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Humidity sensitive property of Li-doped mesoporous silica SBA-15

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Abstract

Mesoporous silica SBA-15 was synthesized by a sol–gel method, and different level of LiCl was doped into SBA-15 by heat-treating process at 550 °C to form a series of samples. These samples and pure SBA-15 were investigated as humidity sensor materials at room temperature within the relative humidity range of 11–95%. It was found that after the doping of LiCl, the humidity sensitivity has been greatly improved, the impedance changed by more than three orders of magnitude over the whole humidity range. This was related to the hydrophilic property of the Li^+, and a possible mechanism was provided to explain the humidity sensitive properties.

Keywords: Mesoporous silica; SBA-15; Humidity sensitivity; Li doped; Sensors

1. Introduction

The humidity control is necessary for various fields of environment detection and monitoring [1–3], and many sensors have been widely used in moisture-sensitive environment, such as libraries, museums, food storages and so on. Many kinds of sensor materials including metal oxides [4–7], polymers [8–10], and organic–inorganic hybrid composites [11–13] have been produced to serve these applications. Among these organic–inorganic composites, the inorganic silica, due to its good mechanical strength and high intrinsic impedance [14], has been successfully combined with different polymers [15,16] to improve the characteristics of the humidity sensors. Pure silica gel also has been studied as humidity sensors by Anderson and Parks [17]. This is because the Si–OH groups and water molecules adsorbed by silica gel play an important role in increasing the conductivity of silica gel. Wang et al. [18] investigated the electrical sensing properties of silica aerogel thin films, but the silica aerogel only showed humidity sensitivity when the relative humidity reached as high as 60%RH. In order to improve the humidity sensitive property, salt-doping was found to be an effective method [19,20]. So, in this paper, LiCl was used as a dopant to the mesoporous silica SBA-15 to improve the sensitivity. The humidity sensing property of pure SBA-15 was given for comparison. In addition, a possible mechanism was discussed to elucidate why the humidity sensitive property of Li-doped SBA-15 was better than that of pure SBA-15.

2. Experimental

2.1. Preparation of mesoporous silica SBA-15

Mesoporous silica SBA-15 was synthesized according to the literature method reported by Li and Zhao [21] using a triblock copolymer surfactant P123 ($EO_{20}PO_{70}EO_{20}$) as a template. The detailed procedure was as follows: 2 g P123 was dissolved in 60 ml HCl solution (2 M) at room temperature. Then 4.4 g tetraethyl orthosilicate (TEOS) was added dropwise under stirring at 40 °C for 24 h. Subsequently the resultant mixture was aged at 60 °C for 24 h without stirring. The product was filtered and washed with distilled water, then dried at 100 °C over night.

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The surfactant template was removed at 550 °C for 8 h to obtain the pure mesoporous silica SBA-15.

2.2. Preparation of Li-SBA-15

The sensor materials of Li-SBA-15 were prepared from different weight ratios of SBA-15 and LiCl. The mixture of LiCl and SBA-15 was ground for 0.5 h in an agate mortar. The grounded mixture was transferred into a crucible and subsequently heated in a muffle furnace with a heating rate of 2 °C/min up to 550 °C, and kept at this temperature for 24 h. Then the Li-SBA-15 samples were obtained, and the products were designated as Li-SBA-15 (*X*), where *X* was the content of LiCl in 1 g of SBA-15. In our experiment, the value of *X* was 0.1, 0.3, 0.5, 0.9, and 1.8 for five Li-SBA-15 samples, respectively.

2.3. Methods of characterization

The powder XRD patterns were measured on a D8 Tools X-ray diffraction instrument using the Cu Kα radiation at 40 kV and 30 mA. N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 m instrument (Micromeritics Instrument Corp., Norcross, GA). Infrared spectra were taken on a Perkin-Elmer series with a resolution of 4 cm^{-1}. The samples were prepared in a form of KBr pellet, the thickness of the pellet being about 1.3 mm. Each spectrum was collected at room temperature under atmospheric pressure. The morphology of products was characterized by a JEOL JSM-6700F field emission scanning electron microscope (SEM). The sample was prepared by distributing the powder samples on a double-sided conducting adhesive tape. The characteristic curves of humidity sensitivity were measured on a ZL-5 model LCR analyzer at room temperature. The controlled humidity environments were achieved using saturated aqueous solutions of different salts: LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3 in a closed glass vessel at ambient temperature, which yielded 11%, 33%, 54%, 75%, 85% and 95% relative humidity, respectively. The power samples were screen printed on a ceramic plate (1 cm × 0.5 cm) in which a pair of interdigitated gold electrodes were printed and then the humidity device was heated at 70 °C for 5 h. A schematic image of this electrode is shown in Fig. 1.

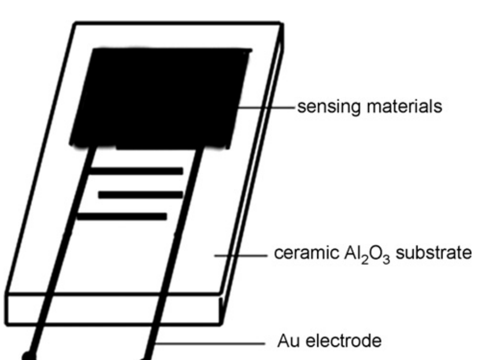

Fig. 1. A schematic image of the humidity sensor.

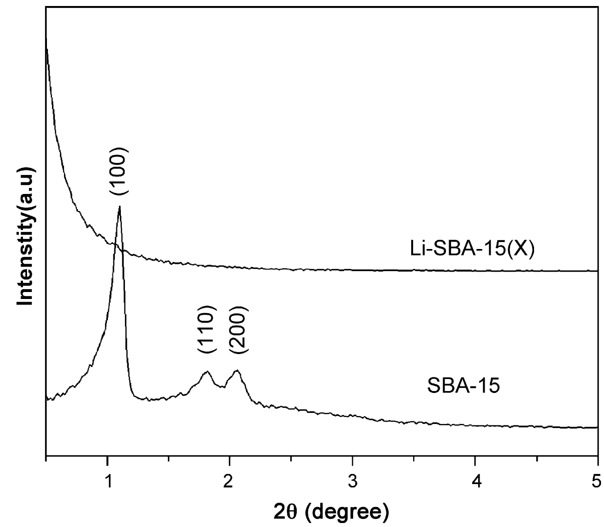

Fig. 2. Lower angle XRD patterns of SBA-15 and Li-SBA-15(0.1). The curves for other Li-SBA-15(*X*) samples were the same as that of Li-SBA-15(0.1).

3. Results and discussion

3.1. Structure and morphology

3.1.1. X-ray diffraction

The lower angle XRD patterns of SBA-15 and Li-SBA-15(*X*) are shown in Fig. 2. We could see that the three peaks attributed to (1 0 0), (1 1 0), and (2 0 0) of SBA-15 were disappeared in Li-SBA-15(*X*), indicating that the mesoporous structure of SBA-15 was destroyed after introducing LiCl into SBA-15. In fact, it was because that LiCl and SBA-15 reacted to form new phases as follows.

Fig. 3 shows the wide angle XRD patterns of SBA-15, pure LiCl, and Li-SBA-15 (*X* = 0.1, 0.3, 0.5, 0.9, and 1.8). As could be seen, a broad peak centered at 22.2° of 2*θ* was observed for the pure SBA-15, indicating that the pore wall of SBA-15 was amorphous. In the pattern of LiCl shown on the top of this

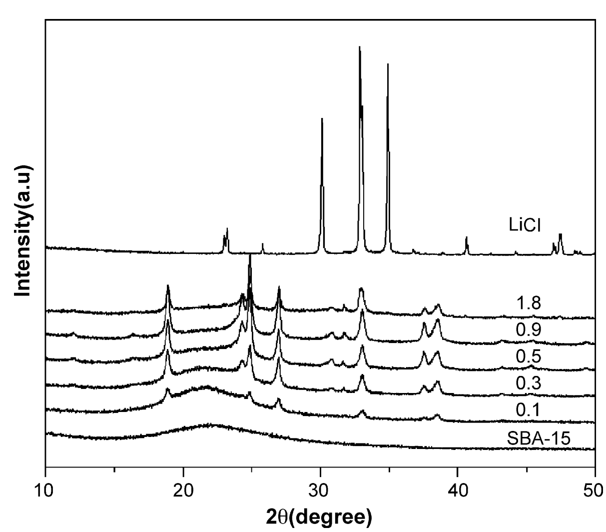

Fig. 3. Wide angle XRD spectra of SBA-15, Li-SBA-15(*X*) of *X* = 0.1, 0.3, 0.5, 0.9 and 1.8, and pure LiCl.