



# Fe modified mesoporous hollow carbon spheres for selective oxidation of ethylbenzene

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**ABSTRACT** Fe modified hollow carbon spheres with large cavity and mesoporous shell (Fe-MHCs) were successfully synthesized by a simple pyrolysis and simultaneous deposition method. The organic molecules gases (carbon species) from pyrolysis of polystyrene deposited in the hard template at the catalysis of Fe species existing in the sample during calcination at high temperature. The obtained Fe-MHCs showed uniform spherical morphology with large surface area ( $924 \text{ m}^2 \text{ g}^{-1}$ ), mesoporous structure and a certain amount of Fe loaded. The Fe species and the special structure endowed the materials excellent catalytic activity in the oxidation of ethylbenzene to acetophenone. The conversion of 94.5% and the high selectivity to targeted product (97.4%) could be achieved and the acceptable recycling stability was also exhibited.

**Keywords:** hollow carbon sphere, Fe modified, catalytic, ethylbenzene oxidation

## INTRODUCTION

Mesoporous hollow carbon spheres (MHCs) have attracted increasing attention due to their low density, high surface-to-volume ratios, hollow interior structures and mesoporous textures [1,2]. Compared with conventional mesoporous carbon or active carbon materials, the large internal volume of MHCs can provide a storage space that can serve many functions [3,4]. Furthermore, the hollow nanostructures with mesoporous shells could facilitate the fast diffusion of reactants and products due to the short diffusion pathway, larger pore, cavity volume, and spherical morphology [5–7]. Templating including hard and soft template method has been widely used to synthesize MHCs [8–11]. Generally, the morphology and the monodispersity of the as-prepared hollow products by soft template method are less satisfactory than that by hard template due to the polydispersity and dynamics [12]. Hence, the method based on hard template has been

commonly employed to prepare MHCs due to the better control of morphology, mesoporous structure and monodispersity. Generally, the crucial process is assembling carbon precursors into hard template by infiltration or polymerization. However, the solvent (e.g., water, ethanol or other organics) is necessary, leading to pollutions and increasing the difficulties for recycle and scale-up production. The chemical vapor deposition (CVD) method is a common hard-templating method using organic small molecule gas (e.g., pyrrole, methane and ethylene) as carbon precursor, which can avoid the impregnation of carbon precursor. However, the high technology in general CVD equipment and accurate control in the flow rate of feed gas limit its extensiveness [13].

One of the most critical issues in the development of MHCs is to select suitable low-cost carbon precursor [14–18]. Some polymers (e.g., resol, pitch, polyaniline, polyacrylonitrile) can act as carbon precursor due to their commercial availability [12]. Polystyrene (PS), a typical polymer, has been widely used in packaging and is a major source of ‘white pollution’ [19]. Nevertheless, PS almost has no carbon residue when directly pyrolysis and was more often used as sacrifice hard template for hollow spheres because it is easy to decompose [20]. Therefore, converting PS into functional carbon materials will provide a possible solution for reusing of polymer waste (e.g., polyethylene, polypropylene) and reducing ‘white pollution’. Some methods (e.g., crosslink) have used PS as carbon precursor for carbon materials [21,22]. In our previous work, we have also fabricated controllable hollow carbon spheres by the ‘dissolution-capture’ method using PS as carbon sources [22]. But those methods have some inevitable limitations, such as the tedious procedure, the use of organic solvent, uncontrollable morphology and the difficulty for scale up. Thus, it is

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significant to expand the utilization of PS as carbon precursor with simple process to prepare carbon materials. In addition, the introduction of iron-based catalyst improved the graphitization degree and pore volume. Moreover, graphitic carbon with a porous structure can provide low-resistant pathways and short ion diffusion channels in chemical reaction.

In this work, the Fe modified MHCs (Fe-MHCs) were fabricated *via* a facile strategy, pyrolysis and simultaneous deposition. The strategy employed Fe modified monodisperse solid silica core and mesoporous shell silica ( $\text{SiO}_2@\text{Fe-mSiO}_2$ ) and PS as hard template and carbon precursor, respectively. In the process of pyrolysis and simultaneous deposition, the organic molecules gases (carbon species) deposited on the hard template at the catalysis of Fe species, existing in the sample, during calcination at high temperature. The hard template and the carbon precursor were mixed without solvent and the impregnation of carbon precursors. The obtained Fe-MHCs features hollow mesoporous structure, high specific surface area and Fe species, ensuring a high performance in the selective oxidation of ethylbenzene reaction.

## EXPERIMENTAL SECTION

### Synthesis of Fe-MHCs

Monodisperse spherical solid core silica particles were synthesized based on the previous work [22]. Typically, 40 mL of aqueous ammonia ( $\text{NH}_4\text{OH}$ , 28 wt.%) was mixed with a solution containing 1000 mL of absolute ethanol (EtOH) and 80 mL of deionized water ( $\text{H}_2\text{O}$ ). After stirring for 30 min, 60 mL of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added to the solution and stirred for 6 h at room temperature. 200 mL of the above prepared suspension was diluted with 400 mL of  $\text{H}_2\text{O}$ , and 60 mL of cetyl trimethylammonium bromide (CTAB) surfactant solution (110 mmol  $\text{L}^{-1}$ , dissolved in a 2:1 mixture of  $\text{H}_2\text{O}$  and EtOH) was quickly added under vigorous stirring. After stirring for 30 min, 4.3 mL of TEOS was added to the reaction mixture and subsequently stirred at ambient temperature overnight. The as-synthesized silica particle suspension was centrifuged and dried at 70°C overnight. The obtained dry composite powder was further calcined at 550°C for 6 h in air in order to remove CTAB selectively from the composites. The calcined silica particles were designated as  $\text{SiO}_2@\text{mSiO}_2$ . 10 wt.%  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was impregnated into mesopores of  $\text{SiO}_2@\text{mSiO}_2$  using ethanol as solvent. After calcined in air at 250°C,  $\text{SiO}_2@\text{Fe-mSiO}_2$  template was obtained.

$\text{SiO}_2@\text{Fe-mSiO}_2$  template and powder of polystyrene were mixed and placed in quartz boat loaded inside the quartz tube.  $\text{N}_2$  was introduced as protective and carrier gas. Then the furnace was heated to 800°C at a rate of 5°C  $\text{min}^{-1}$  and kept at that temperature for 3 h to obtain Fe/silica/carbon composite. After removing silica by 10 wt.% NaOH aqueous solution, the Fe-MHCs was obtained.

### Characterization

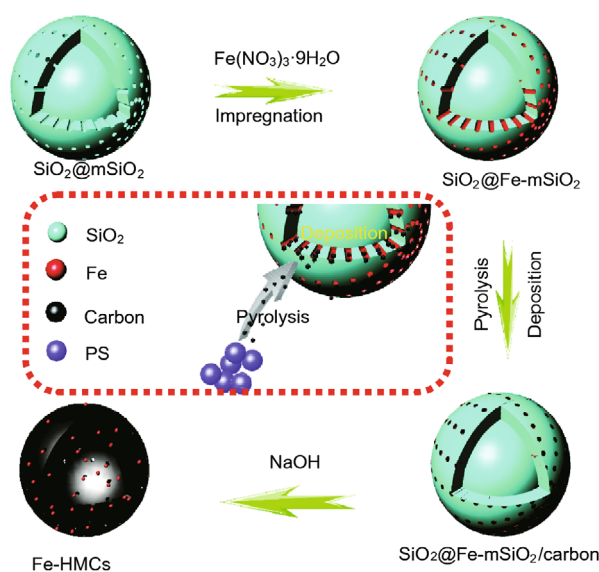
X-ray diffraction (XRD) patterns were achieved using a Rigaku D/MAX-2500 system with Cu-K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ). Nitrogen adsorption-desorption isotherms were carried out on a Micromeritics TriStar 3020 instrument at -196°C. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface area (SSA), while the Barrett-Joyner-Halenda (BJH) method was applied to analyze the pore size distribution using the desorption branch of isotherm. The total pore volume was obtained from the amount of  $\text{N}_2$  adsorbed at the relative pressure ( $P/P_0=0.97$ ). Thermogravimetric analysis (TGA) (Pyris 1 TGA) was performed under air flow from 20 to 800°C at a heating rate of 10°C  $\text{min}^{-1}$ .

### Catalytic reaction

For the catalytic oxidation of ethylbenzene, 10 mg catalyst, 1 mmol ethylbenzene and 3 mmol *tert*-butyl hydroperoxide were dispersed in 3 mL  $\text{H}_2\text{O}$  in a 50 mL sealed glass vessel with magnetic stirring. After reaction at 100°C for 24 h, 50  $\mu\text{L}$  dodecane was added into the tube as the internal standard and 10 mL ethyl acetate was used as extraction liquid, respectively. Upon the removal of catalyst, the mixture was analyzed by an Agilent GC 7820A equipped with a HP-5 column and a flame ionization detector.

## RESULTS AND DISCUSSION

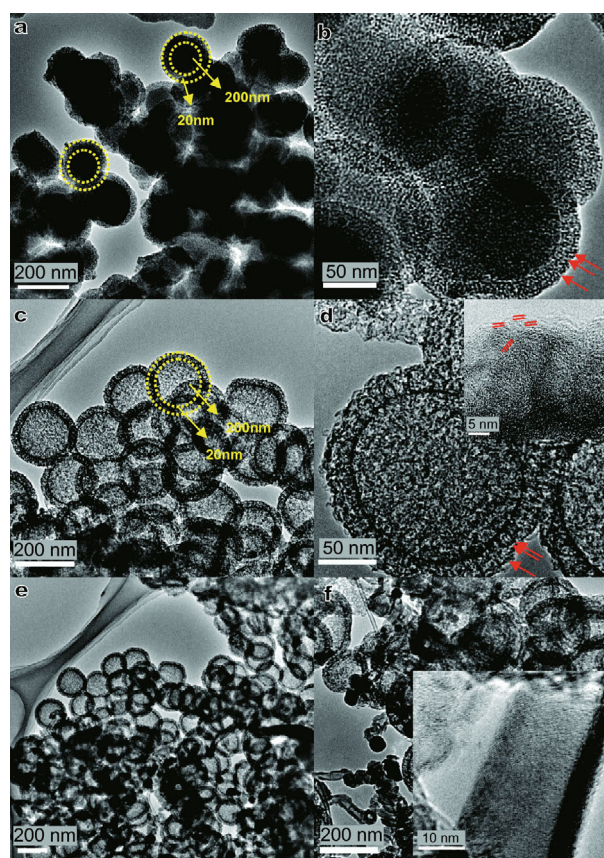
As illustrated in Fig. 1, this method utilized the  $\text{SiO}_2@\text{Fe-mSiO}_2$  as the suitable hard template to provide active sites for pyrolysis simultaneous deposition of PS. Firstly,  $\text{SiO}_2@\text{mSiO}_2$  was produced by adopting silica nanoparticles as the core and the structure-directing agent for the mesoporous silica shell [23]. Subsequently,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was impregnated in the mesopores of the  $\text{SiO}_2@\text{mSiO}_2$ . After calcination in the air, the  $\text{SiO}_2@\text{Fe-mSiO}_2$  template was obtained. This template and PS were mixed for pyrolysis simultaneous deposition under  $\text{N}_2$  protection. The small organic molecules gases (carbon precursor) from pyrolysis of PS can simultaneously deposit on the hard template due to Fe species as catalyst at



**Figure 1** Schematics of the synthesis of the Fe-MHCs.

high temperature, and the mesoporous structure on the shell also provides a space for deposition of carbon precursor. After removal of the silica with NaOH aqueous solution, the uniform Fe-MHCs were obtained. It was noticed that there was no carbon residue when only SiO<sub>2</sub>@mSiO<sub>2</sub> or Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O treated by calcination with PS to pyrolysis simultaneous deposition, indicating the Fe species and porous structure were essential for the deposition of organic molecules gases (carbon species) from pyrolysis of PS. It represented an environment friendly method due to reusing of PS, reducing ‘white pollution’ and avoiding CVD equipment with high technology or complex operation.

The uniform core-shell structure of SiO<sub>2</sub>@Fe-mSiO<sub>2</sub> could be clearly seen in the transmission electron microscopy (TEM) image in Fig. 2a. The size of SiO<sub>2</sub>@Fe-mSiO<sub>2</sub> was about 200 nm and the size of silica core and thickness of the mesoporous SiO<sub>2</sub> shell was 150 and 25 nm, respectively (the yellow dotted circles in Fig. 2a). From the higher resolution TEM image (Fig. 2b), it was clearly that the mesopores in the shell of SiO<sub>2</sub>@Fe-mSiO<sub>2</sub> were developed generally in a uniform and orderly fashion (the yellow dotted circle in Fig. 2a). There was no obvious Fe nanoparticles observed from the template, indicating the Fe species has been highly dispersed in the pores of SiO<sub>2</sub>@mSiO<sub>2</sub>. The wide angle XRD pattern further confirmed the highly dispersion of Fe species (in Fig. 3a). The patterns showed only a wide peak at 23°, ascribed to amorphous silica, and no obvious diffraction peaks owing to Fe species could be found, confirming the



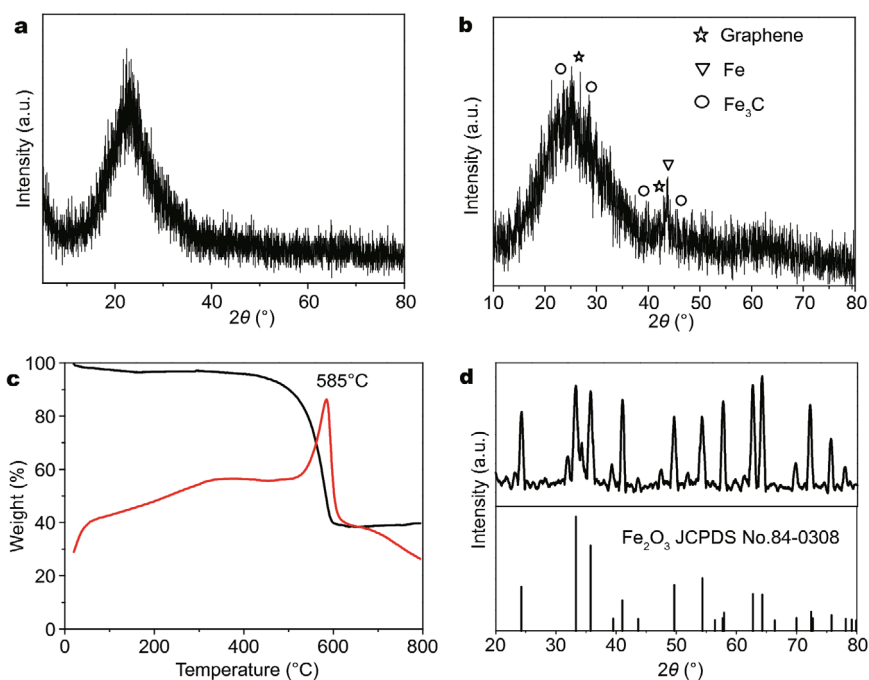
**Figure 2** TEM images of SiO<sub>2</sub>@Fe-mSiO<sub>2</sub> template (a, b) and Fe-MHCs (c-f).

small Fe species was dispersed into the hard template.

TEM was also used to characterize the morphology of the Fe-MHCs. The TEM image showed that the resulting Fe-MHCs efficiently retained the spherical morphology of SiO<sub>2</sub>@Fe-mSiO<sub>2</sub> with no obvious collapse observed (Fig. 2c). The TEM images clearly exhibited well monodisperse and hollow nanostructures with a shell thickness of 25 nm and a void in the diameter of 150 nm, which was in agreement with the diameter of the core of template. The higher magnification TEM images of Fe-MHCs in Fig. 2d showed that the sample possesses twisted disordered mesopores (the red sign), indicating Fe species has provided uniform active sites for deposition of carbon species from pyrolysis of PS in the mesopores of the template. The microstructure of these hollow spheres is a part of graphitic structure, as seen in the high resolution TEM images of the Fe-MHCs (red sign inset of Fig. 2d), which was attributed to the catalytic graphitization of the Fe species [24].

In addition, a little number of Fe nanoparticles with large size (20–60 nm) could be observed in the TEM





**Figure 3** Wide-angle XRD patterns of Fe-SiO<sub>2</sub>@mSiO<sub>2</sub> (a) and Fe-MHCs (b), TGA (c) and wide-angle XRD (d) pattern of MHCs-Fe in air.

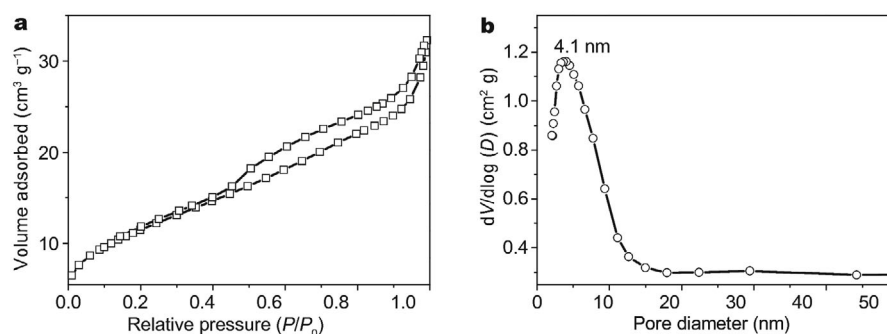
image of Fe-MHCs (Fig. 2e), which might be attributed to Fe aggregation at high temperature. Moreover, some carbon nanotubes (CNTs) (red circle in Fig. 2f) with the diameter of 22 nm also could be ascribed to the catalysis of Fe species at high temperature [25]. The high resolution TEM image (inset of Fig. 2f) of the CNTs showed that the wall was made up of more than a dozen layers of graphite. The graphitic structure could improve the material's mechanical properties and ion transport.

To establish the crystal phases of carbon and the iron-based nanoparticles, the obtained Fe-MHCs were characterized by wide angle XRD. As shown in Fig. 3a, the weak diffraction peak at 26.5° could be assigned to the (002) plane of graphitic carbon [26], in agreement with TEM observation. Generally, the carbon framework with Fe<sup>3+</sup> can turn to Fe<sub>3</sub>C at condition of pyrolysis [27]. At the same time, some Fe<sup>3+</sup> can convert to metal of Fe [28]. Thus, the new diffraction peaks at 44.8° and 65.1° indicated the presence of α-Fe (JCPDS No. 06-0696). The rest of the diffraction peaks correspond to the crystal planes of Fe<sub>3</sub>C species (JCPDS, No. 89-2867) [29,30]. The results showed that a certain amount of Fe species has been loaded in the carbon framework. To further investigate the content of Fe in the Fe-MHCs, the TGA in air atmosphere was performed and XRD was used to determine the type of iron after calcination. As depicted in Fig. 3c during the temperature from 20 to 200°C, the

mass loss was correlated to the evaporation of water. The significant mass loss occurs from 300 to 600°C, which could be attributed to oxidation and gasification of carbon framework in the air. Carbon framework can be completely decomposed in the air and Fe<sub>2</sub>O<sub>3</sub> is obtained at high temperature as seen from XRD (JCPDS No. 84-0308) (Fig. 3d) [31,32]. Clearly, the content of Fe<sub>2</sub>O<sub>3</sub> was 39.7 wt.% measured by TGA. The corresponding Fe contents was about 27.8 wt.%.

The N<sub>2</sub> adsorption experiments were performed to examine the pore characteristics and surface area of Fe-MHCs. Fig. 4a presents a type IV isotherm with a hysteresis loop at  $P/P_0 > 0.4$ , indicating the presence of mesopores. The BET surface area and pore volume of the composite Fe-MHCs is 924 m<sup>2</sup> g<sup>-1</sup> and 1.12 cm<sup>3</sup> g<sup>-1</sup> respectively. The higher BET surface area compared with some other hollow carbon spheres [27,33] ensures a large storage space. The Fe-MHCs possessed mesopore with size of 4.1 nm, calculated by the conventional BJH method on the N<sub>2</sub> adsorption isotherm as shown in Fig. 4b.

The C-H bond oxidation is significant in the chemical industry, which could directly transform the hydrocarbons to some oxygen-containing chemicals. In general, the transition metal catalysts were usually essential in the C-H bond oxidation. Besides, the reaction conditions such as high temperature and pressure increased the risk



**Figure 4** Nitrogen adsorption-desorption isotherms (a) and pore size distribution curves (b).

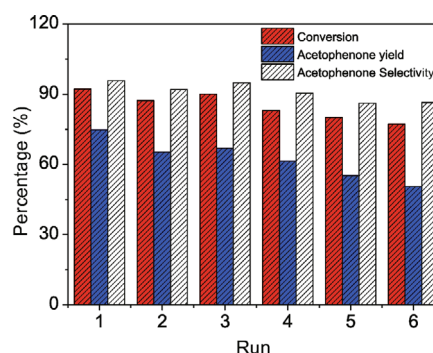
**Table 1** Comparison of the catalytic results of products of Fe-MHCs with related results reported in the literature

Catalyst	Conversion (%)	Yield (%) <sup>a</sup>	Selectivity (%) <sup>b</sup>	Ref.
Fe-MHCs	94.5	79.3	97.4	This work
Mesoporous carbon	88.3	53.4	NA	[22]
Active carbon	NA	55.9	NA	[8]
Boron doped polymeric carbon	10.6	NA	99.9	[9]
MnCl <sub>2</sub>	5	NA	79	[10]
ZJU-19	9	NA	80	[10]
ZJU-20	69	NA	95	[10]
N-doped carbon	94	80.4	NA	[11]

<sup>a</sup>Acetophenone yield; <sup>b</sup>acetophenone selectivity; NA: not available.

for the C–H oxidation. So it is important to develop a new strategy for the catalytic oxidation of C–H bonds in hydrocarbon. The carbon nanomaterials catalyse the oxidation of C–H bonds as reported in an other works [2]. In this regard, the mesoporous hollow feature of Fe-MHCs can prevent the low-cost Fe nanoparticles from leaching. Inspired by those properties of Fe-MHCs, it was used as catalyst in the selective oxidation of ethylbenzene to ethylbenzene. The reaction results with Fe-MHCs as catalyst and some reported results with other catalysts were summarized in Table 1. It was worth noting that the Fe-MHCs exhibited good catalytic performance in the selective oxidation of ethylbenzene. The conversion of ethylbenzene could reach 94.5% and the selectivity of product acetophenone was 97.4%, which were better than the other results reported in some literatures [8–11,22].

In addition, the stability of Fe-MHCs catalysts was also evaluated. The conversion of ethylbenzene and selectivity to acetophenone were achieved even when the catalyst was used in the sixth run (Fig. 5). In brief, Fe-MHCs, as an efficient catalyst, exhibited excellent catalytic activity in the selective oxidation of ethylbenzene and will be a promising alternative to the traditional expensive metal and metal oxide catalysts. Moreover, the unique uniform cavity and mesoporous structures may provide a good



**Figure 5** The stability of the MHCs-Fe catalyst.

condition for their catalytic capabilities.

## CONCLUSION

In summary, we have prepared the Fe modified mesoporous hollow carbon spheres by pyrolysis and simultaneous deposition method. The Fe species and mesoporous structure of hard template were critical to deposition of carbon species from pyrolysis of PS. As catalyst, the Fe-MHCs exhibited high selectivity in the oxidation of ethylbenzene. This strategy represents an environmental-friendly and simple preparation method without high technology or complex operation. In addi-

tion, the efficient utilization of PS as carbon precursor provides a new orientation for preparing carbon materials with controllable morphology.

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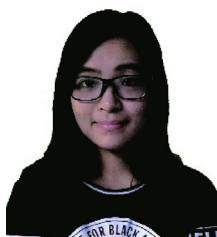
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**Author contributions** Chen A and Gao Y proposed the research

direction and guided the whole project. Du J designed and performed the experiments and wrote the manuscript; Zhang L, Zhang Y and Yu Y helped draft the manuscript and analyze the data. All authors contributed to the general discussion and reviewed the manuscript.

**Conflict of interest** The authors declare that they have no conflict of interest.



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## 铁修饰的中空介孔碳球用于乙苯催化氧化

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**摘要** 本文通过简单的热解沉积方法成功地制备了具有大空腔和介孔壳壁的铁修饰中空碳球. 在高温碳化过程中, 聚苯乙烯分解出的小分子有机气体(碳物种)会被介孔硅模板上的铁所捕获并沉积在模板上, 从而得到铁修饰的中空介孔碳球(Fe-MHCs). 制备的Fe-MHCs具有均一的球形形貌, 大的比表面积(924 m<sup>2</sup> g<sup>-1</sup>)和一定的铁负载量. Fe-MHCs样品中的铁及其形貌使其在乙苯氧化反应中展现了良好的催化性能. 作为催化剂时, Fe-MHCs展现了良好的转化率(94.5%), 高的选择性(97.4%)以及好的循环再利用性.