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Short Report

β-Cyclodextrin Coated Fe_3O_4 Nanoparticles: a Simple Preparation and Application for Selective Oxidation of Alcohols in Water

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Um catalisador magnético foi sintetizado *via* proceso de ativação da carboimida em β-ciclodextrina funcionalizada com nanopartículas *core-shell* (Fe_3O4/SiO_2/CM-β-CD). O catalisador apresenta elevada atividade na oxidação seletiva de vários álcoois usando NaOCl como oxidante e água como solvente. Foi obtido um processo seletivo na ausência de metal de transição e de fácil separação do catalisador.

A magnetically separable catalyst was synthesized *via* a carbodiimide activation process with β-cyclodextrin functionalized by core-shell nanoparticles (Fe_3O4/SiO_2/CM-β-CD). The catalyst presented high activity for selective oxidation of various alcohols with NaOCl as oxidant and water only as the solvent. A substrate-selective and transition metal-free process was achieved with easy separation of the catalyst.

Keywords: β-cyclodextrin, magnetic, oxidation

Introduction

The selective oxidation of primary and secondary alcohols into the corresponding aldehydes and ketones is undoubtedly one of the most important and challenging transformations in organic chemistry.[1,2] Many efforts have been devoted to the field with a variety of catalysts been developed such as metal complexes,[3-6] tetramethylpiperidinyloxide (TEMPO),[7-9] heteropoly acids[10,11] and so on. Nevertheless, organic solvents are usually used to promote the reaction process, which is considered to be contrary to the concept of green chemistry.

On the other hand, water as an abundant, cheap and nontoxic reaction medium has attracted great attention and gradually has become an active area of research.[12,13] The use of water as environmentally benign solvent also reduces the harmful effects of organic solvents thus minimizing the cost of waste disposal.

To perform oxidation reactions in water, the solubility problem of substrates or catalysts must be conquered, since the limited mutual solubility between water and organic agents. For solutions, β-cyclodextrin (β-CD) appears to be an ideal choice as a phase transfer catalyst.[14-16] Cyclodextrins are cyclic oligosaccharides possessing hydrophobic cavities, which can bind substrates selectively and catalyze chemical reactions with high selectivity. The oxidation of alcohols in the presence of β-CD has also been reported. Particular examples were presented with o-iodoxybenzoic acid (IBX),[17] N-bromosuccinimide (NBS),[18,19] NaOCl,[20] as oxidant in water. Despite of the high efficiency of reaction, easy separation and recovery of β-CD, however, still remains a problem.

Recently, a possible strategy to circumvent these problems is to use supported materials that have magnetic properties, thus allowing easy separation of the catalysts by simply applying an external magnetic field.[21-24] So herein we presented a magnetically separable β-CD (Scheme 1, Fe_3O_4/SiO_2/CM(carboxymethyl)−β-CD), which was modified by magnetic silica nanoparticles and used for oxidation of various alcohols. Water was used as the only solvent and NaOCl as a cheap and green oxidant. Facilitated recovery of β-CD and excellent efficiency for selective oxidation of alcohols were achieved. As far as we know, only adsorption property of the material has been studied,[2,26] and it was the first time to use it in oxidation reactions.

Experimental

The detailed description of the preparation of Fe_3O_4/SiO_2/CM−β-CD was listed in the Supplementary Information

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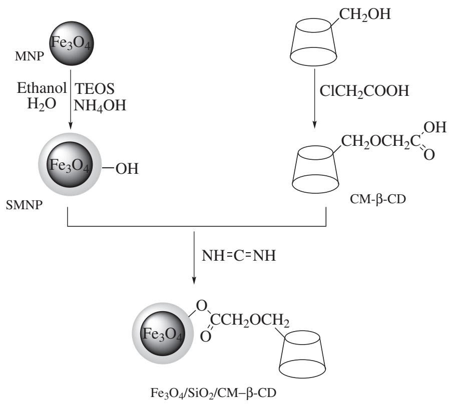


Scheme 1. The synthesis of $Fe_3O_4/SiO_2/CM-β-CD$.

(SI) section. For the oxidation process, Fe_3O_4/SiO_2 MNPs coated CM-β-CD (1 mmol) was dissolved in deionized water (25 mL) and sonicated for 15 min. To the mixture, alcohol (1 mmol) was added at 50 °C, followed by the addition of NaOCl (10%, 5 mL) dropwisely over 20 min. When the reaction was finished, the mixture was extracted by ethyl acetate and dried over anhydrous sodium sulfate. Then ethyl acetate was removed in vacuum. The crude product was analyzed by gas chromatography (GC).

Results and Discussion

Magnetic nanoparticles (Fe_3O_4) (MNPs) were chosen as the core magnetic support because of their simple synthesis, low cost, and relatively large magnetic susceptibility. To prepare the catalyst, β-CD was allowed to react with monochloroacetic acid before immobilized onto MNP. The resulting CM−β-CD was coated on MNP successfully with the help of cyanamide by dehydration (Scheme 1). IR spectrum of MNP coated CM−β-CD (Figure 1) shows detectable changes that are characteristic of β-CD group, which clearly differs from that of the bare magnetic nanoparticles (bare MNPs) and unfunctionalized silica-coated nanomagnets (SMNP). Comparing Figures 1a and 1c it is possible to suggest that there was formation of a silica shell, since the existence of the characteristic Si−O−Si stretching at 1082 and 1095 cm^{-1} on Fe_3O_4/SiO_2 MNPs (Figure 1c) and $Fe_3O_4/SiO_2/CM-β-CD$ MNPs (Figure 1d). In the spectrum of $Fe_3O_4/SiO_2/CM-β-CD$ MNPs (Figure 1d), the most important asymmetric and symmetric C−H stretching bands are found at 2866 and 2936 cm^{-1} respectively, which prove successful grafting of CM−β-CD on silica coated magnetic particles[27] and the characteristic peaks of CM−β-CD in the region of 900-1200 cm^{-1} might be overlapped with the broad and strong peak due to silica coating.

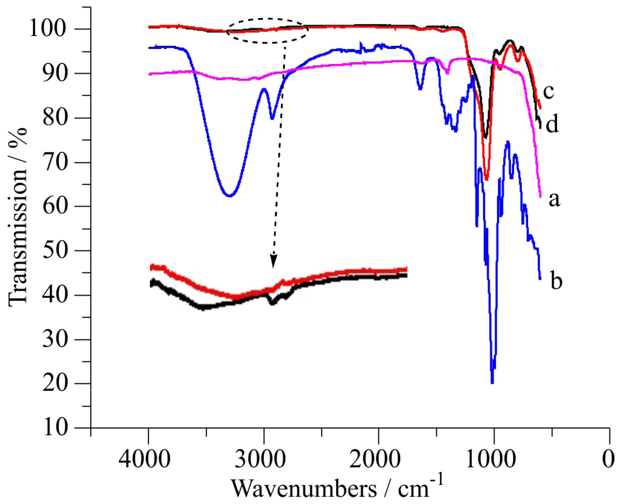


Figure 1. FTIR spectra of (a) bare MNPs; (b) β-CD; (c) Fe_3O_4/SiO_2 MNPs and (d) $Fe_3O_4/SiO_2/CM-β-CD$ MNPs.

XRD analyses were also applied to the prepared Fe_3O_4, Fe_3O_4/SiO_2 MNPs and $Fe_3O_4/SiO_2/CM-β-CD$ core-shell nanoparticles. The coating process of silica shell has been confirmed by IR spectrum in Figure 1 and as shown in Figure 2, a diffuse peak in (b) and (c) at about 20 degree that belong to it are also exhibited. Furthermore, the XRD patterns show characteristic peaks of Fe_3O_4 and the coating process did not induce any phase change of Fe_3O_4. In other words, the IR analysis indicated the successful anchoring of the β-CD group on the surface of magnetic nanobeads, and the XRD analysis suggested the phase maintenance of Fe_3O_4. Raman analyses were also applied to confirm the synthesis of $Fe_3O_4/SiO_2/CM-β-CD$ (SI section).

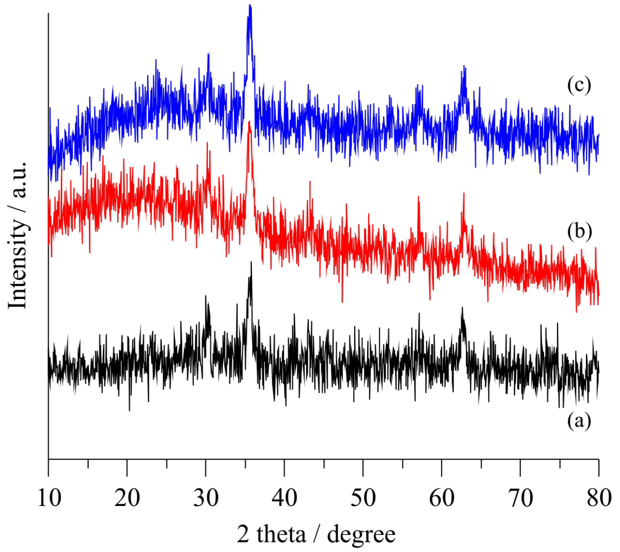


Figure 2. XRD patterns of (a) Fe_3O_4; (b) Fe_3O_4/SiO_2 MNPs and (c) $Fe_3O_4/SiO_2/CM-β-CD$ MNPs.

To further characterize the catalyst, TEM images were obtained as shown in Figure 3. It is clear that the synthesized catalysts are well dispersed, but also in some areas bigger structures with are observed, more likely coming from aggregation/coalescence of individual nanoparticles. It can be seen that dark Fe_3O_4 cores were surrounded by grey silica shells, suggesting the successful coating process. As for the catalyst after being used for 10 times, aggregation phenomenon is clearly presented, which may be a problem that inhibits the recycling for more times.

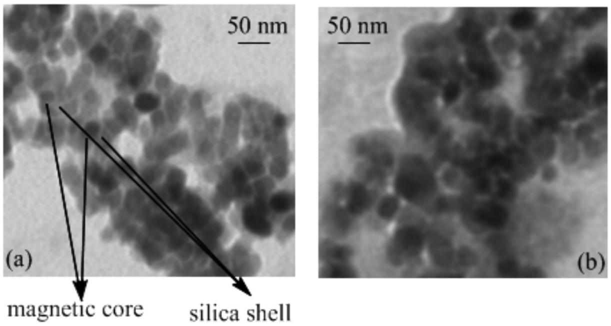


Figure 3. TEM images of (a) $Fe_3O_4/SiO_2/CM-\beta-CD$ MNPs and (b) $Fe_3O_4/SiO_2/CM-\beta-CD$ MNPs after being used for 10 times.

A thermogravimetric study showing the TG curves for β-CD, Fe_3O_4/SiO_2 and $Fe_3O_4/SiO_2/CM-\beta-CD$ were carried out to help to show the immobilization of β-CD. As shown in Figure 4, Fe_3O_4/SiO_2 had almost no weight loss from 50 to 800 °C (curve a). The catalyst $Fe_3O_4/SiO_2/CM-\beta-CD$ went through a similar process of weight loss compared with that of pure β-CD, indicating the successful anchoring of β-CD onto Fe_3O_4/SiO_2 MNPs. Within 200 °C, the weight loss was probably attributed completely to the absorbed water molecules. Around 300 °C, the TG curve of $Fe_3O_4/SiO_2/CM-\beta-CD$ was not as sharp as that of pure β-CD with a little advanced weight loss as well, which was supposed to due to the introduction of carboxymethyl (CM) group for every β-CD.

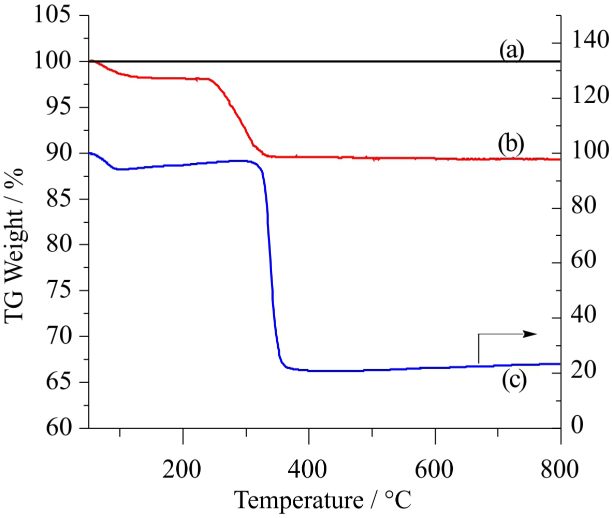


Figure 4. TG curves of (a) Fe_3O_4/SiO_2, (b) $Fe_3O_4/SiO_2/CM-\beta-CD$ and (c) β-CD.

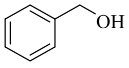
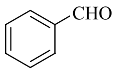
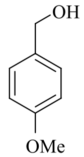
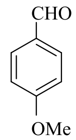
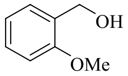
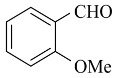
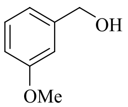
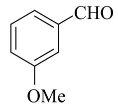
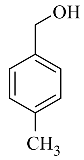
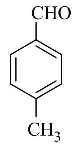
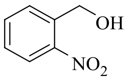
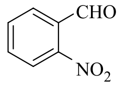
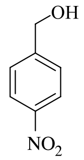
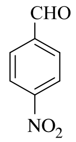
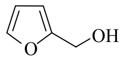
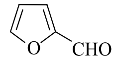
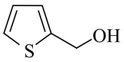
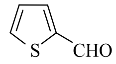
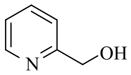
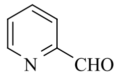
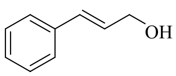
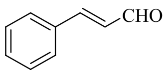
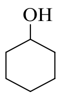
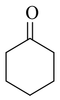
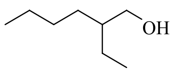
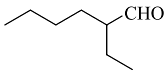
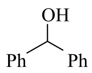
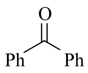
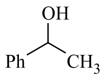
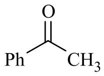
The catalytic activity of functionalized β-CD was first tested in the oxidation of benzyl alcohol using NaOCl as an oxidant with water as the only solvent. The reactions do not need any other additives and different reaction conditions including the amount of NaOCl, β-CD and reaction temperature were investigated (Table 1). The reaction conversion increased directly along with the amount of β-CD and was almost free form the affection of Fe_3O_4/SiO_2 (entries 4-7 and 12). It is known that β-CD and substrates can form host-guest complex. This complexation depends on the size, shape and hydrophobicity of the guest molecule. In our work, the oxidation reaction proceeded smoothly, which confirms the role of β-CD as a phase-transfer catalyst to accelerate the pseudo homogeneous reaction. When the mol ratio between β-CD and substrate reached 1, best result was achieved. Further increase of β-CD showed no benefit, and on the contrary decreased the opportunity for contact.

Table 1. The influence of reaction conditions on benzyl alcohol oxidation[a]

Entry	NaOCl / mL	$Fe_3O_4/SiO_2/CM-\beta-CD$ / mmol	T / °C	Conv. / %	Yield / %
1	1	1	50	24	23
2	5	1	50	98	97
3	10	1	50	99	97
4	5	0	50	trace	trace
5	5	0.1	50	8	7
6	5	0.5	50	33	33
7	5	2	50	97	96
8	5	1	30	30	30
9	5	1	40	61	61
10	5	1	60	98	97
11	5	1	70	98	97
12[b]	5	1	50	99	99

[a]With benzyl alcohol 1 mmol, 10% NaOCl aqueous solution was added dropwisely over 20 min and then the reaction was continued for 1.5 h; [b]unfunctionalized β-CD was used instead of $Fe_3O_4/SiO_2/CM-\beta-CD$.

Table 2. Oxidation of various alcohols[a]

Entry	Alcohol	Products	t / h	Conv. / %	Yield / %
1			1.5	98	97
2			2	98	93
3			2	96	94
4			2.5	96	95
5			1	99	99
6			4	92	90
7			4	93	89
8			1.5	95	92
9			2	93	91
10			2	86	83
11			5	47	47
12			6	50	49
13	1-$C_8H_{17}OH$	1-$C_7H_{13}CHO$	24	Trace	trace
14			24	Trace	trace
15			24	Trace	trace
16			24	Trace	trace

[a]Reaction conditions: alcohol 1 mmol, Fe_3O_4/SiO_2/CM−β-CD 1 mmol, H_2O 25 mL, NaClO (10%) 5 mL added dropwisely, 50 °C.

On the other hand, high temperature favored the oxidation process but may lead to the decomposition of NaOCl. So the oxidant was added dropwisely over 20 min to alleviate the unwanted decomposition. As a result, 1 mmol of β-cyclodextrin, 5 mL NaOCl (10%) and 50 ºC were chosen as a suitable reaction condition for the following reactions.

To examine the utility and generality of this methodology for the oxidation of alcohols, we applied the present catalyst system to a variety of alcohols as shown in Table 2. Obviously, all the primary benzylic alcohols tested were converted into their corresponding aldehydes in high yields and no overoxidation to acids was observed (entries 1-7). It is noteworthy that a type of heterocyclic alcohol (entries 8-10), being less active in many reported systems, worked well in the Fe_3O_4/SiO_2/CM−β-CD/H_2O/NaClO system (entries 8-10). Together with the fact that substituted groups in benzene ring lowered the reactivity, the space configuration of guest molecules was proposed to be an important factor to initiate the reaction. Unfortunately, in the case of aliphatic alcohols such as 1-$C_8H_{17}OH$ and isooctyl alcohol, the result was unsatisfactory even after elongating the reaction time (entries 13-14), probable due to the difficulty in forming complexation between long chain aliphatic alcohol and β-CD. This may also account for the ineffective of benzhydrol and 1-phenylethanol.

The advantage of the magnetic phase-transfer catalyst lies in not only the reaction with water as the sole solvent attributed to the formation of complexation between substrates and β-CD , but also in the ease of separation and recyclability provided by the Fe_3O_4/SiO_2 support. Simply by applying an external magnet to the reaction vessel a separation of the catalyst is achieved within 5 s and the resulting clear supernatant can be decanted (Figure 5). The recovered Fe_3O_4/SiO_2/CM−β-CD can be reused for at least 10 times without great loss of activity (the details can be seen in supporting information). The coated SiO_2 ensured the stability of Fe_3O_4 core against oxidation in the reaction, so as to achieve a high recyclability. After 10 times of reuse, SiO_2 may be dropped off. The Fe_3O_4, losing the protection of SiO_2 was easy to be oxidized. As the principal part of magnetism was destroyed, the catalyst would be lost in the solution and recovery decreased gradually.

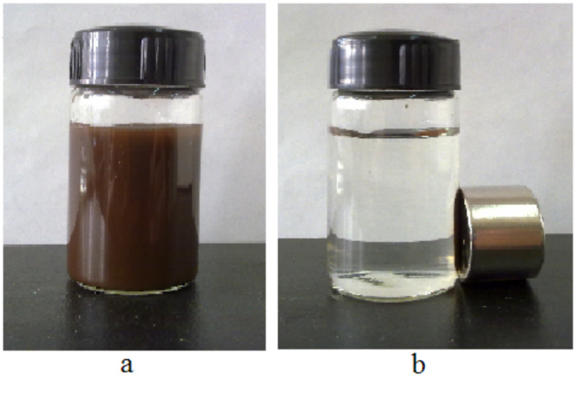


Figure 5. Easy separation of magnetic Fe_3O_4/SiO_2/CM−β-CD MNP catalyst within 5 s (a) during reaction; (b) after separation.

All synthesized particles have small coercivities, which indicate they are superparamagnetic in nature. As shown in Figure 6, saturation magnetizations for Fe_3O_4, Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2/CM−β-CD are 62.56, 37.98 and 30.28 emu g^{-1}, respectively. The order is due to the increasing amount of nonmagnetic material (organic ligands) on the particle surface, which makes up a larger percentage of the nonmagnetic fraction. A direct result of this effect is that it takes longer time to separate Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2/CM−β-CD than bare Fe_3O_4 nanoparticles from particle solution.

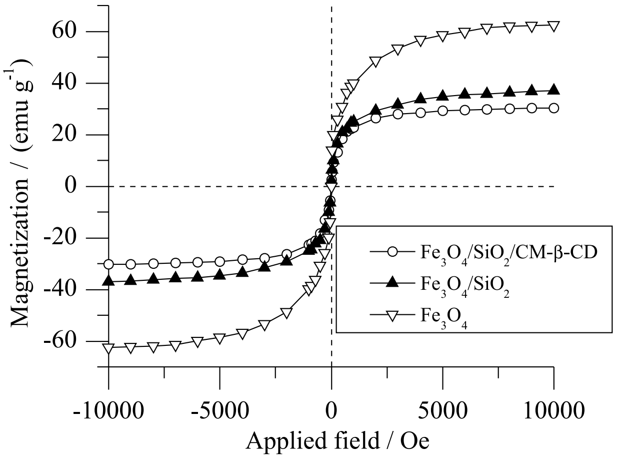
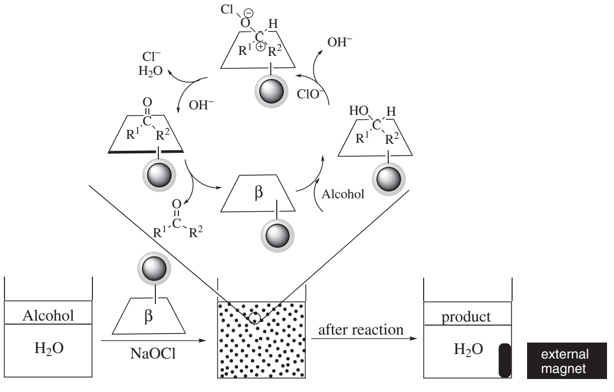


Figure 6. Magnetization curves for Fe_3O_4, Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2/CM−β-CD.

Based on the previous studies,[20] a possible mechanism for the aerobic oxidation of alcohols in the system was proposed as shown in Scheme 2. The formation of aldehydes might be occurred through a SN1 mechanism. Firstly, a β-CD inclusion complex between β-CD and



Scheme 2. A possible mechanism for the oxidation of alcohols.

substrate was formed in situ with the help of hydrogen bond,[17] which was dispersed in water as a pseudo homogeneous phase. Carbonium ion was then formed and attacked by ClO^- anion on carbon atom. Further elimination of Cl^- gave the corresponding aldehydes. After reaction, Fe_3O_4/SiO_2/CM−β-CD was easily recovered with the help of external magnet to be reused.

Conclusions

In summary, we have presented an elegant, simple and transition metal-free methodology for substrate selective oxidation of alcohols, catalyzed by Fe_3O_4/SiO_2/CM−β-CD with cheap NaOCl oxidant using water as the sole solvent. In particular, the present catalytic system shows excellent activity with β-CD served as a phase transfer catalyst. The system also couples the advantages of heterogeneous (easy separation, and excellent reusability) attributed to magnetic Fe_3O_4/SiO_2 system.

Supplementary Information

The experimental details are provided as Supplementary Information, available free of charge at http://jbcs.sbq.org.br as PDF file.

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