Preparation of Fe2O3/CC catalyst and its catalytic reduction performance of o-bromonitrobenzene

Hui Fang [1], Ruishen Xie [1], Chundong Mi [1], Aiquan Jia [1],
and Qianfeng Zhang [1, *]

[1] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology,
Ma'anshan, Anhui, 243002, P. R. China

Abstract. o-Bromoaniline, as an important organic chemical raw material and intermediate, is widely used in the synthesis of pharmaceuticals, pesticides, dyes and functionalized polymers. There is an urgent need to develop green and efficient alternatives to traditional production methods due to high energy consumption, high pollution and poor catalyst stability. In this study, the Fe2O3/CC composite catalyst was innovatively prepared by using carbon cloth (CC) as a carrier combined with the activity of iron oxide (Fe2O3), and systematically evaluated in the multiphase catalytic reduction reaction of o-bromonitrobenzene. The experiments showed that the Fe2O3/CC catalysts possessed excellent catalytic activity and cyclic stability, and their catalytic efficiency did not decrease significantly after multiple recycling. In addition, the significant effect of hydrothermal temperature on the morphology and performance of the catalyst provided a new idea to optimize the catalyst performance. This study provides a new method for the green synthesis of o-bromoaniline and lays a theoretical foundation for the development of environmentally friendly and efficient catalysts in organic synthesis.

Keywords: o-bromoaniline; multiphase catalysis; iron oxide; carbon cloth; green chemistry.

1. Introduction

o-Bromoaniline is an important organic chemical raw material and intermediate with a wide range of applications, which plays an irreplaceable role in the synthesis of pharmaceuticals, pesticides, dyes and functionalized polymers[1-4]. For example, o-bromoaniline is used in the preparation of antibiotics and other drugs, and as a key precursor for pesticides, its contribution to the agricultural chemical industry is particularly significant. Meanwhile, it is also a basic component of many dyes and pigments, and is widely used in the textile industry. With the rapid development of the chemical industry and the growing demand for downstream products, the market demand for o-bromoaniline continues to climb. However, its traditional production process has a series of problems such as high energy consumption, high pollution and insufficient catalyst stability. This not only limits its production efficiency, but also poses a serious challenge to environmental protection. Therefore, the development of an efficient, green and environmentally friendly synthesis method has become an important issue for current research and industrial development.

Traditional production processes for o-bromoaniline are usually based on o-bromonitrobenzene, which is prepared by catalytic reduction reaction. However, these traditional methods usually require the use of organic solvents or high-temperature and high-pressure conditions, accompanied by a large amount of waste gas and liquid emissions, which have serious negative impacts on the environment and resources[5]. In addition, the performance of catalysts in the reaction is crucial, but the traditional homogeneous catalysts have the problem of being difficult to be recycled, while some of the multiphase catalysts are unable to meet the requirements of industrial production due to their low activity or poor stability[6-8]. Based on this, the development of a green, environmentally friendly multiphase catalyst with industrialization potential has become the key to solve the above problems.

Multiphase catalysis has gained wide attention in the field of green chemistry due to its advantages of easy separation and reuse. Compared with the traditional homogeneous catalytic system, multiphase catalysts can effectively reduce the waste of resources and environmental burden in the production process, and have higher economy and sustainability. In

recent years, iron-based catalysts have gradually become a research hotspot due to their advantages of low cost, abundant resources and environmental friendliness[9]. The active components of iron-based catalysts mainly include metal salts, metal oxides and metal hydroxides. However, different types of active components exhibit significant differences in catalytic performance[10]. Although metal salts have high initial activity, they are easy to be lost during the reaction, resulting in poor cycling performance; metal hydroxides are less stable than metal oxides, and thus are not suitable as catalysts for long-term use. In contrast, iron oxide (Fe2O3) is considered to be the ideal active component due to its high stability, low cost, magnetic recyclability, and environmental friendliness[11,12].

In addition to the selection of active components, the carrier material also plays an important role in the overall performance of the catalyst. High-quality carrier materials can improve the dispersion of the active components, enhance the stability of the catalyst, and may synergize with the active components to improve the catalytic efficiency. In this study, carbon cloth (CC) was selected as the carrier material. Carbon cloth is a material with good dimensional stability, high thermal stability and excellent mechanical strength, which has been successfully commercialized in several industrial fields. Its stable source and low price make it a promising carrier for catalyst applications. In addition, the multifunctionality of carbon cloth enables it not only to provide physical support, but also to form a synergistic effect with the active components through its unique surface properties, which can further enhance the performance of the catalyst[13,14].

In this paper, Fe2O3/CC composite catalysts were prepared for the first time by combining the activity of iron oxides with carbon cloth as a loading material, and their performances were comprehensively evaluated in a multiphase catalytic system. The catalysts were prepared by a one-step hydrothermal method, which is a simple, efficient and controllable synthesis method, and the loading condition and morphology distribution of the active components on the surface of the carbon cloth can be precisely controlled by adjusting the reaction conditions (e.g., hydrothermal temperature).

It was found that the Fe2O3/CC composite catalyst exhibited excellent catalytic activity in the reduction reaction of o-bromonitrobenzene with good cyclic stability. The catalytic efficiency of the catalysts did not show any significant decrease after multiple recycling and reuse, indicating that they have good potential for industrial application. Further characterization showed that the hydrothermal temperature had a significant effect on the morphology and loading state of Fe2O3. By regulating the hydrothermal temperature, the distribution of active components on the carrier surface can be effectively optimized, thus improving the overall performance of the catalyst. This finding provides theoretical support for the design of efficient catalysts.

Not only a new method for the green synthesis of o-bromoaniline was provided, but also a new idea for the design and optimization of the loaded iron-based catalysts was put forward. The excellent performance of the Fe2O3/CC composite catalysts shows the potential of its wide application in multiphase catalysis. In addition, the present study provides a theoretical foundation and practical basis for the green synthesis of other organic compounds.

2. Experimental section

In the catalyst preparation system adopted in this paper, CC not only acts as a substrate, but also as a reducing agent reacting with iron nitrate to produce iron oxide, as shown in Figure 1.

$$Fe(NO_3)_3 + 3H_2O \xrightarrow{\qquad} Fe(OH)_3 + 3HNO_3 \qquad (1)$$

$$HNO_3 + C \xrightarrow{\qquad} NOx + CO_2 \qquad (2)$$

$$2Fe(OH)_3 \xrightarrow{\qquad} Fe_2O_3 + 3H_2O \qquad (3)$$

Figure. 1 Hydrothermal reaction formula

2.1 Reagents

o-Bromonitrobenzene, ferric nitrate hydrate nine ($Fe(NO3)3-9H2O$), carbon cloth, anhydrous ethanol, hydrazine hydrate ($N2H4-H2O$), dextrose ($C6H12O6$), urea ($CH4N2O$), silicon dioxide ($SiO2$), ammonia, and activated carbon (C).

2.2 Experimental instruments

The reaction was stirred with a magnetic heating stirrer; the samples were pumped with a vacuum pump; the catalysts were roasted in a chamber muffle furnace; the catalysts were prepared hydrothermally with an autoclave reactor; the catalytic performance of the catalysts was evaluated with a GS/MS gas chromatography; and Nuclear Magnetic Resonance (NMR) tests were carried out on a fully digitalized nuclear magnetic resonance spectrometer instrument for NMR testing.

2.3 Preparation of catalyst

$Fe2O3$ was prepared at 160 °C reaction conditions by the controlled variable method without using carbon cloth as a carrier.

The carbon cloth was first pre-treated by cutting it into 1 cm × 2 cm sizes, and deionized water to ultrasonic for half an hour to remove the surface oxides, and then put it into the reaction kettle equipped with concentrated nitric acid in a hydrothermal bath at 130 °C for 5 h. At the end of the reaction, rinse with deionized water for several times, and then put it into a vacuum oven at 60 °C to dry for 15 min.

2.5 mmol $Fe(NO3)3-9H2O$ was added into 40 mL of deionized water, stirred for 30 min at room temperature, and then the reaction solution was loaded into the reaction kettle and hydrothermally reacted for 5 h at 140 °C, 160 °C and 180 °C respectively, then the reaction kettle was cooled down to room temperature, and the reactants were taken out, and washed with water and ethanol for 2 times, and vacuum dried for 2 h at 60 °C. The final synthesized $Fe2O3$/CC.

2.4 Characterization of catalyst

X-ray diffraction (XRD) patterns were recorded with Cu Kα radiation using a D8 Advance diffractometer from Bruker, Germany at a tube voltage of 40 kV and a tube current of 30 mA. FEI Nova NanoSEM 430 field emission scanning electron microscope (SEM) was used to observe and analyze the product surface. A laser confocal Raman spectrometer (inVia) from Renishaw was used for Raman spectral analysis (Raman) to study the catalyst chemical structure, phase and morphology. An ASAP-2460 nitrogen adsorption-desorption analyzer was used to analyze the specific surface area, pore volume, and pore size distribution of the samples Specific surface area and porosity. The nitrogen adsorption-desorption isotherm data were obtained at 77 K. The specific surface area and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) equation and Barret-Joyner-Halenda (BJH) model. The samples were pretreated and dried under vacuum at 200 °C for 7 h before testing. The chemical composition and elemental valence of the samples were studied by X-ray photoelectron spectroscopy (XPS) analysis using Thermo Scientific K-Alpha instrument. Thermogravimetric analysis (TG) was carried out in $N2$ atmosphere using a Netzsch STA 4449 F3 instrument to study the thermal stability of the catalysts and quantitatively analyze them. The products of the catalysis experiments were quantitatively and qualitatively analyzed using a GC/MS gas-mass spectrometer model MSQ8100 from Shanghai Shunyu Hengping Scientific Instrument.

2.5 Experimental of catalytic reduction

The catalytic transfer hydrogenation reduction was carried out in ethanol solution with $N2H4-H2O$ as the hydrogen source and o-bromonitrobenzene as the reactant. The specific experimental steps were as follows: add 10 mL of anhydrous ethanol solution into a 25 mL three-necked flask, then add 1.5 mL of N2H4-H2O, add 0.5 g of o-bromonitrobenzene with stirring, and then add 0.06 g of the catalyst Fe2O3/CC, and then condense and reflux the reaction at 80 ℃ for 3~5 h, filter the reaction solution. The reaction solution was filtered and analyzed by GS/MS for quantitative and qualitative analysis to obtain the catalytic conversion and selectivity.

The stability of the catalyst was explored by six cycle experiments. The catalyst was recovered and disposed of by alternately washing the catalyst with ethanol and water at the end of the reaction before drying it in an oven at 100 ℃. In order to better investigate the cycling performance of the catalyst, the amount of raw materials such as reaction substrate, hydrogen donor, ethanol and the experimental reaction time were kept constant.

3. Results and Discussion

3.1 Characterization and analysis of Fe2O3/CC

Figure 2 shows the XRD patterns of the catalyst Fe2O3/CC synthesized under different hydrothermal conditions, the peaks located near 25.6° and 22.8° are characteristic diffractions from the carrier CC. The intensity of this peak changed as the hydrothermal temperature increased, but the position of the peak did not change. The peaks located near 33.2° and 35.8° are attributed to the characteristic diffraction from Fe2O3.

To further confirm the inference, laser Raman spectroscopy was used to further characterize the crystal structure of the substance. As shown in the Raman profile of Figure 3, two characteristic peaks of the carrier CC can be found in the Fe2O3/CC curve at 1346 cm-1 and 1580 cm-1, which are the peaks in the D-band (atomic lattice defects) and the characteristic peaks in the G-band (stretching vibration of the carbon atoms with sp2 hybridization in the plane), respectively[15,16]. Three characteristic peaks at 218, 298, and 412 cm-1 were also found, which corresponded to the characteristic peaks of Fe2O3, and the intensity of these peaks became larger and the half-widths became smaller when the hydrothermal temperature was increased from 160 ℃ to 180 ℃, which indicated that the dispersion of Fe2O3 was reduced. The Raman spectra of the products further confirmed that the carbon fiber cloth was loaded with Fe2O3.

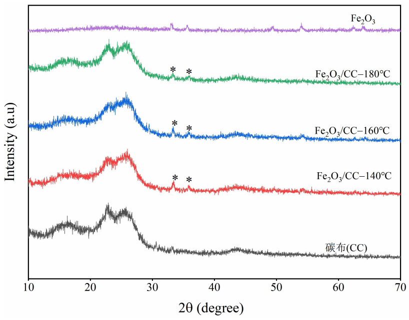

Figure. 2 XRD of Fe2O3/CC and CC under different hydrothermal conditions

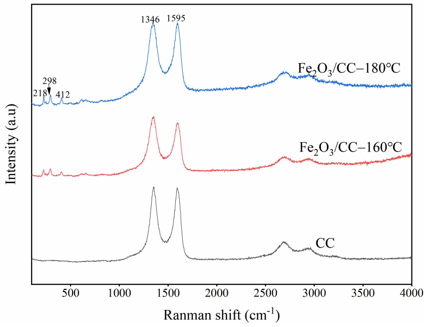

Figure. 3 Raman of Fe2O3/CC and CC under different hydrothermal conditions

Figure 4 shows SEM plots of carbon cloth and Fe2O3/CC prepared at different hydrothermal temperatures. From the figure, it can be seen that there exists a strong relationship between the morphology of Fe2O3 synthesized in situ on carbon cloth and the hydrothermal temperature. When the hydrothermal temperature is 140 °C, blocky Fe2O3 nanosheets grow vertically on the carrier carbon cloth, and when the hydrothermal temperature is 160 °C, the nanosheets on the carrier carbon fiber become fine and uniform. When the hydrothermal reaction temperature was raised to 180 °C, the nanosheets of Fe2O3 wrapped the carbon fibers completely and distributed evenly on the carrier carbon cloth, because the catalyst synthesized by the hydrothermal method could make the powder evenly distributed on the carrier, and the degree of reaction would be more and more intense and the dispersion would be increased when the reaction temperature was gradually raised.

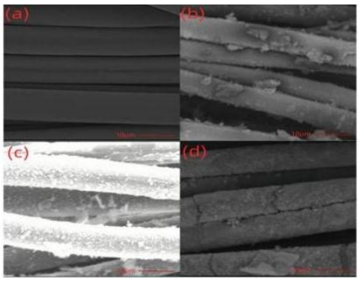

Figure. 4 SEM patterns, (a) CC; (b) Fe2O3/CC-140°C; (c) Fe2O3/CC-160°C; (d) Fe2O3/CC-180°C

Because the XRD patterns of Fe2O3 and Fe3O4 are very similar and it is difficult to completely distinguish them by XRD tests alone, the XPS patterns of Fe2O3/ CC-160°C was subjected to XPS tests to investigate the chemical composition of the elements on the catalyst surface and the valence states of each element. As shown in Figure 5, the full spectrum of Fe2O3/CC and the XPS spectra of Fe 2p orbitals after Gaussian-Lorentz function peak splitting to fit the curves by XPSPEAK4.1 software, it can be seen that Fe2O3/CC consists of the elements of Fe, O, and C in Figure 4(a). Using the C 1s at 284.8 eV as a reference peak, the XPS spectrum of Fe 2p of the catalyst is shown in Figure 4(b). Two broad peaks attributed to Fe 2p3/2 and Fe 2p1/2 were found at binding energies of 710.2 eV and 723.6 eV, respectively. In addition, satellite peaks of Fe2O3 can be clearly seen at binding energies of 718.7 eV and 732.3 eV[17].

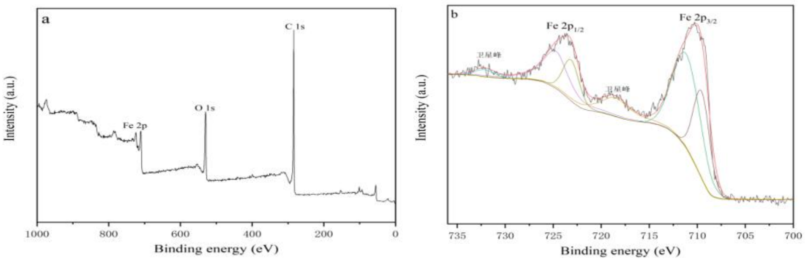

Figure. 5 (a) XPS of Fe2O3/CC-160°C; (b) XPS of Fe 2p

The thermal stability of the samples can be observed through the TG patterns, such as Figure 6, which shows the TG patterns of Fe2O3/CC prepared on carbon cloth and at different hydrothermal temperatures. From the thermal decomposition diagram, it can be seen that the simple carbon cloth starts to lose weight at 420 °C, and when Fe2O3 is loaded onto the carbon cloth, the thermal stability is significantly improved, and the weight loss temperature is increased from 420 °C to 520 °C. Due to the difference in the hydrothermal temperature during the preparation, the weight loss rate is different from 520 °C to 800 °C, and the weight loss rate varies with the increase of the hydrothermal temperature. The rate of weight loss at 520 °C-800 °C was different due to the different hydrothermal temperatures during preparation, and the rate of weight loss decreased with the increase of hydrothermal temperature.

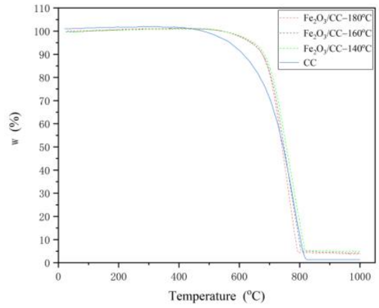

Figure. 6 TG of Fe2O3/CC and CC

3.2 Performance evaluation of Fe2O3/CC catalyzed reduction of o-bromonitrobenzene by hydrazine hydrate

The catalytic performance of Fe2O3/CC-catalyzed reduction of o-bromonitrobenzene by N2H4-H2O prepared at different hydrothermal temperatures was examined. As shown in Table 1, the conversion of o-bromonitrobenzene at a reaction time of 3 h was chosen as the criterion for the examination of the catalytic performance. The experimental results show that the catalytic performance of the prepared Fe2O3/CC is best when the hydrothermal temperature is 160 °C, and the change in the catalytic activity is in accordance with the change in the loading of Fe2O3 as shown by SEM, and XRD results. This is significantly higher than the reported conversion of iron powder with acid reduction. Moreover, all the prepared catalysts showed excellent selectivity. This also just shows that carbon cloth has application value as a carrier.

Table 1. Results of Fe2O3/CC catalyzed reduction of o-bromonitrobenzene by hydrazine hydrate prepared at different hydrothermal temperaturesa

Sample	Time(h)	Conversion(%)	Selection(%)
Fe2O3/CC–140°C	3	70	>98
Fe2O3/CC–160°C	3	86	>98
Fe2O3/CC–180°C	3	75	>98

a Reaction conditions: 0.5 g o-bromonitrobenzene, 10 mL anhydrous ethanol, 1.5 mL N2H4-H2O, 0.06 g catalyst, reaction temperature 80 °C.

Cycling performance is often the key point of investigation when considering the industrial application of catalysts, because excellent cycle times can significantly reduce the production cost of the industrialization. The catalytic cycling performance of Fe2O3/CC was investigated using o-bromonitrobenzene as substrate. The reaction conditions were as follows: 0.5 g of o-bromonitrobenzene, 10 mL of anhydrous ethanol, 1.5 mL of N2H4-H2O, and 0.06 g of catalyst in a 25 mL three-necked flask fitted with a condenser tube, and the reaction was carried out at 80 ℃ for 3 h. The stability of the catalysts was explored by 6 cycle experiments.

The stability of the catalysts was investigated by 6 cycle experiments. The catalyst was recovered and disposed of by alternately washing the catalyst with ethanol and water at the end of the reaction before drying it in an oven at 100 °C. From Figure 7, it can be seen that Fe2O3/CC maintains a catalytic conversion of 80 % or more for at least five times and has good selectivity with selections up to 98 % or more. This indicates that Fe2O3/CC exhibits the advantages of being highly stable and re-cyclable in catalyzing the hydrogen transfer of o-bromonitrobenzene using N2H4-H2O as a reductant.

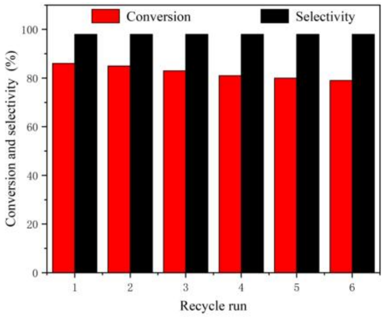

Figure. 7 Cyclic experimental results of the reduction of o-bromonitrobenzene by hydrazine hydrate catalyzed by Fe2O3/CC at 160 °C

4. Future prospects

In further comparison with the current production of iron powder plus acid reduction method, it can be found that it not only has the advantages of more excellent catalytic activity and cycling performance, but also has the advantages of no iron sludge and numerous by-products in the production process, which is in line with the concept of green environmental protection. Future research can be further deepened from the following aspects: (1) Explore the synergistic effect of different carrier materials (e.g., graphene or carbon nanotubes) with the iron-based active components, and evaluate their influence on the catalytic performance; (2) To develop other preparation methods (e.g., sol-gel method or vapor phase deposition method) to further improve the catalyst performance; (3) To extend the application of this catalyst system in other organic transformation reactions to explore its versatility and multifunctionality.

In summary, this study provides an important reference for the green and efficient synthesis of o-bromoaniline by designing and preparing Fe2O3/CC composite catalysts. This multiphase catalytic system based on carbon cloth carrier and iron-based active components not only possesses remarkable catalytic activity and cyclic stability, but also demonstrates good potential for industrial application. The results fit the development trend of green chemistry and lay a solid foundation for the design and application of environmentally friendly catalysts, as well as being of great significance for the promotion of sustainable development in the field of fine chemicals.

5. Summary

In this paper, the effect of hydrothermal temperature on the morphology and activity of the prepared Fe2O3/CC catalysts was investigated in detail. The results showed that the hydrothermal temperature had a significant effect on the morphology and structure of the monolithic catalysts obtained, and the catalytic activity was improved as the hydrothermal temperature was increased from 140 °C to 180 °C, and the loaded iron oxides changed from lumps to fine particles uniformly distributed on the carriers, which surrounded the carriers. Among them, the catalytic reduction performance of Fe2O3/CC obtained at 160 °C was the best, and the results of cycling experiments showed that it had good stability in the catalytic reduction of o-bromonitrobenzene. Although its catalytic activity was slightly inferior compared with that of the Pt-based noble metal catalysts, it has the advantages of low production cost and abundant raw materials, and therefore has more prospects for industrial application.

References

[1] D. B. Tiz, Č. Podlipnik. A Review of FDA-Approved Antiparasitic Drugs in USA for Sheep and Goats: Their Synthesis and Pharmaceutical Use[J].Trends in Pharmaceutical Sciences, 2023, 9(3), 221-236.

[2] A. Mahudeswaran, J. Vivekanandan, P. S. Vijayanand. A study on silver nanoparticles embedded DBSA doped nanostructured poly (aniline-co-2-bromoaniline)[J]. Materials Today: Proceedings, 2021, 47, 2154-2158.

[3] J. C. Obi, I. V. Emmanuel, L. N. Okoro, et al. Synthesis, spectroscopic studies and fastness properties of monoazo dyes derived from substituted ar-ylamines[J]. Science World Journal, 2022, 17(1), 143-147.

[4] Y. Yamamoto, S. Mita, Y. Sato, et al. Practical synthesis of 1, 3-benzoaza-phosphole analogues[J]. Frontiers in Chemistry, 2023, 11, 1174895.

[5] J. Klausen, J. Ranke, R. P. Schwarzenbach. Influence of solution compositin and column aging on the reduction of nitroaromatic compounds by zerovalent iron[J]. Chemosphere, 2001, 44(4), 511-517.

[6] M. L. Kantam, R. Chakravarti, U. Pal, et al. Nanocrystalline Magnesium Oxide-stabilized Palladium(0): An Efficient and Reusable Catalyst for Selective Reduction of Nitro Compounds[J]. Advanced Synthetic Catalysis, 2008, 350, 822-827.

[7] P. Serna, M. Boronat, A. Corma. Tuning the Behavior of Au and Pt Catalysts for the Chemoselective Hydrogenation of Nitroaromatic Compounds [J]. Topics in Ctalysis, 2011, 54.

[8] I. Sorribes, L. C. Liu, and A. Corma. Nanolayered Co-Mo-S Catalysts forthe Chemoselective Hydrogenation of Nitroarenes[J]. ACS Catalysis, 2017, 7, 2698-2708.

[9] M. Xiao, J. Zhu,L. Feng, et al. Meso/macroporous nitrogen-doped carbon architectures with iron carbide encapsulated in graphitic layers as an efficient and robust catalyst for the oxygen reduction reaction in both acidic and alkaline solutions[J]. Advanced Materials, 2015, 27(15): 2521-2527.

[10] E. Pabón, J. Retuert, R. Quijada, et al. TiO2-SiO2 mixed oxides prepared by a combined sol–gel and polymer inclusion method[J]. Microporous and Mesoporous Materials, 2004, 67(2-3), 195-203.

[11] Y. Li, Y. X. Zhou, X. Ma, et al. A metal–organic framework-templated synthesis of γ-Fe2O3 nanoparticles encapsulated in porous carbon for efficient and chemoselective hydrogenation of nitro compounds[J]. Chemical Communications, 2016, 52(22): 4199-4202.

[12] S. Guo, G. Zhang, Y. Guo, et al. Graphene Oxide-Fe2O3 Hybrid Material as Highly Efficient Heterogeneous Catalyst for Degradation of Organic Contaminants[J]. Carbon, 2013. 60, 437-444

[13] Z. Yao, M. Zhu, F. Jiang, Y. Du, C. Wang, P. Yang. Highly efficient electrocatalytic performance based on Pt nanoflowers modified reduced graphene oxide/carbon cloth electrode[J]. Journal of Materials Chemistry, 2012, 22(27), 13707-13713.

[14] Y. C. Chen, Y. K. Hsu, Y. G. Lin, Y. Y. Horng, L. C. Chen, et al. Highly flexible supercapacitors with manganese oxide nanosheet/carbon cloth electrode. Electrochim Acta, 2011, 56, 7124-7130.

[15] X. Cui, Y. Long, X. Zhou, G. Yu, J. Yang, M. Yuan, J. Ma, Z. Dong. Pd-doped Ni nanoparticle-modified N-doped carbon nanocatalyst with high Pd atom utilization for the transfer hydrogenation of nitroarenes[J]. Green Chemistry, 2018, 20(5), 1121-1130.

[16] Y. Duan, T. Song, X. Dong, Y. Yang. Enhanced catalytic performance of cobalt nanoparticles coated with a N,P-codoped carbon shell derived from biomass for transfer hydrogenation of functionalized nitroarenes. Green Chemistry, 2018, 20(12), 2821-2828.

[17] Z. Dong, X. Le, Y. Liu, et al. Metal organic framework derived magnetic porous carbon composite supported gold and palladium nanoparticles as highly efficient and recyclable catalysts for reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol[J]. Journal of Materials Chemistry, 2014, 2(44),18775-18785.