Silver/manganese dioxide nanorod catalyzed hydrogen-borrowing reactions and tert-butyl ester synthesis

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Abstract
Silver/manganese dioxide (Ag@MnO2) nanorods are synthesized and characterized by scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray powder diffraction, and X-ray photoelectron spectroscopy. It was discovered that Ag@MnO2 nanorods can realize hydrogen-borrowing reactions in high yields and are also effective for the synthesis of tert-butyl esters from aryl cyanides and tert-butyl hydroperoxide in a short period of time. Mechanistic experiments revealed that this catalytic system acts as a Lewis acid in hydrogen-borrowing reactions, while the synthesis of tert-butyl esters occurs through a radical pathway. This is the first report on the excellent catalytic activity of Ag@MnO2 nanorods as a catalyst.

Keywords
alkylation, dehydrogenation, hydrogen-borrowing, nanoparticle, nanorod

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Introduction
Hydrogen-borrowing methodology, also known as hydrogen auto-transfer, is a powerful strategy for reduction reactions that avoids using molecular hydrogen directly and the synthesis of complexes using other reactions.1–3 This methodology has been developed for many years as a useful tool in synthetic organic chemistry.4 It also provides a sustainable and cost-effective approach for the synthesis of substituted amines and ketones, which are important groups in many bioactive molecules (Figure 1), without the need for toxic alkyl halides or borohydrides.5 It has been demonstrated that transition-metal complexes are effective catalysts for hydrogen-borrowing reactions, as are noble and non-noble metals.6–15 Besides, biocatalysts, such as known enzymes and Aspergillus oryzae, are also used in hydrogen-borrowing reactions along with the development of enzymes.16 Although some homogeneous noble metals are effective catalysts, there are catalyst-product separation and recycling issues involved in the use of these catalytic systems. Therefore, heterogeneous catalysts with recyclability have been developed such as supported catalysts. Our group has engaged in developing heterogeneous catalysts for dehydrogenation and hydrogen-borrowing reactions that are recyclable, such as polymer Zr-CIA,17 POP-Ir,18 Cu(binap)I,19 TTA-Au-NG,20 NQ-MR,21 and Au@HT.22 However, some catalytic systems are effective as catalysts, but demonstrate poor recyclability and stability, for example, catalysts with noble metal cores, such as iridium and gold, while others have reduced catalytic ability after several cycles. Inspired by this, we decided to study nanorods as heterogeneous catalysts in hydrogen-borrowing reactions and in the synthesis of tert-butyl esters, a functional group present in many natural products, polymers, and pharmaceuticals.23 Nanoparticles, in the form of nanorods, are novel sustainable nano catalysts that solve many issues in modern synthesis and catalysis.24,25 Such nano catalytic systems have effective active sites and usually demonstrate much better catalytic performance and good recovery characteristics.26 Manganese oxides (MnO2) nanorods are known as inexpensive and nontoxic materials, which can be used as...
environmentally friendly catalysts.\textsuperscript{27–30} A recent survey of manganese oxide (MnO\textsubscript{2}) nanorods indicates that when incorporating noble metals, for example, Pt, Au, and Ag, the nano particles have improved activity. In addition, Ag nano particles have been shown to have outstanding ability as catalyst in many organic reactions.\textsuperscript{30–33} Based on our recent discoveries on hydrogen-borrowing reactions\textsuperscript{34–38} and the properties of manganese oxides (MnO\textsubscript{2}) nanorods and Ag nanoparticles, we herein report the synthesis and application of Silver/manganese dioxide (Ag@MnO\textsubscript{2}) nanorods as a catalyst, which has higher catalytic activity after several cycles and which is much cheaper than other catalysts. The Ag@MnO\textsubscript{2} nanorods are characterized by several physical techniques. This synthetic catalytic system was successfully utilized in hydrogen-borrowing reactions and for the synthesis of tert-butyl esters.

**Results and discussion**

**Characterization of the Ag@MnO\textsubscript{2} nanorod**

The supported Ag@MnO\textsubscript{2} nanorods were synthesized by a hydrothermal method\textsuperscript{39} and were characterized through scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The SEM and TEM images in Figure 2 reveal that silver nanoparticles are supported on \(\alpha\)-MnO\textsubscript{2} nanorods. The morphologies and structural characteristics of the Ag@MnO\textsubscript{2} nanorods could be observed diametrically by SEM and TEM. As shown in Figure 2, it is clearly observed that the surface of the MnO\textsubscript{2} nanorods is coated with many small silver particles. The EDS images revealed a peak at 2.93 keV demonstrating that metallic silver nanoparticles are present on the MnO\textsubscript{2} nanorods (Figure 3).

Figure 4 shows the X-ray diffraction patterns of the synthetic \(\alpha\)-MnO\textsubscript{2} and Ag@MnO\textsubscript{2}. By comparing to previous

**Figure 1.** Examples of biologically active amines.

**Figure 2.** (a) and (b) SEM images of Ag@MnO\textsubscript{2}. (c) and (d) TEM images of Ag@MnO\textsubscript{2}.
The XRD pattern of Ag@MnO$_2$ revealed the presence of α-MnO$_2$ (JCPDFS 44-0141) and metallic silver (JCPDFS 87-0597). There is no Ag, AgO x, or other silver oxide species’ diffraction signal, which may reveal good dispersion of silver particles on the surface of α-MnO$_2$. From the two patterns delineated in Figure 4, the diffraction peaks at 38.12°, 44.28°, 64.43°, and 81.54° were assigned to the (111), (200), (220), and (222) crystal faces of silver indicating that silver nanoparticles had been successfully supported on the α-MnO$_2$ nanorods.

The chemical composition and surface chemical states of the Ag@MnO$_2$ composite were also examined by XPS. Four elements (C, Ag, Mn, and O) were identified from the full-survey-scan spectrum of the Ag@MnO$_2$ composite (Figure 5(a)). The Ag 3d spectrum shows two obvious peaks located at 368.1 eV for Ag 3d$_{3/2}$ and 374.2 eV for Ag 3d$_{5/2}$, with a spin energy separation of 6.1 eV, which explains that silver is present in the metallic state.

Catalytic activity. In order to test the catalytic activity of the Ag@MnO$_2$ nanorods, the classical hydrogen-borrowing reaction between benzyl alcohol (1a) and aniline (2a) was selected (Table 1). After a series of experiments, it was found that Ag@MnO$_2$ revealed catalytic activity in toluene (entry 8), with only small amount of the target product, N-benzylaniline (3a) produced in solvents such as EtOAc, DCM, and MeOH (Table 1, entries 1–7), which indicates that there may be a similar solvent effect to our previous work.$^{37,38}$ Besides, compared to room temperature and 60 °C, it was observed that this reaction produced a higher yield at 110 °C (Table 1, entries 8 and 9). This result may disclose that it has a slightly higher energy barrier. Further screenings showed that N-benzylniline (3a) is obtained in a higher yield by replacing Na$_2$CO$_3$ with NaOH as the base (Table 1, entries 9–13). It seems that the stronger the alkalinity is, the higher the isolated yield of N-benzylniline (3a) is. Therefore, the optimal conditions are as follows: Ag@MnO$_2$ as the catalyst, NaOH as the base, and at reflux in toluene.

Having established the optimum reaction conditions, the substrate scope of this hydrogen-borrowing reaction was explored. As shown in Table 2, all of the results are similar to the previous work,$^{43}$ different amines and alcohols could be employed, and it was found that this transformation was not influenced to any great extent by donating or withdrawing groups on the aromatic ring of the amine substrates such as methoxy (–OCH$_3$), hydroxyl (–OH), chloro (–Cl), bromo (–Br), and fluoro (–F) (Table 2, 3a–c and 3e–h). However, for the alcohol substrates, a benzyl alcohol containing the electron-withdrawing group, chloro (–Cl) (Table 2, 3l) gave a lower yield than examples with an electron-donating group such as methyl (–CH$_3$) and methoxy (–OCH$_3$) (Table 2, 3j and 3k). Comparing the yields of 3b, 3c, and 3g, there was no apparent steric hindrance effect in this reaction. A substrate with a heteroatom, 2-aminopyridine (Table 2, 3d), could also be tolerated in this transformation. In addition, furfuryl alcohol (Table 2, 3o) and alkyl 1-substituted products 3i, 3m, and 3n were isolated in good-to-high yields.
Considering the importance and application of tert-butyl esters in organic synthesis,23 the reaction of aryl cyanides with tert-butyl hydroperoxide (TBHP) using the Ag@MnO2 catalytic system was explored. A range of phenylacetonitriles and TBHPs containing electron-rich or electron-deficient groups were employed. The desired products were obtained through C–CN bond cleavage and esterification in good to excellent yields and the results are summarized in Table 3. Phenylacetonitrile derivatives bearing electron-rich groups, like methoxy, methyl, and hydroxyl, reacted smoothly and were transferred into the corresponding esters 6a, 6b, 6g, and 6h in high yields, while the substrates containing electron-withdrawing groups, such as nitro, bromo, and chloro, were also converted into desired products in moderate-to-high yields (6d–f and 6i–k). Comparing the yields of 6f and 6i, it was found that the ortho-substituted arylacetanilide substrate produced a slightly lower yield of the desired product, which indicated that a weak steric hindrance effect might exist in this reaction. Similar results were also observed by comparing 6e, 6j, and 6k, with the yields being slightly lower for meta- and ortho-substituted substrates. To our surprise, tert-amyl hydroperoxide and (2-hydroperoxypropan-2-yl)benzene could also be converted into the corresponding esters 6n and 6o, respectively, in high yields. A substrate with a hydroxy group, 4s, was also compatible providing an excellent yield of product 6g.

Control experiments and activity explorations

To gain further insight into the mechanism, control experiments were performed (Scheme 1). Therefore, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was used in the Ag@MnO2 nanorod catalyzed reactions as a radical scavenger, and the experiments revealed that nearly the same yields of the desired products were obtained. However, totally different results were observed for the reaction of arylcyanide 4a, with TBHP. Therefore, these control experiments imply that radicals are not involved in the hydrogen-borrowing reaction, but that they are involved in the synthesis of tert-butyl esters.

Based on these experiments and the work of other groups,33–35 we propose a tentative mechanism for the hydrogen-borrowing reaction (Scheme 2). First, the alcohol is oxidized to an aldehyde via dehydrogenation by the Ag@MnO2. At the same time, a silver-hydride complex is formed by hydride coordination. Next, the aldehyde condenses with the amine to form imine. Finally, the imine intermediate is reduced to give the target product.

Table 1. Optimization of reaction conditions.a,b

| Entry | Solvent | Base          | T (°C) | Yield (%)b |
|-------|---------|---------------|--------|------------|
| 1     | Toluene | Na2CO3        | rt     | 13         |
| 2     | EtOAc   | Na2CO3        | rt     | <5         |
| 3     | DCM     | Na2CO3        | rt     | <5         |
| 4     | MeOH    | Na2CO3        | rt     | <5         |
| 5     | Et2O    | Na2CO3        | rt     | <5         |
| 6     | DMF     | Na2CO3        | rt     | <5         |
| 7     | DCE     | Na2CO3        | rt     | <5         |
| 8     | Toluene | Na2CO3       | 110    | 21         |
| 9     | Toluene | Na2CO3       | 110    | 56         |
| 10    | Toluene | NaOH          | 110    | 88         |
| 11    | Toluene | Cs2CO3        | 110    | 81         |
| 12    | Toluene | K2CO3         | 110    | 67         |
| 13    | Toluene | NaOAc         | 110    | 73         |

Table 1: Optimization of reaction conditions.a,b

DCM: dichloromethane; DMF: dimethylformamide; DCE: dichloroethane.

*Conditions: 1a (0.5 mmol), 2a (0.75 mmol), catalyst (10 mg), base (1.0 mmol), solvent (3.0 mL), and 12 h.

*Isolated yields.
Table 2. Substrate scope experiments.\textsuperscript{a,b}

|   |   |   |
|---|---|---|
|   |   |   |

\textsuperscript{a}Conditions: 1 (0.50 mmol), 2 (0.75 mmol), Ag@MnO\textsubscript{2} (10 mg), NaOH (0.75 mmol), toluene (3.0 mL), 12 h, and 110 °C.

\textsuperscript{b}Isolated yields.

II could be oxidized by TBHP to form intermediate III. The target ester is finally obtained through the attack of tert-butyl alcohol on III.

Recyclability of the catalyst

Recycling the Ag@MnO\textsubscript{2} nanorods was explored by repeating the hydrogen-borrowing reaction of benzyl alcohol (1a) and aniline (2a). The Ag@MnO\textsubscript{2} nanorods were separated conveniently by centrifugation, followed by washing with EtOH and H\textsubscript{2}O, and then vacuum freeze-drying for 12 h. Subsequent experiments with the recovered catalyst revealed that only slightly lower yields of product 3a were achieved over five cycles (Figure 6).

To help explain these observations involving the Ag@MnO\textsubscript{2} nanorod catalyst, SEM studies on recycled nanorod catalyst showed that the recovered catalyst had excellent stability (Figure 7).

**Conclusion**

In conclusion, we have reported the synthesis and application of Ag@MnO\textsubscript{2} nanorods, which have been characterized through SEM, TEM, EDX, XRD, and XPS. This synthetic catalytic system was successfully applied in hydrogen-borrowing reactions and for the synthesis of tert-butyl esters in moderate-to-high yields. Further investigation on the application of this catalyst in other reactions systems is in progress.

**Experimental**

**Synthesis of Ag@MnO\textsubscript{2}**

The α-MnO\textsubscript{2} nanorods were synthesized by hydrothermal method according to the reported procedure. Next, 400 mg of α-MnO\textsubscript{2} nanowires and 130 mg of PVP (polyvinyl
Table 3. Expansion of the substrate scope of arylcyanides with hydroperoxides.$^{a,b}$

| R     | R² | Product | Yield (%) |
|-------|----|---------|-----------|
| MeO   |     | 6a       | 86%       |
| O₂N   |     | 6d       | 87%       |
| HO    |     | 6g       | 94%       |
| Br    |     | 6j       | 79%       |
| Cl    |     | 6l       | 80%       |
| OMe   |     | 6h       | 88%       |
| Br    |     | 6k       | 81%       |
| O      |     | 6m       | 89%       |
| O      |     | 6n       | 82%       |
| O      |     | 6o       | 91%       |

$^a$Conditions: 4 (1.0 mmol), 5 (3.0 mmol), Ag@MnO₂ (10 mg), KOH (3.0 mmol), CH₃CN (3.0 mL), 60 °C, and 1.5 h.
$^b$Isolated yields.

Scheme 1. Control experiments.

Scheme 2. The proposed reaction pathway.

pyrrolidone) were added to 100 mL of EG (ethylene glycol). The obtained suspension was transferred to a 250 mL round-bottom flask and kept under vigorous stirring at 90 °C for 20 min. Then, NaBH₄ (1.0 mmol) and 2 mL of 0.1 M AgNO₃ (aq., 5%) solutions were sequential added to the reaction flask. This mixture was kept under vigorous
stirring for another 12 h to produce Ag@MnO₂ (Ag: 5% w/w), which were washed three times with ethanol (15 mL) and water (15 mL) by successive rounds of centrifugation at 7000 r/min for 8 min and removal of the supernatant. Finally, the product was dried under vacuum condition.

Scheme 3. A possible reaction mechanism for the synthesis of the tert-butyl esters.

General procedure for synthesis of 3a. To 20-mL colorimetric tube was added 1a (46.5 mg, 0.5 mmol), 2a (81 mg, 0.75 mmol), Ag@MnO₂ nanorod catalyst (10 mg), NaOH (30.0 mg, 0.75 mmol), and toluene (3.0 mL). The mixture was refluxed in air for 12 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product N-benzylaniline (3a). Colorless oil (80.5 mg, 88%), 1H NMR (400 MHz, CDCl₃) δ 7.34–7.24 (m, 4H), 7.23–7.17 (m, 1H), 7.11 (t, J = 7.8 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 7.8 Hz, 2H), 4.26 (s, 2H), 4.07–3.81 (m, 1H); 13C NMR (101 MHz, CDCl₃) δ 148.2, 139.5, 129.3, 128.7, 127.5, 117.6, 112.9, 48.4.

General procedure for synthesis of 6a. To 20 mL colorimetric tube was added 4a (147.1 mg, 1.0 mmol), 5a (270.3 mg, 3.0 mmol), Ag@MnO₂ (10 mg), KOH (168.3 mg, 3.0 mmol), and CH₃CN (3.0 mL). The mixture was stirred at 60 °C for 1.5 h and then cooled to room temperature. After removing the solvent, the resulting residue was directly purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product tert-butyl 4-methoxybenzoate (6a). Colorless oil (178.9 mg, 86%), 1H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 1.51 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 165.6 (s), 163.0 (s), 131.4 (s), 124.6 (s), 113.4 (s), 80.5 (s), 55.4 (s), 28.3 (s).

Declaration of conflicting interests
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Figure 6. Recyclability of the Ag@MnO₂ nanorods in hydrogen-borrowing reactions.

Figure 7. SEM images: (a) fresh Ag@MnO₂ nanorods catalyst and (b) Ag@MnO₂ nanorod catalyst after five runs.
**Supplemental Material**

Supplemental material for this article is available online.

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