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ETHANOL SENSOR OF $CdO/Al_2O_3/CeO_2$ OBTAINED FROM Ce-DOPED LAYERED DOUBLE HYDROXIDES WITH HIGH RESPONSE AND SELECTIVITY

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In this paper, Ce-doped CdAl layered double hydroxide (LDH) was first synthesized and the derivative $CdO/Al_2O_3/CeO_2$ composite oxide was prepared by calcining Ce-doped CdAl LDH. The structure, morphology and chemical state of the Ce doped CdAl LDH and $CdO/Al_2O_3/CeO_2$ were also investigated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), solid state nuclear magnetic resonance (SSNMR), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The gas sensing properties of $CdO/Al_2O_3/CeO_2$ to ethanol were further studied and compared with CdO/Al_2O_3 prepared from CdAl LDH, CeO_2 powder as well as the calcined Ce salt. It turns out that $CdO/Al_2O_3/CeO_2$ sensor shows best performance in ethanol response. Besides, $CdO/Al_2O_3/CeO_2$ possesses short response/recovery time (12/72 s) as well as remarkable selectivity in ethanol sensing, which means composite oxides prepared from LDH are very promising in gas sensing application.

Keywords: Layered double hydroxides; composite oxides; ethanol sensing.

For many years, gas sensors have always played an important role in industrial emission, household security, vehicle emission control, environmental monitoring, etc.[1–3] Particularly, ethanol sensors have shown great application values in detecting alcohol on human breath to prevent drunk driving or detecting leaks in industrial distribution lines to avoid loss.[4–6] Therefore, more and more attentions have been paid on the design and fabrication of gas sensors with high response and selectivity. Conventional gas sensors, mostly based on semiconductor metal oxides, for instance ZnO,[7] SnO_2,[4] TiO_2,[8] In_2O_3,[9] Fe_2O_3,[10] WO_3,[11] CeO_2,[12] etc., have shown great performances in gas sensing field due to their low cost and flexibility in production, simplicity in use and large number of detectable gases.[13] Recently, more and more studies have been focused on composite materials, for example $ZnO-CeO_2$,[14,15] $CdO-SnO_2$ and $CdO-Fe_2O_3$,[16,17] etc., since sensors based on two or more components may possess a synergistic effect and/or a heterojunction interaction between these components which would result in the enhanced gas sensing properties in comparison with the sensors containing one component.[18]

Layered double hydroxides (LDHs) are synthetic two-dimensional nanostructured anionic clays with a general formula $[M(II)_{1-x}M'(III)_x(OH)_2]\ (A^{n-})_{x/n} \cdot yH_2O$ (M(II) = divalent metal; M′(III) = trivalent metal; A = anion).[19] Calcination of LDHs is a well-known way to give rise to mixed metal oxides (MMOs).[20] Because of both kinds and atomic ratio of metal elements in LDHs can be changed under certain conditions, more and more composite oxides based on LDHs precursors have been prepared successfully and used widely as magnetic materials,[20] catalysts or catalyst supports,[21] electrode materials,[22] etc.

As the composite oxides obtained from LDHs precursors have always shown high distribution of metal elements, small

crystallite size and high stability against sintering,[23] it would be promising in gas sensing field if using LDHs precursors to prepare composite oxides. To the best of our knowledge, there are few reports using LDHs as the precursors to prepare composite oxides for gas sensing application.[24] Herein, in our paper, we first prepared Ce-doped CdAl LDH as the precursor. Based on the elemental analysis for metals, C, H, N, S elements and XPS analysis, the chemical formula of the Ce-doped CdAl LDH was confirmed as $Cd^{(II)}_{0.65}\ Al^{(III)}_{0.19}Ce^{(III)}_{0.064}Ce^{(IV)}_{0.096}$ $(C_{12}H_{25}SO_4)_{0.26}(OH)_{2.186} \cdot 0.7\,H_2O$. Afterwards, the composite oxide $CdO/Al_2O_3/CeO_2$ was obtained by calcinating the precursor of Ce-doped CdAl LDH for gas sensing studies.

As shown in Fig. 1(a), the XRD pattern of Ce-doped CdAl LDH exhibits the characteristic reflections of LDH materials with a series of (001) peaks, which are evidences for the layered structure. The interlayer spacing determined from the (003) reflection of the samples (23.23 Å) is shorter than the sum of the calculated lengths of the DS molecule (21.3 Å) and the layer thickness (about 4.8 Å), which indicates that the DS molecules are oriented with a certain angle arrangement, closing to 90° between the layers. After calcination, the characteristic peaks for the layered structure of LDH disappear in $CdO_2/Al_2O_3/CeO_2$ (Fig. 1(b)), while the new conspicuous peaks are respectively attributed to the diffraction of hexagonal CdO phase at 33.31° (111), 38.40° (200), 55.65° (220) and to the cubic CeO_2 phase at 28.50° (111) and 47.48° (220).

The morphologies of Ce-doped CdAl LDH and $CdO/Al_2O_3/CeO_2$ are characterized by SEM (Fig. 2). Many sheets can be distinguished, which are the typical morphologies of LDHs. After calcination, a number of small particles are clearly observed while the sheets of LDH are destroyed badly.

^{27}Al solid-state NMR is a very direct way to probe the coordination environment of aluminum. As shown in

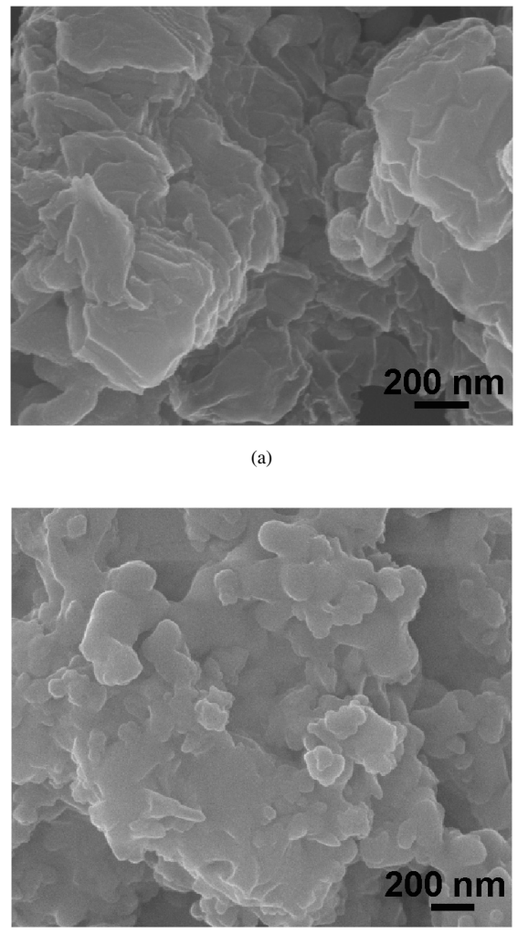

Fig. 2. SEM images of Ce-doped (a) CdAl LDH and (b) $CdO/Al_2O_3/CeO_2$.

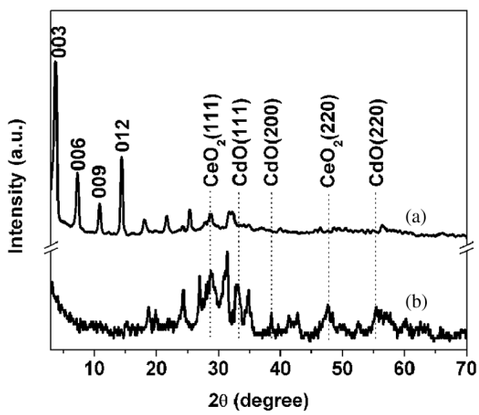

Fig. 1. X-ray diffraction patterns of Ce-doped (a) CdAl LDH and (b) $CdO/Al_2O_3/CeO_2$.

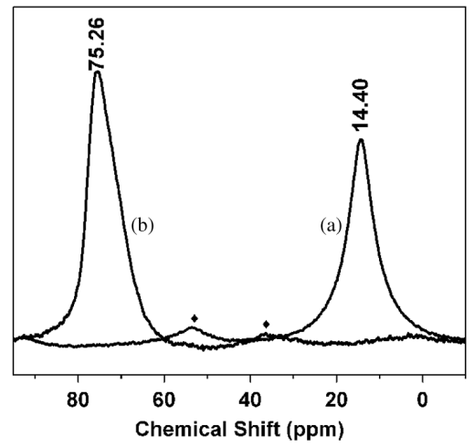

Fig. 3. ^{27}Al solid-state NMR spectra of Ce-doped (a) CdAl LDH and (b) $CdO/Al_2O_3/CeO_2$ (♦: spinning sidebands).

Fig. 3(a), ^{27}Al MAS NMR spectrum of Ce-doped CdAl LDH shows a single intensive resonance at about 14.4 ppm, which corresponds to the six-fold coordinated aluminum ions in octahedral positions within the layer of LDH.[25] For $CdO/Al_2O_3/CeO_2$, four-fold coordinated aluminum ions of Al_2O_3 show up with chemical shift in the center of 75.3 ppm (Fig. 3(b)). Since there are no resonances of six-fold coordinated aluminum ions after calcination, it can be deduced that aluminums in the LDH have been completely converted to the form of Al_2O_3 by calcination.

The gas responses to 1000 ppm ethanol of the composite oxides at various temperatures are shown in Fig. 4. Normally, the responses would increase with the rise of the operating temperature, which can be explained by the enhanced activation of the materials at high operation temperatures. If we keep increasing the operation temperature, the gas sensing responses would reach a highest peak value, then decrease with the further elevation of the working temperatures, which is likely due to the extent of adsorption decreases at high temperatures. Therefore, every sensor has its optimal working temperature. As can be seen in our work, the optimal operating temperature of $CdO/Al_2O_3/CeO_2$ with the max ethanol response ($R_a/R_g = 890$) is at about 190°C. For comparison, CdO/Al_2O_3 was prepared by calcinating the CdAl LDH precursor. The gas sensing of CdO/Al_2O_3 have been measured and the max response of CdO/Al_2O_3 reaches 6.4 at its optimal temperature 250°C. Obviously, $CdO/Al_2O_3/CeO_2$ has a higher ethanol sensing response with a lower working temperature than CdO/Al_2O_3.

Based on the above facts, it can be deduced that CeO_2 plays an important effect on the improvement of the ethanol response and lowering the optimal operating temperature for $CdO/Al_2O_3/CeO_2$. To further investigate the gas sensing performance of $CdO/Al_2O_3/CeO_2$, we have measured the gas sensing properties of the calcined product of $Ce(SO_4)_2$ and chemically grade CeO_2 powder, while the results show that the former nearly has no response to ethanol and the latter only has very low response (1.6) at 230°C (Fig. S1). Therefore, it indicates that the way of using Ce-doped CdAl LDH as precursor to prepare composite oxides may present more excellent gas sensing properties than their independent components.

In addition, electronic sensitization and surface basicity can be further applied to explain the enhancing role of CeO_2 in $CdO/Al_2O_3/CeO_2$ sensor.[15,16,27] On one hand, the introduced CeO_2 would act as a strong acceptor for electrons of the semiconductor CdO/Al_2O_3, and induces an electron-depleted space-charge layer near the interface. By reacting with a reducing analyte, for example ethanol, CeO_2 starts releasing the electrons back to CdO/Al_2O_3. In a great accordance with the XPS spectra (Fig. S2), Cerium has the capability to absorb and release oxygen via the facile creation and diffusion of oxygen vacancies or undergo rapid and repeatable Ce^{4+}/Ce^{3+} redox cycles.[15,28] On the other hand, a stronger basicity of CeO_2 than the composite CdO/Al_2O_3 may be another reason for the enhanced sensitivity of $CdO/Al_2O_3/CeO_2$ sensor. According to the literature, the acid-base properties of oxides will decide the routes of decomposition of ethanol, that is to say, the oxidative dehydrogenation reaction is mainly depended on basic sites and the dehydration is favored on acid sites.[27] For this reason, it is believed that the preferential formation of intermediate products of oxidative dehydrogenation might be another factor to obtain high response to ethanol.

Although $CdO/Al_2O_3/CeO_2$ has a high response (890 to 1000 ppm ethanol) at the operation temperature of 190°C, it also has a long response/recovery time (32/297 s). Therefore, considering the response and the response/recovery time for practical application, we choose 230°C as the working temperature for its short response/recovery time (12/72 s)

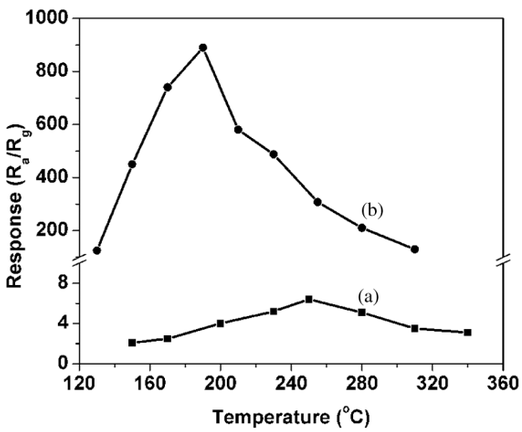

Fig. 4. Response curves of (a) CdO/Al_2O_3 and (b) $CdO/Al_2O_3/CeO_2$ made to 1000 ppm CH_3CH_2OH at different operating temperatures.

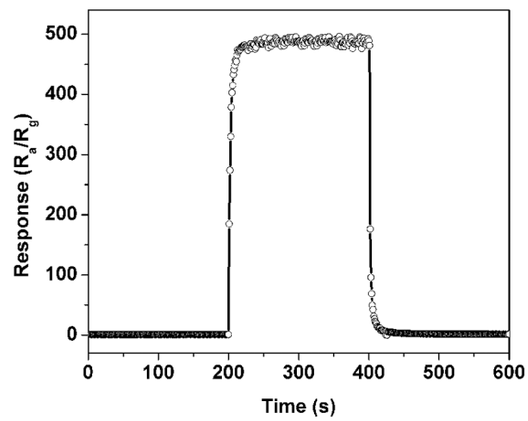

Fig. 5. Response/recovery curve of $CdO/Al_2O_3/CeO_2$ made to 1000 ppm CH_3CH_2OH at 230°C.

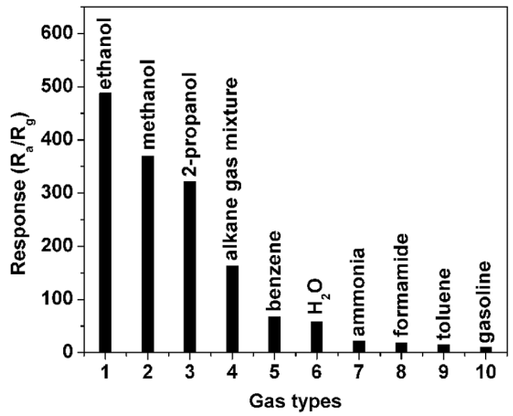

Fig. 6. Responses (R_a/R_g) of $CdO/Al_2O_3/CeO_2$ sensor to 1000 ppm different gases.

and comparative gas sensing response (488). Figure 5 shows the response and recovery curve for $CdO/Al_2O_3/CeO_2$ at 230°C. The first 200 s shows the gas response in the air, after that the air was replaced by 1000 ppm ethanol in air and remained as such for 200 s with the gas response of 488. After 400 s the environment was switched back to air again and the gas response of the sensor drops back to the original value in air.

The selectivity of gas sensors is also an important factor for further application. It is found in Fig. 6 that $CdO/Al_2O_3/CeO_2$ exhibits very high responses to ethanol, methanol and 2-propanol, low response to alkane gas mixture (containing 29.6% methane, 10.0% ethane, 9.90% propane, 1.96% *n*-butane, 4.81% ethylene, 4.88% propylene, 1.97% *n*-butene and 36.88% N_2), but very low responses to benzene, H_2O, ammonia, formamide, toluene, gasoline with the same concentrations of 1000 ppm, which indicates that the $CdO/Al_2O_3/CeO_2$ can be used as a good candidate for highly selective ethanol sensor.

In conclusion, LDHs have been used to prepare composite oxides successfully for gas sensing applications. Especially, the obtained product $CdO/Al_2O_3/CeO_2$ from Ce-doped CdAl LDH can be used as a good candidate for the detection of ethanol in future use. For comparison, it presents much higher sensitivity to ethanol than CdO/Al_2O_3 obtained from CdAl LDH, CeO_2 powder as well as the calcined Ce salt. Since the kinds and proportions of metal ions are changeable under certain conditions in preparation of LDHs, it would definitely provide us with varied composite oxides for gas sensing application by calcination of LDHs.

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