Short Communication

Nanomagnetic double-charged diazoniabicyclo[2.2.2]octane dichloride silica as a novel nanomagnetic phase-transfer catalyst for the aqueous synthesis of benzyl acetates and thiocyanates

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ABSTRACT

Nanomagnetic double-charged diazoniabicyclo[2.2.2]octane dichloride silica hybrid (Fe₃O₄@SiO₂/DABCO) was used as an efficient and magnetically recoverable phase-transfer catalyst (PTC) for nucleophilic substitution reactions of benzyl halides for the synthesis of benzyl acetates and thiocyanates in good to excellent yields at 100 °C in water. No evidence for the formation of by-products, for example, isothiocyanate or benzyl alcohol was observed and the products were obtained in pure form without further purification. The catalyst was easily separated with the assistance of an external magnetic field from the reaction mixture and reused for several consecutive runs without significant loss of its catalytic efficiency.

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1. Introduction

Hybrid xerogel materials, where the organic component is bonded to a polymeric silica skeleton framework, have attracted significant attention over the last decade. In this context, single- and double-charged silica-based hybrid xerogels containing the 1-azonia-4-azabicyclo[2.2.2]octane, DABCO, chloride group have recently drawn particular interest [1–4].

Ionic liquids (ILs) have been widely used in organic synthesis and catalytic reactions as solvents and catalysts. The practical utility of ILs as a catalyst in aqueous media could be extended further if it can be rendered water insoluble. The chemical industry still prefers to use heterogeneous catalyst systems because of the ease of separation, thus supported ILs are highly desirable [5]. Immobilization of ILs on solid supports has been suggested as an alternative way of getting around the problems.

Due to the high surface area to volume ratios, superparamagnetic properties and biocompatibility, magnetic nanoparticles (MNs) can effectively improve the loading and catalytic efficiency of immobilized catalysts. They often encompass the desirable features of both organic and inorganic compounds [6–11]. More than these, they can be easily separated by the simple application of an external magnetic field, which may optimize operational costs and enhance a product's purity [12]. Iron oxides, magnetite (Fe₃O₄), and maghemite (γ-Fe₂O₃) are by far the most used magnetic nanoparticles because they are much less toxic than their metallic counterparts, and they still have high saturation magnetization and superparamagnetic behavior, among which magnetite is a very promising choice due to its already proven biocompatibility. In addition, previous investigations have shown that magnetite has relatively high LD50 values (400 mg/kg in rats) and polymer-coated magnetite has not shown any acute or subacute toxicity in animal studies [13,14].

Phase-transfer catalysis (PTC) is a very useful technique, which is widely used in the synthesis of dyes, pharmaceuticals, perfumes, flavorants, agricultural chemicals, monomers, and polymers, and it has been widely used for organic synthesis, particularly for nucleophilic substitution [15–18]. The design of efficient and recoverable phase-transfer catalysts has become an important issue for reasons of economic and environmental impact, in recent years. In particular, immobilization of the phase-transfer catalyst on a support has considerable advantages, including easy catalyst recovery and product isolation, and employment of a continuous flow method owing to the three-phase nature of the system, which make the technique attractive for industrial applications. Although many phase-transfer catalysts are known, quaternary salts formed from ammonia are practically important and used in many of organic reactions. Its high polarity and ability to solubilize both organic and inorganic compounds can result in enhanced reaction rates and can provide higher selectivity compared with conventional methods [19–22].

Considering these facts and taking all this into account, we decided to use supported nanomagnetic double-charged diazoniabicyclo[2.2.2]octane dichloride silica hybrid (Fe₃O₄@SiO₂/DABCO) as an efficient nanomagnetic phase transfer system for organic transformation.

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2. Experimental

2.1. General

Iron (II) chloride tetrahydrate (99%), iron (III) chloride hexahydrate (98%), benzyl halides and other chemical materials were purchased from Fluka and Merck companies and used without further purification. Products were characterized by comparison of their physical data, such as IR and $^1$H NMR and $^{13}$C NMR spectra, with known samples. NMR spectra were recorded in CDCl$_3$ on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as an internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. The particle morphology was examined by SEM (Philips XL30 scanning electron microscope) and TEM (Zeiss; EM10C; 80 kV).

2.2. Preparation of Fe$_3$O$_4$ superparamagnetic nanoparticles

Superparamagnetic nanoparticles (MNPs) were prepared via improved chemical coprecipitation method [23]. According to this method, FeCl$_2$·4H$_2$O (6.346 g, 31.905 mmol) and FeCl$_3$·6H$_2$O (15.136 g, 55.987 mmol) were dissolved in 640 mL of deionized water. The mixed solution was stirred under N$_2$ at 90 °C for 1 h. Eighty milliliters of NH$_3$.H$_2$O (25%) was injected into the reaction mixture rapidly, stirred under N$_2$ for another 1 h and then cooled to room temperature. The precipitated particles were washed five times with hot water and separated by magnetic decantation. Finally, magnetic NPs were dried under vacuum at 70 °C.

2.3. Synthesis of bis(n-propyltrimethoxysilane)-1,4-diazoniabicycle [2.2.2] octane chloride, BPTDABCOCl

BPTDABCOCl was prepared according to the procedure described by Arenas et al. [3]. Initially, the previously sublimed DABCO (0.897 g, 8.0 mmol) was dissolved in DMF (5 mL). To this solution, 16 mmol of 3-chloropropyltrimethoxysilane (CPTMS) was added. The mixture was stirred for 72 h, under argon atmosphere at 90 °C. The white solid, BPTDABCOCl, was filtered and washed with methanol and then dried for 2 h in an oven at 90 °C.

2.4. Preparation of magnetic double-charged diazoniabicyclo[2.2.2]octane dichloride silica hybrid, Fe$_3$O$_4$@SiO$_2$/DABCO

Fe$_3$O$_4$@SiO$_2$/DABCO was prepared using a sol–gel process. The synthesized magnetite nanoparticles (2.0 g) was first diluted with water.

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Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Benzyl halide</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl</td>
<td>OAc</td>
<td>1.5</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>OAc</td>
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</tr>
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<td>Cl</td>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>Me</td>
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<td>83</td>
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<tr>
<td>5</td>
<td>Cl</td>
<td>OMe</td>
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<td>OAc</td>
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<td>76</td>
</tr>
<tr>
<td>9</td>
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<td>OAc</td>
<td>2.5</td>
<td>80</td>
</tr>
</tbody>
</table>
(40 mL), absolute ethanol (120 mL) and 3.0 mL ammonia aqueous (25%). This suspension was well-dispersed by ultrasonic vibration for 15 min. To this dispersed suspension, BPTDABCOCl (5 g), previously dissolved in DMF (7 mL), was added. Then under continuous mechanical stirring, 1.5 mL of TEOS diluted in ethanol (40 mL) was slowly added to this dispersion, and after stirring for 48 h, the obtained magnetic nanocomposite, Fe₃O₄@SiO₂/DABCO silica was collected by magnetic separation and washed with ethanol.

2.5. Typical procedure for the conversion of benzyl halides to the corresponding benzyl acetates and thiocyanates

To a suspension of alkyl halide (1 mmol) and nucleophilic reagents (NaOAc or KSCN) (2 mmol) in water (5 mL), Fe₃O₄@SiO₂/DABCO (0.225 g) was added and the mixture was stirred at 90 °C for the lengths of time shown in Table 1. After completion of the reaction as indicated by TLC [using n-hexane/ethyl acetate (5:1)], the reaction was allowed to cool to room temperature and the magnetic catalyst was concentrated on the sidewall of the reaction vessel using an external magnet. The reaction mixture residue was poured into water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated in vacuo to give the product in 74% to 91% isolated yields.

3. Results and discussion

Recently, we focused on developing novel PTC systems for organic transformations [24–28] and also successfully performed the one-pot synthesis of pyran annulated heterocyclic compounds in water with nanomagnetic double-charged diazoniabicyclo[2.2.2]octane dichloride silica hybrid (Fe₃O₄@SiO₂/DABCO). Supported nanocomposite (Fe₃O₄@SiO₂/DABCO) was prepared using Fe₃O₄ spheres as the core and the positively double-charged organic-inorganic hybrid silica as the shell (Scheme 1) [29].

In the continuation of our study about developing novel PTC systems for organic transformations, herein, we decided to use Fe₃O₄@SiO₂/DABCO as a new magnetic phase transfer system for the facile preparation of benzyl acetates and thiocyanates in water by nucleophilic substitution reaction (Scheme 2).

![Scheme 1. Synthesis of Fe₃O₄@SiO₂/DABCO.](image1)

![Scheme 2. Postulated roles of Fe₃O₄@SiO₂/DABCO in the nucleophilic substitution.](image2)

![Fig. 1. The FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂/DABCO and BPTDABCOCl.](image3)
First, the Fe$_3$O$_4$@SiO$_2$/DABCO was prepared according to our reported method as shown in Scheme 1. The catalyst has been characterized by scanning electron microscope (SEM), vibrating sample magnetometer (VSM), thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (see the Supplementary Materials for Figs. S1–S3), Fourier transform infrared spectroscopy (FT-IR) (Fig. 1), X-ray diffraction (XRD) (Fig. 2), transmission electron microscopy (TEM) (Fig. 3) and by their comparisons with that of authentic sample. The loading of the catalyst was calculated by TGA analysis (Fig. S3a). The amount of DABCO is 0.5 mmol per gram in Fe$_3$O$_4$@SiO$_2$/DABCO. The FT-IR analysis of Fe$_3$O$_4$@SiO$_2$/DABCO exhibits basic characteristic peak at approximately 580 cm$^{-1}$, which was attributed to the presence of Fe–O stretching vibrations. The presence of peaks at 440, 780 and 990 to 1200 cm$^{-1}$ were most probably due to the symmetric and asymmetric stretching vibrations of framework and terminal Si–O groups. The C–H stretching peaks at 1200 to 1500 and 2870 to 3040 cm$^{-1}$ in the Fe$_3$O$_4$@SiO$_2$/DABCO spectra indicate that the magnetic particles are successfully coated by double-charged diazoniabicyclo[2.2.2]octane chloride silica hybrid. A band at 1465 cm$^{-1}$ is characteristic for the tertiary amine group.

The degree of crystallinity of magnetic iron oxide (Fe$_3$O$_4$) in the synthesized Fe$_3$O$_4$@SiO$_2$/DABCO was obtained from XRD measurement (Fig. 2). According to the database of the Joint Committee on Powder Diffraction Standards (JCPDS; JCPDs, 19-629), the XRD pattern of a standard Fe$_3$O$_4$ crystal with spinel structure has six characteristic peaks at 2$\theta$ = 30.5°, 35.8°, 43.4°, 53.8°, 57.5°, and 63.1° [30]. The pattern of Fe$_3$O$_4$@SiO$_2$/DABCO displays are most intense at 2$\theta$ = 35.83. This line, which corresponds to pure Fe$_3$O$_4$ [31], confirms its presence. It is also apparent that the results of the analysis of Fe$_3$O$_4$@SiO$_2$/DABCO fit the pattern exhibited by standard magnetite. Therefore, it can be concluded that the obtained Fe$_3$O$_4$@SiO$_2$/DABCO show spinel structure and these modifications don’t cause a phase change in Fe$_3$O$_4$ [14].

TEM micrographs provide more accurate information on the particle size and morphology of immobilization silica parts on the magnetic surface. An image of the composite displays dark MNP cores surrounded by an amorphous silica layer (Fig. 3). In order to investigate the possible catalytic properties of Fe$_3$O$_4$@SiO$_2$/DABCO in the nucleophilic substitution reaction, the reaction of benzyl halides with acetate anion in water was chosen. Examination of the catalytic activity catalyst indicated that the use of 2 equiv of NaOAc in the presence of Fe$_3$O$_4$@SiO$_2$/DABCO (0.225 g) in water at 100 °C is the best condition for the conversion of benzyl halides to the corresponding benzyl acetates (Scheme 2; Table 1).$^{1}$H NMR spectra of the crude products clearly showed the formation of acetates and no evidence for the hydrolysis of benzyl halides to the alcohols was observed, which proved that the reactions proceeded cleanly. On the other hand, in the absence of Fe$_3$O$_4$@SiO$_2$/DABCO, the reaction was sluggish and, even after prolonged reaction time, a considerable amount of starting material remained.

### Table 2
Nucleophilic substitution reaction of benzyl halides with thiocyanate anions in water catalyzed by Fe$_3$O$_4$@SiO$_2$/DABCO hybrid.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Benzyl halide</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Cl</td>
<td>SCN</td>
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<td>3</td>
<td>Cl</td>
<td>SCN</td>
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</tr>
<tr>
<td>4</td>
<td>Cl, OMe</td>
<td>SCN</td>
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<td>5</td>
<td>Me, Cl</td>
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<td>7</td>
<td>Br, Cl</td>
<td>SCN</td>
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<td>83</td>
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<tr>
<td>8</td>
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<td>SCN</td>
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<td>80</td>
</tr>
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<td>9</td>
<td>O$_2$N, Cl</td>
<td>SCN</td>
<td>2</td>
<td>81</td>
</tr>
</tbody>
</table>

Moreover, the reaction mixture was contaminated with alcohol. This observation was confirmed with the presence of alcohol on the TLC plate.

With these promising results in hand and establishing the advantages of Fe₃O₄@SiO₂/DABCO as a phase-transfer catalyst, we focused our attention on another nucleophilic substitution reaction, the conversion of benzyl halides to the corresponding thiocyanates (Scheme 2; Table 2).

This catalyst acted very efficiently and, in all cases, a very clean reaction was observed. It is noteworthy that no evidence for the formation of by-products such as alcohols or isothiocyanates was observed and the products were obtained in pure form without further purification. ¹³C resonance of the −SCN and −NCS groups at ~111 and ~145 ppm, respectively, are very characteristic for thiocyanate and isothiocyanate functionalities [14].

The structures of all of the benzyl acetate and thiocyanate products were determined from their analytical and spectral (IR, ¹H and ¹³C NMR) data and by direct comparison with authentic samples (Fig. S4). The high polarity of the catalysts (double-charged silica-based hybrid xerogel containing the 1-azonia-4-azabicyclo[2.2.2]octane, DABCO, chloride group) and the ability to solubilize both organic and inorganic compounds can result in enhanced reaction rates and provide higher selectivity compared with conventional methods.

As shown in Tables 1 and 2, the compounds with both electron donating and withdrawing groups approximately participated in the nucleophilic reaction with equal efficiency. Thus, the nature and position of substitution in the aromatic ring did not affect the reactions much. The meta-substituted aromatic, as well as the sterically hindered ortho-substituted aromatic aldehydes, both undergo condensation reaction without any difficulty.

It is worthy to note that Fe₃O₄@SiO₂/DABCO does not suffer from extensive mechanical degradation after operating and could be quantitatively recovered without filtration since the Fe₃O₄@SiO₂/DABCO was rapidly concentrated as soon as an external magnet was set close to the sidewall of the reaction vessel. The residual catalyst was washed with water and methanol and dried, then immediately reused for the next run. The recovered resin was reused four times for the nucleophilic substitution reaction of benzyl bromide with thiocyanate anion. The results showed that the catalyst does not reveal any loss in its activity and produced benzyl thiocyanate in 88%, 85%, 84% and 84% yield, respectively.

4. Conclusion

In the present work, the performance of Fe₃O₄@SiO₂/DABCO as a solid–liquid phase-transfer catalyst for nucleophilic substitution reactions of benzyl halides in water was investigated. The catalytic system can combine the advantages of homogeneous and heterogeneous catalysts and therefore they can be selective, reactive and recyclable. In conclusion, we have developed an easy to operate, safe and cost-effective method for the preparation of benzyl acetates and thiocyanates in water by nucleophilic substitution.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.07.040.

References
