Synthesis of Fe_3O_4 core/alumina shell nanospheres for partial hydrogenation of benzene

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Abstract. We report a novel synthesis of Fe_3O_4 core/alumina shell nanosphere composite for partial hydrogenation of benzene. Fe_3O_4 core/alumina shell (MFeCA) structured nanospheres were obtained by reducing a hematite core/alumina precursor shell (HFeCAP) nanosphere precursor under H_2/N_2 gas flow. The magnetic alumina nanospheres (MFeCAs) possess not only uniform size (180~350nm) but also adjusted saturation magnetization value. A novel Ru-based magnetic catalyst was synthesized for the partial hydrogenation of benzene in magnetically stabilized bed (MSB). The performance of magnetic catalyst in MSB demonstrates that it's an effective and highly selective method for partial hydrogenation of benzene. The chain regime of the MSB reactor's operation conditions is responsible for the high selectivity of cyclohexene.

1. Introduction

The selective hydrogenation of benzene to cyclohexene has been extensively investigated [1–3], which is considered to be ideal reaction process due to their simple, environmental process and great industrial interest. Such liquid-phase selective hydrogenation of benzene to cyclohexene with different catalyst has been demonstrated to be effective method. For its applications, the high cyclohexene yield was achieved. A magnetically stabilized bed (MSB) offer many advantages, including low pressure drop, high mass-transfer efficiency, and the absence of catalyst attrition and catalyst separation step [4-6]. Therefore, the applications of MSB have been investigated widely in the chemical industry. MSB has been demonstrated to be effective hydrogenation method, such as selective acetylene hydrogenation [7], purification of caprolactam [8] and CO methanation [9], etc. The fabrication of microsphere from alumina and magnetic particles has been reported due to their unique magnetic responsivity and excellent physical strength [10-12]. The results showed that magnetic alumina microsphere could be used in a magnetically stabilized bed (MSB) as a catalyst or catalyst support [10, 11].

In this paper, the combination of MSB and magnetic core-shell Ru-based catalyst were employed, and one new method for selective hydrogenation of benzene in an MSB reactor was developed. Firstly, we fabricated uniform nanocomposite sphere with a hematite core/alumina precursor shell (HFeCAP) structure. The alumina shell was formed via a combination of the aluminum isopropoxide sol-gel process and stearic acid self-assembly. After reducing of the nanosphere hematite core in gas flow mixture of H2 and N2, this novel magnetic carrier named as MFeCA (magnetic core/alumina shell)

nanosphere was employed to synthesis Ru/Fe_3O_4-Al_2O_3 catalysts, which were investigated in the partial hydrogenation of benzene in MSB.

2. Materials and methods

2.1. Materials
1-propanol, aluminum isopropoxide(Al[OCH(CH3)2]3),ruthenium chloride, zinc sulfate and ethanol were all of analytical grade and purchased from the Shanghai Chmeical Corp.

Hematite particles were hydrothermally synthesized by a surfactant-directing approach previously reported16. In a typical synthesis of hematite core/porous alumina shell composite particles, hematite particles (diameter 300 nm) were dispersed by ultrasonication into 100 mL of 1-propanol containing stearic acid. Aluminum isopropoxide was added under vigorous stirring, and the reaction was stirred at 70°C for 6 h. The resulting stearic acid-incorporated core-shell particles were separated by filtration, and dried at room temperature. This intermediate product was named HFeCAP (hematite core/alumina precursor shell spheres). The thermal treatment of HFeCAP in a mixed H2 (4 vol %) /N2 atmosphere at 673 K for 3 h, yielded the final magnetic core/alumina particles (MFeCA). The preparation of magnetic Ru/Fe3O4-Al2O3 catalyst was by impregnation method with RuCl3 solution, followed by drying at 373 K for 8 h and calcination in air at 573 K for 2 h, and them loading was about 0.3 wt %. Before using catalyst, the reduction of catalyst was performed in H2 fluid (30 ml min-1) at 473 K for 10 h. Subsequently, 2 h of preliminary treatment in the hydrogen 4/5000 hydrogen atmosphere at 423 K with a ZnSO4 aqueous solution at the flow velocity of 1ml min-1 was investigated. The process was employed at 3.0 MPa and 423 K. Samples were analyzed by GC-FID.

2.2. Analysis and characterization
X-ray powder diffraction (XRD) was investigated by a PANalytical X' Pert Pro MPD diffractometer. The magnetic properties of the samples were measured at room temperature by a Lake Shore vibrating sample magnetometer (VSM). Particle morphology and size were examined by a Hitachi S-4800 scanning electron microscope (SEM) and a JEM-2100UHR transmission electron microscope (TEM). Low temperature N2 sorption experiments were investagited by a Micromeritics ASAP-2020 Quantachrome Autosorb-1 system.

## 3. Results and discussion

3.1. Characterization
TEM images of samples are shown in figure 1. It can be seen that the sizes of samples s are quite uniform. The average sizes of samples vary in a range of ca. 180-250nm as seen from the TEM images. TEM images show that magnetic microspheres are successfully embedded in the MFeCAs. A TEM image of the MFeCA nanospheres (figure 1(a)) showed that most cores shrunk while their shell remained unbroken. The EDX spectrum of the product core–shell nanospheres (figure 1(b)) revealed the containing of Fe, Al, and O, further indicating the existence of the alumina shell on the Fe3O4 nanosphere surface. Elemental analysis indicated an Al/Fe mass fraction of 0.34, which was consistent with that of the synthesis mixture. Nitrogen sorption isotherm of the MFeCAs samples in figure 2 displays typical type II adsorption isotherms with the superposition of type H1 and H3 hysteresis loops [13]. The products have high Brumauer–Emmett–Teller (BET) surface areas (140 m^2g^{-1}) and large pore volumes (0.22 cm^3g^{-1}). The narrow and sharp pore size distribution curves (inset of figure 2) suggest that the mesopores possess very uniform sizes.
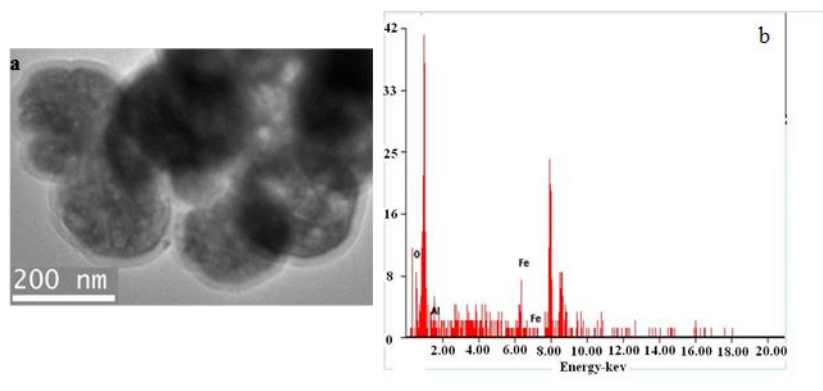
**Figure 1.** (a) TEM image of MFeCA nanospheres; (b) EDX of MFeCA nanospheres.
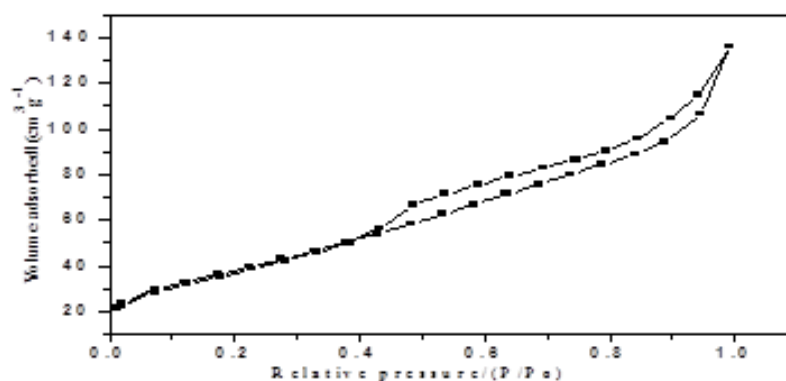
**Figure 2.** N_2 adsorption isotherms of MFeCA nanospheres.
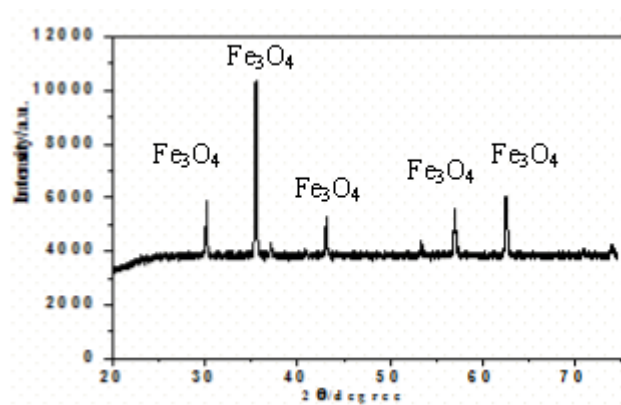
Figure 3. XRD pattern of MFeCA nanospheres.

Figure 3 shows the wide-angle XRD patterns of magnetic nanospheres. The characteristic diffraction peaks of Fe3O4 are clearly observed, which is consistent with TEM observations and further confirms the existence of magnetic microspheres in MFeCAs. The composition of the product could be adjusted by altering the reduction temperature or time, as described previously [14]. The magnetization curve at room temperature (figure 4) shows an obvious magnetic hysteresis loop, which possess a rapid magnetic response to the magnetic field. The saturation magnetization value of the MFeCA nanospheres (~50.2 emu g-1) could also be adjusted by reduction temperature or time, according to the typical reduction processes of hematite. The intrinsic ferromagnetism of MFeCA provided one straightforward way to separate particles from miscible liquids.
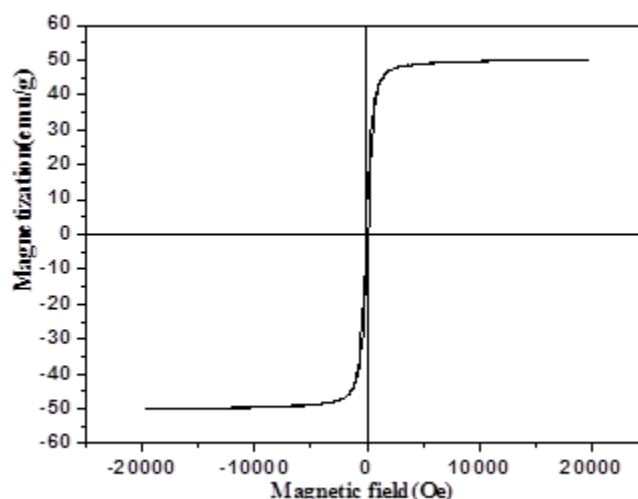
**Figure 4.** Magnetization hysteresis loops of MFeCA nanospheres.
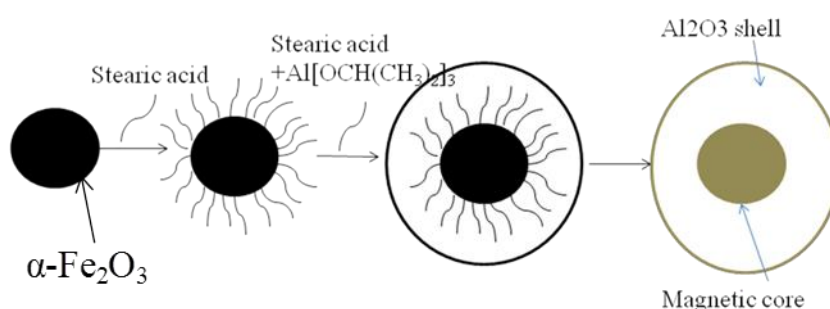
Scheme 1. The formation process of the MFeCA nanospheres.

Scheme 1 illustrates the formation process of the $Fe_2O_3@Al_2O_3$ core-shell nanospherestructure. We propose that HFeCA nanospheres were produced by the self-assembly of mixture α-Fe2O3-surfactant particles and surfactant/alumina compound. The nanosphere/stearic acid capped particles contained a negative charge[15,16], due to the carboxyl groups of the anionic surfactant. Hydrolyzed alumina and template directed self-assembly of alumina/template phases. A specific description is as follows: hydrolyzed aluminum isopropoxide monomers condense to form oligomeric alumina precursors. When the precursors reach a certain size, precursors and surfactants are assembled to produce an alumina shell on the surface of the nanosphere-surfactant composites. The residual alumina/template compound then react favorablly with alumina hydroxyl groups on the surface of the crystal that have been formed, preventing the generation of any additional crystals, thus forming uniform magnetic core-shell alumina nanospheres.

3.2. Performances of the catalyst
In order to assess the activity of the magnetic core–shell $Ru/Fe_3O_4-Al_2O_3$ catalyst, a number of experiments were employed in MSB under operation conditions ranged within a liquid hourly space velocity (LHSV) of 3h-1 to7h-1, a reaction temperature of 423 K, a system pressure of 3.0 MPa, and a magnetic field intensity of 5 Oe – 20 Oe.
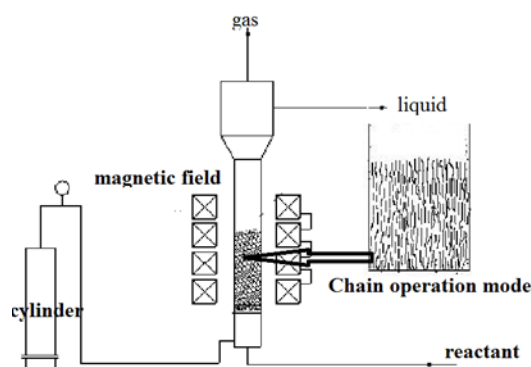
Scheme 2. Diagram of magnetic stable bed in the cold-mode experiment.

Scheme 2 shows the flow chart of of magnetic stable bed in the cold-mode experiment. Its includes the reactor part, magnetic field, current control Parts, feed parts as well as test parts. The reactor is a glass tube with a diameter of 20 mm.The inner diameter is 10mm and Length for 500 mm. The axial uniform magnetic field is generated by the four shafts of the Helmholtz copper wire. The number of turns per coil is 400. The current strength in the coil is controlled by the transformer.
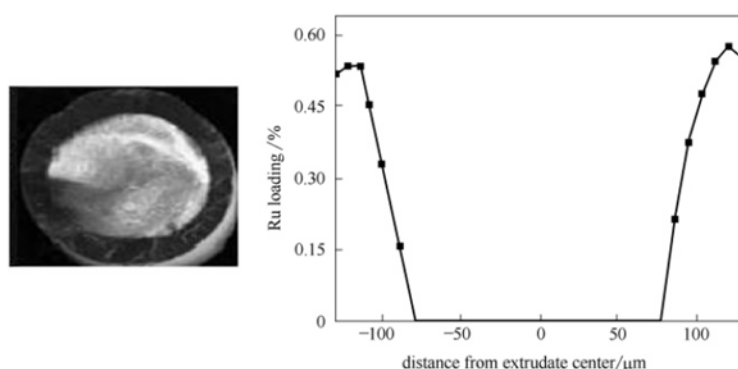
Figure 5. Distribution of Ru/Al_2O_3 by SEM.

According to the figure 5, The dark area in the edge, which is the region of the active constituent Ru. The distribution of the active component is mainly distributed in the outer surface of the catalyst. The EDS element analysis of the scanning electron microscope was analyzed in figure 5, which is further confirmed the surface distribution of the catalyst.

Table 1. Effect of the LHSV on selective hydrogenation of benzene.

（LHSV/h^{-1}）	conversion of benzene, %	selectivity of cyclohexene, %	yield of cyclohexene, %
3.0	17.4	35.8	6.2
4.0	13.0	56.0	7.3
5.0	8.8	61.2	5.4
6.0	5.5	63.1	3.5
7.0	3.2	64.3	2.1

[a]Reaction conditions: P = 3.0MPa, H_2O/benzene = 1 (v/v), H_2/benzene = 2 (mol/mol), T =423K, catalyst amount=5ml. magnetic field intensity 10Oe，zinc sulfate solution concentration0.3wt%

During the assessment of catalyst performance, the MSB reactor was under the chain regime station, which has advantage of high mass transfer property by adjusting the magnetic field intensity as necessary. The chain regime state of the MSB reactorwere investigated by the cold model experiments in a liquid–solid MSB reactor, which is favor to provide good heat and mass transfer property according to the reaction parameters [17, 18]. So during the catalytic activity assessment, the MSB reactor was controlled under the chain regime according to adjusting the magnetic field intensity. Furthermore, the assessment was employed with different magnetic field intensity. As listed in table 1, under magnetic field of 10 Oe, the MSB maintains the chain regime state, which is favor to desorption of cyclohexene so as to achieve high cyclohexene selectivity.

3.2.1. Effect of LHSV. The relationship between the catalyst activity and the liquid liquid hourly space velocity space velocity reveals the fact of mass transfer in selective hydrogenation of benzene processes [8]. The yield of cyclohexene decreases with an increase of LHSV, as shown in table 1. An increase of LHSV makes the concentration of cyclohexene in the oil phases, which reduces mass-transfer rate of cyclohexene from the oil phase to the catalyst surface and consequently enhances the cyclohexene selectivity. Under much high space velocity, the residence time is so short that it can't provide much reaction time for benzene hydrogenation, so that the benzene conversion would be decreased. The appropriate liquid hourly space velocity (LHSV) is very important for benzene hydrogenation.

3.2.2. Effect of ruthenium loading. Several catalysts $Ru/Fe_3O_4-Al_2O_3$ with ruthenium loadings of 0.25–0.7(mass)% were investigated in partial hydrogenation of benzene. As shown in table 2, benzene conversion follows linear relationship with ruthenium loading from 0.25 to 0.55%, while the selectivity of cyclohexene has one breaking point for the highest cyclohexene selectivity at a ruthenium loading of 0.25%. Indeed, the Ru atom possesses highly dispersed state with many active sites leading to high hydrogenation activity along with the increase of Ru loadings. Therefore, the accelerated rate of hydrogenation of benzene and cyclohexene result in increasing benzene conversion and decreasing cyclohexene selectivity. Thus, the proper content of Ru is significant to ensure the best yield of cyclohexene.

Table 2. Effect of the Ru loadings on selective hydrogenation of benzene.

(Ru loadings, %)	conversion of benzene, %	selectivity of cyclohexene, %	yield of cyclohexene, %
0.25	13.0	56.0	7.3
0.4	14.1	68.5	9.7
0.55	21.5	48.6	10.4
0.70	40.3	45.8	18.5

[a]Reaction conditions: P = 3.0MPa, H2O/benzene = 1 (v/v), H2/benzene = 2 (mol/mol), T =423K, catalyst amount=5ml. magnetic field intensity 10Oe，zinc sulfate solution concentration0.3wt%

3.2.3. Effect of magnetic field. The performance of magnetic catalyst was assessed under different magnetic field. As listed in table 3, benzene conversion was only 9.1% when the magnetic field intensity was 5 Oe, which is so low to maintain the catalyst particles in the apparatus. Under high magnetic field intensities, the MSB reactor are stably in the above-mentioned chain regime, which are superior to mass transfer of reactants and products so that it achieve high yield of cyclohexene. No good result in catalyst performance is found by further increasing the magnetic field intensity; moreover, very large magnetic field intensities caused high operating costs.

Table 3. Effect of the magnetic field on selective hydrogenation of benzene.

magnetic field intensity (Oe)	conversion of benzene, %	selectivity of cyclohexene, %	yield of cyclohexene, %
5	9.1	35.5	3.2
10	13.0	56.0	7.3
20	10.5	24.2	2.5

[a]Reaction conditions: P = 3.0MPa,T =423K, LHSV=4h−1, H2/benzene = 2 (mol/mol),H2O/benzene = 1 (v/v), catalyst amount=5ml, zinc sulfate solution concentration 0.3wt%

4. Conclusions

Uniform magnetic core/alumina shell nanospheres were prepared by a combination of the sol-gel process and surfactants self-assembly approach. The magnetic reduced iron core endowed the nanoparticles with magnetic properties. MFeCA possessed a uniform alumina layer of thickness ~30 nm, a large pore volume (~ 0.22 $cm^3 g^{-1}$) and a large surface area (~140 m2g-1). Through studying selective hydrogenation of benzene in MSB, it was noted that high selectivity of cyclohexene can be obtained due to the chain regime. Magnenetic Ru catalyst with MSB provides a convenient and useful means method for selective hydrogenation by magnetic field. The materials prepared in this work may also have applications prospect in hydrogenation.

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