烷基羧甲砜基氢氧化铁热脱羧和热分解法制备纳米氧化铁

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摘要：十六烷基羧甲砜基氢氧化铁和丁基羧甲砜基氢氧化铁通过热脱羧方法,合成了纳米氧化铁颗粒。采用 X 射线衍射、红外光谱及透射电镜等手段对纳米氧化铁的合成过程和结构特征进行了表征。制备的纳米氧化铁具有 8~18 nm 的晶粒尺寸。羧甲砜基的热脱羧过程使得表面活性剂从纳米颗粒表面去除相对容易,特别是丁基羧甲砜基化合物。十六烷基羧甲砜基氢氧化铁制备纳米氧化铁颗粒存在脱羧有机分子还原 Fe^{3+} 过程,而丁基羧甲砜基氢氧化铁通过热脱羧分解的方式合成纳米氧化铁颗粒。

关键词：热脱羧；烷基羧甲砜基；纳米颗粒；红外光谱
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Magnetite Nanoparticles Prepared by Thermal Decarboxylation and Decomposition of Iron Hydroxide Alkylsulfonyl Acetate

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Abstract: Magnetite nanoparticles were prepared by thermal decomposition of iron hydroxide cetylsulfonyl acetate and butylsulfonyl acetate under the protection of nitrogen. The morphology, crystallinity and oxidation state of Fe were studied using TEM, XRD and FTIR. The results reveal that magnetite nanoparticles are 8~18 nm in diameter, and the thermal decarboxylation of carboxymethylsulfonyl in both precursors makes the removal of organic compounds easy, especially in the one with short carbon chain. The final nanoparticles are formed in two different ways, where C16 samples magnetite is derived from the reduction of Fe^{3+} by organic fractions, whereas the nanoparticles of ferric oxides are derived in C4 product from the thermal decomposition.

Key words: thermal decarboxylation; alkylsulfonyl acetate; nanoparticles; infrared spectroscopy

Nanoscale metals, metal oxides and semiconductors are of great interest because they possess physical and chemical properties that are characteristic neither of the atoms nor of their bulk counterparts. Nanoparticles large ratio of surface area to volume can contribute to some of their unique properties, including novel electrical, optical, magnetic, and catalytic properties[1-4].

Magnetite(Fe_3O_4), a common magnetic iron oxide, has a cubic inverse spinel structure with oxygen forming a closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites [5]. Magnetites nanoparticles have attracted attention due to current and potential applications as a Magnetic Resonance Imaging(MRI)contrast agent[6], as well as in catalysis[7]

and biomedicine[8,9]. Several methods have been developed for their preparation including precipitation of Fe^{2+} and Fe^{3+} with alkaline solutions and thermal decomposition of Fe-bearing precursors[10~12]. Gržeta et al.[13] synthesized 10~21 nm magnetite nanoparticles using the common method of thermal decomposition of iron-organic compounds, specifically thermal decomposition of iron choline citrate using nitrogen and quenching in double distilled water.

Removal of organic compounds from a nanoparticles surface, important in catalysis [14], can be hard to achieve because of the strong interaction between capping ligands and substrates. Liu et al.[15] prepared sulphonic acid sodium salt(DBS) and cetyltrimethyl ammonium bromide(CTAB) coated γ-Fe_2O_3 nanoparticles by a microemulsion process. Surfactants remained on the surface of nanoparticles can not be removed even after heat treatment under nitrogen at 350 ℃ because of the strong interaction between -SO_3^{2-} and Fe^{3+} or N^+ and O^{2-}. Pan et al.[16,17] have studied carboxymethylsulfonyl, a group containing a methene between the groups of sulfonyl and carboxyl, in the field of temporarily water-soluble disperse dye, because of its easy decarboxylation, mainly affected by the sulfonyl group, when heated below 200 ℃. Recently our group synthesized cetylsulfonyl acetic acid and its thermal analysis showed that the compound would decarboxylate when heated to 150 ℃ under nitrogen[18]. To the best of our knowledge , there has been no reports on the preparation of nanomaterials assisted by this kind of carboxylic acid. This paper presents the formation of uncoated magnetite nanoparticles by thermal decomposition of iron hydroxide alkylsulfonyl acetate with short and long carbon chains under the protection of nitrogen. An outstanding property of the iron-organic compounds is the thermal decarboxylation of carbonyl at low temperature, making it easy to break the interaction between iron and the organic compounds.

1 Experimental

All chemicals were analytical grade and were used as received without further purification. Cetylsulfonyl acetic acid and *n*-butylsulfonyl acetic acid were synthe-

sized as per the route reported by Pomerantz [19] and purified by column chromatography (ethyl acetate/petroleum 3/1 as the eluent). The preparation of iron hydroxide alkylsulfonyl acetate was similar to that outlined by Bourlinos et al. [20]. 4.04 g Fe (NO$_3$)$_3$H$_2$O was added to a 30 mL ethanol solution containing 3.48 g cetylsulfonyl acetic acid at 40 ℃. After the dissolution of nitrate, 6 mL ammonia(25%) was added, followed by agitation for 20 min. The precipitate was filtered and washed with water and ethanol, then dried at room temperature overnight to obtain iron hydroxide cetylsulfonyl acetate. The compound was calcined at different temperatures for 1 h with a heating rate of 5 ℃·min^{-1} under nitrogen flow in a tube furnace (C16). For the preparation and decomposition of iron hydroxide *n*-butylsulfonyl acetate was essentially equivalent except that the preparation of precursors was carried out at ambient temperature(C4).

XRD measurements were performed using a Rigaku D/max 2400 X-ray diffractometer operated at 40 kV and 25 mA using Cu $K\alpha$ radiation(λ =0.154 18 nm). Samples were scanned between 10° and 80°(2θ) with a scanning rate of 1°·min^{-1}. A Bruke EQUINOX55 FTIR spectrometer recorded infrared spectra of the samples in KBr pellets in the range of 4 000~400 cm^{-1}. TEM images were taken with a FEI Tecnai 20 transmission electron microscope using an accelerating voltage of 200 kV. TEM samples were prepared by placing a drop of dilute ethanol dispersion onto a carbon film coated copper grid and dried at room temperature.

2 Results and discussion

Fig.1 and 2 show the XRD patterns of precursors and sample after calcining at different temperatures. Both iron-organic precursors are amorphous. After heating to 200 ℃, C16 sample remains amorphous, but a broad diffraction peak appears around 2θ=35° in C4 samples, indicating the appearance of an iron oxide with a certain crystalloid. The diffraction peaks become sharper with higher temperatures, suggesting the formation of magnetite(PDF 19-629). There is a tiny difference in the peaks of C4 and C16 samples: In C16, the
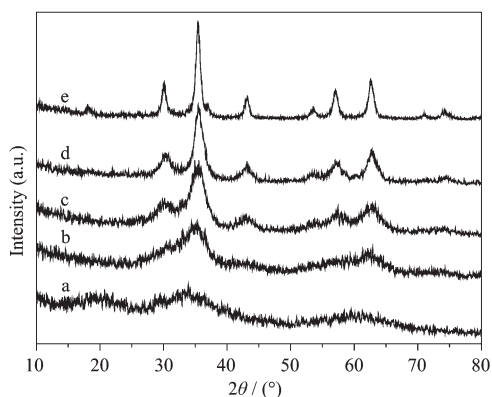
(a) iron hydroxide *n*-butylsulfonyl acetate; (b) 200 ℃;
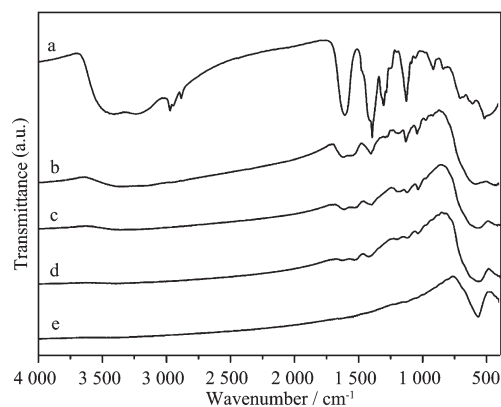(c) 250 ℃; (d) 300 ℃; (e) 400 ℃

Fig.1　XRD patterns of C4 samples
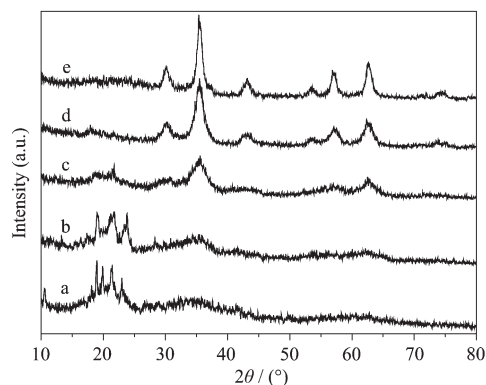
(a) iron hydroxide cetylsulfonyl acetate (b) 200 ℃;
(c) 250 ℃; (d) 300 ℃; (e) 400 ℃

Fig.2　XRD patterns of C16 samples

(a) iron hydroxide cetylsulfonyl acetate; (b)200 ℃;
(c) 250 ℃; (d)300 ℃; (e)400 ℃

Fig.3　FTIR spectra of C4 samples

(a) iron hydroxide cetylsulfonyl acetate; (b) 200 ℃;
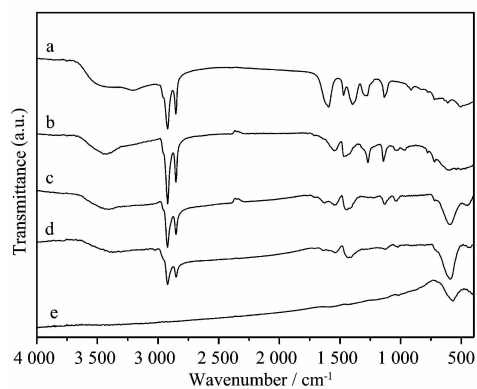(c) 250 ℃; (d) 300 ℃; (e) 400 ℃

Fig.4　FTIR spectra of C16 samples

strongest peak is at $2\theta=35.4°$ without a shift after heating to 250, 300 and 400 ℃. However, the peaks change gradually from $2\theta=35.6°$, relates to maghemite(PDF 25-1402), to $2\theta=35.4°$ in the corresponding patterns of C4. According to the Scherrer formula, the mean sizes of the grain can be calculated from the peak width at half-maximum; the narrowed diffraction peak indicates larger crystallite sizes, as confirmed by TEM. The average grain sizes of C4 and C16 samples calcined at 400 ℃ from the(311) reflection are 11.2 nm and 11.5 nm, respectively, which matches well with values obtained from TEM.

　　The process of thermal decarboxylation and formation of magnetite was monitored by FTIR spectroscopy. Fig.3 and 4 display the spectra for C4 and C16 samples. The regions above 3 000 cm^{-1} become flat after calcining at higher temperatures, and are associated with vibrations of -OH or H_2O. The regions below 3 000 cm^{-1} indicate the vibrations of the $-CH_3$ and $-CH_2-$ groups present in the aliphatic chain. The disappearance of absorption at around 2 900 cm^{-1} in C4 sample after heating to 200 ℃ indicates the decarboxylation of the precursor and the desorption of organic compounds from the particulate surface after thermal decarboxylation. Vibrations of the C16 samples do not vanish until calcining at 400 ℃. Perhaps compounds with short carbon chains after decarboxylation in the C4 samples are able to evaporate and blow away easily with nitrogen, whereas compounds after decarboxylation in the C16 samples have long carbon chains and rarely clear away at low temperatures. Absorptions between 1 600 and 1 380 cm^{-1} indicate the carboxylic acids linked to Fe^{3+} in the form of $-COO^-$ in both precursors. Absorptions in this region, unrelated to the vibrations of

-COO⁻, still exist after the heat treatment. CO_3^{2-} might form after decarboxylation and be decomposed after heating at 400 ℃[21]. Peaks between 1 300 and 1 100 cm⁻¹ denote to the presence of -SO_2- group. Those below 750 cm⁻¹ can be ascribed to Fe-O vibrations; Peaks of C16 samples in this region are sharp, showing the presence of magnetite. Peaks of C4 samples change from broad to sharp with the increase in temperature implying the transformation of crystalloid, as confirmed by XRD[7,22]. Since only Fe^{3+} was employed in the synthesis, the magnetite might have two origins: heating in the presence of unoxidized organic material or firing at high temperature [13,23]. Magnetite in the C16 sample might come from the reduction of Fe^{3+} by organic fractions. But in the C4 sample, organic compounds flow away with nitrogen as soon as the occurrence of decarboxylation and the reduction does not take place in low temperature. When the temperature is high enough, ferric oxide transforms to magnetite by the emission of molecular oxygen[24]. Combined with FTIR results, the samples would be a Magnetite because the Magnetite usually provides a sharp peak in the region of Fe-O stretching. The diffraction peaks are distinct and the width of the peaks narrows if the temperature is increased.

　　White powders appeared on the wall of furnace after heat treatment of the C16 sample to 250 ℃ was characterized by FTIR. As shown in Fig.5, the peaks mainly indicate the vibrations of C-H and -SO_2- groups. The structure of RSO_2CH_3 was also confirmed by proton NMR spectroscopic analysis, and the chemical shifts of the methylsulfonyl and methylenesulfonyl protons (-$CH_2SO_2CH_3$) were observed at 1.84 and 2.89
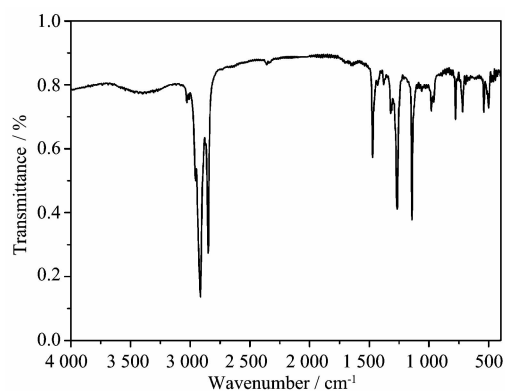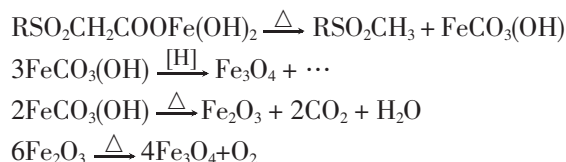

Fig.5　FTIR spectra of sample collected on the wall of the furnace

ppm(Not shown in the paper). These analyses prove that the compound is successfully synthesized by our designed procedure.

　　Kataby et al. studied the thermal desorption of various carboxylic acids from the surface of amorphous iron nanoparticles, showing that dimeric keto compounds were formed by the reaction of two monomers and the elimination of CO_2[25]. In the current study, the spectrum shows no absorption of the C=O group. The substrates are notable, for the amorphous iron has no hydroxide groups; the precursors exhibit excess hydroxide groups, which could offer hydrogen atoms to the reaction of decarboxylation. The whole process from decarboxylation to the formation of magnetite could be described as follows:

$$RSO_2CH_2COOFe(OH)_2 \xrightarrow{\triangle} RSO_2CH_3 + FeCO_3(OH)$$
$$3FeCO_3(OH) \xrightarrow{[H]} Fe_3O_4 + \cdots$$
$$2FeCO_3(OH) \xrightarrow{\triangle} Fe_2O_3 + 2CO_2 + H_2O$$
$$6Fe_2O_3 \xrightarrow{\triangle} 4Fe_3O_4 + O_2$$

　　The TEM images of the C4 and C16 samples obtained at 300 and 400 ℃ are shown in Fig.6. The prod-
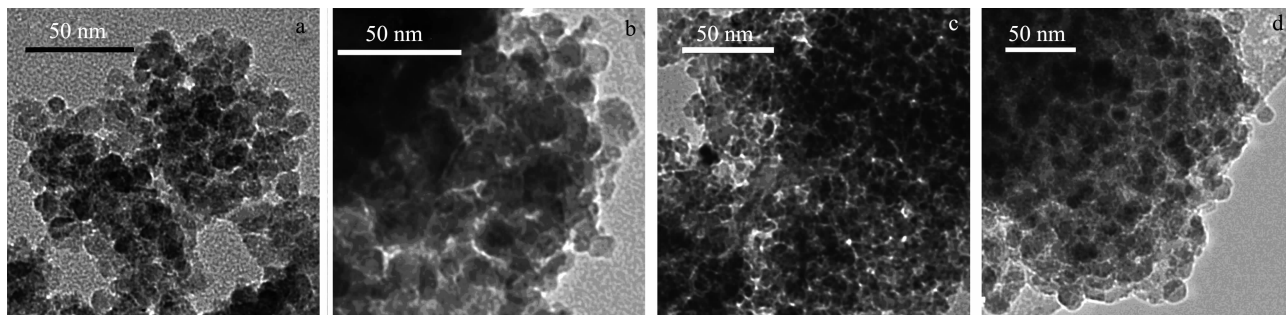
(a) 300 ℃/ C4; (b) 400 ℃/ C4; (c) 300 ℃/ C16; (d) 400 ℃/ C16

Fig.6　TEM images of samples

ucts, nearly spherical, change from 5~7 nm at 300 ℃ to 8~18 nm at 400 ℃. Unavoidably, the nanograins aggregate seriously, due to the absence of capping ligands and the presence of a large surface/volume ratio that would decrease the surface area. But isolated grains from nanoparticles could be seen after heating to 300 ℃ with slight aggregation, and on the edge of blocks after calcining at 400 ℃.

3　Conclusions

Magnetite nanoparticles with grains in the range of 8~18 nm were synthesized by direct thermal decomposition of iron hydroxide butylsulfonyl acetate and cetylsulfonyl acetate under the protection of nitrogen. The thermal decarboxylation of carboxymethylsulfonyl in both precursors makes the removal of organic compounds easy, especially in the one with short carbon chain. For both samples, XRD patterns confirm the formation of magnetite at 400 ℃. FTIR spectra indicate that the final nanoparticles are formed in two different ways. In C16 samples magnetite is derived from the reduction of Fe^{3+} by organic fractions, whereas in C4 the products are derived from the thermal decomposition of ferric oxide in inert gases. The excess hydroxides in the precursors participate the decarboxylation and are helpful in the removal of organic fractions.

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