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Research Progress on the Application of Fe_3O_4/PI Magnetic Nanoparticles in Catalysts

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The rapid development of the chemical industry has produced a large amount of industrial wastewater, posing a huge threat to the ecological environment and human health. Efficient treatment of sewage is an urgent problem to be solved at present. The combination of efficient nanoparticle catalysts and economical wastewater treatment technologies is an important method to solve water pollution problems. However, nanoparticles have the disadvantages of easy agglomeration, poor stability and difficulty in recovery, which reduces their catalytic performance. Fe_3O_4 magnetic catalyst, because of its structural characteristics of polyimide composite material and its magnetic field reaction characteristics of inorganic nanoparticles, makes the nanocomposite able to disperse and treat rapidly under the influence of an external magnetic field and can be reused. This paper provides a review of the preparation methods and their applications of Fe_3O_4 magnetic catalysts in recent years, and analyzes and prospects the application and existing problems of future research development.

Keywords: magnetic, catalysts, nanoparticle.

1. INTRODUCTION

Over the past century, with the rapid development of the Industrial Revolution and modern society, problems such as the greenhouse effect and environmental pollution of soil, rivers, and the atmosphere have become increasingly serious. Loading them onto suitable carriers can effectively solve these problems, so the selection and optimization of carriers are of crucial importance.

Chemical reduction can decompose organic pollutants into small-molecule organic substances or convert them into substances that are easy to recycle. For instance, Yao et al. [1] prepared rGS/PdxAuy/PPy with different morphologies by controlling the proportion of precious metal salts, which were used to catalyze the $NaBH_4$ reduction of 4-NP. They demonstrated extremely high catalytic activity, with only 3.5 μg of catalyst required and the degradation reaction completed within 3.0 minutes, achieving a reaction rate constant k value of 0.269 min^{-1}. Yang et al. [2] fabricated a stable and easily separable Fe_3O_4/Mn_3O_4/GS synergistic catalyst. Fe_3O_4 and Mn_3O_4 synergistically activated monosulfate (PMS) to generate peroxymonosulfate and hydroxyl radicals, rapidly degrading the organic pollutant MB. When the initial concentration of MB was 50 mg/L, using 100 mg/L of the catalyst, the degradation rate reached 98.8 % within 30 minutes.

TiO_2 is currently the most widely studied and applied photocatalyst. Zhang et al. [3] prepared P25 TiO_2-graphene composite materials, which have excellent degradation effects on MB under ultraviolet or visible light conditions. Compared with P25, due to the large specific surface area of graphene, it can not only enhance the adsorption of organic pollutants but also expand the light response range, accelerate charge separation and transfer, and significantly improve the efficiency of photogenerated carrier utilization of the catalyst. It has excellent effects in the photocatalytic treatment of organic pollutants such as methylene blue (MB), methyl orange (MO), and rhodamine B (RhB). In addition to TiO_2-graphene, SnO_2-graphene [4], ZnO-graphene [5], Bi_2WO_6-graphene [6], Ag/AgCl-graphene [7], and $InNbO_4$-graphene can also be used as photocatalysts for the degradation of organic pollutants. For example, Zhang et al. [8] studied the visible light photocatalytic degradation activity of TiO_2-graphene and SnO_2-graphene on the self-sensitized dye RhB. Due to the high electrical conductivity of graphene and the improvement of charge separation efficiency, the photocatalytic activities of both composite materials are good, but SnO_2-graphene shows higher activity, mainly because the transfer of charges from RhB* to SnO_2 is thermodynamically easier to occur.

Graphene-based catalysts have a high conversion rate for heavy metal ions such as Cr(VI). Adding rGS to TiO_2 [9], CdS [10], and α-FeOOH nanorods [11] can significantly improve the photocatalytic activity of the Cr(VI) reduction reaction. In the α-FeOOH nanorod-graphene composite material, the π-hybridized plane of graphene plays a key role in charge transfer, minimizing the recombination of photogenerated electron-hole pairs and thereby enhancing the photocatalytic activity of α-FeOOH nanorods. Some studies have also shown that PANI/GS can adsorb up to 1149.4 mg g-1 of Cr(VI) and partially reduce Cr(VI) to Cr(III) [12]. Graphene oxide tends to aggregate and stack due to π-π interactions and van der Waals forces, resulting in a decrease in specific surface area. To address this issue, 3D graphene porous structure materials, such as graphene hydrogels or aerogels, have gradually developed. Graphene gels can effectively reduce the stacking of graphene sheets,

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not only increasing the surface area of graphene nanosheets, improving the electron transport channels, and enhancing the electrical conductivity, but also having many micrometer-sized porous structures, reducing the material density, and endowing the material with excellent adsorption performance [13 – 15].Yao et al. [16 – 17] developed a variety of highly efficient nanocomposite catalysts for the reduction reaction of the harmful substance 4-NP to the raw material of painkillers and antipyretics, 4-aminophenol (4-AP). Advanced oxidation processes (AOPs) have been a research hotspot in recent years and can be used to treat pollutants that are difficult to degrade by other methods (such as biotechnology). Galze [18] first proposed the concept of advanced oxidation processes (AOPs), mainly utilizing ·OH to oxidize organic pollutants, converting them into small organic molecules or complete mineralization. The main products of the reaction are CO_2, H_2O, and inorganic ions, with no residual sludge produced [19]. Among them, the Fenton reaction is the most important technology in AOPs, which has the advantages of a mild treatment process, high efficiency, no selectivity, and easy operation [20]. The homogeneous Fenton system (Fe^{2+}/H_2O_2) may lead to iron deposition, making the treatment process complex and expensive, thus limiting its implementation. To overcome the above problems, the heterogeneous Fenton system has gradually developed and replaced the traditional homogeneous Fenton system. Extensive research has been conducted on this, especially on magnetic materials such as Fe_3O_4 [21] and Fe_2O_3 [22], which not only have abundant reserves and low prices but also high activity. Moreover, they can be separated by an external magnetic field, significantly improving the reusability of the catalyst.

The application of magnetic nanoparticles has been investigated for many years, and these materials have been shown to have a wide range of applications inomedicine, drug targeting, gene therapy, the chemical industry, catalytic separation, and water treatment due to their unique physical and chemical properties [23, 24]. In particular, Fe_3O_4-based magnetic nanoparticles have been explored and investigated in multidisciplinary [25 – 27]. Compared with other carriers, magnetic carriers have obvious advantages, and paramagnetism makes it easy to separate them from the reaction solution under the action of an external magnetic field. Polyimide is a class of macromolecular materials with special and excellent thermal properties, and it has been extensively studied due to its special thermomechanical superior properties [28]. Due to the potential applications of high-performance polyimide, various functional nanomaterials based on PI materials have also been developed and manufactured. Among them, PI hollow nanospheres are widely used and investigated in various fields, such as dielectric materials, high-temperature nanocarriers, and nanoreactor vessels with heat resistance [29]. So far, the main technologies for the production of hollow magnetic Fe_3O_4 nanoparticles include suspension polymerization, mini-emulsion polymerization, microemulsion polymerization, dispersion polymerization, precipitation polymerization, etc. to the rigid structure of polyimide [30], there are few reports on wrapping Fe_3O_4 with polyimide, and the current research on Fe_3O_4 nanoparticles focuses the method of synthesizing Fe_3O_4 particles first and then wrapping polymers on the surface of Fe_3O_4 particles. Therefore, it is of both theoretical and practical value to outline the preparation of PI/Fe_3O_4 composite microspheres.

Through a one-step metallization reaction, polyimide microspheres loaded with metal nanocatalysts can be effectively produced without the need for any additional reducing agents (such as sodium borohydride, ammonia, UV radiation, etc.), enabling the efficient reduction of metal ions and subsequent formation of metal particles. By thermal treatment, imide cyclization reactions can yield high-quality polyimide, while aggregating reduced metal atoms on the surface to form a surface metal layer with excellent adhesion, thereby enhancing corrosion resistance and wear resistance. Additionally, this technology can effectively reduce traditional processing steps while improving material corrosion resistance. By incorporating nanometals, more uniform particles can be formed, which can be effectively integrated with the polymer structure, resulting in better surface activity and higher stability for superior performance.

2. PREPARATION METHOD OF Fe_3O_4

If magnetic nanocomposites are made with Fe_3O_4 nanoparticles as the core and other structures coated and modified on their surface, the synthesis of Fe_3O_4 nanoparticle materials is particularly important. Currently, the technology for preparing high-magnetic nanoscale iron oxide can be roughly divided into three approaches: biological method, physicochemical method, and chemical method. Among them, the biochemical method is mostly adopted for the preparation of nanoscale iron oxide materials [31 – 33].

2.1. Chemical Co-precipitation method

The co-precipitation method is a relatively common and simple method for preparing magnetic nanoscale Fe_3O_4. This method is relatively mature, and its basic principle is as follows:

$$Fe^{2+}+2Fe^{3+}+8OH^{-}\rightarrow Fe_3O_4+4H_2O. \quad (1)$$

The commonly used experimental method is to mix iron chlorides containing a certain proportion of iron ions (Fe^{3+} and Fe^{2+}), then form a mixed solution, and use NaOH solution or ammonia water as the precipitating agent. By controlling the appropriate experimental conditions and separating under a strong magnetic field at high speed, the reaction is carried out, and then the precipitate is washed and dried to obtain magnetic Fe_3O_4 nanoparticles. The magnetic particles prepared by this method are low-cost, but the particle size is difficult to control, and too fast a precipitation rate can lead to overly large particle diameters. Li Xiao [34] et al. found through research that the optimal conditions for preparing the Fe_3O_4 nanoparticle dispersion system are: at a reaction temperature of 30 °C, adjusting the pH value to 5 – 6, and adding the alkaline solution at a rate of 10 mL/min, which yields better results. At this time, the Fe_3O_4 nanoparticles have a uniform particle size.

2.2. Sol-gel method

The sol-gel method also involves mixing solutions containing Fe^{3+} and Fe^{2+} ions in an appropriate ratio, adjusting the pH value to an appropriate level, and then carrying out hydrolysis, condensation, nanoparticle growth, and aggregation in a certain amount of organic medium to form a network in the liquid phase. The gel is formed by slow evaporation, and during this process, Fe_3O_4 gel is obtained. The residual organic acid is removed by heating, and after high-temperature treatment, magnetic Fe_3O_4 products are finally obtained. The Fe_3O_4 nanoparticle materials synthesized by this method can be fully industrialized on a large scale, with a relatively low reaction temperature, but the cost is high, and the toxicity of the organic substances used as raw materials is relatively high.

2.3. Microemulsion method

The particle size in the microemulsion method is controlled by the size of the droplets. The microemulsion particle system is a thermodynamically stable system, mainly divided into water-in-oil (W/O) and oil-in-water (O/W) types [35]. The main feature of this method is that by controlling the size of the microemulsion droplets, the particle size of Fe_3O_4 can be effectively controlled [36], and long-term stable storage of nanoparticle microemulsions can be achieved. However, due to the extensive use of surfactants, which increases environmental pressure, and the very low synthesis yield, it cannot be widely used in reality.

2.4. Solvothermal method

The solvothermal method involves high-temperature and high-pressure reactions of iron in the form of inorganic compounds, such as dissolving anhydrous ferric chloride in an organic solvent like ethylene glycol. Under the presence of stabilizers and other additives, the reaction is carried out in the solvent with the aid of a high-pressure reaction vessel. $HOCH_2CH_2OH$ acts as both a solvent and a reducing agent to partially reduce Fe^{3+}, and the generated Fe^{2+} continues to react with Fe^{3+} to form Fe_3O_4. In the solvothermal reaction for preparing Fe_3O_4, the crystallization and crystal growth are extremely complex processes. Factors such as the pH value of the reaction system, the temperature during the reaction, the heating rate, and the reaction time all affect the particle size of the nanoparticles. Due to the strict experimental conditions and high cost of the solvothermal method, it may be subject to certain limitations in practical applications [37 – 40].

3. Fe_3O_4/PI MAGNETIC NANOCOMPOSITES PREPARATION

When producing polyimide solid composite microspheres, a two-step method is usually adopted. First, the precursor polyamic acid is obtained, and then thermal imidization is carried out using electroimidization or chemical imidization methods, or a combination of both, to finally obtain polyimide solid composite microspheres.

Chen Li [17, 18] et al. used methanol as the solvent and polyvinylpyrrolidone as the dispersant, and obtained polyimide solid particles after precipitating the particles.

Kanji Wakabayashi [20] et al. synthesized polyimide solid microspheres at high temperatures. At 240 °C, the dianhydride is dissolved in solvents such as liquid paraffin. The temperature is then raised, and the diamine monomer is added step by step. The reactants undergo a polymerization reaction. After 6 hours, polyimide microspheres precipitate from the solvent. They are then washed with acetone to obtain solid polyimide particles. In the experiment conducted by Jiang Yuanyuan et al., a secondary precipitation method was adopted. The diamine and polyvinylpyrrolidone were dissolved in N,N-dimethylacetamide solution, and then the dianhydride was added in batches to obtain a polyamic acid aqueous solution. Subsequently, piperidine and acetic anhydride were added through chemical imidization to obtain a polyimide solution. Then, a gel of polyvinylpyrrolidone was added to the solution, and finally, the polyimide microspheres were separated from the solution. The amount of polyvinylpyrrolidone affects the size of the microsphere particles.

According to the principle of liquid phase separation, J.K. Xiong et al. [21] dissolved the existing polyimide in a solvent to form a polyimide solution. Then, under stirring conditions, ethanol solution was dropped in sequence to precipitate polyimide microspheres. The greatest advantage of this method is that it can ensure the dispersion of polyimide particles, and the solvent does not contain any surfactants, making the experimental environment relatively environmentally friendly.

The preparation method of pure polyimide microspheres is still in the laboratory research stage. There are many difficult-to-control problems in the preparation process, making it impossible to achieve further industrial production. From a functional perspective, many applications of pure polyimide are limited, and the excellent properties of polyimide materials cannot be fully utilized. Therefore, core-shell structured composite microspheres have emerged, and polyimide and other materials composite nanospheres have become a research hotspot [22, 23].

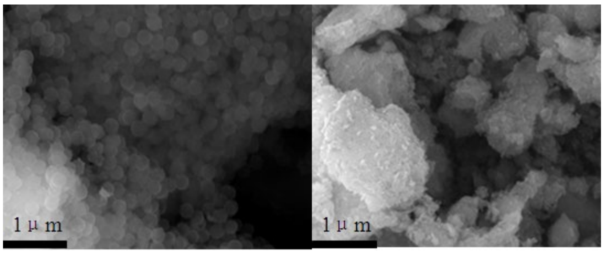
There are many methods for preparing organic/inorganic structured core-shell materials by the template method, and PI hollow microspheres have great potential and can be used in applications such as catalyst carriers. By wrapping PI around other organic or inorganic microspheres and removing the template through physical or chemical methods, PI hollow microspheres with good performance can be prepared. However, whether it is with Fe_3O_4 nanoparticles as the core and PI as the shell, or with PI as the core and Fe_3O_4 as the shell, there are not many reports in current research. This may be due to the rigid structure of polyimide, which limits the composite microspheres, or due to factors such as low solid content in the experimental stage, large solvent consumption, and difficult morphology control, which affect the successful preparation of composite microspheres. Currently, the main methods for preparing Fe_3O_4/PI magnetic nanocomposite microspheres are as follows.

When magnetic nanoparticles reach the nanometer scale, they exhibit common properties of nanomaterials such as the small size effect, surface effect, and quantum size effect. Among them, there is a large magnetic dipole interaction between Fe_3O_4 nanoparticles. By establishing a shell with good magnetic dipole interaction, Fe_3O_4 nanoparticles can be better stabilized and effectively resist agglomeration, thereby improving their adsorption performance. Therefore, we need to establish a core-shell structure on the surface of Fe_3O_4 nanoparticles to prevent their agglomeration [14].

After the preparation of Fe_3O_4 nanoparticles, the shell layer is then coated on their surface. Fe_3O_4 composite microspheres have a wide range of applications. Due to the diversity of polymers and the presence of functional groups in polymers themselves, polymer/Fe_3O_4 composite microspheres can have functional groups without further modification, making them widely studied. However, most polymers have a low thermal decomposition temperature, which limits their application in some fields. Therefore, high-temperature resistant polyimide materials can effectively break through this temperature limitation. Qu Chunyan and Zhou Haoran [6] used Fe^{3+} and polyamic acid triethamine salt as precursors to synthesize PI/Fe_3O_4 composite microspheres in a reactor through a one-step reaction, and explored various influencing factors to optimize the process conditions. Based on the solvothermal method, PI/Fe_3O_4 composite microspheres were synthesized by the reaction of Fe^{3+} with the polyimide precursor-polyamic acid triethamine salt (PAAS), in a reactor under high temperature and high pressure conditions.

If the magnetic composite material has Fe_3O_4 as the shell and polyimide as the core, then using conventional methods, the agglomeration problem of inorganic particles needs to be addressed. Fe_3O_4 nanoparticles need to be specially treated to make them hydrophobic, and adding some dispersants, initiators or emulsifiers in the reaction may weaken the performance of polyimide.

Fig. 1 a shows the scanning electron microscopy (SEM) image of pure Fe_3O_4 particles, revealing their spherical shape with an approximate diameter of 200 nm. Fig. 1 b presents the SEM photograph of Fe_3O_4/PI powder. Comparing the images of pure Fe_3O_4 particles and composite microspheres, it is evident that the surface is clearly covered by polymer fibers. However, the PI/Fe_3O_4 powder no longer maintains a spherical shape [37].



a b

Fig. 1. SEM images: a – Fe_3O_4; b – Fe_3O_4/PI [37]

This is due to the encapsulation of Fe_3O_4 by PI, but the excessive concentration of polyamic acid triethylamine salt causes the composite microspheres to aggregate, resulting in the synthesized PI/Fe_3O_4 powder lacking a spherical structure.

The experiment conducted thermal weight loss tests on Fe_3O_4 and PI/Fe_3O_4 composite powders, and the thermal weight loss curves are shown in Fig. 2. The Fe_3O_4 curve shown in curve a of Fig. 2 shows that the weight loss is due to the loss of oxygen in the metal oxide at high temperatures, as well as the possible residual solvents and hydroxyl groups generated on the surface of Fe_3O_4 during the preparation process. The mass loss is caused by solvent evaporation and group removal under high temperature conditions.

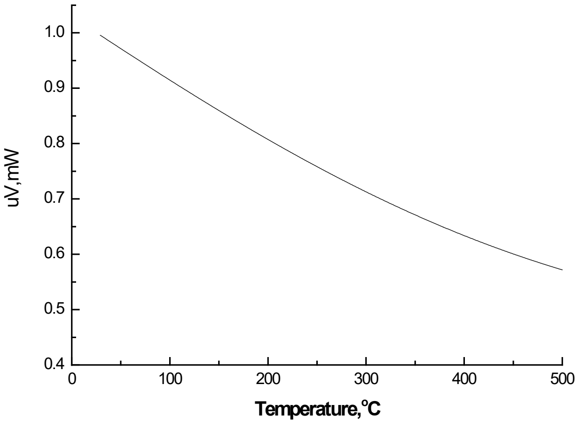


Fig. 2. DSC curve of PI/Fe_3O_4 composite powder [37]

By comparing the TGA curve of PI/Fe_3O_4 composite powder with curve b, it can be seen that the initial decomposition temperature of the composite powder is higher than that of pure Fe_3O_4, and the weight loss of PI/Fe_3O_4 composite powder is basically completed after 620 °C. The final weight loss of PI/Fe_3O_4 composite powder is 47 wt.% [37].

DSC testing was conducted on PI/Fe_3O_4 composite powder to investigate whether PI in PI/Fe_3O_4 composite microspheres had been completely imidized. The DSC curve is shown in Fig. 3 [37].

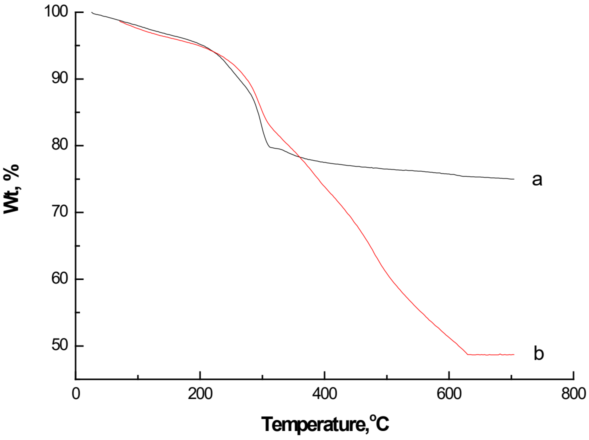


Fig. 3. Thermogravimetric curves: a – Fe_3O_4; b – PI/Fe_3O_4 composite powder [37]

From the DSC curve of PI/Fe_3O_4 composite powder, it can be seen that there is no reaction peak between room temperature and 500 °C, indicating that the polyimide in the PI/Fe_3O_4 composite microspheres has been completely imidized in the reaction vessel [37].

In order to observe the magnetic response of PI/ Fe_3O_4 composite powder more intuitively, the sample was dispersed in ethanol and photos were taken before and after applying a magnetic field. From Fig. 4, it can be seen that the composite powder was uniformly dispersed in the ethanol solution before the application of a magnetic field. After the application of a magnetic field, the sample gathered towards the side closer to the magnet, which intuitively indicates that the synthesized PI/Fe_3O_4 composite powder has a certain magnetic response [37]. A simple one-step solvothermal method was used to prepare PI/Fe_3O_4 composite powder using triethylamine salt as a precursor. Compared with other methods, the preparation process of polymer Fe_3O_4 composite microspheres does not require the preparation of Fe_3O_4 particles in advance, but rather the one-step synthesis of PI/Fe_3O_4 composite powder.


a b

Fig. 4. Photos of composite powder ethanol dispersion before and after external magnetic field: a – without external magnetic field; b – with external magnetic field [37]

Not only is the method simple and the conditions mild, but it also avoids experimental losses caused by coating the surface of Fe_3O_4 after its formation. The results indicate that the surface of Fe_3O_4 can successfully bind with PI, and PI penetrates the entire crystal through self-assembly process. PI/Fe_3O_4 composite powder exhibits certain magnetic properties and excellent thermal performance, and has the potential to be used as high-performance absorbing materials and other applications.

Compared with other methods, the preparation process of polymer Fe_3O_4 composite microspheres does not require the preparation of Fe_3O_4 particles in advance, but rather the one-step synthesis of PI/Fe_3O_4 composite powder. Not only is the method simple and the conditions mild, but it also avoids experimental losses caused by coating the surface of Fe_3O_4 after its formation. The results indicate that the surface of Fe_3O_4 can successfully bind with PI, and PI penetrates the entire crystal through self-assembly process. PI/Fe_3O_4 composite powder exhibits certain magnetic properties and excellent thermal performance, and has the potential to be used as high-performance absorbing materials and other applications.

In previous research projects [37], researchers used chemical co precipitation to prepare Fe_3O_4 particles, and then mixed functionalized polystyrene (PS) nanoparticles with the prepared Fe_3O_4 to obtain PS/Fe_3O_4 magnetic nanocomposites through electrostatic interactions; Next, pyrrole monomer is added to undergo oxidative polymerization on the surface of the composite, resulting in magnetic PS coated with polypyrrole on the surface. Fe_3O_4@PPy compound; Finally, a novel magnetic catalyst was prepared using the sedimentation precipitation method. The results show that PS/Fe_3O_4@PPy/The particle size distribution of Pb magnetic composite is relatively uniform and the dispersibility is good; After adsorbing dye molecules, the magnetic composite can be recycled and reused multiple times.

Qu Chunyan and Zhou Haoran [6] synthesized PI/Fe_3O_4 composite microspheres through a one-step reaction in a reactor using $Fe^{3+}$and triethylammonium polyamide salt as precursors. Various influencing factors were explored and process conditions were optimized. Based on the solvothermal method, PI/Fe_3O_4 composite microspheres were synthesized by reacting $Fe^{3+}$with polyimide precursor PAAS in a reaction vessel under high temperature and pressure conditions.

The UV-Vis spectrum of this process is shown in Fig. 5. The maximum absorption wavelength of the initial methylene blue solution appears at 665 nm and the solution appears dark blue, as shown in curve (a) in Fig. 5. After adding a certain amount of sodium borohydride and reacting for 8 hours, the color of the solution changed from dark blue to light blue, and the absorption intensity at the maximum absorption wavelength decreased but did not completely disappear, as shown in curve (b) in Fig. 5[36].

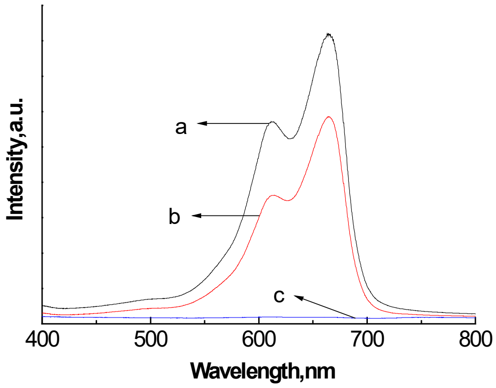
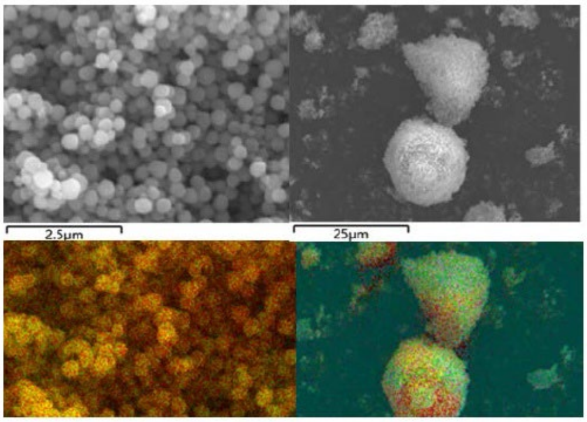


Fig. 5. a – initial solution; b – UV-Vis spectra of catalytic reduction of methylene blue solution in the absence of catalyst; c – in the presence of catalyst [36]

It is difficult to reduce methylene blue solution in the absence of a catalyst. When adding 10 mgPS to the system/Fe_3O_4@PPy After Pb magnetic composite, the absorption intensity completely disappears, as shown in curve (c) in Fig. 5, and the color of the solution changes from dark blue to colorless within 2 minutes. Based on the above UV Vis analysis, it can be concluded that, PS/Fe_3O_4@PPy/Pb magnetic catalyst exhibits excellent catalytic performance.

The EDS analysis in Fig. 6 a shows that oxygen accounts for 35.5 % and iron 64.5 %. Fig. 6 b shows that carbon accounts for 68.3 %, nitrogen 1.2 %, oxygen 23.8 % and iron 6.7 %. Fe_3O_4 composite microspheres have a wide range of applications [37].



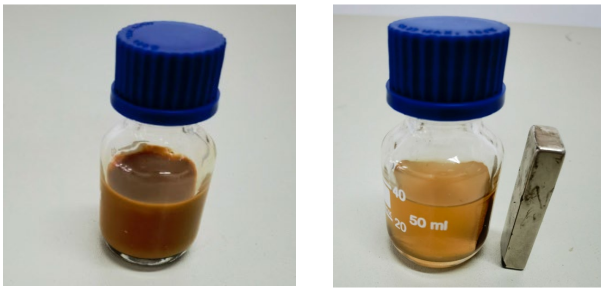
a b

Fig. 6. EDS images: a – Fe_3O_4; b – PI/Fe_3O_4 powders [37]

Due to the variety of polymers and the fact that the polymer itself has functional groups, the PI/Fe_3O_4 composite microspheres can have functional groups without further modification to make them functional. Fe_3O_4 composite microspheres have received extensive attention. However, most polymers have low thermal decomposition temperature, which limits their application in some fields [37].

In order to achieve both heat resistance and magnetic conductivity in polyimide composite materials, Fe_3O_4/PI magnetic polyimide composite powder was synthesized using a one-step solvothermal method. Ether anhydride type polyamide acid was designed and prepared using diphenyl ether tetracarboxylic acid dianhydride and 4,4'-diaminodiphenyl ether as monomers. The PI/Fe_3O_4 composite powder was synthesized by reacting Fe^{3+} with polyimide precursor - triethylamine salt of polyamide acid in a reaction kettle under high temperature and high pressure conditions. On the surface morphology, the PI/Fe_3O_4 composite powder has a complete spherical structure (Fig. 6 b).

In order to observe the magnetic response of PI/Fe_3O_4 composite powder more intuitively, the sample was dispersed in ethanol and photos were taken before and after applying a magnetic field. It can be seen in Fig. 7 that the composite powder was uniformly dispersed in the ethanol solution before the application of a magnetic field [40].



a b

Fig. 7. Photos of composite powder ethanol dispersion before and after external magnetic field: a – without external magnetic field; b – with external magnetic field [40]

After the application of a magnetic field, the sample gathered towards the side closer to the magnet, which intuitively indicates that the synthesized PI/Fe_3O_4 composite powder has a certain magnetic response. The magnetic saturation intensity curve in Fig. 8 shows that the coating of PI has a certain impact on the magnetic saturation intensity [37]. He Jis [7] conducted a polymerization reaction of highly cross-linked sulfonated polystyrene spheres (SPS) and reactants in a solvent. The sulfonation reaction was carried out at 40 °C for 3 hours. PAA was prepared by reacting 4,4'-ODA and s-BPDA at room temperature for 2 hours under a nitrogen atmosphere. PAA was diluted and SPS was added to the DMAc dispersion. The mixture was stirred to coat PAA on the surface of SPS. Then, 5.68 g of $FeCl_3$ and 2.54 g of $FeCl_2$ were added to the PAA-SPS dispersion and stirred at room temperature for 12 hours. During the stirring process, PAA-SPS was coated with Fe^{2+} and Fe^{3+} ions. Then, 0.12 mL of acetic anhydride and 0.05 mL of pyridine were added dropwise to the dispersion and stirred at room temperature for 12 hours.

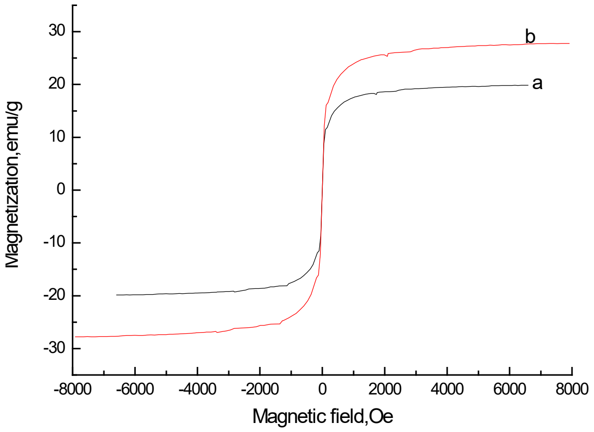


Fig. 8. Magnetic saturation intensity curves: a – Fe_3O_4; b – PI@Fe_3O_4 [37]

After stirring, a small amount of ammonia water was added. The material was washed, centrifuged, washed again, and then separated. All steps except centrifugation were carried out under a nitrogen atmosphere. Finally, it was gradually heated to 350 °C in a muffle furnace to obtain PI-MHNS hollow magnetic microspheres.

This study combined in-situ and template methods to synthesize PI-based hollow magnetic nanospheres. The properties of polyimide will be retained, and the magnetic particles will be uniformly dispersed around the hollow spheres. No special treatment of inorganic particles is required to generate the interaction between PI spheres and inorganic particles. The hollow structure can also be maintained. In addition, the simultaneous occurrence of two reactions, imidization and the formation of Fe_3O_4, will enhance the interaction between Fe_3O_4 and PI.

Hollow composite materials based on polyimide were successfully prepared by in-situ and template methods. PI@PPy were completely coated on the surface of polystyrene nanoparticles. After calcination, PI@PPy/Pd hollow composite materials were obtained through a chemical process. Due to the interaction between the amino groups on the PPy main chain and Pd^{2+} ions, Pd nanoparticles were densely and uniformly anchored on the surface of the PPy shell. Due to their special structure, they are ideal nanoreactor materials for heterogeneous catalysis. The catalytic performance of PI@PPy/Pd hollow composite materials was studied through a reduction reaction using $NaBH_4$ as the reducing agent, and they exhibited excellent catalytic performance in the reduction of methylene blue solution. The preparation process of PI@PPy/Pd hollow composite materials is shown in Fig. 9 [36].

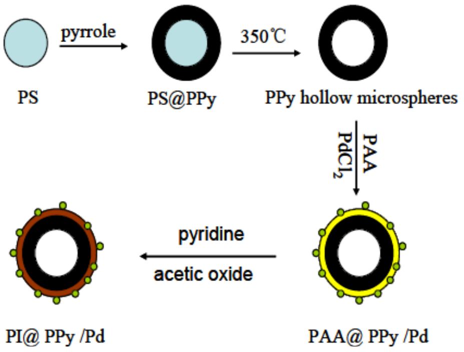


Fig. 9. Flowchart of PI@PPy/Pd composite materials [36]

Another study showed that superparamagnetic Fe_3O_4 nanospheres were used as the magnetic core, and soluble starch resin as the carbon source to prepare Fe_3O_4@C magnetic nanoparticles through a hydrothermal method. By carbonizing organic substances on the surface of Fe_3O_4 nanoparticles, core-shell structured SiO_2-Fe_3O_4 and Fe_3O_4@C carriers were prepared. Pd was loaded onto Fe_3O_4@C to form a core-structured magnetic nanocatalyst, and their catalytic performance was studied. The obtained environmentally friendly magnetic materials can be used for the degradation of dye wastewater. The preparation process diagram of magnetic composite materials is shown in Fig. 10 [40].

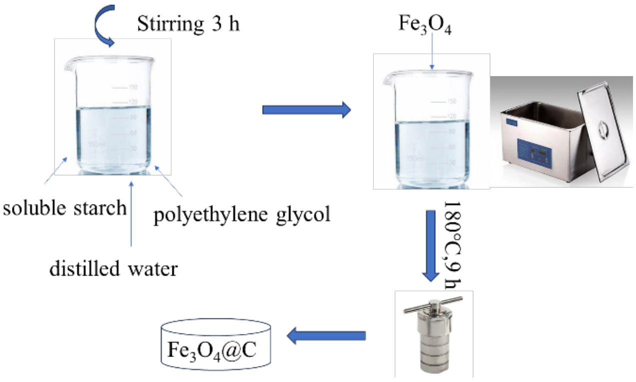


Fig. 10. Preparation process of magnetic composite materials [40]

To prepare a composite material that is both heat-resistant and has magnetic permeability, Fe_3O_4/PI magnetic polyimide composite powder was fabricated by a one-step solvent method. Using 4,4′-diaminodiphenyl ether (OD) as the monomer, ether anhydride polyamic acid was designed and prepared. Through the reaction of Fe^{3+} and polyimide prepolymer-polyamic acid triethylamine salt in a reactor under high temperature and high pressure conditions, PI/Fe_3O_4 composite powder was synthesized.

4. APPLICATION OF Fe_3O_4 CATALYSTS

In recent years, magnetic nanomaterials have been successfully used as catalyst carriers in various organic synthesis reactions. Baylor et al. proposed the use of ruthenium catalysts for the benign and green synthesis of sulfonamide drugs. In this reaction, the formation of C-N bonds occurs with high selectivity and the only by-product is water. Currently, there are many mature application fields, such as magnetic storage materials, catalysis, environmental analysis, stimulus-responsive biotechnology, ultra-high frequency microelectronics, electromagnetic wave absorption, and biomedicine, among others, and there have been in-depth studies in these areas [24 – 26].

Nanomaterials as catalyst materials have a high specific surface area and high catalytic activity and have been widely used in heterogeneous reaction systems. However, due to the small size structure of these materials, it is difficult to separate them from the reaction system, increasing the difficulty of recovery and greatly limiting the application of these nanocatalytic materials in this field. If other nanomaterials are combined with Fe_3O_4 nanoparticles, core-shell structured catalyst nanocomposite materials can be obtained, thereby reducing the separation difficulty, increasing the recovery efficiency, and reducing the cost of the reaction [6].

Magnetic materials have a wide range of applications in biomaterials. Due to their similar scale, magnetic materials can be combined with biological organisms after modification. This includes magnetic implantation for targeted drug release, immobilization of biological proteases, and connection with polymerase chain reaction, among others. Due to the magnetic effect of biological nanomaterials, people can also use the external electromagnetic field to influence the movement of biological nanoparticles, such as cell immunomagnetic separation technology and biological probe imaging methods.

Magnetic polymer composite microspheres are also widely used in the wastewater treatment industry, especially for industrial wastewater rich in heavy metals, dyes, and organic matter. In recent years, due to the rapid development of industry, water pollution caused by industrial wastewater has become increasingly severe, and the harm of heavy metals has attracted widespread attention globally [42, 43]. Due to the low concentration of pollutants in wastewater and the large amount of pollutants in soil, efficient enrichment and separation have become particularly important. Magnetic polymer composite microspheres, due to their magnetic properties of inorganic substances and active groups of polymer substances, can be absorbed by heavy metal molecules in soil and separated from magnetic nanocomposites very quickly under the influence of external electromagnetic fields [27].

5. CONCLUSIONS

Magnetic Fe_3O_4 nanoparticles were prepared by solvothermal synthesis from ferric chloride hexahydrate and coated with silica and carbon, respectively. The Fe_3O_4@C/Pd magnetic nano-catalyst was prepared by loading noble metal components onto the processed Fe_3O_4@C support and fixing the noble metal components on the surface of the support by sodium borohydride reduction. Looking to the future, Fe_3O_4 magnetic nanocomposite microspheres are bound to have broad development prospects. In recent years, researchers have been increasingly involved in the development of magnetic nanocomposites, and the technology has gradually matured. However, in terms of basic theoretical research, there is still a significant lack of theoretical research on the generation mechanism, aggregation principle, and interaction between magnetic substances and polymer composites. In the field of material design, research on the basic structure of polymer microspheres and the acid and alkali resistance of composite materials still needs to be further explored. In terms of specific applications, more research is needed for the development from the laboratory to industrial and environmental protection applications. These studies have provided new directions for the development of novel catalysts for the treatment of organic pollutants. The author has developed a new type of catalyst through research; this catalyst not only has catalytic activity but also features high-temperature resistance and solvent resistance. By using composite technology, the author has overcome the difficulty of metal nanoparticles easily solidifying and broken through the bottleneck that it is difficult for polyimide solid materials to form a spherical appearance, achieving catalytic activity. There are few reports on the research of new catalysts with multiple excellent properties and light weight materials. Some scholars have produced polyimide microspheres loaded with metal nanocatalysts through a one-step metalization reaction without using any additional reducing agents (such as sodium borohydride, hydrazine, etc.). Metal ions can be effectively reduced, and metal particles can be generated. Through thermal treatment, the imide ring closure reaction can produce high-quality polyimide; the reduced metal atoms aggregate on the surface and form a surface metal layer with good adhesion, thereby having better corrosion resistance and wear resistance. This technology can effectively reduce traditional processing procedures and also effectively improve the corrosion resistance of materials. By adding nano-metals, polyimide can form more uniform particles and can effectively combine polyimide with polymer structures, giving polyimide better surface activity and higher stability.

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