Preparation of Magnetic γ-Al_2O_3 Supported Palladium Catalyst for Hydrogenation of Nitrobenzene

Yuqi Lang, Qiaoqiao Wang, Jianmin Xing, Bo Zhang, and Huizhou Liu
Laboratory of Separation Science and Engineering, State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, P.R. China

DOI 10.1002/aic.11553
Published online June 18, 2008 in Wiley InterScience (www.interscience.wiley.com).

Spherical alumina support with magnetic core of 134 nm in diameter was prepared by the controlled hydrolysis of aluminums iso-propoxide. The magnetite Fe_3O_4 nanoparticles were first synthesized by coprecipitation. Later silica film was coated onto the surface of Fe_3O_4 nano particles with the sodium silicate acidification method. Alumina was supported on Fe_3O_4/SiO_2 film by the controlled hydrolysis of aluminum alkoxide in a dilute solution consisting of cyclohexane and 2-propanol. Finally, magnetic alumina supported palladium catalysts were prepared by microemulsion method. The surface morphology and crystal structure of the magnetic alumina and catalysts were characterized by XRD, TEM, BET, and VSM, respectively. The results showed that these kinds of composite particle exhibit superparamagnetic behavior with zero coercivity and remanence. The catalysts show high activity for nitrobenzene directly hydrogenating to aniline under mild conditions. © 2008 American Institute of Chemical Engineers
AIChE J, 54: 2303–2309, 2008
Keywords: magnetic alumina, nanoparticle, superparamagnetic, palladium

Introduction

Aniline is an important chemical raw material, mainly used for production of methylene diphenyl diisocyanate (MDI), as well as additive for rubber process, intermediates dyes and pigments, pesticides and herbicides.[1] About 85% of aniline is produced by catalytic hydrogenation of nitrobenzene. The reaction is usually catalyzed by supported noble metals including Pt, Pd, Ru, and Raney metal,[2] commonly used as heterogeneous catalyst.[3] Large-scale processes involving heterogeneous catalysis often require the recovery of catalyst from product. To minimize loss of expensive catalyst components and to avoid contamination of products with catalyst, the catalyst pellets can normally be retained in reactors or separated from products by conventional filtration or centrifugation techniques.[4] However, it is difficult and expensive to separate fine particles from a solid–liquid slurry system. So the application of nanocatalyst has been restricted in the industry relatively.

High gradient magnetic separation has the potential to provide a useful filtration method for a wide range of catalyst types, like naturally ferromagnetic, ferrimagnetic, and moderately or strongly paramagnetic materials. Its unique aptitude for separations involving small (<l00 μm) particles suggests utility for a range of catalyst recovery problems to which no other filtration technique is easily applicable.[5] Recently, many researchers have studied the preparation of magnetically-responsive carbon-,[6,7] silica-,[8,9] and alumina-magnetite[10] supports. Liu et al.[11,12] and Ma et al.[13,14] prepared and characterized a series of the surface modification magnetic nanospheres. Shan et al.[15] synthesized the magnetic alumina sorbents of about 100–150 μm by the internal gelation method and studied its use in the separation of aromatic compounds from gasoline by a π-complexation mechanism.

Correspondence concerning this article should be addressed to H. Liu at hzliu@home.ipe.ac.cn.

There has not been any report about magnetic alumina nanoparticles produced via the alkoxide route. The formation of monodisperse oxide particles via the alkoxide route in an alcohol solution is analogous to controlled homogeneous precipitation by the hydrolysis of metal salt in an aqueous solution.[16–18] In this article, a novel synthesis method for alumina support with superparamagnetic was developed. Magnetic alumina carriers were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM).

Experimental

Materials

A nonionic surfactant Triton X-100 (toctylphenoxy-polyethoxyethanol) from Sigma chemical was used as a dispersant. Aluminums iso-propoxied (AIP), 2-propanol, cyclohexane, and $NH_3 \cdot H_2O$ were of analytical grade, purchased from Beijing Chemical Reagent Company, China. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) were analytical grade, obtained from Beijing Shuanghuan Chemical Reagent Company, China. $PdCl_2$ (impurities less than 500 ppm in total) was purchased from Sigma Chemical. Other chemicals were of reagent grade and used as received.

Preparation of nanomagnetic alumina with Fe_3O_4/SiO_2 as core

Synthesis of Nanomagnetic Fe_3O_4 Particles and Surfaces Coating with Silica Solution of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O > 99\%$) and ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O > 99\%$) were prepared as iron sources with molar ratio 2:1. Ammonium hydroxide (0.14 mol, 100 ml) was slowly injected into the iron sources under vigorous stirring. The reaction was processed under the protection of N_2 gas at 85°C for 30 min. The black colloidal particles were isolated by magnetic decantation centrifugation and washed several times with mixture of deionized water and acetone (1:1) to remove the excess ammonia cations.

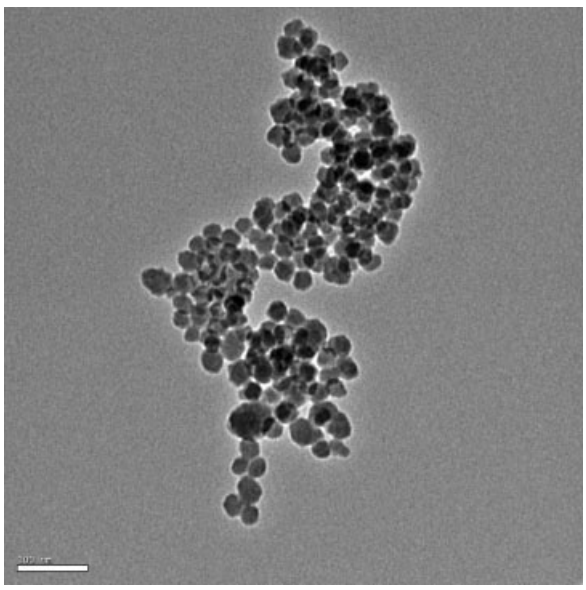

Figure 1. TEM Micrographs of magnetic Fe_3O_4 particles coated.

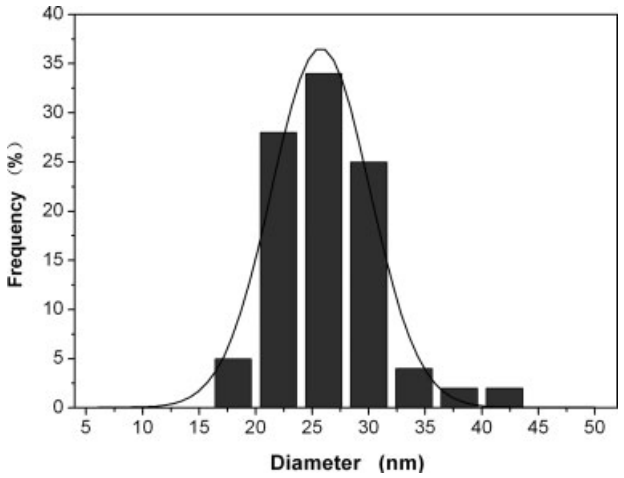

Figure 2. The corresponding particle size histogram for magnetic Fe_3O_4 particles coated with silica.

The Fe_3O_4 nanoparticles were redispersed in pretreated sodium silicate solutions and sonicated for 15 min. The weight ratio of Fe_3O_4 to SiO_2 varies from 50 to 400%. The pH (about 6) value was maintained using 0.5M HCl over ~2 h. The nanomagnetic Fe_3O_4 particles coated with silica were then washed for several times with deionized water and separated by magnetic decantation. It was denoted as sample FS.

Preparation of magnetic alumina carriers

Spherical magnetic alumina was prepared by the hydrolysis of aluminum iso-propoxide (AIP) in a dilute solution of cyclohexane and 2-propanol. The AIP powder (2 g) was first dissolved in the 2-propanol (200 ml) at 80°C for 6 h. The FS nanoparticles were then added in aluminal sol solutions and sonicated for 15 min. It was denoted as sample A1. Mixture of cyclohexane solution and Triton X-100 were added to the A1 solution, with vigorous stirring at 60°C for 2 h, before the 2-propanol water solution (90 to 10 vol %) was mixed in. The precipitation occurred within 30 min and then stabilized for 1 h in the water bath at 25°C. The volume ratio of

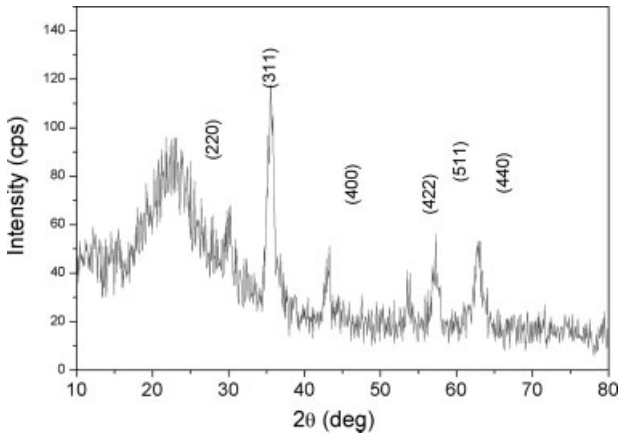

Figure 3. XRD of the Fe_3O_4 particles coated with silica.

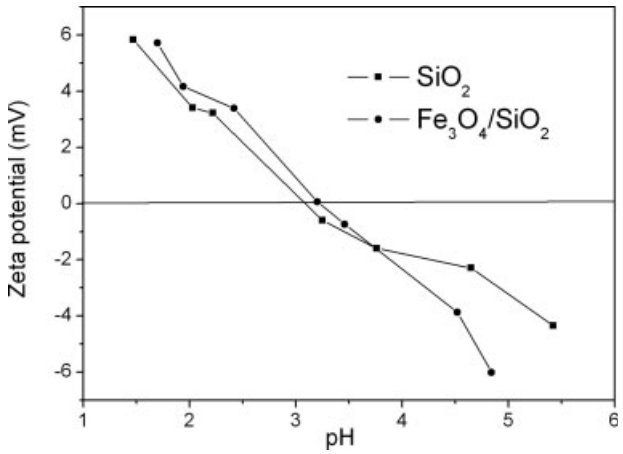

Figure 4. Zeta potential curve vs. pH for SiO_2 and Fe_3O_4/SiO_2 gels.

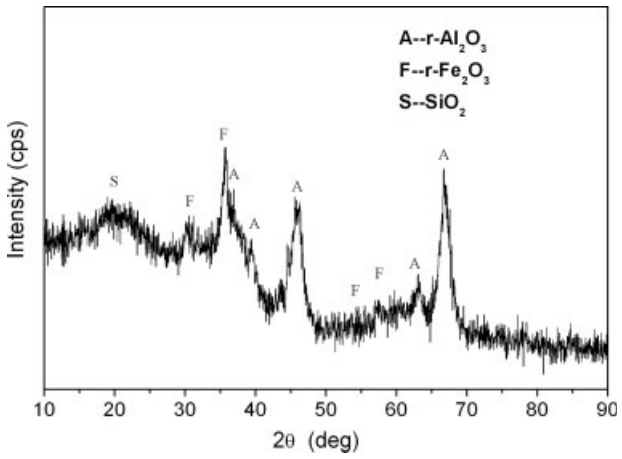

Figure 6. XRD patterns of magnetic Al_2O_3 particles (coated by SiO_2).

2-propanol, cyclohexane, Triton X-100, and 2-propanol water were 50, 43, 2, and 5 vol %, respectively. Particles were separated from the solution by centrifugation at 4500 rpm. To avoid impurities and agglomeration during the process of dry and thermal treatment, the as-prepared powders were thoroughly washed with deionized water, dehydrated using alcohol, and then dried in vacuum at 120°C for 24 h. At last, the dried powder was calcined at 800°C for 4 h to produce highly pure active γ-Al_2O_3 nanoparticles. It was denoted as sample FSA.

Characterization of the magnetic alumina carriers

Size and morphology of magnetic microspheres was observed by transmission electronic microscopy (TEM, Philips Tecnai G. USA). The magnetization curves of samples were measured with a vibrating sample magnetometer (VSM, model-155, Digital Measurement System, USA) at room temperature. Structural identification was performed by using XRD (Philips X'pert, Cu Kα radiation k = 1.5418 Å, USA). Adsorption experiments and specific surface area of the particles were performed on static volume adsorption analyzer (Autosorb-I, Quantachrome, USA).

Catalyst preparation

Synthesis of Pd Nanoparticles by the Microemulsion Technology. The nonionic surfactant Triton X-100, oil (cyclohexane), and the palladium aqueous solution were thoroughly mixed in a flask. The water/surfactant molar ratio was kept at 8 to 1. The oil/surfactant weight ratio was 3 for all the solutions. Clear yellowish orange solutions were obtained after mixing about 10 min and then stirring continually for 12 h. A reducing agent, 1M $NaBH_4$, was added to the prepared microemulsions in a $NaBH_4$: Pd molar ratio of 10:1. The mixtures were stirred for about 2 h. The color of solution changed from yellowish to gray black after a few minutes, which suggests a change in the oxidation state of the palladium, and formation of a colloidal suspension of metallic particles.

Deposition of the metal particles onto a magnetic alumina support was performed by adding FSA powder to the as-prepared palladium colloidal suspension under vigorous stirring. The relative amounts of noble metal particles of 1 wt % in the pure-metal-on-FSA catalysts. After the addition of FSA, a solvent (tetrahydrofuran, $\geq$99.5%), was added dropwise to slowly break the microemulsion and allow the particles to adsorb onto the support material. The total amount of added

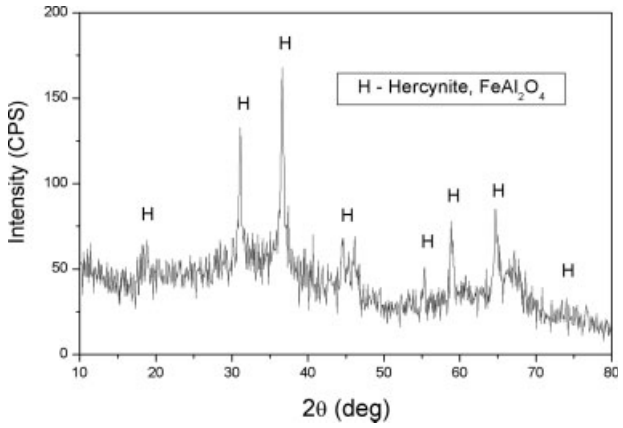

Figure 5. XRD patterns of Fe_3O_4/Al_2O_3 particles after calcined at 600°C (uncoated by SiO_2).

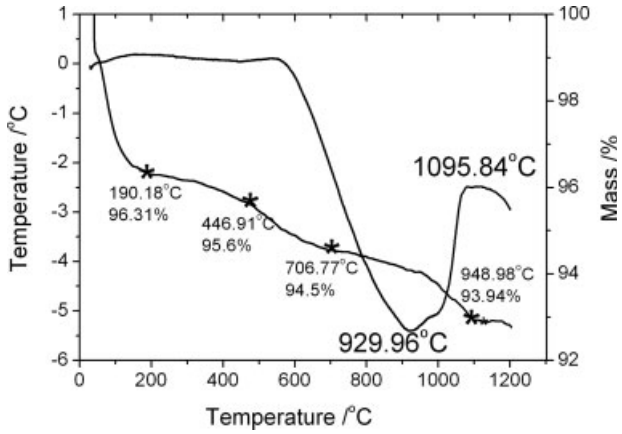

Figure 7. TGA/DTA thermographs of Fe_3O_4/SiO_2.

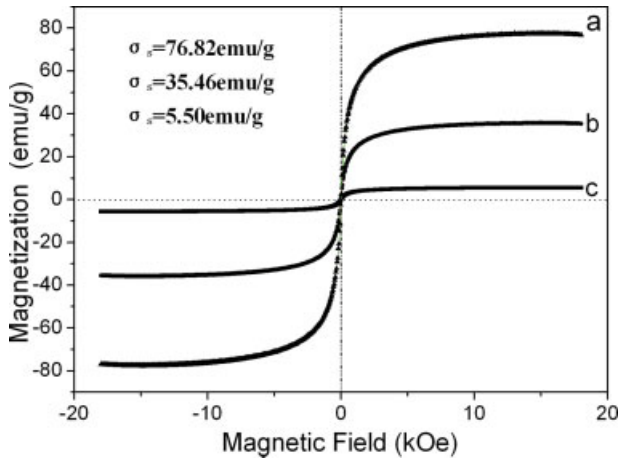

Figure 8. VSM of magnetic nanocomposite, (a) Fe_3O_4; (b) Fe_3O_4/SiO_2; (c) $Fe_3O_4/SiO_2/Al_2O_3$.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

solvent corresponded to three times the volume of the suspension. The mixture was shaken for 4 h and settle to decant overnight. The suspension was filtered out and supernatant washed thoroughly with water and ethanol, followed by centrifugation and drying first at room temperature. Sample was further dried for 6 h at 250°C in air. After calcinations at 600°C for 2 h, FSA supported palladium catalyst samples were obtained.

Activity measurement of Pd/FSA

The selective hydrogenation of nitrobenzene to aniline was carried out in an autoclave containing 1.0 g Pd/FSA at different reaction condition. The catalyst was in situ reduced at 200°C for 2 h. Then 1.0 ml nitrobenzene and ethanol were injected into an autoclave with 1 g catalysts with continuous stirring (at 800 rpm). The reactor was filled with H_2 up to 1.00 MPa and then heated slowly with a magnetic stirrer (1000 rpm). The conversion of nitrobenzene and the selectivity to aniline during the hydrogenation was determined using HPLC. The liquid chromatographic system was equipped with a diode array detector and a stainless steel analytical column (ZORBAX SB-C18, 5-mm particle size, 4.6 mm–250 mm, Agilent Technologies, USA). The mobile phase consisted of methanol–water (70:30, v/v), and the flow-rate was 1.0 ml/min. Separations were carried out at 30°C and 10 μl was injected into the LC system.

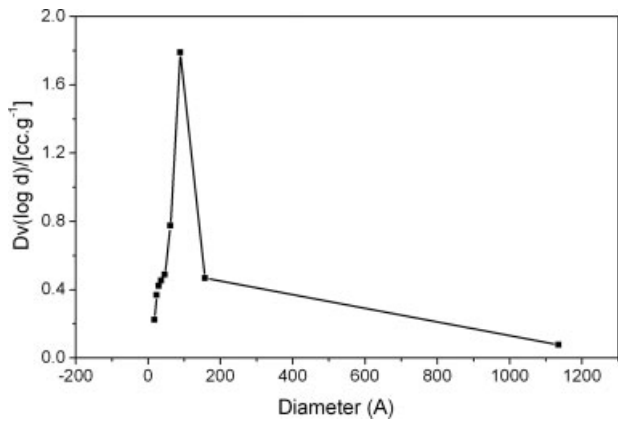

Figure 9. BJH desorption pore size distribution of magnetic alumina carriers.

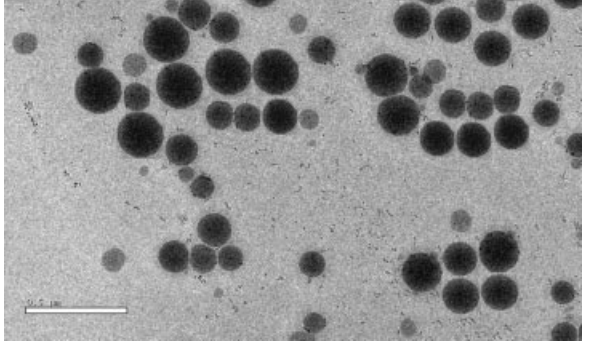

Figure 10. TEM Micrographs of magnetic alumina carriers.

Results and Discussion

Characterization of nano-magnetic Fe_3O_4 particles coated with silica

Particle size and morphology for the sample FS at Fe_2O_3/SiO_2 ratio 0.30, as observed by TEM, is shown in Figure 1. Particles were almost spherical and well dispersed with an average diameter of 25.6 nm (Figure 2). XRD patterns for FS powder before calcined were shown in Figure 3. The six diffraction peaks have been assigned to a spinel structure

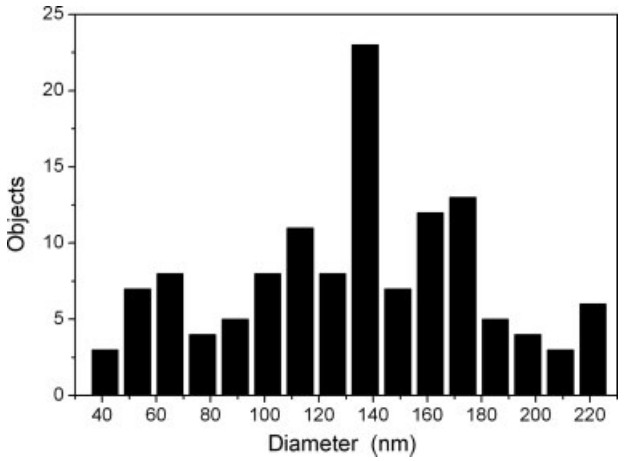

Figure 11. The corresponding particle size histogram for magnetic FSA particles.

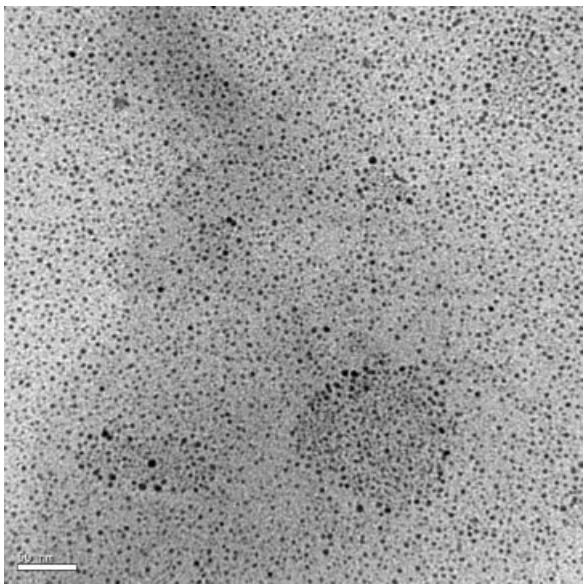

Figure 12. TEM micrographs of palladium nanoparticles.

with the characteristic reflections of Fe_3O_4. In addition, the broad peak appeared in the range from 20° to 30°, indicating the existence of amorphous SiO_2. And the coated particles were characterized by measuring the zeta-potential of particles in the aqueous electrolyte solution. As shown in Figure 4, the measured zeta potential responses to the suspension pH of the silica-coated magnetite particles approached to the case of naturally occurring silica. This finding confirms a full coverage of magnetite by silica, making the coated surface silica-like. The analysis of the main X-ray reflection (311) peak width and position by using the Debye-Scherrer equation[19] led to a mean grain size of 12 nm for Fe_3O_4.

Magnetic property of magnetic alumina carriers

The composition and configuration of the magnetic alumina carriers prepared via the alkoxide route was analyzed by TEM and XRD. Compared the XRD analysis of particles

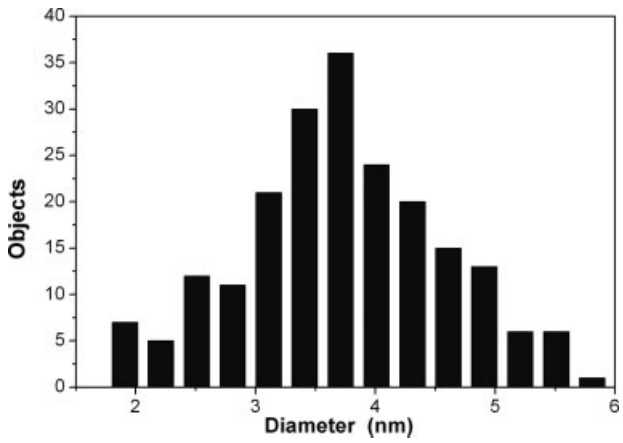

Figure 13. The corresponding particle size histogram for palladium nanoparticles.

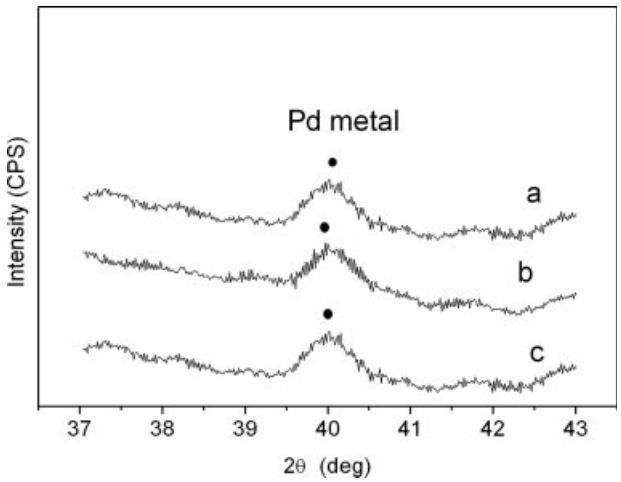

Figure 14. XRD patterns of magnetic Al_2O_3 supported palladium catalyst, (a) 2%Pd, (b) 1%Pd, (c) 0.5%Pd.

coated and uncoated with silica in Figures 5 and 6, the silica coating can protect nanomagnetic Fe_3O_4 particles and prevent further reaction with alumina while calcined at 800°C.[20–22] Figure 5 shows the result of a Fe_3O_4/Al_2O_3 uncoated by SiO_2 particles calcined at 600°C, it can be seen that the presence of Hercynite, $FeAl_2O_4$. And measured by VSM, the sample lost the magnetism. Figure 6 present the XRD pattern of the magnetic carrier coated with silica, which can be deduced that the magnetic nanocomposite is mainly composed of γ-Al_2O_3. The calculated value of the lattice parameter (a_0 =8.33 ± 0.02) and the brown-ochre color of the samples indicate the presence of γ-Fe_2O_3 (a_0 = 8.351) rather than Fe_3O_4 (a_0 = 8.3967). Furthermore, Figure 7 shows the result of a simultaneous DTA/TG analysis of the dried FS particles. There is an obviously exothermic peak at 1095.84°C, which can probably be attributed to the formation of new iron-silicate species under high temperature. Also it means that the Fe_3O_4/SiO_2 can be thermally stable at 800°C and no reaction took place between siilca-Fe_3O_4.

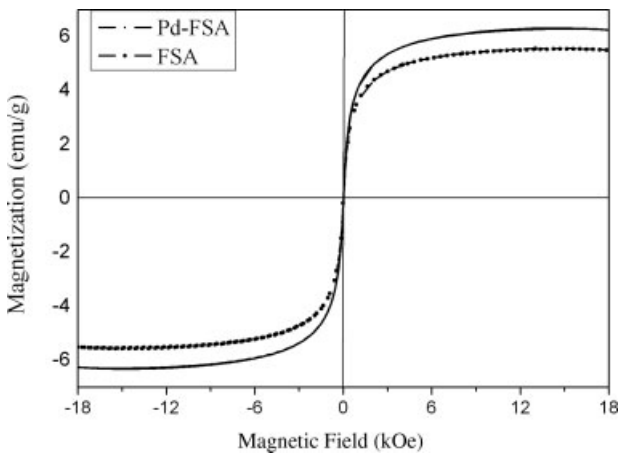

Figure 15. VSM of magnetic alumina supported palladium catalyst.

Table 1. Result of Nitrobenzene Hydrogenation to Form Aniline with Supported 1 wt % Pd Catalyst at Different Reaction Conditions

Reaction Conditions					
Temperature (K)	Ethanol (ml)	Reaction Time (min)	Pressure (MPa)	Conversion (%)	Selectivity of Aniline (%)
293	100	60	1	97.98	87.03
	50	30	0.2	99.00	92.19
	150	90	0.5	99.53	92.96
323	100	90	0.2	100	99.99
	50	60	0.5	99.17	99.84
	150	60	0.5	99.99	98.62
353	50	90	1	99.78	94.55
	150	60	0.2	99.99	99.99
	100	30	0.5	99.29	92.26
393	50	60	1	90.82	91.93
	100	60	1	92.71	93.28
	150	60	1	95.42	93.40

Figure 8 shows magnetic curve of the Fe_3O_4 particles, Fe_3O_4 particles coated with silica (weight ratio of Fe_3O_4/SiO_2 is 0.33) and magnetic alumina, measured at room temperature by VSM. According to the diameter of the magnetic Fe_3O_4 particles, is 12 nm, smaller than the D_p (25 nm) of Fe_3O_4 particles,[23] exhibit superparamagnetic behavior with zero coercivity and remanence. The specific saturation magnetization decrease from 76.82 emu/g Fe_3O_4 uncoated to 5.52 emu/g coated with alumina.

The BET specific surface area of FSA nanoparticles calcined at 800°C for 4 h is 380.3 m^2/g. The pore size distribution is given in Figure 9. It can be seen that there is a maximum value at about 17 nm; most of the pores in the nanoparticles are 10–20 nm in diameter. Figure 10 displays the TEM micrograph of magnetic alumina containing 8.0 wt % Fe_3O_4 prepared by hydrolysis of aluminum alkoxides. The micrograph shows particles with an average diameter of 133.6 nm, and the corresponding particle size histogram for magnetic FSA particles micrograph shown in Figure 11. The particles were spherical and well dispersed because the dispersant physically adsorbed onto the particles prevent agglomeration during growth.

Characterization and tests of Pd/FSA catalysts

Figures 12 and 13 shows the typical TEM micrographs and the size distribution of Pd nanoparticles obtained in a microemulsion. The individual nanoparticles were very fine and essentially monodispersed. The particles had a narrow size distribution about 3.85 nm, illustrated in Figure 12. The XRD results of the magnetic supported different Pd content mixture are well displayed in Figure 14. Although the intensity of peak increased with the Pd content, the half-peak widths were almost identical regardless of Pd. The average particle size, calculated using the Debye-Scherrer equation, was 5.2, 5.4, and 6.8 nm at Pd contents of 0.5, 1, and 2 wt %, respectively. The characteristic peaks for Pd ($2\theta = 40.2$), marked by their indices (111), revealed that the resultant Pd particles were in the face-centered cubic structure.[24] The broad peak indicated by the particles were poor crystalline owing to less-ordered structures, which is usually observed for nanoparticles. The magnetic curves of the FSA and Pd/FSA particles were shown in Figure 15. The particles exhibit superparamagnetic behavior with zero coercivity and remanence. After the situ reduced, part of Fe_2O_3 was reduced to the Fe_3O_4. The specific saturation magnetization of supported palladium magnetic catalyst increased.

Table 1 shows the trend of nitrobenzene hydrogenation to form aniline at the different reaction conditions. The general trend for the reaction is that conversion usually increases with the increase of temperature up to 353 K, then decreased. At the high temperature, the solvent boiling point is lower and the solvent differential pressure increases. Hence the hydrogenation rate drops and conversion of nitro-benzene decreased. All results show that the catalysts, both of low and higher Pd loading, have high activity for nitrobenzene directly hydrogenating to aniline under mild conditions.

Conclusions

The nanomagnetic γ-alumina carriers with size distribution around 134 nm were synthesized by the hydrolysis of aluminum iso-propoxide (AIP) in a dilute solution of cyclohexane and 2-propanol. Furthermore, the palladium nanoparticles were deposited onto a magnetic alumina support by microemulsion method. Support was fully characterized by various techniques such as XRD, TEM, SEM, and VSM, respectively. The nanomagnetic γ-alumina carriers have characteristics of superparamagnetism and good stability at high temperature. Triton X-100 was used as a dispersant to prevent agglomeration during nucleation and growth. Magnetic alumina-supported palladium catalysts show extraordinary activity for nitrobenzene hydrogenation even under mild conditions. Nitrobenzene is directly hydrogenated to aniline. The 90% yield of aniline was produced in 40 min for catalysts with Pd loading of 1 wt %.

Acknowledgments

This work was financially supported by the National High Technology Research and Development Program of China (Grant 2002AA302211) and the National Natural Science Foundation of China (Grant 20021603). And we would like to thank the Center for Biological Electron Microscopy, the Institute of Biophysics for our electron microscopy work.

Literature Cited

1. James AS, Cristian C, Adriana C. Methods for preparation of catalytic materials *Chem Rev*. 1995;95:477–510.
2. Li CH, Yu ZX. Nitrobenzene hydrogenation with carbon nanotube-supported platinum catalyst under mild conditions. *J Mol Catal A: Chem*. 2005;226:101–105.
3. Masatomo Y, Lena KL, Anders EC. Structure and catalytic properties of nanosized alumina supported platinum and palladium particles synthesized by reaction in microemulsion. *J Colloid Interface Sci*. 2003;268:348–356.
4. Whitesides GM, Hill CL, Brunie JC. Magnetic filtration of small heterogeneous catalyst particles. Preparation of ferrimagnetic catalyst supports. *Process Res Dev*. 1976;15:226–227.
5. Rudge SR, Kurtz TL, Vessely CR, Catterall LG, Williamson D. Preparation, characterization, and performance of magnetic iron-carbon composite micropartieles for chemotherapy. *Biomaterials*. 2000;21:1411–1420.
6. Meldrum FC, Heywood BR, Mann S. Magnetoferritin: in vitro synthesis of a novel magnetic protein. *Science*. 1992;257:522–523.
7. Oliveim LC, Rios RV. Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water [J]. *Carbon*. 2002;40:2177–2183.
8. DelMont F, Morales MP. Formation of γ-Fe_2O_3 isolated nanoparticles in a silica matrix. *Langmuir*. 1997;13:3627–3634.
9. Liu QX, Xu ZH, Finch JA, Egerton R. A novel two-step silica-coating process for engineering magnetic nanocomposites. *Chem Mater*. 1998;10:3936–3940.
10. Josephson L. Magenetic Particle for Use in Separation. U.S. Patent No. 4,672,040, 1987.
11. Liu XQ, Guan YP, Ma ZY, Liu HZ. Surface modification and characterization of magnetic polymer nanospheres prepared by miniemulsion polymerization. *Langmuir*. 2004;20:10278–10282.
12. Liu XQ, Ma ZY, Xing JM, Liu HZ. Preparation and characterization of amino-silane modified superparamagnetic silica nanospheres. *J Magn Magn Mater*. 2004;270:1–6.
13. Ma ZY, Guan YP, Liu HZ. Synthesis of magnetic chelator for immobilized metal affinity adsorption of protein with high adsorption capacity by cerium initiated graft polymerization. *Langmuir*. 2005;21:6987–6994.
14. Ma ZY, Guan YP, Liu HZ. Synthesis and characterization of micron-sized monodisperse superparamagnetic polymer particles with amino groups. *J Polym Sci Part A: Polym Chem*. 2005;43:3433–3439.
15. Shan GB, Liu HZ, Xing JM. Separation of polycyclic aromatic compounds form model gasoline by magnetic alumina sorbent based on π-complexation. *Ind Eng Chem Res*. 2004;43:758–761.
16. Catone DL, Matijievie E. Alumina hydrous oxide solsII, preparation of uniform spherical particles by hydrolysis of Al sec-butoxiede. *J Colloid Interface Sci*. 1974;77:291–301.
17. Sordent D, Akinc M. Preparation of spherical monosezed Y_2O_3 precursor particles. *J Colloid Interface Sci*. 1988;122:47–59.
18. Jean H, Ring TA. Processing monosized TiO_2 powders generated with HPC dispersant. *Am Ceram Soc Bull*. 1986;65):1574–1577.
19. Cullity BD. *Elements of X-Ray Diffraction*, 2nd ed. Reading, MA: Addison-Wesley, 1978.
20. Hua Y, Yuan J, Yue L. XPS study and micro-crystal analysis of $CaCO_3$ coated with SiO_2. *J Inorg Chem*. 2001;17:134–138.
21. Cui A, Wang T, Jin Y. TiO_2 surface coated with SiO_2 and Al_2O_3. *Eng Chem Metallurgy*. 1999;20:178–181.
22. Wang QQ, Guan YP, Lang YQ. Preparation of magnetic spherical Al_2O_3 composite particle by hydrolyzation of ures. *Chemistry*. 2007;2:112–116.
23. Lee J, Isobe T, Senna M. Preparation of ultrafine Fe_3O_4 particles by precipitation in the presence of PVA at high pH. *J Colloid Interface Sci*. 1996;177:490–494.
24. Dong H, Chen W, Ting H. Preparation of palladium ultrafine particles in reverse micelles. *J Colloid Interface Sci*. 1999;210:123–129.

Manuscript received Sept. 4, 2007, revision received Mar. 12, 2008, and final revision received May 13, 2008.