

CO₂ Sensing Properties of Zr-Added Porous CaFe₂O₄ Powder

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The gas sensing properties of Zr-added and pure CaFe₂O₄ powders for CO₂ in air were examined in the temperature range of 250–450 °C. The semiconductor-type gas sensor made from pure CaFe₂O₄ powder showed a fairly good response to CO₂. Furthermore, the addition of a small amount of Zr into CaFe₂O₄ powder was found to be effective for enhancing the CO₂ 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 CaFe₂O₄-based sensor at 300 °C was estimated to be 2.5 times higher than that of the sensor made from pure CaFe₂O₄ powder. However, the 90% response time of the Zr-added CaFe₂O₄-based sensor was much quicker at 350 °C than that at 300 °C. Thus, the optimal gas sensing performance of the Zr-added CaFe₂O₄-based sensor is expected to be obtained at the operating temperature of 350 °C, considering the still higher response to CO₂ gas at this temperature. It is noted that the present CaFe₂O₄-based sensor responded reversibly as well as continuously to CO₂ gas. Infrared analysis revealed that the sensing mechanism of the present CaFe₂O₄-based sensor is the change in the electric resistance of CaFe₂O₄ caused by reactive CO₂ adsorption with negatively charged oxide ions (O⁻) resulting in the increase in the hole concentration in the base material of CaFe₂O₄.

1. Introduction

Recently, there has been increasing demands for the monitoring and/or control of CO₂ 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) CO₂ sensors have been intensively investigated. Among these types of CO₂ 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 CO_2 concentration. However, this type of sensor has a problem in that the CO_2 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.⁽⁸⁾ Oxide-semiconductor-type sensors containing La_2O_3 or alkaline earth metal oxides (BaO , SrO , CaO) have been investigated because these La_2O_3 or alkaline earth metal oxides display strong interaction with CO_2 , leading to the enhancement of the electric resistance change, which results in a large output of the sensing signal.^(9–15) The semiconductor-type CO_2 sensor using BaO -containing complex oxides has attracted attention owing to its strong interaction with CO_2 among the alkaline earth metal oxides.⁽¹⁶⁾ 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 (CaFe_2O_4). We have recently reported that the addition of zirconium (Zr) into CaFe_2O_4 forms a characteristic porous structure with smaller grains connected into a three-dimensional network, resulting in a higher specific surface area.⁽¹⁷⁾ The porous structure of Zr -added CaFe_2O_4 is preferable as a semiconductor-type gas sensor material. Therefore, we examined the CO_2 sensing properties of the Zr -added CaFe_2O_4 materials in the present study.

2. Experimental Procedure

CaFe_2O_4 powder was synthesized by a malic acid complex method.⁽¹⁷⁾ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 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 $\text{Zr}[\text{OC}(\text{CH}_3)_3]_4$ 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 $700\text{ }^\circ\text{C}$ for 12 h in air. The heating ratio was $10\text{ }^\circ\text{C min}^{-1}$ in all cases.

Figure 1 shows a schematic drawing of the CO_2 sensor and measuring circuit used in the present study. The CaFe_2O_4 -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 $600\text{ }^\circ\text{C}$ for 2 h in air. The CO_2 sensing properties were measured in a conventional gas flow apparatus equipped with heating facilities in the temperature range of $250\text{--}450\text{ }^\circ\text{C}$. The CO_2 concentration was varied in the range of $0\text{--}5000\text{ ppm}$ by diluting pure CO_2 gas with dry air. The sample gases were allowed to flow over

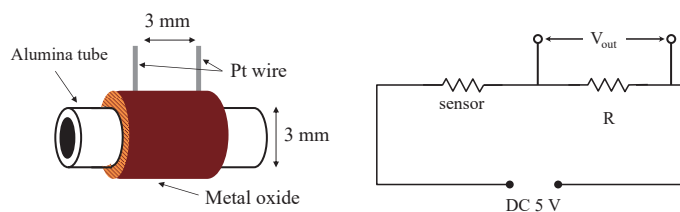


Fig. 1. (Color online) Schematics of the CO_2 sensor with the CaFe_2O_4 -based material and the measuring circuit.

the sensor element at a rate of $0.1 \text{ dm}^3 \text{ min}^{-1}$. The gas response (S) was defined as $R_{\text{air}}/R_{\text{gas}}$, where R_{air} and R_{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 $1100\text{--}2500 \text{ cm}^{-1}$ at $350 \text{ }^\circ\text{C}$ in air, CO_2 , or N_2 .

3. Results and Discussion

3.1 Preparation of Zr-added CaFe_2O_4 powder

Figure 2 shows the XRD patterns for Zr-added and unadded CaFe_2O_4 powders prepared from a malic acid complex. XRD peaks of unadded CaFe_2O_4 powder calcined at $700 \text{ }^\circ\text{C}$ in air could be ascribed to the CaFe_2O_4 phase. On the other hand, the XRD peaks of 5 mol% Zr-added product could also be ascribed to the CaFe_2O_4 phase, and small impurity peaks appeared in the Zr-added CaFe_2O_4 powders. These diffraction peaks of the impurity phase were identified as the $\text{Ca}_2\text{Fe}_2\text{O}_5$. Chemical valence states of Zr-added and unadded CaFe_2O_4 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 Ca^{2+} , Fe^{3+} , Zr^{4+} , and O^{2-} valence states, respectively.⁽¹⁷⁾

3.2 Gas sensing properties

Figure 3 shows the transient responses of the sensors made from pure CaFe_2O_4 and 5 mol% Zr-added CaFe_2O_4 powders to 5000 ppm CO_2 in air at $350 \text{ }^\circ\text{C}$. When the atmosphere was changed from dry air to 5000 ppm CO_2 in air, the electric resistances of the sensor decreased, suggesting that CO_2 adsorbs on the surface of CaFe_2O_4 as a negatively charged species. CaFe_2O_4 is a p-type

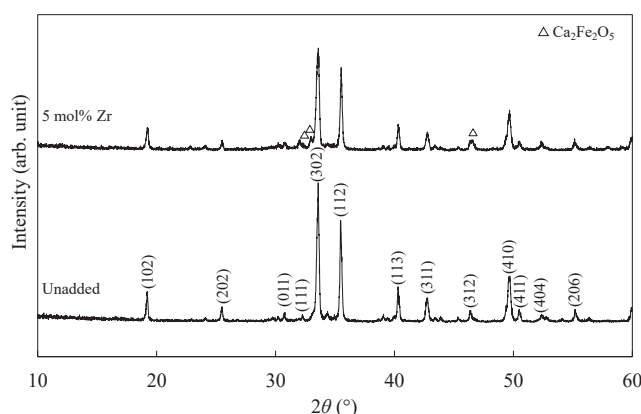


Fig. 2. XRD patterns for sample powders prepared from Zr-added CaFe_2O_4 powders calcined at $700 \text{ }^\circ\text{C}$ for 12 h in air.

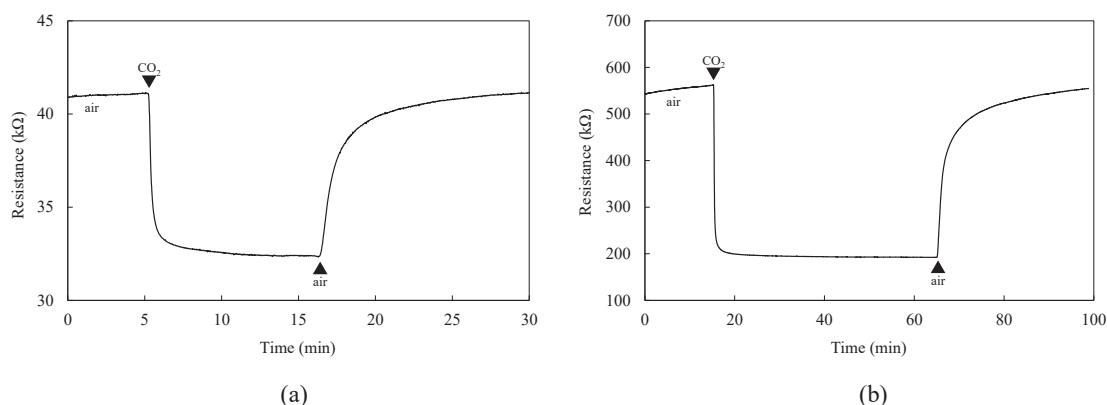


Fig. 3. Transient responses of (a) pure CaFe_2O_4 and (b) 5 mol% Zr-added CaFe_2O_4 powders to 5000 ppm CO_2 in air at 350 °C.

semiconductor so that the hole concentration of CaFe_2O_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_2O_4 has a stronger gas response and a shorter response time compared with pure CaFe_2O_4 . The CO_2 response and 90% response time were 3.0 and 40 s for Zr-added CaFe_2O_4 , respectively, and 1.3 and 70 s for pure CaFe_2O_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_2O_4 at the operation temperature. It is well known that the sensing performance of resistive-type sensors markedly depends on the operation temperature.⁽¹⁸⁾ 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_2O_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_2O_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.

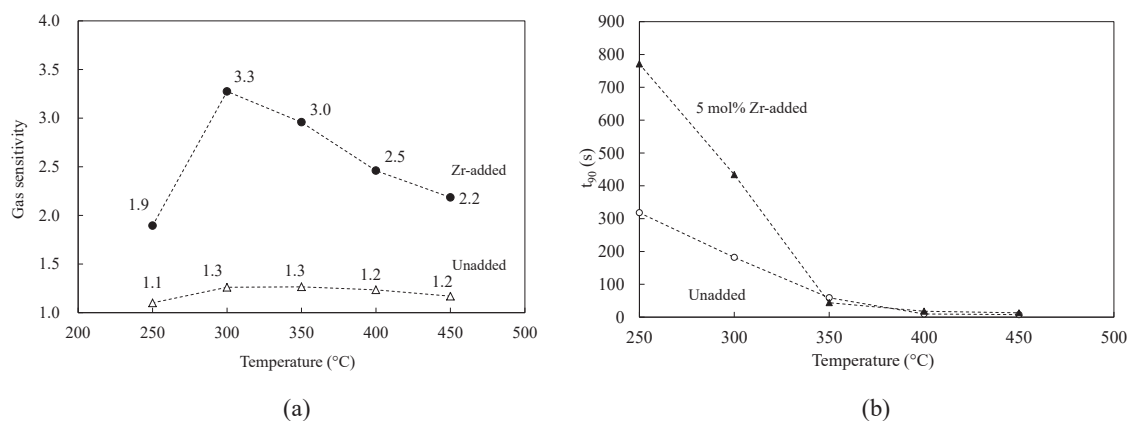


Fig. 4. (a) Operating temperature dependence of the gas response of the pure and 5 mol% Zr-added CaFe₂O₄ powders to 5000 ppm CO₂, and (b) operating temperature dependence of the 90% response time of the 5 mol% Zr-added CaFe₂O₄ powder to 5000 ppm CO₂ (t_{90} : 90% response time).

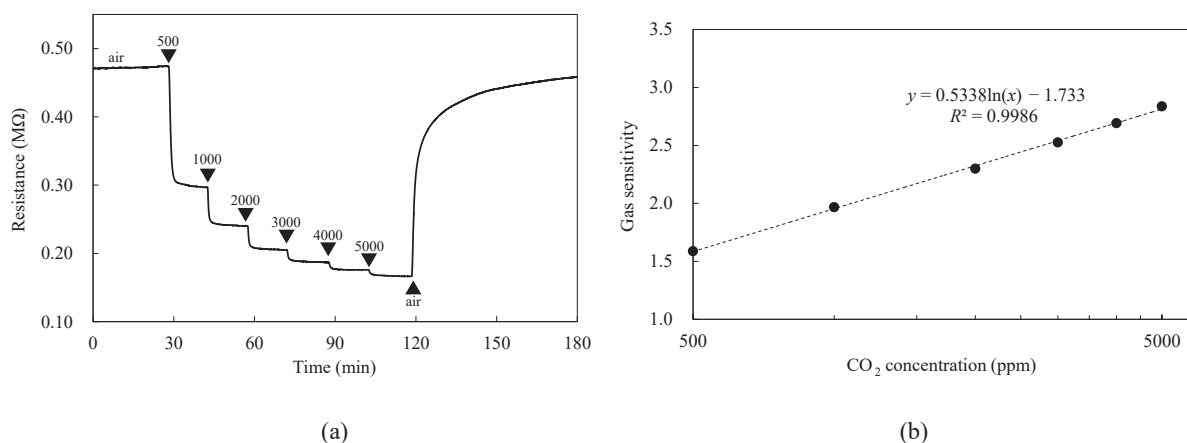


Fig. 5. (a) Transient response to stepwise changes in CO₂ concentration, and (b) the relationship between the gas response and CO₂ concentration for 5 mol% Zr-added CaFe₂O₄ powder in air at 350 °C.

3.3 Gas sensing mechanism

As previously reported, 5 mol% Zr-added CaFe₂O₄ 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 CaFe₂O₄. This increment in the surface area upon Zr-addition might be effective for enhancing the response to CO₂ gas beyond that of pure CaFe₂O₄. However, upon the addition of 5 mol% Zr, the surface increases to only twice that of pure CaFe₂O₄. Thus the enhanced gas response of the Zr-added CaFe₂O₄-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, N₂, and pure CO₂ atmospheres at 350 °C for Zr-added and pure CaFe₂O₄ powders to analyze the CO₂ 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_2O_4 powders, respectively, as shown in Fig. 6. Fukuda and co-workers⁽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} .⁽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.⁽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_2O_4 powders, respectively, so that the configuration of CO_2 adsorption on the CaFe_2O_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_2O_4 powder was almost unchanged. In contrast to the pure CaFe_2O_4 powder, the IR absorption bands of

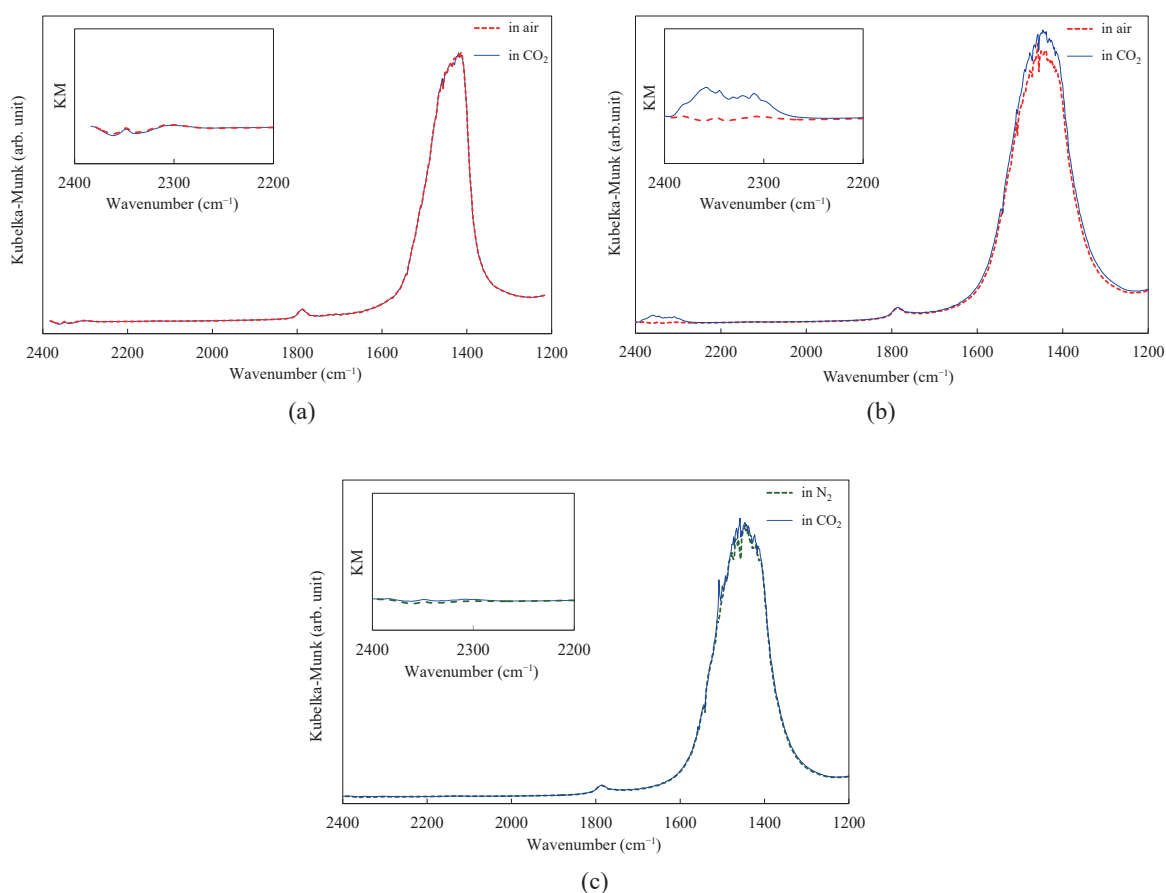


Fig. 6. (Color online) IR spectra: (a) in air atmosphere and CO_2 atmosphere for pure CaFe_2O_4 powder and (b) Zr-added CaFe_2O_4 powder, and (c) in N_2 atmosphere and CO_2 atmosphere for Zr-added CaFe_2O_4 powder.

the Zr-added CaFe_2O_4 powder at $1350\text{--}1550\text{ cm}^{-1}$ and $2300\text{--}2400\text{ cm}^{-1}$ 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_2O_4 were identical to those of pure CaFe_2O_4 powders. This result suggests that, when the oxygen species on CaFe_2O_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_2O_4 sample. These observations also suggest that the oxygen species adsorbed on CaFe_2O_4 are strongly related to the CO_2 sensing properties of the CaFe_2O_4 powders.

It is known that CO_2 shows Lewis acidity and interacts strongly with the surfaces of basic oxides such as CaFe_2O_4 . Schneider reported that CO_2 adhered to the CaO surface by reacting with surface oxygen to form carbonate species (CO_3^{2-}):⁽¹⁶⁾



or



CaFe_2O_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_2O_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_2O_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_2O_4 powder showed a higher CO_2 gas response compared with that of pure CaFe_2O_4 powder and reached a maximum value at $300\text{ }^\circ\text{C}$. At $350\text{ }^\circ\text{C}$, the 90% response time of Zr-added CaFe_2O_4 powder was much faster than that at $300\text{ }^\circ\text{C}$. It is conceivable, on the basis of the IR measurements, that the change in the electric resistance of CaFe_2O_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_2O_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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