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Designed synthesis of multifunctional Fe_3O_4@SiO_2–NH_2@CS–Co(II) towards efficient oxidation of ethylbenzene

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ABSTRACT

The preparation of Co(II) supported magnetic heterogeneous catalyst, i.e. Fe_3O_4@SiO_2–NH_2@CS–Co, and its efficient and selective catalytic properties toward the oxidation of ethylbenzene to acetophenone are presented. The materials were characterized by various physicochemical techniques such as scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, vibrating sample magnetometer, elemental analysis, inductively coupled plasma-atomic emission spectrometer and X-ray photoelectron spectroscopy, etc. The reaction conditions were thoroughly investigated and highly improved catalytic performance (82.5% conversion of ethylbenzene and 80.1% selectivity to acetophenone) was gained under more mild reaction conditions of lower temperature (70 °C), shorter reaction period (60 min) and cheaper and greener oxygen source (H_2O_2). More importantly, it could be reused successively at least 10 times when more than 80% of its catalytic activity maintained.

1. Introduction

The oxidation of relatively cheap hydrocarbons to corresponding value-added fine derivatives, especially the selective oxidation of alkyl aromatic compounds to benzylic ketones, is one of the fundamental and important transformations both in basic researches and industrial manufacturing [1–3]. Among various substrates, acetophenone (AP), the oxidation product of ethylbenzene (EB), imparts high value addition and applied widely in fields such as perfumes, pharmaceuticals, resins, alcohols, tear gas and solvent for cellulose ethers, thus standing out and attracting much research attention [4–6].

In the last few years, the designing of catalytic systems for this kind of selective oxidation reaction with H_2O_2 as oxygen source, due to its cheapness, easy handling and production of only water as by-product, has received increasing attention [7–9]. Simultaneously, there has been an increased interest in developing transition metals, such as Co(II), Mn(II) and Cu(II), involved catalysts for the selective oxidation of EB [10–13]. In particular cobalt-based catalysts, because of their plausible potential as commercial catalysts, are mostly investigated and quite a number of studies have been conducted over both homogenous and especially heterogeneous ones [8,10,11,14–16]. However, the major drawbacks of homogenous catalyst used are the difficulty in product separation, irreversible deactivation, self-aggregation of active sites and low selectivity due to secondary oxidation of AP to corresponding carboxylic acid. To this end, currently the heterogenization of the homogenous catalyst, or rather immobilization of metal complexes on solid supports, e.g. typically silica matrices [17], mesoporous materials [18], mixed-oxide [16,19], organic polymers and polymer-based materials has been addressed to handle the mentioned issues [20–23]. Owing to the nearly similar active sites as their homogeneous phase, these thermally and chemically more stable heterogeneous catalysts, especially with easy separation and recycling character, have recently drawn more attention.

However, there still exist some drawbacks during those oxidation reactions involved with heterogeneous catalyst, for instance harsh reaction conditions, moderate or even poor conversion and selectivity caused by uncontrolled oxidation products [24,25], even the extensive use of costly TBHP as oxidant [6,9,16,23,26–27]. What is more, with the nanosizing of catalysts nowadays, traditional separation techniques, such as filtration and centrifugation, are considered to be time-consuming and energy-inefficient, usually leading to a tedious postprocessing work. At this regard, it is of great demand to develop a high-efficiency,

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environmental friendly catalyst for the selective oxidation of EB which worked under mild conditions with easy recovery procedure.

In contrast, magnetic separation can be taken as a quick, simple, eco-friendly, and more effective method than conventional separation methods. As a major class of advanced materials, magnetic hybrid materials, especially core@shell structure microspheres, that is, with magnetically responsive cores responsible for easy recycling, are being widely explored in catalysis today.

Besides, while chitosan is well-established for metal extraction [28–30], its application as catalyst support was rarely reported [31–33]. However, in view of its capability of effective removal of transition metals ions from aqueous medium, it is impressive that chitosan, with plenty of free amines that could offer platform for deposition of highly active transition metals, be used as support to design multi-functional catalyst.

Thus, aiming to integrate multi-advantages of magnetic matter and chitosan into one composite, this work chose chitosan (CS) enveloped magnetic nanoparticles as platform support to design efficient, durable and recyclable Co-based catalyst. In continuation of our previous work on the synthesis of Fe_3O_4@SiO_2–NH_2@CS-type support [33], we have introduced Co(II) successfully by impregnating the resulting support into the aqueous medium of Co$(OAc)_2 \cdot 4H_2O$. The obtained heterogeneous magnetic catalyst with good dispersibility has a high content of Co(II) ions which were anchored onto the cross-linked chitosan layers. A significantly enhanced catalytic performance in the oxidation of EB to AP in HOAc with H_2O_2 as oxidant and KBr as promoter was demonstrated. Moreover, the amount of $Co(OAc)_2 \cdot 4H_2O$ used in the impregnating process and the reaction conditions, such as the dosage of catalyst, H_2O_2, reaction time, volume ratio of HOAc to EB, reaction temperature, molar ratio of KBr to EB, were varied during the reaction. Remarkable EB conversion of 82.5% was obtained under the optimal reaction conditions with excellent selectivity to AP of 80.4%, especially the recycled catalyst presented an almost constant catalytic activity even with at least 10 runs, clearly demonstrating that this Co-based catalyst is of heterogeneous nature.

2. Experimental

2.1. Materials and instruments

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), tetraethoxysilane (TEOS), ethanol (EtOH), ethylene glycol (EG), acetic acid glacial (CH_3COOH), potassium bromide (KBr), hydrogen peroxide (H_2O_2, 30%), sodium sulfate dehydrate (Na_2SO_4) and dichloromethane (CH_2Cl_2) were all received from Tianjin Kermel Chemical Reagent Factory, China. Tri-sodium citrate dehydrate (Na_3Cit) and chitosan (CS) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium acetate anhydrous (NaOAc) and ammonia water $NH_3 \cdot H_2O$, 25–28 wt%) were supplied by Shenyang Chemical Plant, China. 3-aminopropyl trimethoxysilane (APTMS), glutaraldehyde (50%), cobalt(II) acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$), ethylbenzene (EB), acetophenone (AP) were purchased from Aladdin Chemistry Co., Ltd., China. Toluene was offered by Tianjin Fuyu Chemical Co., Ltd., China. All chemical reagents were analytical grade except AP which is a GR level and used without extra purification. But the concentration of H_2O_2 was titrated according to standard methods before using. All compounds were known and their physical and spectroscopic data were compared with those of authentic samples.

The morphology data of as-prepared series of magnetic nanomaterials was collected on JSM-6460LV and JEM-2000EX to get their SEM and TEM images, respectively. Co content determination was carried out using a Prodigyxp High Dispersion ICP (LEEMAN). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum Two FTIR spectrometer using KBr pressed pellet technique at a resolution 4 cm^{-1} in the region of 400–4000 cm^{-1} and the position of an infrared band is given in reciprocal centimeters (cm^{-1}). The magnetic properties were measured at room temperature using a vibrating sample magnetometer (Lake Shore 7410, VSM). The resulting products from oxidation were identified by a Techcomp 7900 gas chromatograph equipped with a 30m × 0.32 mm DB-WAX capillary column (Agilent Technologies Inc.) and a flame ionization detector, at given conditions (60 °C-2 min-60 °C-200 °C (30 °C/min), Inj. 250 °C, Det. 250 °C). For elemental analysis a EURO-EA 3000CHNS-elemental analyzer was used. In addition, X-ray photoelectron spectroscopy analysis (XPS) were performed using a Thermo Scientific Escalab 250 (Thermo VG,USA) instrument equipped with Al Kα radiation (hv = 1486.6 eV).

2.2. Synthesis of chitosan coated magnetic support (Fe_3O_4@SiO_2–NH_2@CS)

Fe_3O_4@SiO_2–NH_2 was synthesized following the original procedure reported previously by our groups [33–35]. In a typical synthesis, $FeCl_3 \cdot 6H_2O$ (1.62 g), Na_3Cit (1.50 g) and NaOAc (4.00 g) were introduced in EG (60 mL) and magnetic stirred vigorously under ambient temperature for 1 h until all components were entirely mixed to form a homogeneous yellow solution. The resulting mixture was then transferred into stainless-steel autoclave (100 mL) with Teflon-lined, and the highly sealed autoclave was heated at 200 °C for 12 h to acquire the desired magnetic Fe_3O_4 cores and got cooled under ambient condition before using. The precipitate was washed with copious amount of ethanol and deionized water and then suspended into water (80 mL) for the next process.

The modification of the external surface of Fe_3O_4 magnetic particles (MNPs) with amine groups was identified hereafter by using TEOS and APTMS. Magneto-fluid (Fe_3O_4 MNPs dispersed in water, 20 mL) was introduced into ethanol (150 mL) before the addition of $NH_3 \cdot H_2O$ (1 mL) to create a alkaline environment for

Table 1
Chemical composition of studied samples.

Samples	Elemental analyses (wt%)[a]	Co content (mg/g)[b]		
	C	N	H	
Fe_3O_4@SiO_2–NH_2	5.2	1.9	1.7	–[c]
Fe_3O_4@SiO_2–NH_2@CS	6.2	1.8	1.7	–[c]
Fe_3O_4@SiO_2–NH_2@CS-Co	4.6	1.2	1.3	4.448
Catalyst used 10 times	4.6	1.2	1.3	–[d]

[a] CNH were determined by elemental analysis.
[b] Co content determined by ICP.
[c] None.
[d] Not determined.