Received: 2 September 2011

Revised: 4 October 2011

(wileyonlinelibrary.com) DOI 10.1002/aoc.1862

Applied

Selective aerobic oxidation of alcohols catalyzed by iron chloride hexahydrate/TEMPO in the presence of silica gel

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An environmentally friendly and efficient process whereby $FeCl_3 \cdot 6H_2O/2, 2, 6, 6$ -tetramethylpiperidine *N*-oxyl (TEMPO)catalyzed oxidation of alcohols to the corresponding aldehydes and ketones is accomplished in the presence of silica gel using molecular oxygen or air as the terminal oxidant. The electron-deficient benzyl alcohol was smoothly oxidized to the corresponding aldehydes with up to 99% isolated yield. It was found that silica gel not only could enhance the catalytic reaction rate but also increase the selectivity for the product. The high performance of $FeCl_3 \cdot 6H_2O/TEMPO$ catalyst system in the presence of silica gel might be attributed to the surface silanol groups. UV-visible spectra analysis showed that the Fe (III)–TEMPO complex could serve as the active intermediate species in the present catalytic system. A plausible mechanism of the catalytic system is proposed. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords: aerobic alcohol oxidation; iron chloride; molecular oxygen; 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO); silica gel

Introduction

The selective oxidation of alcohols to their corresponding carbonyl compounds is an important functional group transformation in organic synthesis.^[1] Traditionally, the oxidants are required in stoichiometric quantities.^[2] Permanganate, manganese(IV) oxide, chromium(VI) oxide, dichromate, and ruthenium(VII) oxide are also hazardous oxidizing agents. From both an economic and environmental viewpoint, the catalytic oxidation process represents a promising improvement in this protocol. The use of molecular oxygen or air as the oxidant is particularly attractive.

Numerous reports describe aerobic alcohol oxidation using transition metals such as Cu,^[3–8] Pd,^[9–17] Ru,^[18–21] Au,^[22–24] or V,^[25–29] alone or in conjugation with the nitroxy radical 2,2,6, 6-tetramethylpiperidine *N*-oxyl (TEMPO)^[30–34] as catalysts. In these studies, noble metals, halogens, extra bases or complicated ligands are often used. These are typically restricted for use in pharmaceuticals, fragrances and food additives. Therefore the development of procedures with a green, efficient and inexpensive catalytic system for aerobic oxidation of alcohols is a worthwhile challenge. Minisci and co-workers reported an efficient use of Mn(NO₃)₂ and Co(NO₃)₂ or Cu(NO₃)₂ in combination with TEMPO in a CH₃COOH catalytic system for the oxidation of primary, benzylic and secondary alcohols.^[35,36]

Recently, green, inexpensive and readily available iron salts have attracted a great deal of attention in modern chemistry.^[37–40] In contrast, iron salts being employed as the catalyst for aerobic oxidation of alcohols is rarely reported. Martin and Suárez^[41] first reported the Fe(NO₃)₃/FeBr₃ catalytic system for the oxidation of alcohols, which was effective for chemoselective oxidation of secondary aliphatic alcohols. It was reported by Dijksman *et al.*^[18] that Fe(III and II) chlorides in combination with TEMPO showed no catalytic activity for aerobic oxidation of 2-octanol in chlorobenzene.

Wang *et al.*^[42] and Yin *et al.*^[43] have made a great breakthrough in this respect. They developed an efficient three-component catalytic system, consisting of FeCl₃·6H₂O/TEMPO/NaNO₂, in which NaNO₂ as the electron-transfer medium is required for completing the catalytic cycle. We are particularly interested in exploring the potential of the iron-TEMPO catalyst system for aerobic alcohol oxidation without additional co-catalyst. It was reported that silica gel enhances many reaction rates.^[44] Nishiguchi and Asano^[45] reported that metallic nitrates supported on silica gel were able to efficiently oxidize alcohols to the corresponding ketones and aldehydes. In this system, the metallic nitrates were the stoichiometric oxidant. However, according to our knowledge FeCl₃·6H₂O/TEMPOcatalyzed oxidation of alcohols in the presence of silica gel using O₂ as oxidant has never been reported in the literature. We reckoned that a simple alcohol oxidation reaction could be performed using FeCl₃·6H₂O/TEMPO catalyst system in the presence of silica gel using O₂ as oxidant, in which O₂ acts as an ultimate oxidant and water is the only by-product. A possible reaction mechanism is also highlighted.

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Table	1.	FeCl ₃ •6H ₂ O-catalyzed	oxidation	of	benzyl	alcohol	to
benzal	deh	vde ^a					

Entry	FeCl ₃ •6H ₂ O	TEMPO	Silica gel	Conversion (%)/ selectivity (%) ^b
1	No	Yes	Yes	Trace
2	Yes	No	Yes	Trace
3	Yes	Yes	Yes	97/99
4	Yes	Yes	No	35/83
5 ^c	Yes	Yes	No	90/88
6 ^d	Yes	Yes	Yes	55/93
7 ^e	Yes	Yes	Yes	95/95

^aReaction conditions: 5 mmol benzyl alcohol, 8 mol% FeCl₃·6H₂O, 2 mol% TEMPO, 0.2 g silica gel, 5 ml toluene, 0.5 MPa O₂, 80°C, 6 h.

^bConversion and selectivity are determined by GC analysis using *n*-nonane as the internal standard.

^cReaction time: 24 h.

^dReaction performed at 65°C.

^eUnder 0.1 MPa O₂.

Results and Discussion

Effect of silica gel on the benzyl alcohol reaction

Initially, we performed benzyl alcohol oxidation (Table 1). There was very little reaction without $FeCl_3.6H_2O$ or TEMPO (Table 1, entries 1 and 2). The results clearly indicated that the presence of silica gel greatly improved the conversion of benzyl alcohol as well as the selectivity for benzaldehyde (Table 1, entries 3–6). The conversion of benzyl alcohol obtained was 97% with the addition of 0.2 g silica gel for 6 h (Table 1, entry 3), in contrast to only 35% for 6 h in the absence of silica gel (Table 1, entry 4). The conversion of benzyl alcohol obtained was 90% by prolonging the reaction time to 24 h without silica gel (Table 1, entry 5). When the temperature was decreased to 65°C, however, the conversion of benzyl alcohol obtained was only 55% (Table 1, entry 6). The result suggested that elevated temperature was essential for high conversion of the substrate. It is noteworthy that a 95% conversion of benzyl alcohol was also obtained by reducing the



Figure 1. Dependence of the conversion of benzyl alcohol on the amount of silica gel. Reaction conditions: 5 mmol benzyl alcohol, 8 mol% FeCl₃·6H₂O, 2 mol% TEMPO, silica gel, 5 ml toluene, 0.5 MPa O_2 , 80°C, 6 h. Conversions are determined by GC analysis using *n*-nonane as the internal standard.

pressure of oxygen to 0.1 MPa for a slightly longer time (Table 1, entry 7). The effect of the amount of silica gel was also investigated. As shown in Fig. 1, the amount of silica gel modulated the oxidation of benzyl alcohol. The conversion increased with increasing amount of silica gel until 0.2 g, and plateaued when over 0.2 g of silica gel was used.

Optimization of the Aerobic Oxidation of Benzyl Alcohol

The catalytic system was optimized using benzyl alcohol as a test substrate, and the data are summarized in Table 2. The nature of the solvent had a crucial impact on the reaction outcome. Thus, while toluene, PhCF₃, dichloromethane or dichloroethane favored the benzyl alcohol oxidation (Table 2, entries 1-4), n-hexane yielded only moderate conversion (Table 2, entry 5). The use of polar coordinating solvents such as DMF and CH₃CN resulted in low conversions (Table 2, entries 6 and 7), which might be due to the competitive coordination of solvent molecules to the metal center and fewer binding sites for benzyl alcohol and TEMPO.^[46] In order to optimize the environmental properties and to achieve minimal toxicity, toluene was chosen as a solvent. A variety of iron salts were evaluated with toluene as a solvent (Table 2, entries 8-13). Fe₂(SO₄)₃ and Fe (OAc)₃ were the least active catalysts, yielding only 8% and 2% conversion, respectively (Table 2, entries 8 and 9). The conversion obtained in the presence of FeBr₃ was 69% (Table 2, entry 10). It was observed that when anhydrous FeCl3 was employed as a catalyst, this resulted in a lower yield than FeCl₃·6H₂O (Table 2, entry 11). FeCl₃·6H₂O proved to be an excellent catalyst in terms of reaction rate and conversion. The reaction could also be accomplished using FeCl₂·4H₂O as a catalyst with a slightly longer reaction time (Table 2, entries 12 and 13). The results suggested that the iron counterion had a great effect on the oxidation of benzyl alcohol.

Oxidation of Alcohols Catalyzed by FeCl₃·6H₂O/TEMPO

The FeCl₃·6H₂O/TEMPO/silica gel catalytic system exhibits good catalytic activity for primary and secondary benzylic alcohols. As shown in Table 3, primary benzylic alcohols were easily oxidized

Table 2.	ble 2. Optimization of the aerobic oxidation of benzyl alcohol ^a					
Entry	Fe salt	Solvent	Time (h)	Conversion ^b (%)	Yield ^b (%)	
1	FeCl ₃ •6H ₂ O	Toluene	6	97	96	
2	FeCl ₃ •6H ₂ O	PhCF ₃	6	90	89	
3	FeCl ₃ •6H ₂ O	CH_2CI_2	7	97	93	
4	FeCl ₃ •6H ₂ O	$C_2H_4CI_2$	8	93	86	
5	FeCl ₃ •6H ₂ O	<i>n</i> -Hexane	6	62	60	
6	FeCl ₃ •6H ₂ O	DMF	6	5	4	
7	FeCl ₃ •6H ₂ O	CH₃CN	6	32	25	
8	$Fe_2(SO_4)_3$	Toluene	6	8	3	
9	Fe(OAc) ₃	Toluene	6	2	0.9	
10	$FeBr_3$	Toluene	6	69	56	
11	FeCl₃	Toluene	6	94	85	
12	FeCl ₂ •4H ₂ O	Toluene	7	72	70	
13	FeCl ₂ •4H ₂ O	Toluene	8	100	>99	

^aReaction conditions: 5 mmol benzyl alcohol, 8 mol% Fe salt, 2 mol% TEMPO, 0.2 g silica gel, 5 ml solvent, 0.5 MPa O₂, 80°C. ^bDetermined by GC.

Table 3. Oxidation of alcohols catalyzed by EeCl ₂₂ 6H ₂ O/TEMPO ^a						
Entry	Substrate Product		Time (h)	Conversion ^b (%)/Yield ^c (%)		
,			O ₂ /Air	O ₂	Air	
1	ОН	0	7/12	100/98(93)	97/90	
2	- ОН		8/18	100/92(90)	95/80	
3	ОН	0	8/18	100/99(99)	98/87	
4 ^d	O ₂ N-OH	0 ₂ N-	24/26	>99/99(99)	26/22	
5 ^d	O ₂ N OH	O ₂ N O	26/42	>99/99(99)	80/79	
6 ^d	Br	Br	16/24	>99/99(98)	100/98	
7 ^d	CI	ci	16/24	100/98	96/95	
8	МеО	MeO	6/—	100/53(50)	_	
9	ОН		9/18	98/68	93/66	
10	CI	CI	13/—	100/75	_	
11	ОН	0	8/—	>99/91(80)	_	
12 ^e	OH		24/24	72/67	52/40	
13 ^e	ОН	° , , ,	24/—	75/69	_	
14 ^e	OH	° – – – – – – – – – – – – – – – – – – –	24/24	92/90	85/76	

Selective aerobic oxidation of alcohols promoted by silica gel

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=0

24/—

13/8

Table 3. (Continued)							
Entry	Substrate	Product	Time (h)	Conversion ^b ((%)/Yield ^c (%)		
			O ₂ /Air	O ₂	Air		
16 ^e	(→)_OH 6		24/—	11/4	_		
^a Reaction conditions: 5 mmol alcohol, 8 mol% FeCl ₃ -6H ₂ O, 2 mol% TEMPO, 0.2 g silica gel, 5 ml toluene, 0.5 MPa O ₂ or air, 80°C. ^b Conversions are determined by GC. ^c Yields are determined by GC; values in parentheses are yields of the isolated products. ^d Conditions: 5 mol% TEMPO. ^e Conditions: 20 mol% FeCl ₃ -6H ₂ O, 10 mol% TEMPO.							

into their corresponding aldehydes with high conversion and yield (Table 3, entries 1-3). Over-oxidized carboxylic acids were not observed. As expected, the conversion of electron-deficient benzylic alcohols took longer compared with electron-rich benzylic alcohols (Table 3, entries 4-7), whereas a moderate isolated yield was obtained from a benzylic alcohol containing a *p*-methoxy substituent (Table 3, entry 8). Halide-substituted benzyl alcohols showed good tolerance for the oxidation process (Table 3, entries 6 and 7). Cinnamyl alcohol was also successfully oxidized into cinnamaldehyde in 80% isolated yield. It was clear that the conversion of activated secondary benzylic alcohol was high, but with a moderate yield. Ether was formed as the major by-product, presumably because of the strong Lewis acidity of FeCl₃ (Table 3, entries 9 and 10). Compared with benzylic alcohols, aliphatic alcohols were less reactive. Aliphatic secondary alcohols can also be successfully oxidized into ketones with good yields by increasing the loading of FeCl₃·6H₂O and TEMPO (Table 3, entries 12-14). Interestingly, aliphatic secondary alcohols with branched chains gave excellent results (Table 3, entry 14). In contrast, in the case of cyclohexanol, the conversion achieved was only 13% (Table 3, entry 15). Unfortunately, the oxidation of aliphatic primary alcohols resulted in low conversions. For example, with 1-octanol as the substrate, the conversion obtained was only 11% (Table 3, entry 16).

A substantial practical improvement for aerobic oxidation is to replace pure O_2 with air since this reduces cost and is also

safer.^[24] When air was used to replace pure O_2 , we observed a slightly lower conversion rate, which can be easily compensated by prolonging the reaction time (Table 3).

Mechanistic Aspects

Based on the above results, the mechanism of the catalytic system was investigated. Scheme 1 shows the proposed reaction process. First, Fe(III) was dispersed on the surface of silica gel. Next, alcohol coordinated to the Fe(III) to lead to alkoxy species, which dissolved in toluene and partially adsorbed on the silica gel surface. Subsequently, alkoxy species in combination with TEMPO lead to the formation of the species A (Fe(III)–TEMPO complex), which was considered to exist in the surface phase and liquid phase and serve as the active intermediate species in the present catalytic system. Intramolecular transfer of the β -hydrogen would lead to obtaining the carbonyl compound, Fe(II) species, and TEMPOH. The resulting Fe(II) species was oxidized by TEMPO to Fe(III). TEMPOH was oxidized by molecular oxygen to TEMPO and water.^[47] The following sections are described to support the proposed reaction process.

Figure 2 shows the evidence for the formation of Fe(III)–TEMPO complex and the oxidation of Fe(II) to Fe(III) by UV–visible spectroscopy. It should be noted that the UV–visible measurement was performed using toluene and the reaction amount of benzyl alcohol as the solvent. This is due to insolubility of the FeCl₃-6H₂O



Scheme 1. Proposed mechanism for Fe-TEMPO-catalyzed aerobic oxidation of alcohols.



Figure 2. UV-visible investigation of Fe(III)-TEMPO complex formation.

and FeCl₂·4H₂O in pure toluene. As shown in Fig. 2, the UV-visible spectrum of Fe(III) has the maximum at 341 nm; after addition of TEMPO, the maximum at 341 nm disappeared and two new maxima at 312 nm and 351 nm emerged. Actually, the possible coordination mode of [Fe(dmf)₃Cl₂]-TEMPO complex has been studied in detail.^[48] The spectrum of [Fe(dmf)₃Cl₂]-TEMPO exhibited two maxima at 317 nm and 352 nm. These results indicate that Fe (III)-TEMPO was formed in the course of alcohol oxidation. In addition, as the amount of TEMPO is increased, the wavelength is also shifted. The UV-visible spectrum of Fe(II) (under N₂ condition) has a maximum at 333 nm; after addition of TEMPO, the maximum at 333 nm disappeared and two new maxima at 316 nm and 359 nm emerged, which was consistent with the absorbance of Fe(III):TEMPO (4:2). This demonstrated that Fe(II) was oxidized to Fe(III) by TEMPO, and formed the Fe (III)-TEMPO complex with another molecule of TEMPO. The alkoxy-Fe (III)-TEMPO complex could serve as active intermediate species in the present catalytic system. It is noteworthy that the same absorption peak was obtained in the presence of silica gel, indicating that the addition of silica gel did not change the reaction mechanism.

To the best our knowledge, this is the first report of the $FeCl_3-6H_2O/TEMPO$ catalyst system directly activating molecular oxygen without requiring a co-oxidant for the oxidation of alcohols.



Figure 3. Effect of solid additives on the oxidation of benzyl alcohol. Reaction conditions: 5 mmol benzyl alcohol, 8 mol% FeCl₃·6H₂O, 2 mol% of TEMPO, 0.2 g of additives, 5 ml toluene, 0.5 MPa O_2 , 80°C, 6 h. Conversions are determined by GC analysis using *n*-nonane as the internal standard.

The role of silica gel in the catalytic system of FeCl₃·6H₂O/TEMPO was investigated. Figure 3 shows the catalytic performance of FeCl₃·6H₂O/TEMPO in the presence of other solid additives as a comparison to the silica gel. The acidic molecular sieve of HZSM-5, the neutral molecular sieve of SBA-15, neutral alumina and γ -alumina could give good conversions of benzyl alcohol, while the presence of a 3 Å molecular sieve and nano-MgO decrease the catalytic activity. These results indicate that the primary role of silica gel is not to remove the water by-product, since the 3 Å molecular sieve is traditionally used as a dehydrater for organic solvents and that the main role of the silica gel is not to widen the surface of iron salts. The surface hydroxyl groups of the solids appear to be the major contributor in accelerating the reaction. Therefore we speculate that the silanol groups form a special reaction field where alcohols and catalysts are accumulated by adsorption. This speculation is supported by the report that the principal adsorption sites of the silica gel are the surface



Figure 4. Time courses for the oxidation of benzyl alcohol over different activation temperatures of silica gel: (**a**) 800°C; (**b**) 650°C; (**b**) 300°C; (**v**) off the shelf; (**b**) without silica gel. Reaction conditions: 5 mmol benzyl alcohol, 8 mol% FeCl₃·6H₂O, 2 mol% TEMPO, silica gel 0.2 g, 5 ml toluene, 0.5 MPa O₂, 80°C, 6 h. Yields are determined by GC analysis using *n*-nonane as the internal standard.



Figure 5. Effect of the different treatment temperatures of silica gel on oxidation of benzyl alcohol. Reaction conditions: 5 mmol benzyl alcohol, 8 mol% FeCl₃·6H₂O, 2 mol% TEMPO, 0.2 g silica gel, 5 ml of toluene, 0.5 MPa O₂, 80°C, 6 h. Yields are determined by GC analysis using *n*-nonane as the internal standard. (\Box) GC yield.

Figure 5 illustrates the catalytic performance of FeCl₃· $6H_2O/$ TEMPO for the oxidation of benzyl alcohol in the presence of the different treatment temperature of silica gel. In the silica gel treatment temperature range 100–500°C, benzaldehyde yields were essentially unchanged. Up to 600°C the yield of benzaldehyde was obviously reduced. When the treatment temperature of silica gel was raised to 1100°C, the yield of benzaldehyde decreased greatly. This might be attributed to the concentration of silanol groups, which dropped to a certain extent, affecting the reaction results. Based on the above results, it is most likely that the enhancement in catalytic performance of FeCl₃· $6H_2O/TEMPO$ is due to the surface concentration of the adsorbed reactant.^[51,52]

Conclusions

We have developed an environmentally friendly and efficient $FeCl_3-6H_2O/TEMPO/$ silica gel-catalyzed method for the oxidation of alcohols to their corresponding aldehydes and ketones with moderate to excellent yields. In this catalytic system, silica gel, as the additive, plays an important role. Its presence speeds up the oxidation rate to a remarkable degree. A plausible mechanism of the catalytic system is proposed, in which the Fe(III)–TEMPO complex might serve as the active intermediate species. Simple and green catalysts will be very practical and useful in the preparation of fine chemicals.

Experimental

General Chemical Reagents

All chemicals used in this study were analytical grade, commercially available and used without further purification unless otherwise noted. Silica gel was 200–300 mesh, with a surface area of $172.1 \text{ m}^2 \text{ g}^{-1}$ and average pore diameter 2.182 nm.

General Measurement

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer using CDCl₃ as the solvent with tetramethylsilane as an internal reference. ¹H and ¹³C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane (CDCl₃: $\delta_{\rm C}$ =77.0 ppm; residual CHCl₃ in CDCl₃: $\delta_{\rm H}$ = 7.26 ppm). Determination of conversions and yields by gas chromatography (GC) was performed on an Agilent 7890A with a flame ionization detector (FID). All products were confirmed by gas chromatography-mass spectrometry (GC-MS) with an Agilent 6890N GC/5973 MS detector and comparison of their GC retention time with those of authentic samples. The UV-visible spectra were recorded on a Shimadzu-2550 spectrometer with 10 mm path length of guartz sample cells at 298 K. Wavelength range, 240–900 nm; SE-54 capillary column, 30 m imes 250 μ m imes 1 μ m; FID, 300°C; injection, 250°C; carrier gas, nitrogen; carrier gas rate, 2 ml min⁻¹. Benzyl alcohol, 3-methyl-benzyl alcohol, 4-methyl-benzyl alcohol, 4-nitrobenzyl alcohol, 3-nitrobenzyl alcohol, 4-methoxybenzyl alcohol, 4-bromobenzyl alcohol, 4-chlorobenzyl alcohol, cinnamyl alcohol, 1-(4-chlorophenyl)ethanol, DL-1-phenylethanol, 2-octanol,

1-octanol and their corresponding products were detected under the following conditions: column temperature, 100° C for 7 min, rising to 250°C at a rate of 15°C min⁻¹. 2-Pentanol and its corresponding product were detected under the following conditions: column temperature, 30°C for 7 min, rising to 250°C at a rate of 15°C min⁻¹. 4-Methyl-2-pentanol and its corresponding product were detected under the following conditions: column temperature, 80°C for 7 min, rising to 250°C at a rate of 15°C min⁻¹.

General Experimental Procedure

The oxidation of all alcohols was carried out in a Teflon-lined 316 L stainless steel autoclave. The initial air in the autoclave was exchanged three times with oxygen. Typically, FeCl₃·6H₂O (0.4 mmol) and silica gel (0.2 g) were added to the autoclave, followed by 5 ml toluene. After stirring for 2 min, benzyl alcohol (5 mmol) was added and stirred for 5 min, then TEMPO (0.1 mmol) was added. After the autoclave was closed, oxygen was charged to 0.5 MPa. The autoclave was placed in an oil bath which was pre-heated to 80°C. The reaction mixture was monitored by GC. When the reaction was finished, the autoclave was cooled to room temperature and carefully depressurized. The reaction mixture was loaded directly on a small pad of silica flushing with hexane to remove the toluene and the product was eluted with dichloromethane. The solvent was concentrated in vacuo and the product was further purified by column chromatography over silica gel (n-hexane:ethylacetate, 10:1) to afford benzaldehyde (502 mg, yield 93%). $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra data of all isolated products were in accord with the literature.

Sample preparation for UV-visible investigation of Fe(III)-TEMPO complex formation

The UV-visible measurement was performed using toluene and the reaction amount of benzyl alcohol as the solvent. This is due to the insolubility of FeCl₃·6H₂O and FeCl₂·4H₂O in pure toluene. Into a 10 ml A-grade volumetric flask was added precisely 0.108 g FeCl₃·6H₂O. 0.5407 g benzyl alcohol was added, followed by 2 ml toluene. The mixture was swirled vigorously for approximately 2 min, and then 0.0156 g TEMPO was added. The reaction was swirled vigorously for approximately 2 min to allow for complex formation to occur, and then was diluted to volume. 0.1 ml of this solution was transferred to a fresh 10 ml A-grade volumetric flask and diluted to volume. This final solution was then immediately analyzed (See Supporting Information for details).

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

Acknowledgments

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 20643006), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry and the National Basic Research Program of China (2009CB623505).

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