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# Reducing gas-sensing properties of ferrite compounds $MFe_2O_4$ ($M$ = Cu, Zn, Cd and Mg)

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**Abstract**

Four kinds of ferrites, $MFe_2O_4$ ($M$ = Cu, Zn, Cd and Mg), having high specific surface area (40–80 $m^2/g$) were prepared by a coprecipitation method and tested for sensing properties to reducing gases of CO, $H_2$, LPG, $C_2H_5OH$ and $C_2H_2$. The gas sensitivity depended considerably on the kinds of ferrites and the gases to be detected. All of the ferrites were more sensitive to $C_2H_2$, $C_2H_5OH$ or LPG than to $H_2$ or CO. Among the ferrites, the gas sensitivity tended to decrease in the order $MgFe_2O_4 \sim CdFe_2O_4 > CuFe_2O_4 > ZnFe_2O_4$, which was in fact coincident with the increasing (or decreasing) order in specific surface area (or grain size). It was revealed that $MgFe_2O_4$ and $CdFe_2O_4$ were the most sensitive and selective to LPG and $C_2H_2$, respectively, among the ferrites tested. 

*Keywords:* Gas sensitivity; Ferrite; $MFe_2O_4$

## 1. Introduction

Nanometer-sized materials, which have high surface activity due to their small particle size and enormous surface area, have been widely studied in the field of gas sensors in recent years [1–3]. A large number of metal oxides, i.e. $SnO_2$, ZnO, $WO_3$, $TiO_2$, $Fe_2O_3$ and mixed oxides, were reported to be sensitive to certain gas species. Spinel-type oxides with a general formula of $AB_2O_4$ are important mixed oxides in gas sensors, and have been investigated for the detection of both oxidizing and reducing gases. For example [4], $MgFe_2O_4$, $ZnFe_2O_4$ and $NiFe_2O_4$ were studied for oxygen-sensing properties in comparison with those of chromites such as $MgCr_2O_4$, $ZnCr_2O_4$ and $NiCr_2O_4$. The results showed that the p-type chromites are more sensitive to oxygen than the n-type ferrites. As for reducing gases, Liu et al. [5] reported that the n-type semiconductor $CdFe_2O_4$ exhibits high sensitivity and selectivity to alcohol vapor. However, information on the gas sensing properties of nanocrystalline ferrites ($MFe_2O_4$) is still limited. In this paper, nanopowders of several ferrites were synthesized and their gas-sensing properties were studied.

## 2. Experimental

The ferrites $MFe_2O_4$ ($M$ = Cu, Zn, Cd or Mg) were prepared as follows. The nitrate of each constituent metal (Cu, Zn, Cd or Mg) and iron was dissolved in water at the designated molar ratio ($M$/Fe = 1:2). To this solution, a 6 M NaOH solution was added at 70°C under stirring. After standing for 1 h at 70°C under stirring for aging, the resulting precipitate (hydroxides) was collected by filtration, washed thoroughly with distilled water and dried at 120°C. Finally, the precursor was calcined at 400°C for 1 h to form the $MFe_2O_4$ mixed oxide. All the reagents used were of A.R. grade, and the water was distilled twice.

Specific surface area of the samples was determined at 77 K with an ST-03 surface area instrument (Beijing Analytic Instrument Factory, China). X-ray diffraction analysis was performed with CoK$\alpha$ radiation by using a D/max-IIIC powder X-ray diffractometer (Rigaku, Japan). TEM photographs were taken with a JEM-2000EX instrument (Electron-optics, Japan). Elemental analysis was performed by using a P-E 2380 atomic absorption spectrometer (Perkin-Elmer, USA).

Gas-sensing properties were determined with an RQ-2 gas sensitivity instrument (Qingdao University, China) using thick film-type sensors fabricated through a traditional thick film technique. The measurement was proceeded by

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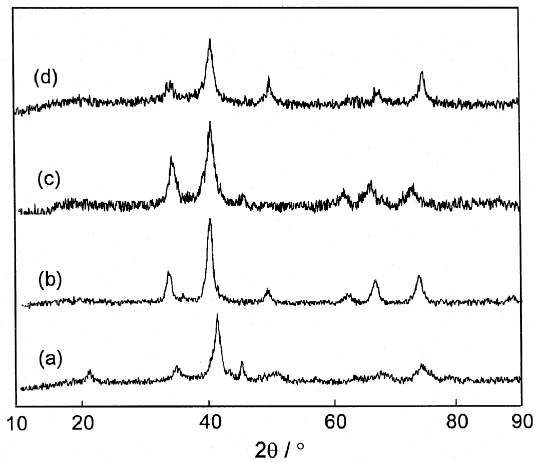


Fig. 1. XRD patterns of the samples. (a) $ZnFe_2O_4$, (b) $CuFe_2O_4$, (c) $CdFe_2O_4$, (d) $MgFe_2O_4$.

a static process: a given amount of the test gas (CO, $H_2$, LPG, $C_2H_5OH$ or $C_2H_2$) was injected into a glass chamber and mixed with air. The electric resistance of the sensors in test gases ($R_g$) and in pure air ($R_a$) was measured respectively, and the gas sensitivity ($S$) was then defined as $S = R_a/R_g$ for the n-type sensors.

## 3. Results and discussion

### 3.1. Characterization

The XRD patterns of the products are displayed in Fig. 1. All the samples have single phase spinel-type structure with $d$-spacing values consistent with those found in the JCPDS files ($ZnFe_2O_4$: 22–1012; $CuFe_2O_4$: 25–283; $CdFe_2O_4$: 22–1063; $MgFe_2O_4$: 36–398). Moreover, the temperature of the heat treatment in this work (400°C) is much lower than that of the solid state synthesis, in which the mixed oxides with spinel structure are often obtained from reactions at about 1000°C. This lowering of crystallization temperature favors the formation of fine powders with larger specific surface area (see Table 1). The widened diffraction peaks in Fig. 1 also conform the existence of rather small crystallites of the samples.

The composition of the samples, determined by atomic absorption spectroscopy and represented by $M$/Fe molar ratio in Table 1, is found close to the theoretical value for

Table 1
The composition ($M$/Fe ratio), specific surface area ($\sigma$) and grain size ($d$) of the samples

| Sample | | $ZnFe_2O_4$ | $CuFe_2O_4$ | $CdFe_2O_4$ | $MgFe_2O_4$ |
|---|---|---|---|---|---|
| $M$/Fe (mol) | Calc. | 0.5 | 0.5 | 0.5 | 0.5 |
| | Found | 0.45 | 0.47 | 0.53 | 0.51 |
| $\sigma$ ($m^2 \cdot g^{-1}$) | | 45.4 | 78.6 | 80.1 | 83.7 |
| $d$ (nm) | | 47 | 35 | 33 | 32 |

$M Fe_2O_4$. Observation of TEM indicates that the samples are spherical particles with a mean diameter within 50 nm. Table 1 shows also the specific surface area ($\sigma$) and grain size ($d$, measured from the TEM photographs) of the samples. Among them, $ZnFe_2O_4$ exhibits the largest grain size (47 nm) and the smallest specific surface area (45.4 $m^2/g$). The other three samples, $CuFe_2O_4$, $CdFe_2O_4$ and $MgFe_2O_4$ have smaller grain size (35, 33 and 32 nm, respectively) and larger specific surface area (78.5, 80.1 and 83.7 $m^2/g$, respectively).

### 3.2. Gas-sensing properties

Fig. 2 illustrates the gas sensitivity ($S$) of the sensors at different operating temperatures ($T$) in 2000 ppm LPG. Each of the curves shows a maximum sensitivity corresponding to an optimum heating temperature. The best sensitivity appears at 350°C for $ZnFe_2O_4$ and at 250°C for $CuFe_2O_4$, $CdFe_2O_4$ and $MgFe_2O_4$. The higher working temperature of $ZnFe_2O_4$ sensor is probably due to its smaller specific surface area and lower surface activity, which results in weaker interaction between the test gases and the material surface. Thus, it needs more excitation for the sensors to show sufficient response to the test gases.

Relationship between the sensitivity ($S$) and the concentration ($C$) of the test gases (Fig. 3) is determined at the optimum working temperature, that is, at 350°C for $ZnFe_2O_4$ and at 250°C for the others. It is found that, in general, the sensors are much more sensitive to alcohol vapor, LPG and $C_2H_2$ gas and less sensitive to CO and $H_2$. However, there are differences in the sensitivity to various gases of the four samples. $ZnFe_2O_4$, $CuFe_2O_4$ and $CdFe_2O_4$ are most sensitive to acetylene of the five test gases, and $MgFe_2O_4$ is most sensitive to LPG. $CdFe_2O_4$ shows considerable sensitivity to hydrogen and poor response to carbon monoxide, while similar sensitivity to $H_2$ and CO is observed for the other three samples.

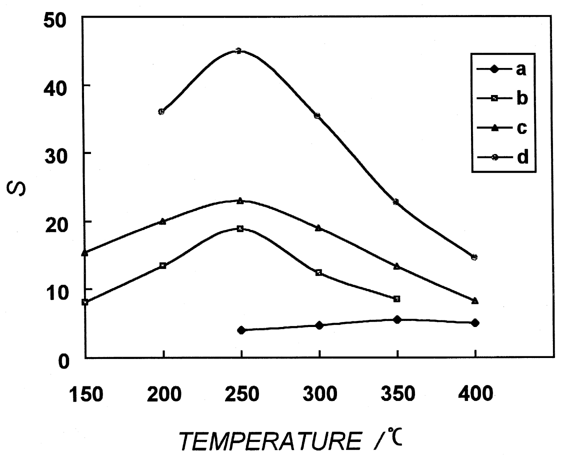


Fig. 2. The optimum working temperature of the sensors in 2000 ppm LPG. (a) $ZnFe_2O_4$, (b) $CuFe_2O_4$, (c) $CdFe_2O_4$, (d) $MgFe_2O_4$.

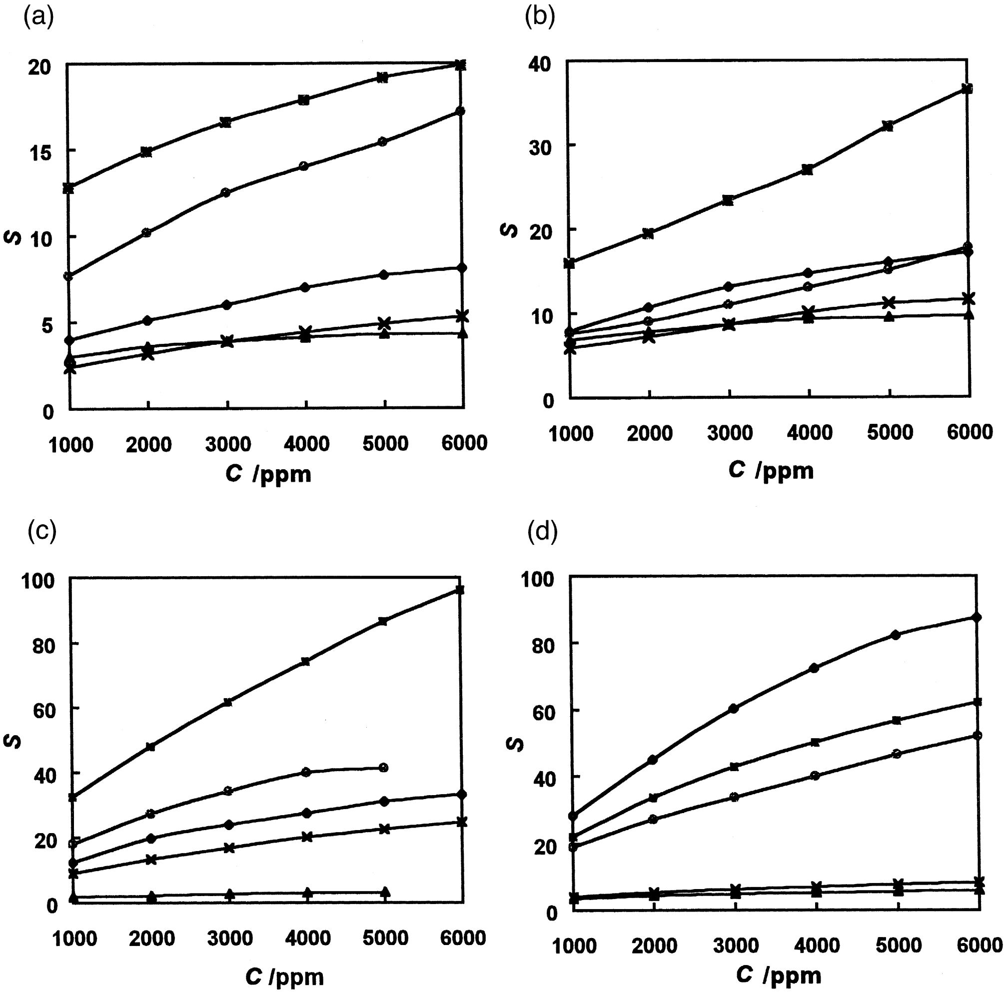


Fig. 3. Relationship between the sensitivity ($S$) and the gas concentration ($C$) at the optimum operating temperatures. (a) $ZnFe_2O_4$ (350°C), (b) $CuFe_2O_4$ (250°C), (c) $CdFe_2O_4$ (250°C), (d) $MgFe_2O_4$ (250°C). ■ $C_2H_2$, ♦ CO, ♦ LPG, × $H_2$, ○ $C_2H_5OH$.

On the other hand, the gas sensitivity of the samples is related to their grain size and specific surface area. The sensitivity decreases in the order $MgFe_2O_4 \sim CdFe_2O_4 > CuFe_2O_4 > ZnFe_2O_4$, while the grain size of the samples increases approximately in the order $ZnFe_2O_4 < CuFe_2O_4 < MgFe_2O_4 \sim CdFe_2O_4$. Samples that have smaller grain size (or larger surface area) have larger gas sensitivity, and vice versa. Therefore, it would be an efficient way to increase the specific surface area of the materials for the purpose of improving their gas-sensitive performance.

## 4. Conclusions

Four spinel-type mixed oxide nanopowders were prepared by chemical coprecipitation method at lower temperature. Measurement of the gas sensitivity of the samples was related to the kinds of the ferrites and their specific surface area (or grain size). $MgFe_2O_4$ and $CdFe_2O_4$ were the most sensitive and selective to LPG and $C_2H_2$. The sensitivity decreased in the order $MgFe_2O_4 \sim CdFe_2O_4 > CuFe_2O_4 > ZnFe_2O_4$, while the grain size of the samples increased approximately in the order $ZnFe_2O_4 < CuFe_2O_4 < MgFe_2O_4 \sim CdFe_2O_4$.

## References

[1] L. Bruno, C. Pijolat, R. Lalauze, Tin dioxide thin-film gas sensor prepared by chemical vapour deposition, Sens. Actuators, B 18–19 (1994) 195–199.

[2] Y. Liu, W. Zhu, M.S. Tse, S.Y. Shen, Study of a new alcohol gas sensor made from ultrafine $SnO_2$–$Fe_2O_3$ powders, J. Mater. Sci. Lett. 14 (1995) 1185–1187.

[3] H. Suo, F. Wu, Q. Wang, G. Liu, F. Qiu, B. Xu, M. Zhao, Study on ethanol sensitivity of nanocrystalline $La_{0.7}Sr_{0.3}FeO_3$-based gas sensor, Sens. Actuators, B 45 (1997) 245–249.

[4] Y. Shimizu, S. Kusano, H. Kuwayama, K. Tanaka, M. Egashira, Oxygen-sensing properties of spinel-type oxides for stoichiometric air/fuel combustion control, J. Am. Ceram. Soc. 73 (1990) 818–824.

[5] X.Q. Liu, Z.L. Xu, Y.S. Shen, A new type ethanol sensing material on $CdFe_2O_4$ semiconductor, J. Yunnan Univ. 19 (1997) 147–149, [in Chinese].