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Self-assembled three-dimensional flower-like α-Fe_2O_3 nanostructures and their application in catalysis

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Three-dimensional flower-like α-Fe_2O_3 nanostructures have been successfully synthesized by a simple surfactant-free environmental friendly solvolthermal process. The as-prepared products were investigated by X-ray powder diffraction, transmission electron microscopy, and field emission scanning electron microscopy. By adjusting the synthetic parameters, the shape of the α-Fe_2O_3 nanostructures can be controlled. The three-dimensional flower-like α-Fe_2O_3 nanostructures were found to be highly active as catalysts for phenol alkylation. The effects of various parameters, such as reaction temperature, reaction time and the amount of catalyst, were studied. The catalyst was stable and could be reused three times in normal atmosphere without suffering appreciable loss in catalytic activity. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: iron oxide; nanostructure; alkylation; phenol

Introduction

α-Fe_2O_3 (hematite) is a semiconductor ($E_g = 2.1$ eV) which is environmentally friendly, nontoxic, corrosion-resistant and easily obtainable. The use of α-Fe_2O_3 has been demonstrated as a photoanode for photoassisted electrolysis of water,[1] an active component of gas sensors,[2–5] a photocatalyst[6] and an ordinary catalyst.[7–9] Because of its excellent properties, considerable efforts have been focused on the properties and synthesis of hematite nanomaterials with controllable size and shape, such as nanocrystals,[10] nanoparticles,[11] nanocubes,[12] nanospindles,[13] nanoflakes,[14] nanorods,[15] nanowires,[16] nanobelts[17] and nanotubes.[18] Three-dimensional (3D) nanostructures have attracted much attention due to their unique properties and potential applications.[19,20] Zhong *et al*. reported the synthesis of novel 3D flower-like iron oxide nanostructures mediated by an ethylene glycol (EG) and then calcined at 450 °C for 3 h.[21] It is therefore still a big challenge to develop simple and reliable synthetic methods for self-assembled 3D flower-like α-Fe_2O_3 nanostructures, which will strongly affect their properties.

Alkylation of phenol has attracted much attention due to alkylphenols are important intermediates and can be used as raw materials in chemical industry and for further syntheses of fine chemicals. Various kinds of agrochemicals, plastics, dyes, antioxidants, flavoring agents, emulsifiers, non-ionic detergents, pharmaceuticals, etc., are produced from them.[22] 4-*tert*-butyl Phenol (4-TBP) imparts improved performance properties to the class of metallic detergents used in lubricating oils, and in the production of substituted tri-aryl phosphates.[23] The Friedel–Crafts reaction is known to be an important method of introducing alkyl and acyl groups into aromatic compounds. The *tert*-butylation of phenol is a typical Friedel–Crafts alkylation and usually catalyzed by homogeneous Lewis acids ($AlCl_3$, BF_3) or strong mineral acids (HF, H_2SO_4), which are highly toxic, generate a substantial amount of waste and cause severe corrosion problems. A few studies have been reported on the *tert*-butylation of phenols using various solid acids such as micro-porous molecular sieves, cation exchange resins, clays, zeolites and supported metal oxides.[24–27]

In this paper 3D flower-like α-Fe_2O_3 nanostructures were synthesized under simple surfactant-free solvothermal conditions at relatively low temperature in one step. Furthermore, it was found to be highly active as a catalyst for phenol alkylation with *tert*-butyl chloride.

Experimental

Materials

All reagents were of high analytical purity and used without any further purification. $FeCl_3 \cdot 6H_2O$, urea, isopropanol, phenol, *tert*-butyl chloride and petroleum ether were purchased from Shanghai Chemical Company.

Preparation of 3D Flower-like α-Fe_2O_3 Nanostructures

In a typical process, α-Fe_2O_3 flower-like structures were obtained as follows: 0.5 mmol $FeCl_3 \cdot 6H_2O$ and 0.15 g urea were dissolved in 40 ml isopropanol in a 50 ml beaker with constant stirring. After 10 min, the mixture was transferred into a 60 ml Teflon-lined stainless steel autoclave and maintained at 200 °C for 24 h, then air cooled to room temperature. Finally, the red precipitates were obtained by centrifugation, washed with absolute ethanol several times and dried in vacuum at 60 °C for 4 h.

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Preparation of α-Fe_2O_3 Nanoparticles

A similar procedure was used to obtain α-Fe_2O_3 nanoparticles: 0.5 mmol $FeCl_3 \cdot 6H_2O$ and 0.15 g urea were dissolved in 40 ml distilled water in a 50 ml beaker with constant stirring.

Catalytic Alkylation of Phenol

The alkylation of phenol with *tert*-butyl chloride was investigated using the obtained flower-like α-Fe_2O_3 nanostructures as catalyst. The catalytic reaction was carried out in a 50 ml flask fitted with a water-cooled condenser and magnetic stirrer. In a typical process, 0.03 mol phenol was dissolved in 20 ml petroleum ether, and 0.3 mmol of α-Fe_2O_3 powders were added. Then 0.03 mol *tert*-butyl chloride was added while the reaction mixture was heated at 60 °C with continuous stirring until the reaction was completed, then centrifuged. The solutions was separated and washed with water three times. The white product (m.p.: 99–101 °C) was obtained after recrystallization with ethanol. The precipitate was washed with absolute ethanol then dried and used in the next catalytic cycle without additional treatment.

Characterization of Catalyst and Alkylation Product

The synthesized products were characterized by X-ray powder diffraction (Shimadzu XRD-6000) with graphite monochromatized Cu-K_α radiation ($\lambda = 0.15406$ nm), employing a scanning rate of 0.02 deg s^{-1} in the 2θ range from 10 to 70°. Figure 1 presents the XRD pattern of the as-prepared sample. All of the detectable diffraction peaks can be indexed to (012), (104), (110), (113), (024), (116), (214) and (300) reflections of the hexagonal-phase α-Fe_2O_3, in good agreement with the standard value (JCPDS card no. 86–0550). To further investigate the structural and textural properties of the α-Fe_2O_3, the synthesized catalysts were characterized by field-emission scanning electron microscopy (FESEM). FESEM images were obtained on an S-4800 field-emission scanning electron microscopy of Hitachi with an accelerating voltage of 5 kV. It is clearly shown in Fig. 2(a) that the product possesses a flower-like morphology with diameter about 2 μm. The flowers are composed of thin nanosheets which are joined to each other in such a special fashion that the flowers exhibit spherical-shaped morphologies. The thickness of the nanosheet is about 15 nm. The morphology of the as-prepared α-Fe_2O_3 sample was further characterized by transmission electron microscopy (TEM) which operated on a Jeol-2010 instrument with a tungsten filament using an accelerating voltage of 200 kV. A typical TEM image of the sample is shown in Fig. 3, which also confirmed the flower-like structure.

^1H NMR spectra were obtained at 25 °C on a Bruker Avance-300. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.27–7.24 (d, $J = 8.6$ Hz, 2H), 6.79–6.76 (d, $J = 8.6$ Hz, 2H), 1.29 (s, 9H).

Results and Discussion

The possible reaction in the formation of α-Fe_2O_3 nanostructures might be expressed as follows: soluble ferric chlorides firstly dissociate in isopropanol into ferric ions which then attach by isopropanol neutral ligands. Urea was used as a precipitator in the reaction. The ferric complexes may be decomposed under high pressure in the Teflon-lined stainless steel autoclave. If the solvent was changed to water, α-Fe_2O_3 nanoparticles [Fig. 2(b)] could be obtained.

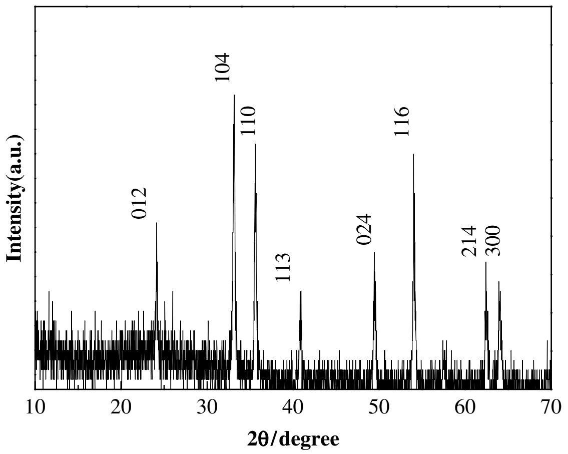


Figure 1. XRD pattern of the as-prepared sample.

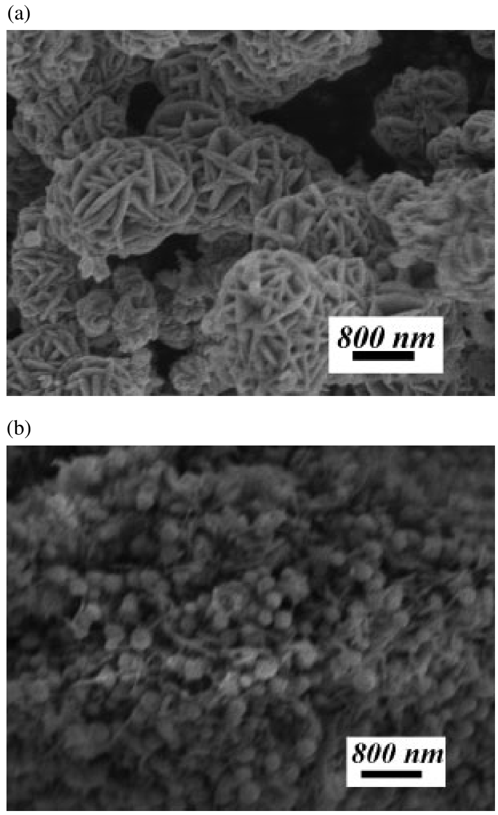


Figure 2. FESEM images of (a) flower-like α-Fe_2O_3 nanostructures; (b) α-Fe_2O_3 nanoparticles.

The flower-like α-Fe_2O_3 nanostructures catalyzing alkylation of phenol and *tert*-butyl chloride in petroleum ether was chosen as a model reaction. The effects of the amount of catalyst, temperature and reaction time were investigated and the results were summarized in Table 1. It can be seen that the yield of product was increased with an increase in the amount of catalyst (Table 1, entries 1–5). At 0.1 mmol, the yield of 4-*tert*-butyl phenol was found to be 41.7% and it is increased to 69.3% at 0.3 mmol. However, when the amount of catalyst increased to 0.4 mmol, the yield of 4-*tert*-butyl phenol was slightly increased. Therefore, a further increase in the amount of catalyst had little effect on the

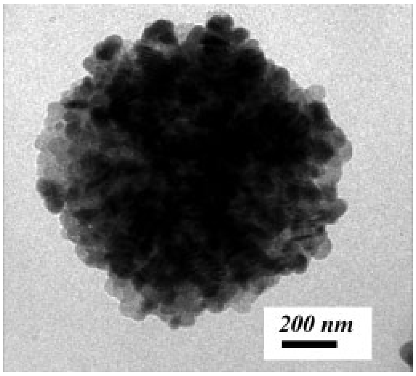


Figure 3. Typical TEM image of the flower-like α-Fe_2O_3 nanostructure.

Table 1. Phenol alkylation with different amount of catalyst, different temperature and different times[a]

Entry	Catalyst (mmol)	Time (h)	Temperature (°C)	Yield[b] (%)
1	0	4	60	0
2	0.1	4	60	41.7
3	0.2	4	60	51.4
4	0.3	4	60	69.3
5	0.4	4	60	69.5
6	0.3	4	0	0
7	0.3	4	50	58.2
8	0.3	4	80	62.6
9	0.3	2	60	18.6
10	0.3	3	60	52.0
11	0.3	5	60	64.3

[a] Reaction conditions: phenol (0.03 mol), *tert*-butyl chloride (0.03 mol); [b] isolated yield.

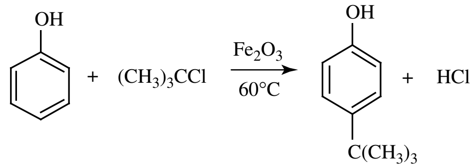
yield of phenol alkylation. Accordingly, 0.3 mmol of catalyst could catalyze the reaction sufficiently from the experiment results.

The effect of the reaction temperature on the yield of 4-*tert*-butyl phenol was studied at various temperatures from 0 to 80 °C (entries 6, 7, 4 and 8). It was found that no products were observed when the temperature was under 25 °C. The yield of product was 58.2% at 50 °C and it increased to 69.3% at 60 °C. However, further increase of reaction temperature to 80 °C resulted in a slight decrease in yield of the product. This behavior is often observed in alkylation reactions and is mainly due to the thermodynamics of alkylation and de-alkylation.[27]

It is noteworthy that the reaction time was a key parameter of the process. It revealed that the reaction yield is increased with the increase of reaction time in the time range of 2–4 h (entries 9, 10, 4 and 11). However, the yield decreases slightly if the reaction time is prolonged to 5 h. It is also mainly due to the thermodynamics of alkylation and de-alkylation.[27]

Accordingly, the reaction scheme may be depicted as shown in Scheme 1. The reusability of the catalyst was investigated because it is very important to industrial and pharmaceutical applications. The flower-like α-Fe_2O_3 nanostructures showed good efficiency of reusability, and could be recycled three times without obviously decrease in activity.

Furthermore, the flower-like α-Fe_2O_3 catalyst could also be applied to 2-naphthol alkylation reaction. A yield of 61.3% 4-*tert*-butyl 2-naphthol could be obtained under the optimized reaction conditions.



Scheme 1. α-Fe_2O_3 catalyzed *tert*-butylation of phenol.

Conclusions

In conclusion, the 3D flower-like α-Fe_2O_3 nanostructures were synthesized under surfactant-free solvolthermal conditions at 200 °C in only one step. The method is easy and friendly to the environment. It brings forward a broad idea to synthesize nanostructures of α-Fe_2O_3. The flower-like α-Fe_2O_3 nanoparticles were found to be highly active as a catalyst for phenol alkylation with *tert*-butyl chloride. The alkylation of phenol catalyzed with flower-like α-Fe_2O_3 nanostructures was successful. High yields of the 4-*tert*-butyl phenol could be obtained with this catalyst. The optimum reaction condition for this reaction was using 0.3 mmol catalyst at 60 °C for 4 h. At this time, the yield of 4-*tert*-butyl phenol was 69.3%. The α-Fe_2O_3 catalyst could also be applied to alkylation of 2-naphthol.

Acknowledgments

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