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La_2O_3-loaded SnO_2 Element as a CO_2 Gas Sensor

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Among SnO_2 elements modified by various metal oxides, La_2O_3-loaded SnO_2 element was found to show promising sensing properties to CO_2 in dry air at 673 K, rather high sensitivity and quick response. The sensitivity to CO_2 depended on the operation temperature and the amounts of metal oxides loaded. A linear relationship between the sensitivity and the concentration of CO_2 was observed for La_2O_3-loaded SnO_2 element.

Detecting the concentration of CO_2 at ppm level by a simple method has been desired not only in various industrial processes but also in environmental technology.[1-7] Although semiconductor gas sensors have been widely used for detecting CO, town gas, or LPG in air, they are not useful for sensing CO_2 because much less reactivity of CO_2 causes no change of the properties of oxides. At present, solid electrolyte,[1,3] mixed oxide capacitor,[4,5] and K_2CO_3-polyethylene glycol solution supported on porous ceramics[7] have been reported to show good sensing properties for the CO_2 detection. These sensors, however, have more complex structure than that of oxide resistors. Therefore, if the resistance of metal oxides changes much with the concentration of CO_2, the metal oxides will be able to provide a simpler and more feasible CO_2 sensor system. Here we wish to report a promising sensing ability of La_2O_3-loaded SnO_2 element.

The structure of the sensor element fabricated is the same as that reported elsewhere.[8] SnO_2 powder was obtained from the Catalysis Society of Japan. The powder was impregnated with various metal oxides in three different ways (I) - (III). In the procedures I and II the SnO_2 powder was mixed with water and the resulting paste was applied on an alumina tube having two Pt-wire electrodes, and calcined at 973 K for 4 h. Then the resultant element was impregnated with aqueous solution of metal nitrate or acetate by coating with a brush (I), or by soaking the element into the solution (II). The elements were dried and again calcined at 773 K for 5 h before use. In the procedure III the SnO_2 powder was first impregnated with aqueous solution of metal nitrate by an incipient wetness method and dried. The resulting powder was applied on an alumina tube after being mixed with water into paste, and calcined at 973 K for 4 h. Sample gas containing 2080 ppm CO_2 in dry air balance was commercially obtained. It was confirmed that no water vapor was detected in the gas by gas chromatography. Prior to each resistance measurement, each metal oxide-

loaded SnO_2 element was exposed to dry air (60 $cm^3 \cdot min^{-1}$) at 773 K for 60 min. A CO_2 gas (≤ 2080 ppm, dry air balance, 60 $cm^3 \cdot min^{-1}$) was then introduced. The sensitivity to CO_2 was defined as the ratio of resistance of an element in dry air to that in a sample gas, R_{air}/R_{CO_2}.

At first effect of the sample preparation methods was examined. The sample prepared by the method I showed the highest sensitivity to CO_2. This would be due to the difference of the distribution of the additives, though the reason should be clarified in the future study. In addition, the reproducibility of the results on samples prepared by the method I is very good; therefore, the procedure I is preferentially employed hereafter.

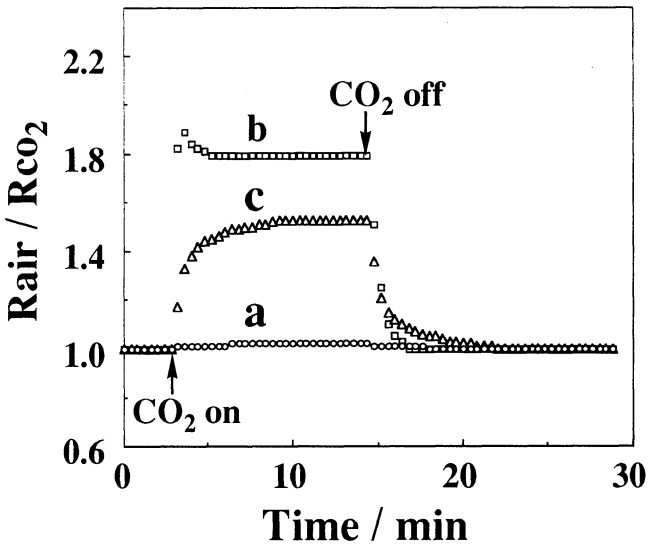

Fig. 1. Response transients to 2080 ppm CO_2 on the pure, La_2O_3-, and SrO-loaded SnO_2 elements at 673 K. (a) Pure SnO_2. (b) La_2O_3(4.2 wt%)-SnO_2. (c) SrO(1.1 wt%)-SnO_2.

Figure 1 shows response transients to 2080 ppm CO_2 at 673 K on the pure, La_2O_3-, and SrO-SnO_2 elements. On turning CO_2 flow on the resistance of each sensor decreased more or less. The sensitivity of pure SnO_2 element was small (R_{air}/R_{CO_2} = 1.02). On the other hand, the sensitivity of La_2O_3- or SrO-loaded SnO_2 elements show higher sensitivity to CO_2 than pure SnO_2 element. Repeating turning-on and -off little changed the response transient of La_2O_3- or SrO-loaded SnO_2 elements. The decrease in the resistance by the exposure of the element to the CO_2 flow may be due to the desorption of O^- or O_2^- by the adsorption of CO_2 to yield oxygen molecules and free electrons. Further mechanistic studies on the CO_2 sensing of these elements are in progress.

The sensing properties for 2080 ppm CO_2 at 673 K was compared among the SnO_2 elements loaded with various metal oxides. Table 1 summarized the sensitivity and the 90% response time. R_{air}/R_{CO_2} increased by the loading of metal oxides on SnO_2, except for the K_2O-loaded SnO_2 element, approximately in the following order; SnO_2 only ≈ alkaline metal oxides ≤ transition metal oxides < alkaline earth oxide ≤ rare earth oxides. The order is of interest and probably related with the sensing mechanism though the details would be clarified by the experiments in progress. Among the elements listed in Table 1, the La_2O_3-loaded SnO_2 element showed the highest sensitivity to CO_2 at 673 K, R_{air}/R_{CO_2} = 1.79. On the other hand, 90% response times are much improved by the addition of rare earth oxide, while become longer by the addition of alkaline earth oxide. For example, La_2O_3-loaded SnO_2 element the response to turning CO_2 on was so quick (90% response time was about 0.4 min) and the response to turning-off (time to recover the initial level completely) was within 2 min. These

Table 1. CO_2 sensing characteristics[a] of metal oxide-loaded SnO_2 element at 673 K

Metal oxide	Amount of metal oxide loaded / wt%	R_{air} / R_{CO_2}	90% Response time[b] / min
Pure SnO_2	-	1.02	2.4
Li_2O	0.6	1.41	0.7
Na_2O	5.9	1.02	0.3
K_2O	2.8	0.82	-
MgO	0.6	1.24	7.8
CaO	1.3	1.53	4.3
SrO	1.1	1.53	4.2
BaO	0.5	1.68	4.5
Cr_2O_3	1.2	1.33	2.6
Fe_2O_3	0.5	1.34	1.4
CoO	2.4	1.17	2.7
NiO	1.4	1.32	3.4
CuO	1.8	1.16	1.4
ZnO	2.9	0.97	-
La_2O_3	4.2	1.79	0.4
Pr_2O_3	3.4	1.54	0.5
Nd_2O_3	4.2	1.76	0.4

a) CO_2 concentration, 2080 ppm. b) 90% Response time for the increase of CO_2 concentration.

results, i.e., rather high sensitivity and rapid response to CO_2, indicate that La_2O_3-loaded SnO_2 element has a promising salient feature as a CO_2 gas sensor. Hereafter the La_2O_3-loaded SnO_2 element is investigated in more detail.

The sensing ability of La_2O_3-loaded SnO_2 element depended on the operation temperature. In the range of operation temperature 633 - 773 K, the sensitivity and 90% response time decreased with the increment in the operation temperature.

The sensor characteristics depended not only on the operation temperature but also on the amount of metal oxide loaded. The

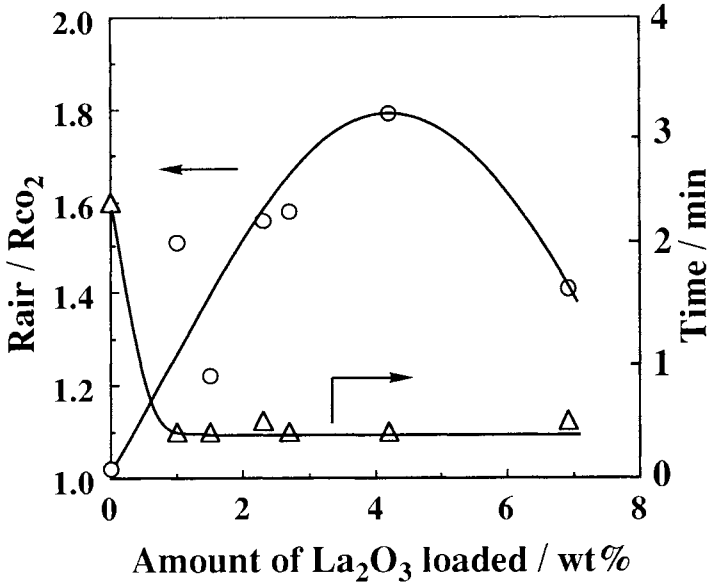

Fig. 2. Dependence of sensitivity (○) and 90% response time (△) of La_2O_3-loaded SnO_2 element on the amounts of La_2O_3 loaded at 673 K.

dependence of the sensitivity and 90% response time of La_2O_3-loaded SnO_2 element on the amount of La_2O_3 loaded is shown in Fig. 2. The sensitivity (○) of La_2O_3-SnO_2 element at 673 K increased monotonously in the range of the amount of La_2O_3 loaded 0 - 4.2 wt% and decreased beyond 4.2 wt%. The 90% response time (△) was much decreased by the loading of 1.0 wt% La_2O_3 and was not changed with more loading.

The sensitivity of La_2O_3-loaded SnO_2 element is depicted in Fig. 3 as a function of CO_2 concentration. Clearly, below 2080 ppm a linear relationship between the sensitivity and the concentration of CO_2 can be recognized. The correlation enables us to measure the concentration of CO_2 by the change in the resistance of the sensor element.

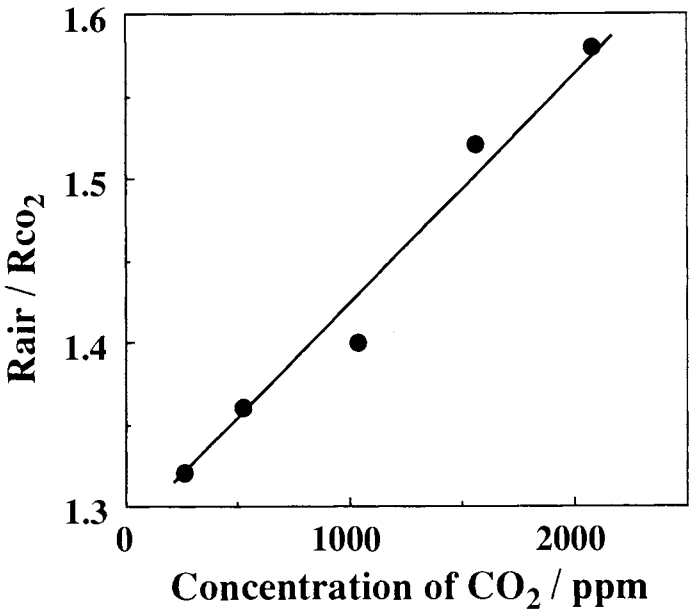

Fig. 3. Dependence of sensitivity of La_2O_3(2.7 wt%)-loaded SnO_2 element on the CO_2 concentration at 673 K.

In conclusion, the CO_2 sensing property of SnO_2 element was improved by the loading of various metal oxides; in particular, La_2O_3-SnO_2 showed the rather high sensitivity and the quick response.

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