

Research Article

Synthesis of Monolithic $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ Composite Aerogels via Organic Solvent Sublimation Drying

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Monolithic $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ composite aerogels have been prepared successfully via organic solvent sublimation drying method. The results show that a new phase forms when the right amount of ferric oxide is added to the alumina aerogel. From the TEM pictures we can see a shuttle-type structure with the length of about 15 nm forms, which leads to the high surface areas of composited aerogel.

1. Introduction

Aerogel is an extremely porous material prepared by using air replacing the liquid component of the wet gel [1–3]. Its unique structure makes it have extraordinary properties like low density, large porosity, low thermal conductivity, and high specific surface area, which lead it to receive much attention in a wide range of applications [4–8]. In particular alumina aerogel, which provides thermal insulation over a large temperature range and large specific surface area, would be a very useful material [9–12]. In order to make it better applied to some specific areas, we need to add other special materials to improve the characteristics of alumina aerogel. After adding iron oxide, alumina aerogel shows high magnetic strength and porosity. Thus $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ composite aerogel can be used as an absorbent, magnetic carrier, and high efficient reaction catalyst [13, 14]. In addition, this composite aerogel has been used for selective hydrogenation reaction of sulfur dioxide because of good heat insulation performance [15]. But preparation of monolithic narrow pore size distribution mesoporous composite aerogel is very difficult. Recently we developed a new drying method to prepare inorganic oxide aerogels. That is organic solvents sublimation drying (OSSD) method [16]. This method can avoid the influence of surface tension of gas-liquid phase transformation during the drying process.

In this paper we applied it to prepare stable $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ composite aerogels with different ratio of iron oxide and investigate the effect of iron oxide on alumina aerogel through X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, nitrogen sorption isotherms, and transmission electron microscopy (TEM).

2. Experimental

2.1. Preparation. First, appropriate amount of ethanol and water was mixed and heated to 80°C in a beaker, and a certain amount of aluminum chloride hexahydrate (Sinopharm Chemical Reagent Co., Ltd.) was added with vigorous stirring until being dissolved. Then certain amount of hydrochloric acid (Shanghai Lingfeng Chemical Reagent Co., Ltd.) was added with stirring and reflux condensation for 4 h. At last the sample was cooled to room temperature and the alumina clear sol was obtained.

The second step was the preparation of clear iron oxide sol. The detailed procedures are as follows: a certain amount of iron chloride (Sinopharm Chemical Reagent Co., Ltd.) was dissolved in anhydrous ethanol and then stirred at room temperature for 4 hours until getting Fe alcohol sol.

Then alumina sol and iron oxide sol were mixed according to the desired mole ratio of Fe and Al and reacted at room temperature for 5 h to get composite sol. A certain amount

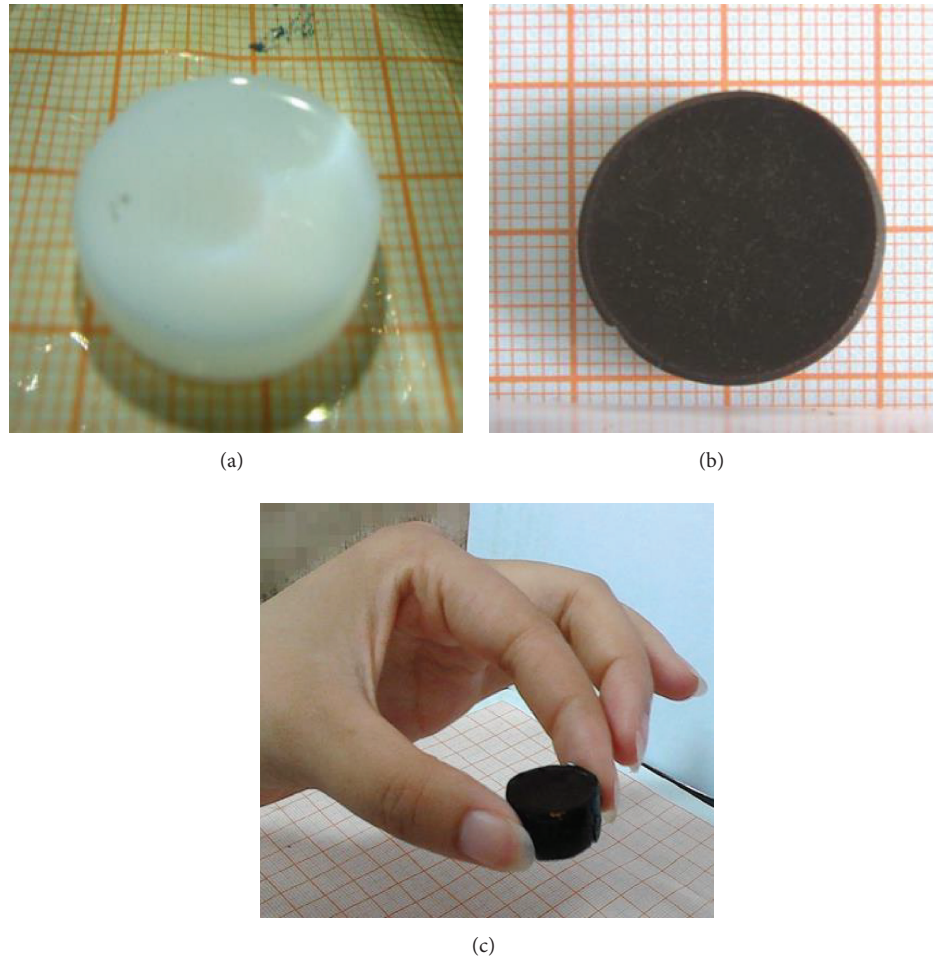


FIGURE 1: The picture of alumina aerogels (a), Fe_2O_3 aerogels (b), and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ aerogel (c).

of epoxy propane (Shanghai Lingfeng Chemical Reagent Co., Ltd.) as a gelation agent was slowly added into the alumina, iron oxide, and composite sols, respectively, and then sealed at 25°C and let them turn into gels.

The obtained wet gel was dried through organic solvent sublimation drying technology (OSSD) [16]. The detailed procedure is as follows: the samples were aged in EtOH for 48 h at 50°C and then washed in 50%, 80%, and 100% acetonitrile/EtOH (v/v) exchanged solvents for 24 h at 50°C , respectively. After that, the wet gel was stored in a beaker and dried under the low vacuum condition.

2.2. Characterization. The pore size distribution and specific surface area of the samples were measured using a N_2 adsorption analyzer (ASAP 2020). Before test, the samples were heated at 473 K in 10^{-6} Torr for 1 h for degassing. The Barrett-Joyner-Hollander (BJH) method was used to calculate the pore size distribution. The morphology and microstructures of the samples were characterized by a transmission electron microscope (TEM, JEOL-1230). Organic groups were investigated by a Fourier transform infrared

spectroscopy (FT-IR, TENSOR27). X-ray diffraction (XRD) data were recorded on D8-Discover (Bruker) using $\text{Cu K}\alpha$ radiation at a scanning speed of $2^\circ/\text{min}$ within the 2θ range of $10^\circ\text{--}80^\circ$.

3. Results and Discussions

Through OSSD drying method, we successfully prepared monolithic alumina, Fe_2O_3 , and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ aerogels, as shown in Figure 1. All of the three aerogels are shiny and have no crack. The colour of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ composite aerogel is shallower than pure iron oxide. We synthesized a series of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ aerogels with different molar ratio of Fe and Al to investigate the effect of iron oxide on alumina aerogel.

Table 1 shows the BET surface area and pore structure parameters for different aerogels. From Table 1, we can find the pore volume and average pore diameter for $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ aerogels are between those of the Al_2O_3 and Fe_2O_3 aerogels, in addition to the BET surface area. When a little of iron oxides are added into Al_2O_3 aerogel, the surface area has a little change. With the increase of content of Fe_2O_3 ,

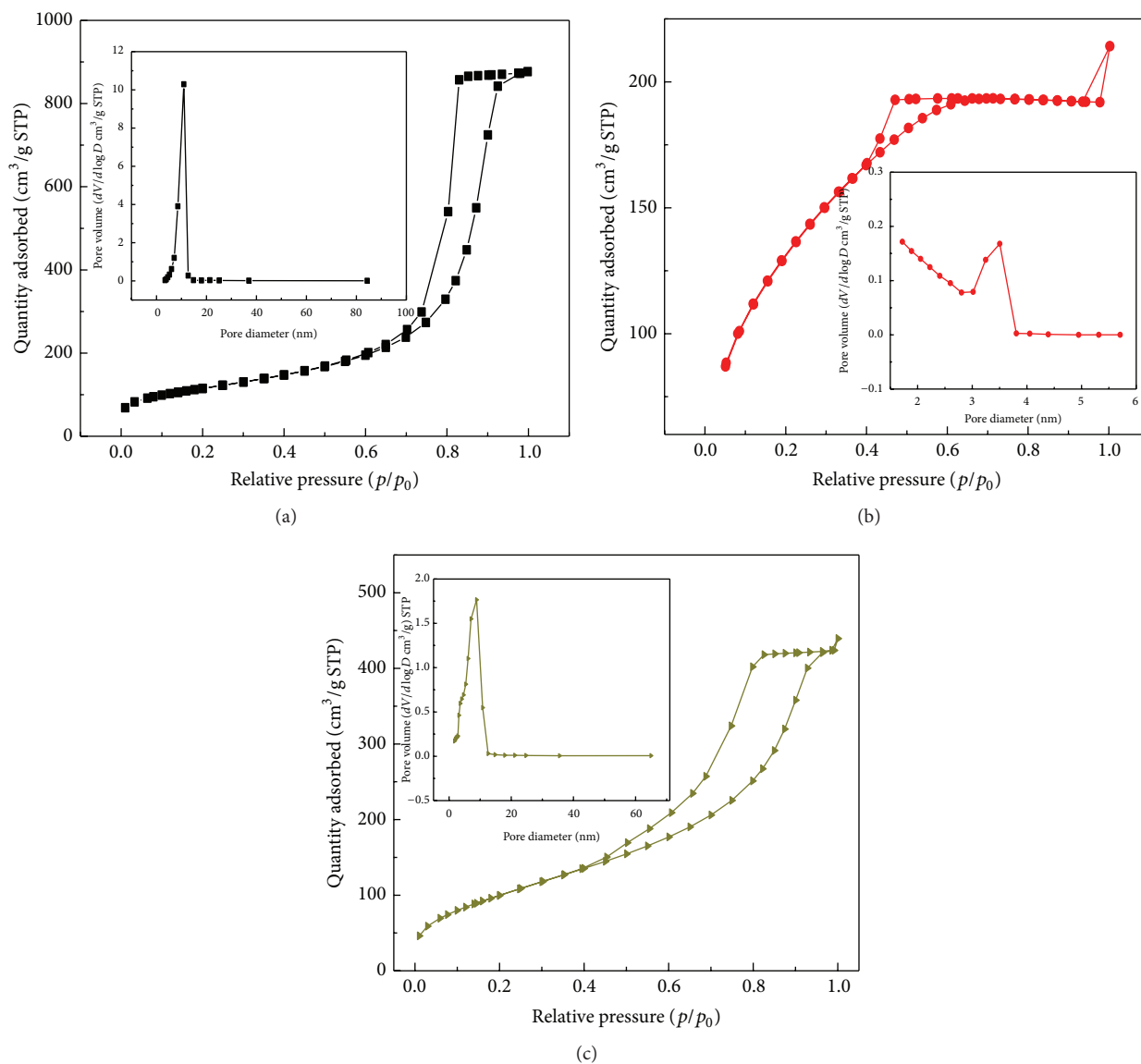


FIGURE 2: Nitrogen adsorption-desorption isotherms and pore size distribution of alumina aerogel (a), Fe₂O₃ aerogel (b), and Fe₂O₃-Al₂O₃ aerogel (c).

the surface area suddenly increases to 545.66 m²·g⁻¹. Then as the further increase of content of Fe₂O₃, the specific surface areas of composite aerogels begin to decrease little by little. So for Fe₂O₃-Al₂O₃ composite aerogels, appropriate proportion can make it have the largest specific surface area.

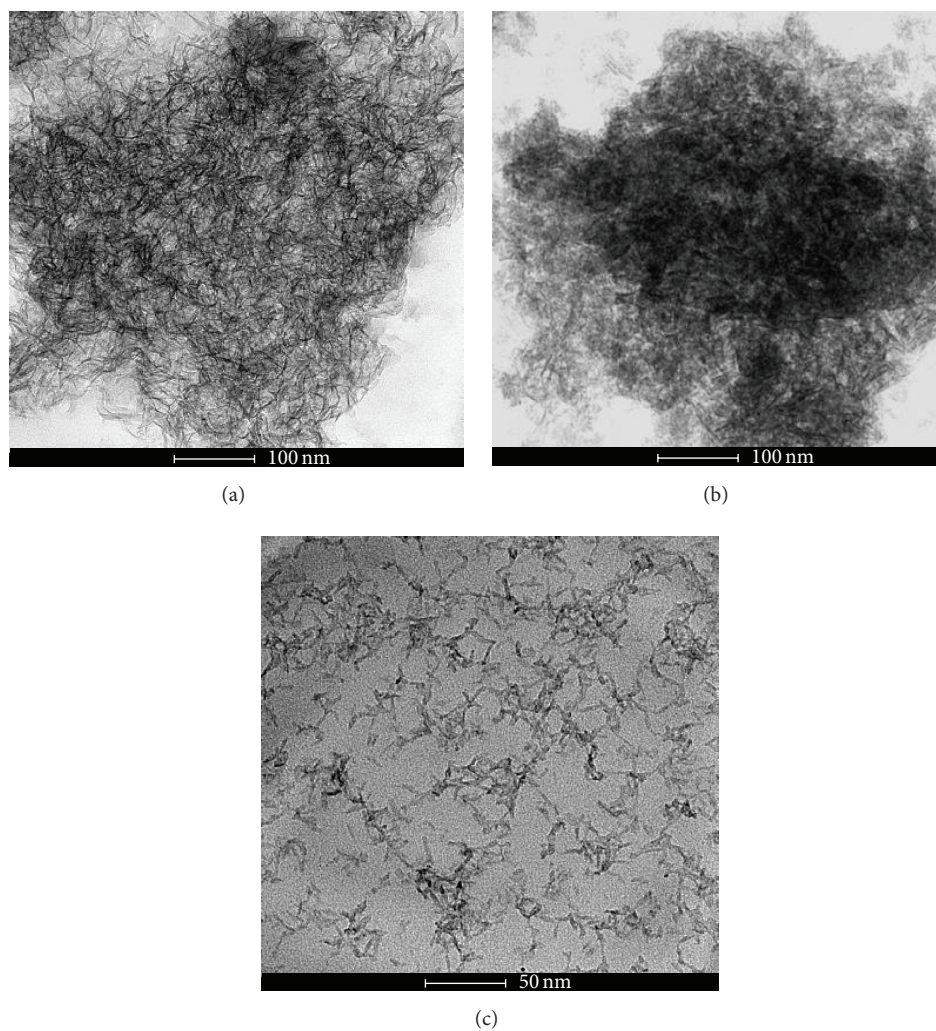
Figure 2 shows the nitrogen adsorption-desorption isotherms and pore size distribution of alumina aerogel, Fe₂O₃ aerogel, and Fe₂O₃-Al₂O₃ aerogel with 1:2 molar ratio of Fe to Al, respectively. The pore structure and the BET surface area of Fe₂O₃-Al₂O₃ composite aerogel were close to those of pure alumina aerogel, rather than iron oxide which gave priority to micropores. The Fe₂O₃-Al₂O₃ composite aerogel and alumina aerogel had pronounced mesoporosity in the range of 3–15 nm with a narrow pore size distribution, which made them have high internal surface areas.

Figure 3 shows the TEM pictures of three aerogels. From Figure 3 we can see that when floc structure Fe₂O₃ aerogel is added into thread-like structure alumina aerogel, shuttle-type structure with the length of about 15 nm forms, which leads to the composite aerogel having the high surface area. At the same time, the figure also hints that a new form appears at composite aerogel, which is different from the pure alumina and Fe₂O₃ aerogel.

In order to further investigate the aerogels' composition, we carried out the FT-IR experiment, as shown in Figure 4. For alumina aerogel, boehmite is the main component for its infrared absorption peak at 1050 cm⁻¹ and 616 cm⁻¹. For Fe₂O₃ aerogel, the main composition should be FeOOH for its infrared absorption peak at 2920 cm⁻¹, 1105 cm⁻¹, and 1404 cm⁻¹. When Fe₂O₃ is added into alumina aerogel,

TABLE 1: Pore structure parameters of alumina aerogels doped with various amounts of Fe_2O_3 .

Samples	BET ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Average pore diameter (nm)
Al_2O_3	413.46	1.3562	11.7480
Fe_2O_3 - Al_2O_3 mol(Fe) : mol(Al)	1:10	404.92	0.9007
	1:6	408.27	0.8189
	1:4	419.45	0.8025
	1:2	545.66	0.7229
	3:5	471.15	0.7059
	7:10	429.89	0.7357
	4:5	418.94	0.7620
	1:1	376.07	0.6798
Fe_2O_3	317.75	0.1891	2.3807

FIGURE 3: TEM photos for alumina aerogel (a), Fe_2O_3 aerogel (b), and Fe_2O_3 - Al_2O_3 aerogel (c).

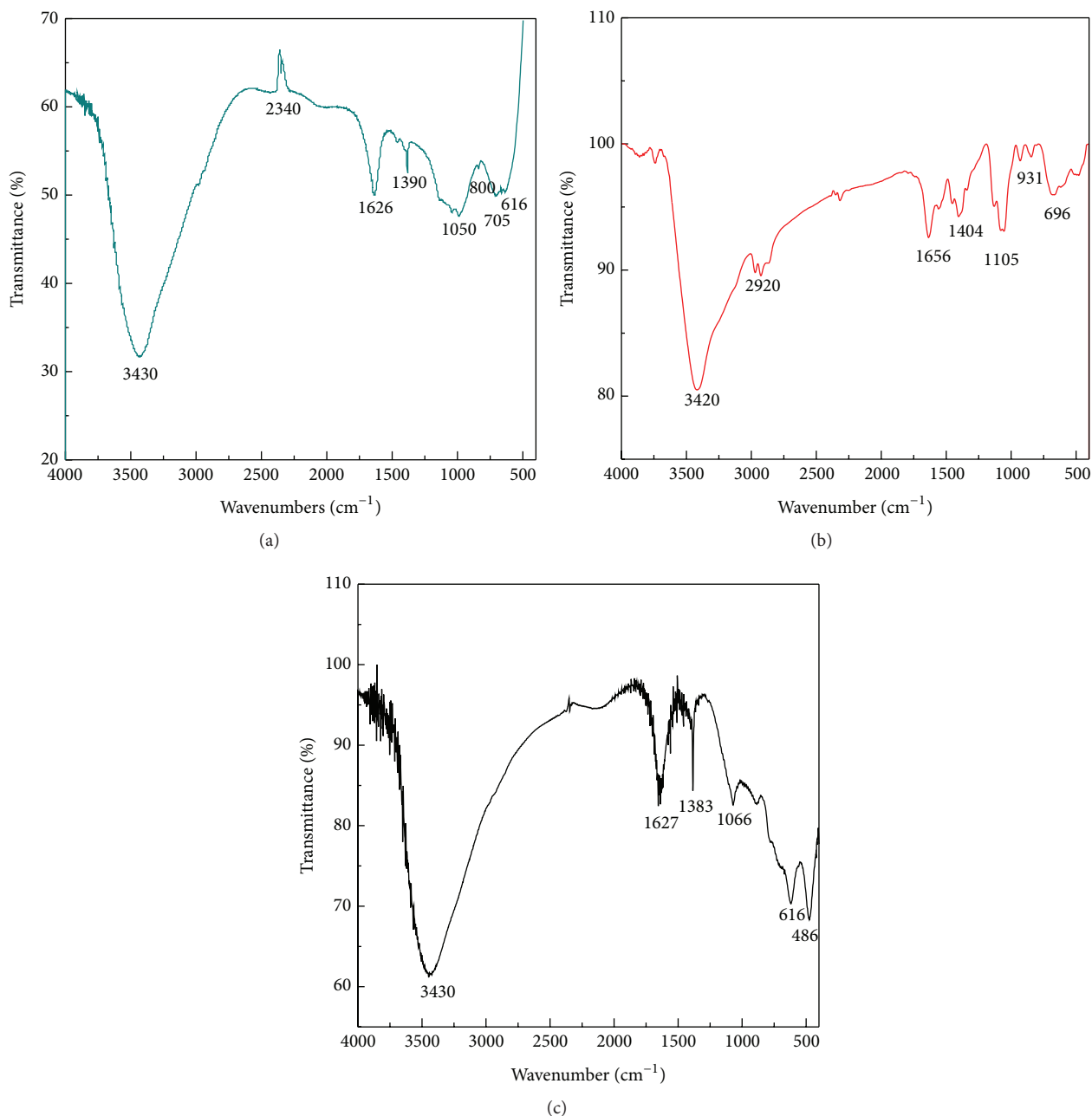


FIGURE 4: FT-IR spectrum of alumina aerogels (a), Fe₂O₃ aerogels (b), and Fe₂O₃-Al₂O₃ aerogel (c).

the IR spectra characteristic absorption peaks of boehmite and FeOOH are both reflected. In addition, there is an absorption peak at 496 cm⁻¹, caused by the presence of the Al-O stretching vibration in FeAl₂O₄. Figure 5 shows a set of XRD patterns of above samples. The XRD patterns reveal the same information with the results of FT-IR experiment. For Fe₂O₃-Al₂O₃ aerogel, the peaks corresponding to FeAl₂O₄ appear obviously.

We think that FeAl₂O₄ is formed after mixing two kinds of sol. Hydrochloric acid was used in the preparation of alumina sol. When alumina sol was mixed with iron oxide

sol, acidic condition would lead to some FeAl₂O₄ formation. Therefore, FeAl₂O₄ can be found in the characterization.

4. Conclusions

We successfully synergized monolithic alumina, Fe₂O₃, and Fe₂O₃-Al₂O₃ aerogels through OSSD drying method. Combined with IR spectra, TEM images, and pore structure parameters of aerogels, we found that the Al₂O₃-Fe₂O₃ composite aerogel with the appropriate proportion would form a new structure, which made it have the higher specific

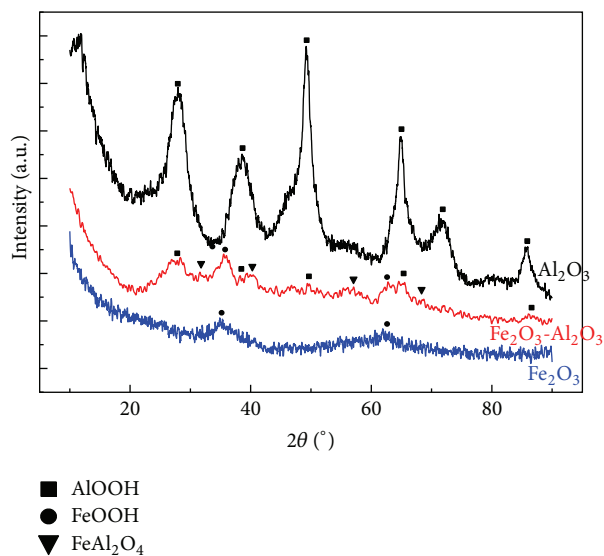


FIGURE 5: XRD patterns of alumina aerogels (black), Fe_2O_3 aerogels (blue), and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ aerogel (red).

surface area than the pure Al_2O_3 and Fe_2O_3 aerogels. And its particle size focused on about 15 nm and average pore diameter was about 4 nm.

Competing Interests

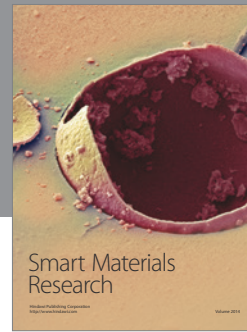
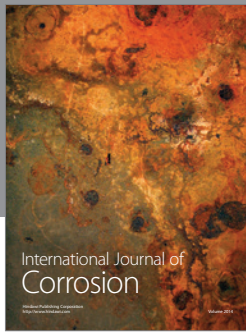
The authors declare that they have no competing interests.

Acknowledgments

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