CO$_2$ Sensing Properties of Zr-Added Porous CaFe$_2$O$_4$ Powder

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The gas sensing properties of Zr-added and pure CaFe$_2$O$_4$ powders for CO$_2$ in air were examined in the temperature range of 250–450 °C. The semiconductor-type gas sensor made from pure CaFe$_2$O$_4$ powder showed a fairly good response to CO$_2$. Furthermore, the addition of a small amount of Zr into CaFe$_2$O$_4$ powder was found to be effective for enhancing the CO$_2$ response of the present gas sensor. It was also found that the gas response, defined by the ratio of the resistance in air and that of the target gas reached maximum at the operating temperature of 300 °C. The gas response of the Zr-added CaFe$_2$O$_4$-based sensor at 300 °C was estimated to be 2.5 times higher than that of the sensor made from pure CaFe$_2$O$_4$ powder. However, the 90% response time of the Zr-added CaFe$_2$O$_4$-based sensor was much quicker at 350 °C than that at 300 °C. Thus, the optimal gas sensing performance of the Zr-added CaFe$_2$O$_4$-based sensor is expected to be obtained at the operating temperature of 350 °C, considering the still higher response to CO$_2$ gas at this temperature. It is noted that the present CaFe$_2$O$_4$-based sensor responded reversibly as well as continuously to CO$_2$ gas. Infrared analysis revealed that the sensing mechanism of the present CaFe$_2$O$_4$-based sensor is the change in the electric resistance of CaFe$_2$O$_4$ caused by reactive CO$_2$ adsorption with negatively charged oxide ions (O$^-$) resulting in the increase in the hole concentration in the base material of CaFe$_2$O$_4$.

1. Introduction

Recently, there has been increasing demands for the monitoring and/or control of CO$_2$ concentrations in the office, home, agriculture field, and bio related processes, for example. To date, solid-state electrolyte-based(1-4) and oxide semiconductor-based(5-7) CO$_2$ sensors have been intensively investigated. Among these types of CO$_2$ sensors, an electric-resistance-type sensor

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using oxide semiconductor has attracted much attention because their electric signal output is directly related to the CO₂ concentration. However, this type of sensor has a problem in that the CO₂ response is fundamentally low owing to its sensing mechanism, i.e., electric resistance change caused by the gas adsorption on the surface of the semiconductor oxide. In order to improve the gas response of this type of sensor, the synthesis of a mesopore structured oxide semiconductor with high specific surface area has been attempted. Oxide-semiconductor-type sensors containing La₂O₃ or alkaline earth metal oxides (BaO, SrO, CaO) have been investigated because these La₂O₃ or alkaline earth metal oxides display strong interaction with CO₂, leading to the enhancement of the electric resistance change, which results in a large output of the sensing signal. The semiconductor-type CO₂ sensor using BaO-containing complex oxides has attracted attention owing to its strong interaction with CO₂ among the alkaline earth metal oxides. However, a material which is abundant, inexpensive, and nontoxic is preferable from the viewpoint of reducing environmental load. As a material which satisfies these conditions, we have focused on calcium ferrite (CaFe₂O₄). We have recently reported that the addition of zirconium (Zr) into CaFe₂O₄ forms a characteristic porous structure with smaller grains connected into a three-dimensional network, resulting in a higher specific surface area. The porous structure of Zr-added CaFe₂O₄ is preferable as a semiconductor-type gas sensor material. Therefore, we examined the CO₂ sensing properties of the Zr-added CaFe₂O₄ materials in the present study.

2. Experimental Procedure

CaFe₂O₄ powder was synthesized by a malic acid complex method. Ca(NO₃)₂·4H₂O, Fe(NO₃)₃·9H₂O, and malic acid in a 1:2:3 molar ratio were dissolved in ethanol to form a mixed solution. The addition of Zr was accomplished by introducing Zr[OC(CH₃)₃]₄ solution into the abovementioned mixed solution. The amount of Zr was set at 5 mol% with respect to Fe. The mixed solution was heated on a hot plate to prepare the precursor. The precursor was calcined at 700 °C for 12 h in air. The heating ratio was 10 °C min⁻¹ in all cases.

Figure 1 shows a schematic drawing of the CO₂ sensor and measuring circuit used in the present study. The CaFe₂O₄-based powders were mixed with α-terpineol containing 5 wt% ethyl cellulose, and the resulting paste was applied on an alumina tube attached to a pair of Pt-wire electrodes. The sensor element was fabricated by heating the entire assembly at 600 °C for 2 h in air. The CO₂ sensing properties were measured in a conventional gas flow apparatus equipped with heating facilities in the temperature range of 250–450 °C. The CO₂ concentration was varied in the range of 0–5000 ppm by diluting pure CO₂ gas with dry air. The sample gases were allowed to flow over

![Fig. 1. (Color online) Schematics of the CO₂ sensor with the CaFe₂O₄-based material and the measuring circuit.](image-url)
the sensor element at a rate of 0.1 dm³ min⁻¹. The gas response (S) was defined as \( R_{\text{air}} / R_{\text{gas}} \), where \( R_{\text{air}} \) and \( R_{\text{gas}} \) were the electric resistances of a sensor element in air and in a sample gas, respectively. The electrical resistances were measured on the basis of a conventional circuit in which the element was connected with an external resistor in series. The output voltage across the external resistor at a circuit voltage of 5 V was used to evaluate the electric resistance of the element.

Diffuse reflectance spectra (DRS) were collected for the sensor materials using an IR spectrometer in the wavenumber range of 1100–2500 cm⁻¹ at 350 °C in air, CO₂, or N₂.

3. Results and Discussion

3.1 Preparation of Zr-added CaFe₂O₄ powder

Figure 2 shows the XRD patterns for Zr-added and unadded CaFe₂O₄ powders prepared from a malic acid complex. XRD peaks of unadded CaFe₂O₄ powder calcined at 700 °C in air could be ascribed to the CaFe₂O₄ phase. On the other hand, the XRD peaks of 5 mol% Zr-added product could also be ascribed to the CaFe₂O₄ phase, and small impurity peaks appeared in the Zr-added CaFe₂O₄ powders. These diffraction peaks of the impurity phase were identified as the Ca₂Fe₂O₅ phase. Chemical valence states of Zr-added and unadded CaFe₂O₄ powders were analyzed by an XPS measurement. As a result, it was found that the binding energies of the Ca 2p, Fe 2p, Zr 3p, and O 1s spectra are in good agreement with those of the Ca²⁺, Fe³⁺, Zr⁴⁺, and O²⁻ valence states, respectively.(17)

3.2 Gas sensing properties

Figure 3 shows the transient responses of the sensors made from pure CaFe₂O₄ and 5 mol% Zr-added CaFe₂O₄ powders to 5000 ppm CO₂ in air at 350 °C. When the atmosphere was changed from dry air to 5000 ppm CO₂ in air, the electric resistances of the sensor decreased, suggesting that CO₂ adsors on the surface of CaFe₂O₄ as a negatively charged species. CaFe₂O₄ is a p-type
semiconductor so that the hole concentration of CaFe$_2$O$_4$ increases with increasing adsorption of negatively charged species such as CO$_3^{2-}$, as discussed below. When the CO$_2$ flow was turned off, the resistances of the two elements returned to their original levels. It is clear from Fig. 3 that Zr-added CaFe$_2$O$_4$ has a stronger gas response and a shorter response time compared with pure CaFe$_2$O$_4$. The CO$_2$ response and 90% response time were 3.0 and 40 s for Zr-added CaFe$_2$O$_4$, respectively, and 1.3 and 70 s for pure CaFe$_2$O$_4$, respectively.

Figure 4 depicts the dependence of the gas response and 90% response time ($t_{90}$) to 5000 ppm CO$_2$ of the sensors made from pure and 5 mol% Zr-added CaFe$_2$O$_4$ at the operation temperature. It is well known that the sensing performance of resistive-type sensors markedly depends on the operation temperature. As for the reducing gases such as H$_2$, the temperature dependence of the gas response reaches maximum in accordance with the mixed effect of gas diffusion and reaction at the sensor surface. This is because the resistance change was caused by the reaction between target gases and the negative charged adsorbed oxygen on the surface of the sensor. On the other hand, the present response to CO$_2$ would be caused by the adsorption of CO$_2$ to form negatively charged species. It is speculated that the temperature dependence toward less active gases such as CO$_2$ would be determined by the rate of adsorption and desorption of the target gas. In the present study, the CO$_2$ gas response reached a maximum at 300 °C. On the other hand, the 90% response time was too slow for practical use at 300 °C. Thereafter, the CO$_2$ sensing properties of Zr-added CaFe$_2$O$_4$ were mainly examined at 350 °C owing to the quick response, although the CO$_2$ gas response was slightly lower than that at 300 °C. Figures 5(a) and 5(b) show the response transients to stepwise changes in CO$_2$ concentration and the relationship between the gas response and the CO$_2$ concentration for 5 mol% Zr-added CaFe$_2$O$_4$. When the CO$_2$ concentration was changed from 0 to 500 ppm in the measuring chamber, the gas response was 1.6. The gas response became higher as the CO$_2$ concentration was increased to 5000 ppm and finally reached 3.0. Each 90% response time for stepwise changes in the CO$_2$ concentration was estimated to be within 90 s. The gas response showed a linear correlation with the logarithm of CO$_2$ concentration in the range of 500–5000 ppm.
Fig. 4. (a) Operating temperature dependence of the gas response of the pure and 5 mol% Zr-added CaFe$_2$O$_4$ powders to 5000 ppm CO$_2$, and (b) operating temperature dependence of the 90% response time of the 5 mol% Zr-added CaFe$_2$O$_4$ powder to 5000 ppm CO$_2$ ($t_{90}$: 90% response time).

Fig. 5. (a) Transient response to stepwise changes in CO$_2$ concentration, and (b) the relationship between the gas response and CO$_2$ concentration for 5 mol% Zr-added CaFe$_2$O$_4$ powder in air at 350 °C.

3.3 Gas sensing mechanism

As previously reported, 5 mol% Zr-added CaFe$_2$O$_4$ powder exhibited three-dimensional porous structures formed by small grains connecting with each other, resulting in a higher specific surface area compared with that of pure CaFe$_2$O$_4$. This increment in the surface area upon Zr-addition might be effective for enhancing the response to CO$_2$ gas beyond that of pure CaFe$_2$O$_4$. However, upon the addition of 5 mol% Zr, the surface increases to only twice that of pure CaFe$_2$O$_4$. Thus the enhanced gas response of the Zr-added CaFe$_2$O$_4$-based sensor might originate not only from the increased surface area but also from the effect of Zr itself. Thus, infrared (IR) measurements were conducted in dry air, N$_2$, and pure CO$_2$ atmospheres at 350 °C for Zr-added and pure CaFe$_2$O$_4$ powders to analyze the CO$_2$ related species on these samples. In dry air, IR absorption bands
were observed at 1350–1550 cm$^{-1}$ and 2300–2400 cm$^{-1}$ for Zr-added and pure CaFe$_2$O$_4$ powders, respectively, as shown in Fig. 6. Fukuda and co-workers\cite{19} reported the possible adsorption configurations of CO$_2$ on the CaO surface to be unidentate and bidentate carbonate complexes.

They pointed out that the IR band derived from the Ca–O–C complex configuration appears in the range of 1350–1550 cm$^{-1}$. This IR band might be due to Ca–O–C asymmetric vibration. When CO$_2$ adsorbs on carbonate in a bidentate complex configuration, on the other hand, the adsorption peak is expected to appear at approximately 1750 cm$^{-1}$.\cite{19} The results shown in Fig. 5 revealed significant IR bands at around 1350–1550 cm$^{-1}$. The IR spectra were also observed in the range of 2300–2400 cm$^{-1}$. Dietzel et al. reported that the IR band derived from the O=C=O configuration is observed from 2300 to 2400 cm$^{-1}$ for the metal oxide surface.\cite{20} This IR band might be derived from the O=C=O stretching vibration. In the present study, IR absorption bands were observed at 1350–1550 cm$^{-1}$ and 2300–2400 cm$^{-1}$ for Zr-added and pure CaFe$_2$O$_4$ powders, respectively, so that the configuration of CO$_2$ adsorption on the CaFe$_2$O$_4$ powder might be a unidentate complex judging from the slight increment in the intensity in the range of 2300–2400 cm$^{-1}$. As shown in Fig. 6, when the atmosphere was changed from dry air to CO$_2$, the IR spectra of pure CaFe$_2$O$_4$ powder was almost unchanged. In contrast to the pure CaFe$_2$O$_4$ powder, the IR absorption bands of

Fig. 6. (Color online) IR spectra: (a) in air atmosphere and CO$_2$ atmosphere for pure CaFe$_2$O$_4$ powder and (b) Zr-added CaFe$_2$O$_4$ powder, and (c) in N$_2$ atmosphere and CO$_2$ atmosphere for Zr-added CaFe$_2$O$_4$ powder.
the Zr-added CaFe$_2$O$_4$ powder at 1350–1550 cm$^{-1}$ and 2300–2400 cm$^{-1}$ became stronger when the atmosphere was changed from dry air to CO$_2$ [Fig. 6 (b)]. On the other hand, by switching between N$_2$ and CO$_2$ atmospheres, the IR spectra of the Zr-added CaFe$_2$O$_4$ were identical to those of pure CaFe$_2$O$_4$ powders. This result suggests that, when the oxygen species on CaFe$_2$O$_4$ was removed by N$_2$ treatment, CO$_2$ adsorption becomes negligible, resulting in a vanishing Ca–O–C asymmetric vibration and O=C=O stretching vibration for the Zr-added CaFe$_2$O$_4$ sample. These observations also suggest that the oxygen species adsorbed on CaFe$_2$O$_4$ are strongly related to the CO$_2$ sensing properties of the CaFe$_2$O$_4$ powders.

It is known that CO$_2$ shows Lewis acidity and interacts strongly with the surfaces of basic oxides such as CaFe$_2$O$_4$. Schneider reported that CO$_2$ adhered to the CaO surface by reacting with surface oxygen to form carbonate species (CO$_3^{2-}$):\(^{(16)}\)

$$\text{O}^2- + \text{CO}_2 \rightarrow \text{CO}_3^{2-} \quad (1)$$

or

$$\text{O}^- + \text{CO}_2 + e^- \rightarrow \text{CO}_3^{2-} \quad (2)$$

CaFe$_2$O$_4$ is known as a p-type semiconductor, and its majority carriers are holes.\(^{(21)}\) Accordingly, it is expected that the reaction of adsorbed CO$_2$ with a negatively charged oxide ion would bring about an increase in the hole concentration. The sensing signal would originate from the negatively charged CO$_2$ adsorption, taking into account the results of the IR measurement, although the detailed mechanism requires further study. The present IR analysis and previously reported slight increment in the surface area indicates that the addition of Zr is effective not only for increasing the surface area but also for enhancing the CO$_2$ adsorption on CaFe$_2$O$_4$. In other words, added Zr accelerates the adsorption of the CO$_2$ that is produced by the reaction of CO$_2$ with negatively charged oxygen species. This implies that the change in electric resistance caused by CO$_2$ adsorption on the CaFe$_2$O$_4$ surface is enhanced by the mixed effect of Zr addition, i.e., the increment in the surface area, and the enhancement of oxygen-species-assisted CO$_2$ adsorption.

4. Conclusion

It was demonstrated that 5 mol% Zr-added CaFe$_2$O$_4$ powder showed a higher CO$_2$ gas response compared with that of pure CaFe$_2$O$_4$ powder and reached a maximum value at 300 °C. At 350 °C, the 90% response time of Zr-added CaFe$_2$O$_4$ powder was much faster than that at 300 °C. It is conceivable, on the basis of the IR measurements, that the change in the electric resistance of CaFe$_2$O$_4$ is caused by the reaction of adsorbed CO$_2$ with a negatively charged oxide ion, because of the increase in the hole concentration. Furthermore, the strong gas response of Zr-added CaFe$_2$O$_4$ to CO$_2$ can be attributed to its high specific surface area as well as enhanced adsorption on the sensor material.

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