Magnetically Separable Core–Shell-structured γ-Fe_2O_3–SiO_2 Catalyst with High Activity and Selectivity for Oxidizing Benzyl Alcohol to Benzaldehyde

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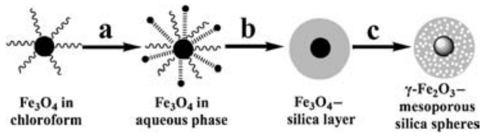
Uniform core–shell-structured γ-Fe_2O_3–mesoporous silica spheres (F-MSS) catalyst was prepared by hydrolyzing TEOS in the presence of CTAB. The structure, shape, formation mechanism, and catalytic performance of F-MSS catalyst were investigated. The results showed that F-MSS catalyst had high BET surface area, excellent catalytic activity and selectivity for oxidizing benzyl alcohol to benzaldehyde. The F-MSS catalyst can be reused three times at least and has potential application in industry in the place of noble metal.

Nanocatalysis is an active front area in chemistry and is a bridge between homogeneous and heterogeneous catalysis.[1] Progress has been made in activity, selectivity, and recyclability of catalysts.[1,2] However, there are several common problems to resolve, such as aggregation of nanoparticles and isolation of catalyst from the reaction solution. Magnetic separation is considered a convenient way for removing and recycling magnetic catalytic species by applying an appropriate magnetic field.[3] Metal and metal oxides with both magnetism and catalytic activity are desirable. In order to prevent nanoparticles from aggregation, the core–shell structure is preferable to adopt, in which a mesoporous shell plays dual roles: permitting molecules to pass through the pore freely and preventing cores from coming into direct contact each other, whereas the core is the catalytic active species and the magnet for separation.

Up to now, several works about the preparation of core–shell-structured nanoparticles have been reported, such as gold nanoparticles encapsulated in mesoporous ZrO_2 as CO oxidation catalyst,[4] Fe_3O_4–SiO_2 as adsorbent for removal of microcystals,[5] and magnetic and semiconductor nanocrystals coated with mesoporous silica acting as magnetic fluorescent delivery vehicle.[6] However, few of them are used as catalyst in organic synthesis, such as selective oxidation of alcohol or hydrogenation.

Selective oxidation of benzyl alcohol is a fundamentally important reaction in the synthesis of fine chemicals.[7] Aldehydes are valuable both as intermediates and as high-value components for the perfume industry and food additives. Until now, the synthesis of aldehydes in industry has been mainly based on the use of stoichiometric amounts of chromate or permanganate, but these reagents are expensive and cause serious environmental problems. To overcome these problems, many efforts have been paid to supported catalysts for selective oxidation of alcohol, such as Au–Pd/TiO_2,[1a] hydroxyapatite (HAP) bound RuHAP[8] and PdHAP,[9] as well as Ru/Al_2O_3.[10] However, these catalysts all need noble metals or their composite with oxide. It is desirable to exploit an effective and inexpensive catalyst for selective oxidation of alcohol.



Scheme 1. Synthetic process of γ-Fe_2O_3 wrapped by mesoporous silica spheres. (a) The transferation of Fe_3O_4 nanocrystals from chloroform to aqueous phase using CTAB as phase-transfer agent (•). (b) The formation process of silica sol–gel on the surface of the Fe_3O_4 nanocrystals in aqueous phase. (c) The formation of F-MSS by calcination at 500 °C.

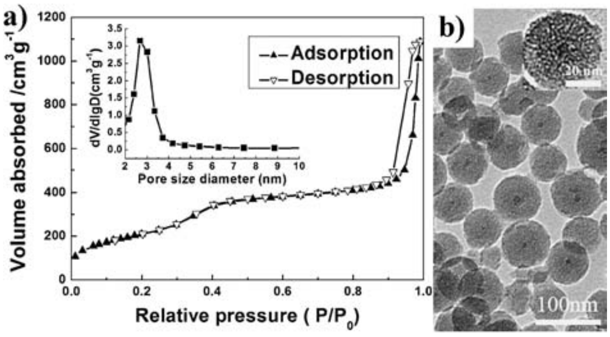


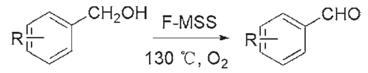
Figure 1. (a) Nitrogen adsorption/desorption isotherm and Barrett–Joyner–Halenda (BJH) pore-size distribution plot (inset) of F-MSS. (b) TEM images of F-MSS (the enlarged individual F-MSS in inset).

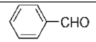
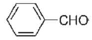
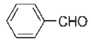
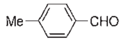
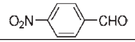
In this paper, we report the preparation of γ-Fe_2O_3–mesoporous silica spheres (F-MSS) and the excellent catalytic activity and selectivity for oxidizing benzyl alcohol to benzaldehyde.

The synthetic process is indicated in Scheme 1. Figure S1 is the X-ray diffraction (XRD) pattern of γ-Fe_2O_3 nanocrystals wrapped by mesoporous silica. It can be seen that a broad peak at 20–30 degree (2θ) corresponds to the amorphous SiO_2. Other peaks are good in agreement with the standard XRD pattern of γ-Fe_2O_3 (Maghemite, JCPDS 39-1346). Figure 1a shows the N_2 adsorption/desorption isotherm and the pore-size distribution (inset) of mesoporous silica shells. The isotherm belongs to type IV with a hysteresis loop, demonstrating their mesoporous characteristics. The BET surface area and single point total pore volume are $770\,m^2\,g^{-1}$ and $0.93\,cm^3\,g^{-1}$, respectively. The pore size is about 2.8 nm, which can be seen in the inset of Figure 1a.

Figure S2 is the TEM image of Fe_3O_4 nanocrystals synthesized by pyrolysis in nonaqueous system (see Support Information).[11] The average size of Fe_3O_4 nanocrystals is about 10 nm. They are homogeneously dispersed in chloroform with the assistance of oleic acid and octadecylamine. In order to make a silica

Table 1. The oxidation of alcohols using F-MSS as catalyst



Entry	R	product	*t*/h	Conv./%	Select./%
1	H		12	76	84
2[a]	H		24	94	92
3[b]	H		24	83	84
4	CH_3		24	60	84
5	NO_2		24	71	98

[a] Fresh catalyst, O_2 as oxidant (bubbling through the reaction system at 5 sccm S^{-1}). The reacting mixture composed of 10 mmol of benzyl alcohol, 10 mL of PEG200, and 0.05 g of F-MSS reacted at 130 °C for 24 h. [b] The catalyst is used for three times.

shell on the oxide nanoparticles, it is necessary to transfer these nanocrystals from chloroform to aqueous phase by using a phase-transfer agent. CTAB is a good candidate because it can serve as not only the stabilizing surfactant for the nanoparticles in the aqueous phase but also the structure-directing agent for the formation of the mesoporous silica. Organic template can be removed by calcination in order to obtain F-MSS. Figure 1b shows uniform F-MSS with a diameter around 50 nm. From the insert in Figure 1b, about 3 nm disordered pore and the core of γ-Fe_2O_3 can be seen clearly. The energy-dispersive spectrum (EDS, Figure S3) shows that the mass percent of Fe, Si, and O are 5.3%, 42.4%, and 52.3%, respectively.

Table 1 shows the experimental results of the oxidation reaction of benzyl alcohol using F-MSS as catalyst. The conversion and selectivity are up to 94% and 92% respectively when reacted at optimum conditions, such as 130 °C for 24 h. Oxidation of benzyl alcohol can produce many by-products, such as toluene, benzene, benzyl benzoate, and acetal.[1a] In our reaction system, the main product is benzaldehyde, only a little ester present as an esterification product of benzylic acid and benzyl alcohol. As a comparison, the oxidation of *p*-methylbenzyl alcohol and *p*-nitrobenzyl alcohol has been completed under the same reaction conditions. The lower conversion, which is lower than that of unsubstituted benzyl alcohol after reacting for 12 h, might be related to the bulk of the molecules which hinders molecules from passing through the shell freely. Conversion seems independent from the electronic properties of the substituents, because conversion is similar for methyl and nitro groups, but the selectivity is substituent-dependent, *p*-nitrobenzyl alcohol giving excellent selectivity.

Recyclability is important for industrial application of catalyst; therefore, not only excellent catalytic activity but also easy separation is needed. The magnetization characterization at 300 K indicates no hysteresis loop of the F-MSS (Figure 2a), which demonstrates the superparamagnetic characteristics for application to separation. F-MSS can be removed from the reaction solution easily by employing a magnet (shown in Figure 2b). What is more, the reuse performance of the catalyst is quite good due to protection of the shell. The conversion and selectivity both exceed 80% after being used three times. The TEM image of F-MSS catalyst we prepared (Figure S4) shows no obvious changes after use. It is the reason that catalytic performance can be maintained at a high level after use.

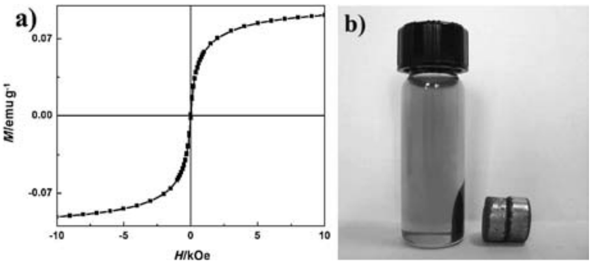


Figure 2. (a) Hysteresis loop of the F-MSS at 300 K. (b) The picture of the F-MSS isolated from reaction solution by a magnet after reaction.

In summary, we have synthesized size uniform F-MSS catalyst with γ-Fe_2O_3 core and mesoporous silica shell. The catalytic results show that the F-MSS catalyst has excellent activity and selectivity for oxidizing benzyl alcohol to benzaldehyde. The mesoporous silica shells not only ensure reactants and products pass through the pores freely but also protect the γ-Fe_2O_3 nanoparticles from aggregation. The magnetism of F-MSS makes the catalyst easily isolable from reaction solution. The F-MSS catalyst is a good alternative for noble metal and has potential application in industry.

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11 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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