (α-CO_2) and 650 K (β-CO_2) and one ascent of O_2 desorption. Based on the IR measurements of CO_2 adsorbed on pure SnO_2 sample,[11] α-CO_2 can be attributed to the carbonate or bicarbonate species. The adsorbed species corresponding to β-CO_2 is unknown. The IR studies to make β-CO_2 clear are in progress. The ascent of O_2 is assignable to the desorption of O^- or O^{2-} similarly to that of SnO_2.[12]

The results of CO_2 desorption from the other La_2O_3-loaded SnO_2 samples are summarized in Fig. 2. The desorption peaks of O_2 were not shown to avoid the complicated Fig. 2. Clearly, all La_2O_3-SnO_2 samples prepared with a brush gave two desorption peaks of CO_2, while SnO_2 or La_2O_3-SnO_2 prepared by the incipient wetness method gave only one desorption peak around 473 K (α-CO_2). The profile from SnO_2 is in good agreement with that previously reported.[8] Thus, the addition of La_2O_3 with a brush produced the site for the adsorption of β-CO_2. It was reported that $La_2(CO_3)_3$ decomposes to $La_2O_2CO_3$ at 701 - 758 K and further to La_2O_3 at 1179 - 1203 K[13]: The role of La_2O_3 added should be clarified.

The surface La/Sn atomic ratio obtained by XPS for La_2O_3(3.5 wt%)-SnO_2 element prepared with a brush was about ten times greater than that of La_2O_3(4.0 wt%)-SnO_2 element prepared by the incipient wetness method. The

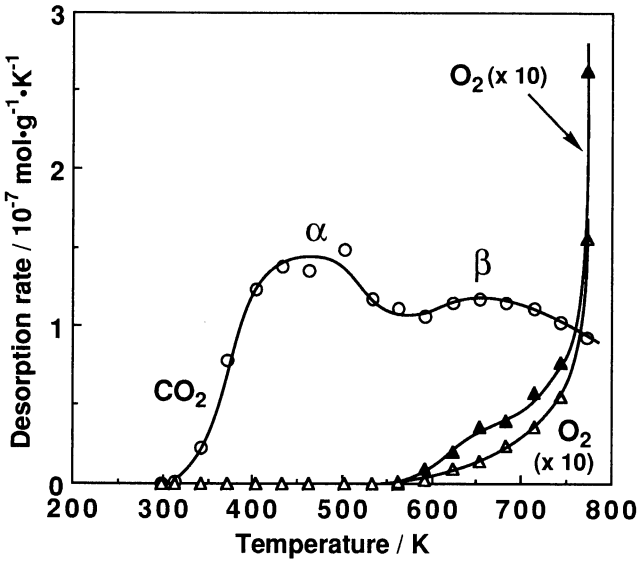

Fig. 1. TPD profile of CO_2 and O_2 from La_2O_3(4.1 wt%)-SnO_2 exposed to 2080 ppm CO_2 in dry air (○ and △) or to dry air alone (▲) at room temperature.
○, CO_2; △ and ▲, O_2.

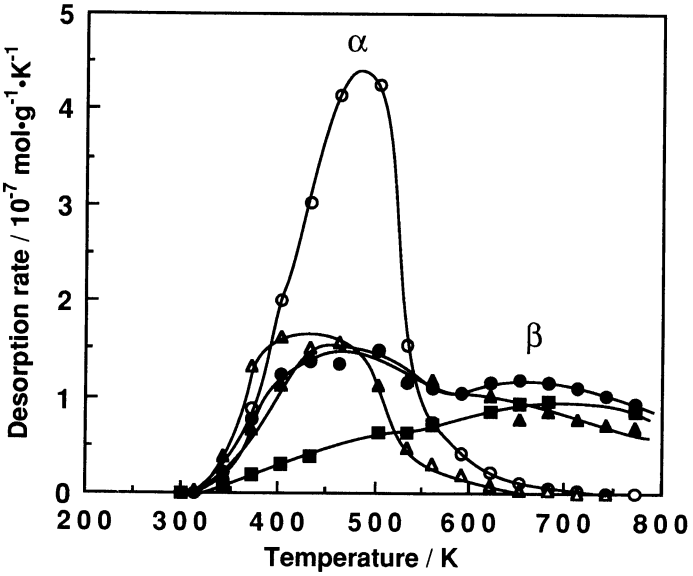

Fig. 2. TPD profile of CO_2 after exposure to 2080 ppm CO_2 (in dry air) at room temperature.
○, ▲, ●, and ■ correspond to La_2O_3-SnO_2 samples with the loading amount of La_2O_3 of 0.0 (pure SnO_2), 2.8, 4.1, and 9.6 wt%, respectively. △, La_2O_3(4.0 wt%)-SnO_2 prepared by the incipient wetness method.[9]

distribution of La may result in the different TPD profiles of CO_2.

We have presented previously that the resistance of La_2O_3-SnO_2 element decreased on the exposure to 2080 ppm CO_2 at 673 K, while the resistance of SnO_2 element little changed.[9] It was also reported that the resistance of SnO_2 increased on the introduction of CO_2 at 373 - 438 K.[8] The difference of the sensitive temperature regions to CO_2 between SnO_2 and La_2O_3-SnO_2 elements and the TPD results in Fig. 2 suggest that at the operation temperature of 673 K, β-CO_2 is responsible for the change in the resistance and not α-CO_2. This is strongly supported by the finding that La_2O_3-SnO_2 prepared by the incipient wetness method shows little change in resistance on the exposure to CO_2,[9] and has no β-CO_2 peak in the TPD profile (Δ, Fig. 2).

The sensitivity and the amount of β-CO_2 desorbed between 573 - 773 K are plotted against the amount of La_2O_3 loaded in Figs. 3a and 3b, respectively. Similar volcano-shaped dependencies on the amount of La_2O_3 loaded were observed for the sensitivity and the amount of β-CO_2, and the maximum of the former is in harmony with that of the latter. The correlations bear out that the sensitivity of the La_2O_3-loaded SnO_2 element at 673 K depends on the amount of β-CO_2.

From the comparison of Δ with ▲ in Fig. 1, it is clear that the amount of O_2 desorbed below 773 K decreased when CO_2 adsorption was carried out at room temperature on the O_2-preadsorbed surface. The amount of the decrement of O_2 desorption is plotted as a function of the amount of β-CO_2 in Fig. 4. It increased with the amount of β-CO_2, suggesting that the decrease in the amount of

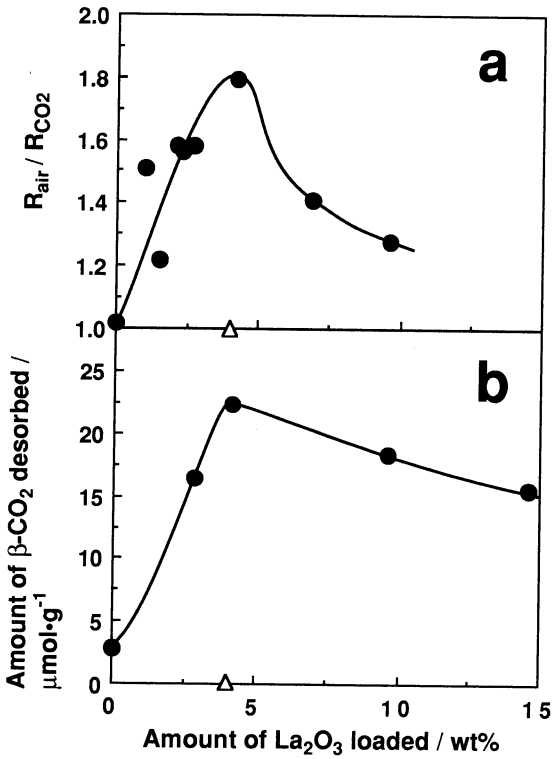

Fig. 3. Correlation between the sensitivity or the amount of β-CO_2 and the amount of La_2O_3 loaded.
●, La_2O_3-loaded SnO_2; Δ, the same as that in Fig. 2. The sensitivity was measured at 673 K and cited from ref. (9).

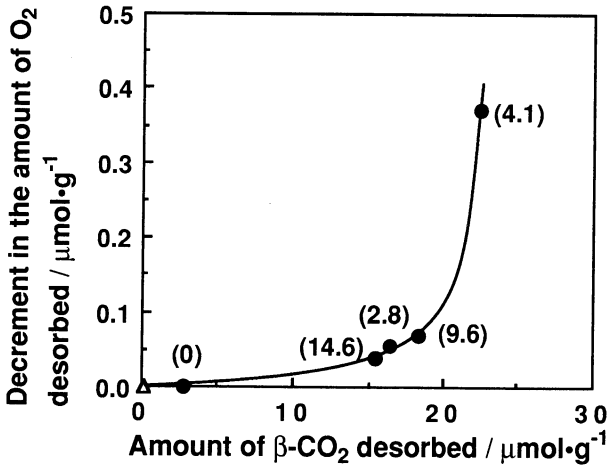

Fig. 4. Relationship between the decrement in the amount of O_2 desorbed (≤ 773 K) and the amount of β-CO_2 desorbed.
● and Δ, the same as that in Fig. 3. Numbers in parentheses were the amounts of La_2O_3 loaded.

O_2 desorption is caused by the adsorption of β-CO_2.

The resistance of La_2O_3-SnO_2 element increased and decreased to the original level in the presence and absence of oxygen at 673 K, respectively. The fact indicates that the La_2O_3-SnO_2 element is a n-type semiconductor. On the basis of above results, the decrease in the resistance of La_2O_3-loaded SnO_2 element on the exposure to CO_2 gas at 673 K can be understood by the following reaction,

$$2O^-(a) \text{ (or } 2O^{2-}(a)) + CO_2(g) \longrightarrow O_2(g) + (\beta\text{-})CO_2(a) + 2e \text{ (or } 4e).$$

Namely, the adsorption of β-CO_2 results in the desorption of oxygen negatively charged and the release of electrons. When the working temperature of the sensor is low, the α-CO_2 species would take part in the response for CO_2 by the following reaction as previously reported,[8]

$$O^- + CO_2 + e \longrightarrow CO_3^{2-}.$$

The adsorption of CO_2 would form a carbonate species and bring about the increase of the electric resistance.

All the findings in this work lead to the conclusion that the decrease in the resistance of semiconductors at 673 K upon the exposure to CO_2 gas results from the adsorption of β-CO_2 and the desorption of O^- or O^{2-} to generate oxygen molecules and free electrons.

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