Facile Preparation and Reactivity of Magnetic Nanoparticle-Supported Hypervalent Iodine Reagent: A Convenient Recyclable Reagent for Oxidation

Chenjie Zhu^a and Yunyang Wei^{a,*}

^a School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

Fax: (+86)-25-8431-7078; phone: (+86)-25-8431-5514; e-mail: ywei@mail.njust.edu.cn

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Abstract: A simple three-step preparation of magnetic nanoparticle-supported (diacetoxyiodo)benzene starting from 4-iodobenzoic acid is described. The nanoparticle reagent was obtained with good loading levels and has been successfully used for efficient oxidation of a wide range of alcohols. The supported reagent demonstrated comparable activity with that of its homogeneous counterpart (diacetoxyiodo)benzene and could be simply recycled with the assistance of an external magnet.

Keywords: alcohols; aldehydes; hypervalent iodine compounds; oxidation; supported catalysts

In recent years, hypervalent iodine compounds have been used extensively for a variety of chemical transformations and particularly as reagents in several oxidation reactions.^[1] As a result of their non-toxic nature, affordability, and safety profile, hypervalent iodine compounds are nowadays popular reagents for the formation of carbon-carbon bonds, carbon-heteroatom bonds, and heteroatom-heteroatom bonds. Activation of carbon-hydrogen bonds, rearrangements, and fragmentations can be also induced by these reagents. Despite the synthetic importance of hypervalent iodine compounds, their broader application has been restricted due to the low atom economy, because the use of stoichiometric amounts of hypervalent iodine reagents leads to the production of equimolar amounts of organic iodine waste, such as PhI, which is difficult to recover and reuse because of the high volatility and solubility in organic solvents. A possible solution would be the development of catalytic systems based on hypervalent iodine.^[2] Another is the application of recyclable reagents, whose by-products can be efficiently separated from reaction mixtures and reused.^[3] Taking PhI(OAc)₂ as an example to address the recovery issue, many highly efficient strategies have been used to immobilize this reagent onto various supports such as organic and inorganic polymers $(\mathbf{a}-\mathbf{d})$,^[4] perfluorous alkyl chains (\mathbf{e}) ,^[5] and ionic liquids (\mathbf{f}, \mathbf{g}) ^[6] (Figure 1). However, substantial decreases in activity (or efficiency) of these immobilized reagents are frequently observed due to the heterogeneous nature of these support materials in reaction media. Furthermore, in many instances recovery of heterogenized reagents through filtration is cumbersome, especially in the case of air-sensitive or high toxicity products. To overcome the low reactivities of heterogeneous recyclable hypervalent reagents, soluble recyclable alternatives having comparable reactivities to $PhI(OAc)_2$ have also been developed by the groups of Kita,^[7a,b] Togo,^[7c] and Zhdankin.^[7d]

On the other hand, magnetite or maghemite $(Fe_3O_4/\gamma - Fe_2O_3)$ nanoparticles (MNP) have drawn considerable attention as heterogeneous catalytic supports for their good stability, high surface area and easy synthesis.^[8] The direct use of MNP without modification as magnetically recoverable catalysts for organic reactions has also been explored.^[9] An attractive feature of MNP-supported catalysts is that they can be easily separated with the aid of an external magnet, thus facilitating easy catalyst recycling without using extra organic solvents and additional filtration steps.^[10] In addition, crystalline nanoparticles with appropriate surface coatings are readily dispersible in organic solvents and catalysts are usually immobilized on the surface of nanoclusters. Reactants in solution have easy access to the active sites on the surface of nanoparticles, avoiding the problems encountered in many heterogeneous support matrixes where a great portion of the catalysts are present deep inside the matrix backbones and reactants have



Figure 1. Examples of supported PhI(OAc)₂ reagents.

only limited access to the catalytic sites. Furthermore, the magnetically functionalized reagents often show identical and sometimes even higher activity than their corresponding homogeneous analogues due to the high accessible surface area.^[11]

To the best of our knowledge, no example of a magnetic nanoparticle-supported hypervalent iodine reagent has been reported. Therefore, we envisaged that use of MNP as a support would properly address the efficiency issues in hypervalent iodine reagents by providing a readily recyclable and reusable oxidant with reasonably high activity. In continuation of our efforts to develop new applications of hypervalent iodine reagents,^[12] here, we would like to report our exploration of the design of MNP-supported PhI(OAc)₂ and its application in oxidation of alcohols.

MNP-supported $PhI(OAc)_2$ (3; MNP-PIDA) was synthesized according to the procedure shown in Scheme 1. Organic silane groups were chosen for immobilization of PhI complexes to the surface of magnetite nanoparticles because silanes were known to have a large affinity for under-coordinated surface sites of metal oxide particles.^[13] Reaction of 3-aminopropyltriethoxysilane with 4-iodobenzoic acid using diisopropylcarbodiimide (DIC) in combination with 1-hydroxybenzotriazole (HOBt) afforded 1 in excellent yields. Polyvinylpyrrolidone (PVP, average MW: 40,000)-protected magnetic nanoparticles of 8-20 nm were prepared by coprecipitation of iron(III) and iron(II) ions in basic solution following the published procedure.^[14] The obtained MNP were sonicated for one hour before being treated with excess 1 in anhydrous toluene under reflux. Subsequent oxidation to derivative 3 was accomplished using freshly prepared peracetic acid at 40°C overnight. The loading of 3 is 0.68 mmol/g as determined by elemental analysis. Using a similar strategy, SiO₂-supported PhI(OAc)₂ (5; SiO_2 -PIDA) was also prepared for the purpose of comparison.

The MNP-PIDA (3) and SiO₂-PIDA (5) were characterized by FT-IR spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), vibrating



Scheme 1. Synthesis of the MNP-supported $PhI(OAc)_2$ (3) and SiO_2 -supported $PhI(OAc)_2$ (5).

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Figure 2. TEM images of MNP-PIDA (3): (*left*) before reaction and (*right*) after reusing 8 times.

sample magnetometer (VSM), thermogravimetric analysis (TG-DTG) and elemental analysis.^[15] Unfortunately, due to the magnetic properties of 3 it is actually impossible to further characterize this material by using solid state NMR spectroscopy.^[16] From the transmission electron microscopy (TEM) analyses of MNP-PIDA 3, it was confirmed that well separated nanoparticles with a size distribution ranging from 8 to 20 nm were homogeneously dispersed over the entire area (Figure 2, *left*), such polydispersity is expected from of the protocol chosen for the synthesis of magnetic nanoparticles. Note that the particles showed slight aggregation after 8 times recycling (Figure 2, right), presumably because the moieties on the MNP surfaces are less effective in preventing the aggregation of the MNP (upon solvent evaporation). However, powder X-ray diffraction (XRD) indicated that the final MNP-PIDA was oxidized from magnetite (Fe₃O₄) to maghemite (γ -Fe₂O₃),^[15] on the basis of the calculations with the Debye-Scherrer formula, the mean grain size of maghemite was 18.3 nm, which is consistent with the TEM images. The magnetic properties of MNP-PIDA were determined by vibrating sample magnetometer (VSM), the magnetization curve of MNP-PIDA exhibited typical superparamagnetic behavior, showing no observed hysteresis (Figure 3). The saturation magnetization value (σ_s) is 51.32 emu/g. The value is slightly smaller than that of bulk magnetite (92 emu/g), which is probably due to the increasing amount of non-magnetic material (organic ligands) on a particle surface which makes a larger percentage of the particle mass non-magnetic. However, this value is sufficiently high for magnetic separation. The final MNP-PIDA is well dispersed in common organic solvents and can be efficiently attracted with a small magnet.

In order to check the efficiency of MNP-PIDA, the known PIDA/TEMPO oxidation system was selected.^[17] The MNP-PIDA was then tested for the oxidation of a wide range of alcohols, including benzylic, allylic, heterocyclic, alicyclic, and aliphatic alcohols. As shown in Table 1, most alcohols underwent oxida-



Figure 3. Magnetization curve of MNP-PIDA measured at room temperature.

tion to afford the corresponding aldehydes or ketones in excellent yield. The present protocol afforded aldehydes from primary alcohols and ketones from secondary alcohols. Excellent chemoselectivity was observed under the present system. We detected no phenol oxidation products (Table 1, entry 6), which are well known to form in reactions with aryl- λ^3 -iodanes.^[18] In the oxidation of primary alcohols to the corresponding aldehydes, no signs of any over-oxidation to their carboxylic acids, even after prolonged reaction times, were detected. An allylic alcohol such as cinnamyl alcohol (Table 1, entry 9) was also oxidized efficiently without any observable reaction at the double bond functionality. In the present research benzylic alcohols underwent smooth oxidation (Table 1, entries 1–7). The electronic properties of the substituents in the aromatic ring had A relatively minor influence on the oxidation of alcohols (Table 1, entries 2 and 4). Strong electron-withdrawing groups, such as nitro group, improve the oxidation of alcohol (Table 1, entry 2). Strong electron-donating groups, such as the OCH_3 group, lowered the reaction rate (Table 1, entry 4). This is different from previously reported procedures where the OCH3 group favors alcohol oxidation.^[19] Heteroaryl alcohols such as 2furyl, 2-thienyl, and 3-pyridinyl alcohols also gave good yields (Table 1, entries 11–13). It is worth mentioning that together with the good results with benzylic, allylic and heteroaryl alcohols, the yields obtained from the reaction of aliphatic alcohols under the same conditions are also quite high (Table 1, entries 15 and 16). In view of the fact that the reaction of an aliphatic alcohol is much more difficult than the reaction of a benzylic alcohol, the results obtained with the present procedure were very satisfactory.

As can be seen in Table 1, the use of SiO_2 -PIDA (5) instead of MNP-PIDA (3) in the oxidation of alco-

Entry	Alcohols	Products	System ^[a]	Time [h]	Yield [%] ^[b]
1	ОН	0	A B	1.0 2.0	94 92
2	O ₂ N OH	O ₂ N O	A B	0.5 1.5	96 90
3	СІОН	CI CI	A B	1.0 2.0	94 90
4	ОН		A B	2.5 4.0	90 87
5	ОН		A B	1.0 2.0	92 88
6	НОСОН		A B	1.0 1.5	93 91
7	ОН		A B	2.0 3.0	95 92
8	ОН		A B	4.0 5.0	90 86
9	ОН		A B	1.5 2.0	96 93
10	ОН	0	A B	4.0 6.0	88 80
11	ОН	↓ ↓ ↓ ↓ ↓ ↓	A B	3.0 5.0	91 87
12	С	⟨s↓o	A B	2.0 4.0	88 81
13	С ОН N	(N O	A B	2.0 4.0	93 90
14 ^[c]	ОН	o − o	A B	5.0 7.0	78 70
15 ^[c]		Ŭ ())4	A B	4.0 6.0	88 82
16 ^[c]	∕ t∕)₅ OH	<u>∕</u> √ <u>√</u> 5 0	A B	5.0 7.0	85 79

^[a] Oxidation system A: MNP-PIDA/TEMPO, B: SiO₂-PIDA/TEMPO.

^[b] Yields of isolated products unless otherwise noted.

^[c] Yields were determined by GC-MS.

hols led to similar results, albeit a longer reaction time was needed. For a comparison of the activities of **3**, **5**, and PhI(OAc)₂, the experiments on the reaction rate were carried out using benzyl alcohol as the model substrate. The MNP-PIDA showed excellent activity toward the oxidation of alcohol, which is comparable to that of its homogeneous counterpart PhI(OAc)₂, as presented in Figure 4. Although the activity of **3** is a little lower than that of its homogeneous counterpart, probably due to steric and diffusion rate differences, the relative activity of **3** seems to be extraordinarily higher than that of SiO₂-PIDA (**5**), suggesting the importance of a nanosized support. This is because when the size of the support materials is decreased to the nanometer scale, the surface area of nanoparticles will increase dramatically. For example, spherical nanoparticles of 10 nm diameter have a calculated surface area of $600 \text{ m}^2 \text{ cm}^{-3}$, which is comparable to that of many porous supports for reagent immobilization. As a consequence, nanoparticle supports could have a higher loading capacity than many other conventional support matrixes, leading to the improved activity of the nanoparticle-supported reagents. Another and far more important reason for this phenomenon is that the nanometer-sized supports will even be dispersible in solution, forming an emul-



Figure 4. Comparison of the oxidation activities of PIDA, MNP-PIDA and SiO₂-PIDA.



Figure 5. (1) Reaction mixture containing MNP-PIDA; (2) MNP-PIDA collected using an external magnet after the reaction.

sion (see Figure 5), therefore, the present nanomagnet-supported reagent 3 can be regarded as a "quasi-homogeneous" reagent.

Table 2 shows the results of the competitive oxidation of primary and secondary alcohols. The competing oxidation of an equimolar mixture of benzyl alcohol and 1-phenylethanol resulted in a 92% yield of benzaldehyde and less than 5% yield of acetophenone (Table 2, entry 1). Oxidation of an equimolar mixture of octan-1-ol and octan-2-ol gave 85% caprylic aldehyde, whereas no ketone could be detected (Table 2, entry 2). These results suggest that the chemoselective oxidation of a primary alcoholic functionality in the presence of a secondary alcoholic functionality is possible with the present oxidation system.

Product separation and recycling of the MNP-PIDA were indeed quite easy and simple (see

 Table 2. Competitive oxidation of primary and secondary alcohols.^[a]

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Entry	Substrate	Product	Time [h]	Yield [%] ^[b]
1	ОН	0	1	92 +
2	+ \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow	+ 0 $+$ 0 $+$ 0 $+$ 0	4	85 + -

^[a] The reactions were carried out on a 1:1 mixture of primary and secondary alcohols, on a 1 mmol scale.

^[b] GC-MS yield.

Figure 5). After the reaction, the organic layer was simply decanted, assisted by a nearby magnet, to afford the desired products. The MNP-PIDA was quickly concentrated to the side wall of the reaction vial once a magnet is placed nearby. The separated MNP-PIDA was then washed and regenerated by treatment with peracetic acid. The reusability of the reagent was investigated by the oxidation of benzyl alcohol. The procedure was repeated and the results indicated that the reagent could be recycled for 8 times with no apparent loss of acitivity (Figure 6). TEM shows that the MNP-PIDA still maintained the nanostructure after repeated reuse, proving its robustness (Figure 2). More importantly from the point of view of an application, it is possible to remove the reagent completely after the reaction. This aspect was checked by the following experiment. During the reaction, the MNP-PIDA was attracted to the bottom of the reactor by the application of a magnetic field. Then, about half of the supernatant was transferred to a new reactor. The solution was averagely divided into two sections S1 (without MNP-PIDA) and S2 (containing MNP-PIDA). The conversion of the alco-



Figure 6. Recycling esperiments for the oxidation of benzyl alcohol.

hol in S1 and S2 was 27% *via* GC-MS. After an additional one hour, the conversions of the alcohol in S1 and S2 were 29% and 91%, respectively. These experiments prove that the MNP-PIDA can be almost completely separated from the reaction solution. This could be further supported by the fact that only 0.8% loss of weight in MNP-PIDA was observed after eight times recycling. The possibility for recovery of the MNP-PIDA by magnetic decantation is clearly advantageous in comparison to conventional filtration protocols for SiO₂-PIDA which, in our experience, always go along with some loss of weight.

In conclusion, we have prepared MNP-PIDA as a first maghemite nanoparticles-supported hypervalent iodine reagent. The prepared MNP-PIDA allowed the oxidation of alcohols to aldehydes or ketones in excellent yields and high selectivity without remarkable over-oxidation to carboxylic acids. It is noteworthy to mention that the reagent could easily be recycled and reused without loss of activity. This new reagent can be regarded as a readily available alternative or as a complement to the known supported hypervalent iodine reagents.

Experimental Section

General Methods

¹H NMR spectra were obtained with TMS as internal standard in CDCl₃ using a Bruker DRX 500 (500 MHz) spectrometer. GC-MS were recorded on a Thermo Trace DSQ GC-MS spectrometer using a TRB-5MS $(30 \text{ m} \times 0.25 \text{ mm} \times$ 0.25 µm) column. ESI-MS were recorded on a Thermal Finnigan TSQ Quantum ultra AM spectrometer using a TRB-5MS ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) column. The shape and surface morphology of the samples were examined on a scanning electron microscope (SEM) (Hitachi S-3400N, Japan). Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2010 instrument. X-ray diffraction (XRD) images were obtained from a Rigaku D/max-2400PC instrument with Cu Ka radiation. Elemental analysis was performed on an Elementar Vario MICRO spectrometer. Magnetic measurements of particles were made using a vibrating sample magnetometer (Lake Shore 7410). Thermogravimetric analysis was carried out in nitrogen using a Shimadzu TGA-50 spectrometer. IR spectra were recorded on a Nicolet IS10 spectrometer. Silica gel (60-100 mesh) was dried at 200°C for 5 h before use. All solvents used were strictly dried according to standard operations and stored over 4 Å molecular sieves. All other chemicals (AR grade) were obtained from commercial resources and used without further purification.

Synthesis of Compound 1

To a stirred solution of 4-iodobenzoic acid (1.24 g, 5.0 mmol) in CHCl₃ (20 mL) was added 3-aminopropyltriethoxysilane (1.11 g, 5.0 mmol), diisopropylcarbodiimide (0.63 g, 5.0 mmol), 1-hydroxybenzotriazole (0.68 g, 5.0 mmol), and the solution was stirred at room temperature for 12 h. After completion, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 3/1) to give the product **1**; yield: 2.08 g (92%). ¹H NMR (500 MHz, CDCl₃): δ = 7.99 (s, 1 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.51 (d, *J* = 8.5 Hz, 2 H), 3.82 (q, *J* = 7.0 Hz, 6 H), 3.41–3.45 (m, 2 H), 1.71–1.77 (m, 2 H), 1.21 (t, *J* = 7.0 Hz, 9 H), 0.68– 0.71 (m, 2 H).

Synthesis of PVP-Stabilized Magneitite Nanoparticles

 $FeCl_3 \cdot 6H_2O$ (11.0 g, 40.7 mmol) and $FeCl_2 \cdot 4H_2O$ (4.0 g, 20.4 mmol) were dissolved in 60 mL deionized water under nitrogen gas with vigorous stirring at 85°C. The pH value of the solution was adjusted to 9 by addition of concentrated NH₃·H₂O. After 4 h, the magnetite precipitates were washed to pH 7 by deionized water. The black precipitate was collected with a permanent magnet under the reaction flask, and the supernatant was decanted. The sediment was re-dispersed in 50 mL of deionized water. The PVP aqueous solution (5.0 mL, 25.6 g/L) was added, and the mixture stirred for 1 day at room temperature. The PVP-stabilized magnetite nanoparticles were separated by addition of aqueous acetone (H₂O/acetone = 1/10, v/v) and centrifugation at 10000 rpm for 5 min. The supernatant solution was removed, and the precipitated particles were washed by ethanol twice. The particles were dried under vacuum.

Synthesis of MNP-PIDA (3)

1.0 g of PVP-stabilized magneitite nanoparticles was dispersed in 30 mL dry toluene by sonication for 1 hour. Compound 1 (1.35 g, 3.0 mmol) was then added. The reaction mixture was refluxed under nitrogen gas for 3 days. After being cooled to room temperature, the products were sedimented on a magnet and washed successively with dry toluene ($50 \text{ mL} \times 3$) and dry acetone ($50 \text{ mL} \times 2$), then dried under vacuum. Acetic anhydride and hydrogen peroxide solution (30%) were mixed in a 2:1 ratio and stirred for 5 h at 40 °C. This peracetic acid solution was added to the compound 2 (about 20 mL per gram) at 40 °C and the mixture stirred overnight. After reaction, the product was collected by a magnet and washed with toluene. The loading of 3 is 0.68 mmolg⁻¹ as determined by elemental analysis.

Synthesis of SiO₂-Supported PhI(OAc)₂ (5)

Silica gel (60–100 mesh) was dried at 200 °C for 5 h before use. Then 1.0 g of active silica was dispersed in 30 mL dry toluene by sonication for 1 hour. Compound **1** (1.35 g, 3.0 mmol) was then added. The reaction was refluxed for 3 days under nitrogen gas. After being cooled to room temperature, the products were collected by filtration and washed successively with dry toluene (50 mL×3) and dry acetone (50 mL×2). The obtained powder was then dried under vacuum. After completion, a similar work-up procedure was followed as mentioned above to afford **5**. The loading of **5** is 0.53 mmolg⁻¹ as determined by elemental analysis.

Oxidation of Alcohols by MNP-PIDA

Reagent 3 (1 mmol) was added to a solution of alcohol (1 mmol) and TEMPO (0.01 g, 0.05 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature and monitored by gas or thin-layer chromatography. After completion, 3 was collected at the side of the flask using a small magnet, and the supernatant carefully decanted. Particles were then washed and regenerated by treatment with peracetic acid. The organics were concentrated under vacuum to yield the corresponding carbonyl compound.

Oxidation of Alcohols by SiO₂-PIDA

Reagent 5 (1 mmol) was added to a solution of alcohol (1 mmol) and TEMPO (0.01 g, 0.05 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature and monitored by gas or thin-layer chromatography. After completion, 5 was collected by filtration for reuse. The filtrate was evaporated to give the corresponding carbonyl compound.

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