Preparation of Cu-SiO$_2$ composite aerogel by ambient drying and the influence of synthesizing conditions on the structure of the aerogel

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A copper-doped silica composite aerogel with high specific surface area was prepared using a sol-gel method at ambient pressure. A drying control chemical additive (DCCA) *N,N*-dimethylformamide (DMF) was introduced to the composite sol of tetraethyl orthosilicate (TEOS) and copper nitrate (Cu(NO$_3$)$_2$·3H$_2$O) during the synthesizing process. The influence of the preparation conditions including Cu loading, catalyst concentration and heat treatment on the structure of copper-doped silica was investigated. The results showed that the obtained aerogel particles were uniformly distributed. The pore diameter was in a range of 2 to 15 nm. Heavier Cu loading benefited the formation of CuO crystalline, and reduced the specific surface area and pore diameter. When the catalyst concentration was high, the aggregation of Si-O network was reduced with the increase of it. The composite aerogel exhibited a good thermal stability after the heat treatment at high temperature.

Silica aerogel is a kind of new material with many unique properties and a wide potential application [1,2]. Metal-doped silica composite aerogel has been applied successfully in many reactions of catalytic oxidation, hydrogenation and dehydrogenation as high efficiency catalysts [3,4]. The conventional preparation techniques for synthesizing metal-doped silica composite are the chemical dipping and the high temperature calcination [5]. The aerogel material prepared by the conventional techniques has lower utilization efficiency, and the active components prefer to agglomerate in the matrix network. But using a sol-gel method, the composite material with high dispersibility and stability of active species can be synthesized [6]. Combining with supercritical drying technology, the sol-gel method is frequently applied to the synthesisis of metal-doped silica composite aerogel [7]. However, it is not worth being widely used in industry for the high-cost of supercritical drying. Therefore, how to synthesize silica aerogel using ambient pressure drying has become a hotspot in current researches [8–11]. For example, Shi and his coworkers [10] have prepared silica aerogel with low density and high specific surface area by using speedy drying technique. SiO$_2$ and TiO$_2$-SiO$_2$ aerogel with high specific surface area have been synthesized by Zhu and his coworkers [11] by acid-base catalysis at ambient pressure.

In recent years, the preparation of metal-doped silica composite materials at ambient pressure has attracted increasing research interest. A composite gelation synthesized through doping of polar solvent formamide in sol-gel system, and its influence on optical properties was discussed by Sales group [12]. *N, N*-dimethylformamide (DMF) is an applicable drying control chemical additive (DCCA) [13]. Using metal tetrasulphophthalocyanines as raw material, DMF was added to silica composite and a composite material with well optical properties was synthesized at atmospheric pressure by Garcia-Sanchez et al. [14]. The influence of Cu loadings on the composition of Cu-SiO$_2$ nano-aerogel was studied by Zhao et al. [15] under supercritical drying

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condition. But the prepared aerogel has lower specific surface area. The influence of different preparation conditions on the structure of the composite aerogel, which is synthesized with DMF additive by ambient drying, has never been reported in detail. In the present paper, a copper-doped silica composite aerogel with high specific surface area was synthesized by using the sol-gel method at normal atmosphere. A drying control chemical additive (DCCA) *N, N*-dimethylformamide (DMF) was introduced to the composite sol system of tetraethyl orthosilicate (TEOS) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) during the synthesizing process. The influence of the preparation conditions including Cu loadings, catalyst concentration and heat treatment on structure of the copper-doped silica was investigated. The results will provide important basic information for the catalyzed materials of enzymatic synthesis of diphenyl carbonate (DPC) and it can be used in other fields of catalysis.

1 Experimental

1.1 Reagents and apparatus

The reagents used in the experiment are as follows: Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) (Tianjin Bodi Chemical Co. Ltd, Tianjin, China), tetraethyl orthosilicate (TEOS) (Tianjin Kemiou Chemical Reagent Co. Ltd, Tianjin, China), *N, N*-dimethylformamide (DMF) (Tianjin Baishi Chemical Co. Ltd, Tianjin China), nitric acid (HNO_3) and absolute ethyl alcohol (Xi'an Sanpu Fine Chemical Company, Xi'an, China). All the chemicals are analytical grade reagent. De-ionized water was used in the experiment as solvent.

The morphologies and particle sizes of the samples were observed using a transmission electron microscope (TEM) (Hitachi, H-600, Japan), operated at 100 kV. Its infrared absorption spectra (FT-IR) were measured by an infrared spectrometer (Thermo Nicolet, Avatar360 E.S.P., USA), scan scope from 4000 to 400 cm^{-1}. The structures of the samples were characterized by X-ray diffractometer (XRD) (Rigaku, D/Max2550, Cu, 40 kV, 50 mA, Japan). The specific surface area and pore structures of the composite aerogel were determined by N_2 physical adsorption apparatus (ASAP 2020M, USA).

1.2 Preparation of composite aerogel

Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was dissolved into absolute ethyl alcohol and stirred as copper source, the solution mixed above was added into the mixture of TEOS and deionized water slowly, and was stirred by magnetic stirrers at 50°C for several minutes. Then *N, N*-dimethyl- formamide (DMF) and nitric acid with different concentrations (as catalyst) were dropped into the mixed solution formed by the last step. The mole ratio of TEOS: DMF: ethyl alcohol: deionized water was kept at 1∶0.5∶3∶6. After 6 h of stirring,

the sol, formed by mixed solution above, was poured into culture dish to age for several days to form blue alcogel at room temperature. After successive aging of the alcogel for 12 h, the alcogel was dipped in absolute ethyl alcohol and the mixture of TEOS and absolute ethyl alcohol (the volume ratio is 1∶1) to age for 24 h at 40°C, respectively. Then, the aging repeated once to displace the water in alcogel further. After washing in absolute ethyl alcohol for several times, the alcogel was dried for 12 h at 40°C and 48 h at 70°C, respectively. In order to remove water and organic substance inside the alcogel further, the dried alcogel was placed in an electric stove to heat, the resulting metal-doped silica composite aerogel was obtained.

To discuss conveniently, the composite aerogel was marked as *C*-Cu-*X*, where *C* represents the mol quantity of the concentrated nitric acid (14.75 mol/L) used in the experiment (*C*=0.05, 0.00035 mol), and *X* represents the mass fraction of Cu loadings, m_{Cu}/m_{SiO_2} (*X*=5,10).

2 Results and discussion

2.1 Analysis of morphology and specific surface of composite aerogel

Figure 1 is the TEM images of the composite aerogel for 0.05-Cu-5 and 0.05-Cu-10 annealed at 500°C. It can be observed that the aerogel particles, generally speaking, are almost spherical, and uniformly dispersed.

Figure 2 shows the distribution curves of pore diameters
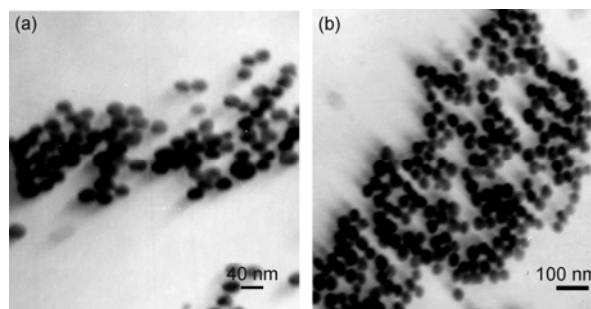
Figure 1 TEM images of the composite aerogels. (a)Aerogel sample 0.05-Cu-5; (b) aerogel sample 0.05-Cu-10.
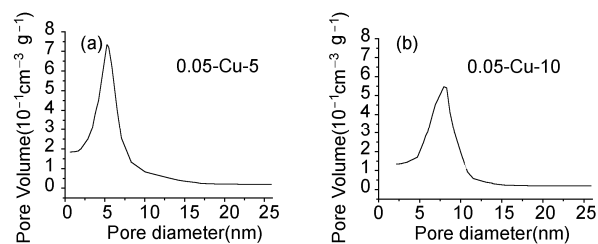
Figure 2 Pore diameter distribution of the composite aerogel. (a)Aerogel sample 0.05-Cu-5; (b) aerogel sample 0.05-Cu-10.

of the composite aerogels for 0.05-Cu-5 and 0.05-Cu-10 annealed at 500°C. It can be observed from Figure 2 that the pore diameter distribution of the composite aerogels is in a range of 2–15 nm. With the increase of Cu loadings, the average pore diameter of the composite aerogels increases and the pore volume decreases.

The structure change of the composite aerogel for 0.05-Cu-5 and 0.05-Cu-10 annealed at 500°C is presented in Table 1.

It can be seen that the composite aerogel has larger specific surface area, and with the increase of Cu loadings the specific surface and pore volume of composite aerogel decrease, the particle size increases. The results agree with that from [16], which was obtained under supercritical drying condition in the experiment. The results indicate that all kinds of microstructures of composite aerogel with high specific surface area can be influenced by the factor of Cu loadings.
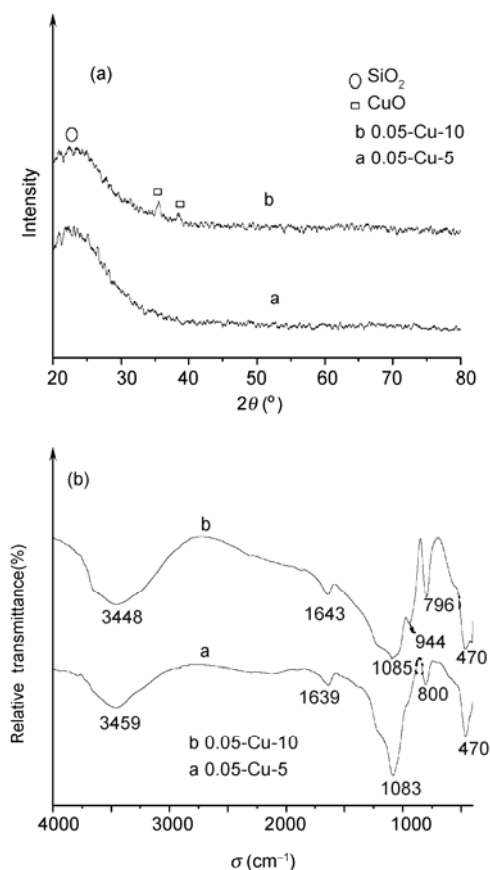
2.2 The influence of Cu loadings on the component and pore adsorption of composite aerogel

The XRD patterns and FT-IR spectra of the composite aerogel annealed at 500°C, with catalyst concentration $C=0.05$ mol at different Cu loadings, are presented in Figures 3(a) and (b). The broadening peak at $2\theta=23°$ is the diffraction peak of SiO_2, which indicates that SiO_2 is amorphous. None of CuO's diffraction peak observed at 5% Cu loading suggests that the aerogel, with very well active components dispersed in the matrix, can be synthesized by sol-gel process. As Cu loading increases to 10%, two weak peaks that represent characteristic crystal phase of CuO occur at around 23° and 38.5°. This suggests that there are CuO crystal grains existing in composite aerogel, that is to say, some active components are well dispersed in the matrix in the form of CuO crystal grains or clusters. All the results above indicate that the amount of Cu loading has an effect on the phase composition of $Cu-SiO_2$ composite aerogel, and the active components present well dispersive state in matrix and has stronger interaction with matrix.

Compared with the spectrum a in Figure 3(b), the vibrational absorption peak of Si-OH appears obviously in the spectrum b at 944 cm^{-1} [17] , and it becomes stronger at around 3459 cm^{-1}. The reason for this is the increase of silicon-hydroxy originated from the heavier Cu loading. Besides, the stretching vibration absorption peak of Si-O-Si at around 796 cm^{-1} increases noticeably, and the shift of its center to lower wavenumber indicates that heavier Cu loading can

Figure 3 XRD patterns (a) and FT-IR spectra (b) of the composite aerogels with different Cu loadings.

affect the formation of Si-O-Si network and the interaction between Cu and SiO_2. The vibration peaks of Cu-O bond appear commonly at 575, 500, 470 cm^{-1}, which is hard to be observed due to the overlapping of the broadening band at around 470 cm^{-1} corresponding to SiO_2 matrix.

Figure 4 plots the isotherms of nitrogen adsorption-desorption of the composite aerogel annealed at 500°C. It shows that the samples are of absorption characteristics with porous structure, and that the adsorption-desorption isotherms are closed to *I* type. The material exhibits a strong capability of adsorbing at relative pressure p/p_0 within 0.01–0.12. So the relatively smooth curve has a sharp rise which corresponds to mono-molecule layer adsorption on the pore surface. As p/p_0 exceeding 0.12, the adsorption isotherm is approximately horizontal, which is an adsorption behavior of porous solid. A retardation phenomenon existing in the desorption process with an open back-loop indicates that absorbed nitrogen can not be desorbed entirely. The possible reason for this may be that some pores with strong capability of adsorbing are exposed due to the volatilization of some organic materials during the anneal of the aerogel at 500°C. While the exposed pores have relatively strong adsorbability of nitrogen, which results in a difficult desorption during the process of depressurization. The comparative

Table 1 Effect of copper loading content on the structures of the composite aerogels

| Sample	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})	d (nm)
0.05-Cu-5	560.7	0.27	19.1
0.05-Cu-10	456.8	0.12	28.2
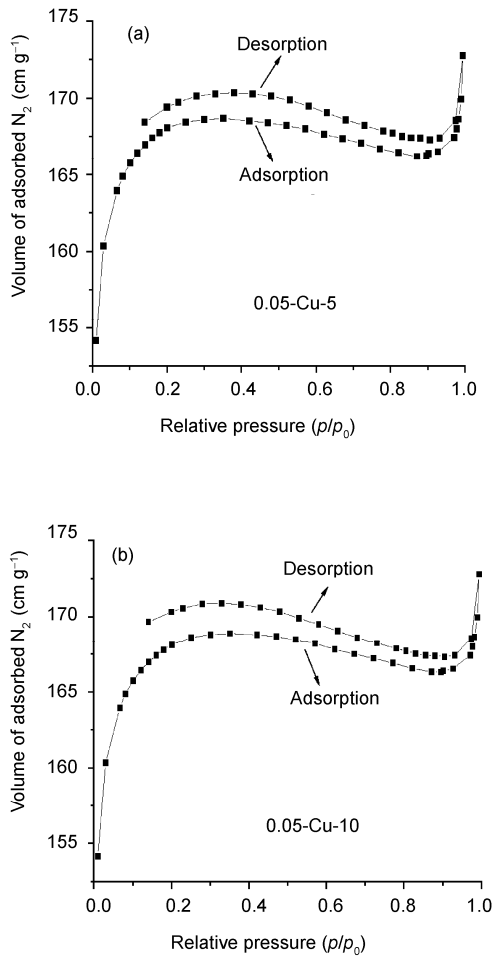
Figure 4 Nitrogen adsorption-desorption isotherms of the composite aerogel. (a) Aerogel sample 0.05-Cu-5; (b) aerogel sample 0.05-Cu-10.

closeness of the adsorption-desorption isotherm in Figure 4 suggests that Cu loading has a certain effect on the uniformity of pore structure.

2.3   The influence by catalyst concentration

Figure 5 presents FT-IR spectra of the composite aerogel for 0.05-Cu-10 and 0.00035-Cu-10 annealed at 500°C. It can be observed that the absorption peaks at around 1641 and 3446 cm^{-1} are relatively weak for the composite aerogel
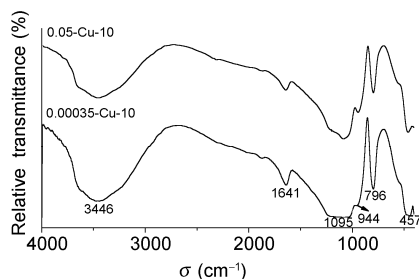

Figure 5   FT-IR spectra of the composite aerogel.

with a higher catalyst concentration. It is because the higher concentration of catalyst is, the lesser silicon-hydroxide group adsorbed during the polycondensation of matrix for the sample with the same volume of catalyst. In addition, the intensities of vibrational absorption peaks of Si-O-Si at around 1095 and 796 cm^{-1} are also weak. The possible reason is that the hydralysis of TEOS under acid catalytic condition is an electrophilic reaction. The higher H$^+$ concentration is, the faster hydrolysis rate of TEOS monomers is. Due to the slower polycondensation rate, it leads to a slowing down of the polycondensation speed of Si-O-Si network and a decline of its agglomeration.

2.4   The influence by heat treatment

For preparing the composite aerogel, heat treatment is one of the important factors. The distribution, combination and formation of aerogel crystal grains are usually influenced by heat treatment at high temperatures. Figure 6 shows the XRD patterns of the composite aerogel for 0.05-Cu-10 with different heat treatment temperatures and times. The XRD patterns of the samples, with different heat treatment temperatures for 3 h and heated at 700°C for various times, are presented in Figure 6(a) and (b), respectively. A diffraction peak of SiO$_2$ with broad band appeared at around 22° indicates that SiO$_2$ is still amorphous after heat-treatment at high temperature. This peak becomes sharper and narrower after the heat treatment for 3 h at 900°C and 7 h at 700°C, indicating the crystallization of SiO$_2$. With regard to the diffraction peaks of CuO phase, they are weak and of dispersive state for the sample heated at 300°C. The weak diffraction peaks appear at around 35.5° and 38.5° after the heat treatment at 500°C for 3 h, and their intensities get strong even though the peaks are relatively broad. This results show that the CuO has smaller crystal grains and are well dispersed in the matrix in the form of crystallite. An obvious enhancement of diffraction peaks for an increase of temperature from 700°C to 900°C indicates that the sizes of active components gradually increase with a rise of the temperature. After heat treatment at 700°C for 7 h, the diffraction peak of CuO appears at around 43.1°. Compared with those after heat treatment for 3 h and 5 h at 700°C, the sizes of CuO crystal grains become larger further. All the results above show that active components are still well dispersed in the matrix and have relatively strong interaction with matrix, together with better thermal stability of sample after heat treatment at higher temperatures and longer times.
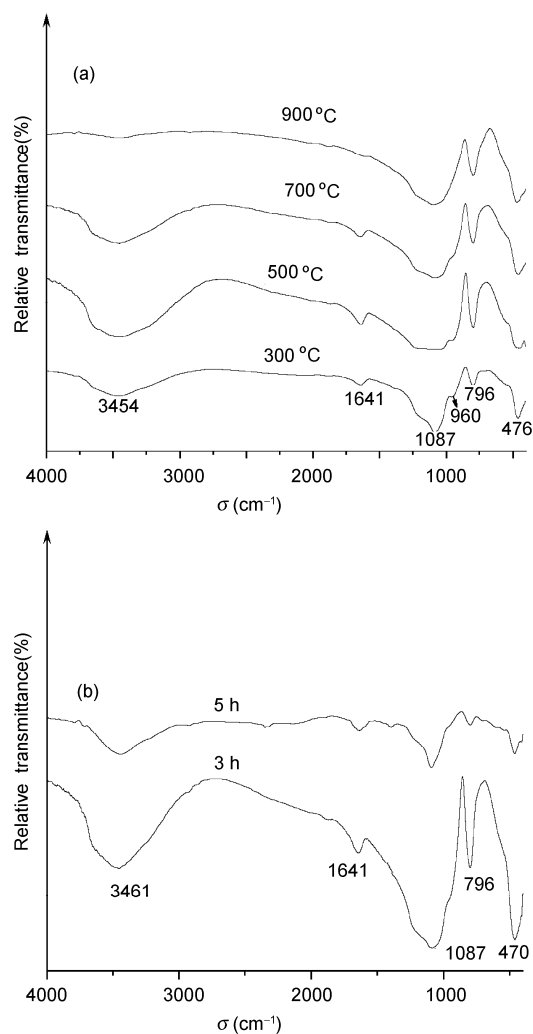
The FT-IR spectra of the composite aerogel for 0.05-Cu-10 with different heat temperatures and times are shown in Figure 7(a) and (b). The absorption peaks emerging at around 476, 796 and 1087 cm^{-1} correspond to Si-O-Si's flexural vibrations, symmetrical stretching vibration and antisymmetric stretching vibration, respectively [18]. The appearance of those absorption peaks shows that the composite
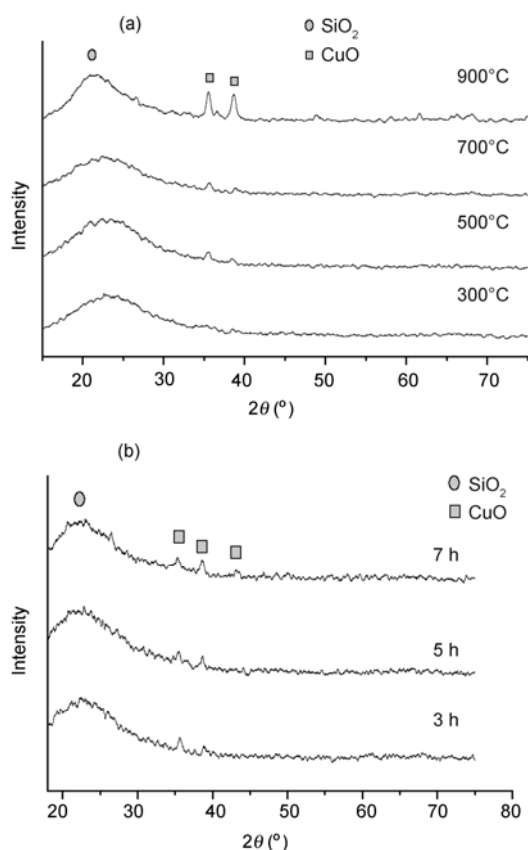
Figure 6   XRD patterns of composite aerogel with different heat temperatures and times. (a)Heated at different temperatures for 3 h; (b) heated at 700°C for different times.

aerogel has IR absorption characteristic of SiO_2 in amorphous state.

It can be observed in Figure 7(a) that the intensities of Si-OH vibrational absorption peaks at around 960, 3454 and 1641 cm^{-1} decrease with the rising temperatures. The phenomena that the absorption peaks at around 3454 and 1641 cm^{-1} become very weak and the absorption peak at 960 cm^{-1} disappears completely indicate a significant reduction of Si-OH bond in quantity. The absorption intensity at 796 cm^{-1} becomes stronger with the changing of heat treatment temperature from 300°C to 500°C. This phenomenon suggests that the moisture and organic substance in pore structure were volatilizing during the process of heat treatment, and its thermal analysis is presented in Figure 8. Condensation and polymerization lead to an enlargement and enhancement of silica network. With a continuing rise of temperature, the absorption peak starts to decrease. The reason for this is the collapse of part of silica network during the higher heat treatment. It can be seen that the absorption peaks corresponding to each functional group of the composite aerogel become weaker when the heat treatment time increases from 3 to 5 h at 700°C. The observation from IR spectra shows that the composite aerogel becomes stable,

Figure 7   FT-IR spectra of composite aerogel with different heat temperatures and times. (a) Heated at different temperatures for 3 h; (b) heated at 700°C for different times.
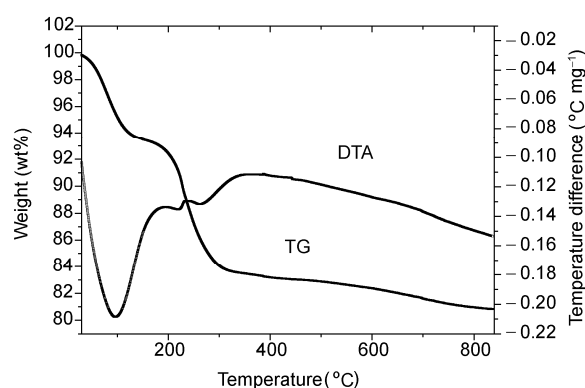
Figure 8   Thermal analysis curves of the composite aerogel for 0.05-Cu-10.

which is made up of the network formed by Si-O-Si bonds after a high-heat treatment for a longer time.

The thermal analysis curves of the composite aerogel for 0.05-Cu-10 are shown in Figure 8. We can see from Figure

8 that the curve of differential thermal analysis (DTA) has endothermic peaks and the corresponding thermogravimetric (TG) curve shows weight loss around 98℃ and 220°C, respectively. It is ascribed to the evaporation of the water absorbed and organic substance including alcohol [19]. The curve of DAT also has exothermic peaks around 236°C and 320°C, respectively. It is probably due to the burning of TEOS and small quantity of NO_3^- which remains in the aerogel. The corresponding TGA curve shows a continuous weight loss. With an increase of the heat treatment temperature, the weight loss rate of the composite aerogel reduces.

3 Conclusions

A copper-doped silica composite aerogel with high specific surface area was prepared by using a sol-gel method at normal atmosphere. *N,N*-dimethylformamide (DMF) was introduced to the composite sol system of tetraethyl orthosilicate (TEOS) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) during the synthesizing process. The influence of the preparation conditions including Cu loadings, catalyst concentration and heat treatment on the structure of the copper-doped silica was investigated. The results show that the pore diameter of composite aerogels is in a range of 2 to 15 nm.

Copper is of diffuse state for low Cu loading. The specific surface area and pore volume of the composite aerogel decrease with the increase of Cu loadings, and some oxide crystal grains are well dispersed in the matrix. The formation of Si-O network is affected by the concentration of catalyst. The more concentration of catalyst is, the weaker polycondensation of Si-O-Si network is. After the heat treatment of the composite aerogel at 500°C, the obtained aerogel grains are distributed uniformly. The material tends towards stable and it indicates a good thermal stability after higher heat treatment.

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