Research Paper



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

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Huanhuan Luo¹, Yike Yang^{1,2}, Bobin Yang¹, Zhaojun Xu¹ and Dawei Wang¹

Abstract

Silver/manganese dioxide $(Ag@MnO_2)$ 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 $Ag@MnO_2$ 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 $Ag@MnO_2$ nanorods as a catalyst.

Keywords

alkylation, dehydrogenation, hydrogen-borrowing, nanoparticle, nanorod

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High catalytic activity, Easy recyclability

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 hydrogenborrowing reactions along with the development of enzymes.¹⁶ Although some homogeneous noble metals are

¹Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, P.R. China

²Department of Criminal Science and Technology, Henan Police College, Zhengzhou, P.R. China

Corresponding author:

Dawei Wang, Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P.R. China Email: wangdw@jiangnan.edu.cn

Creative Commons Non Commercial CC BY-NC: This article is distributed under the terms of the Creative Commons Attribution-NonCommercial 4.0 License (https://creativecommons.org/licenses/by-nc/4.0/) which permits non-commercial use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en-us/nam/open-access-at-sage). 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]₂,¹⁹ 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



Figure 1. Examples of biologically active amines.

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 environmental friendly catalysts.^{27–30} A recent survey of manganese oxide (MnO₂) 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.³⁰⁻³³ Based on our recent discoveries on hydrogen-borrowing reactions³⁴⁻³⁸ and the properties of manganese oxides (MnO₂) nanorods and Ag nanoparticles, we herein report the synthesis and application of Silver/manganese dioxide (Ag@MnO₂) nanorods as a catalyst, which has higher catalytic activity after several cycles and which is much cheaper than other catalysts. The Ag@MnO₂ nanorods are characterized by several physical techniques. This synthetic catalytic system



Figure 2. ((a) and (b)) SEM images of Ag@MnO₂. ((c) and (d)) TEM images of Ag@MnO₂.



Figure 3. EDS images of Ag@MnO₂.

was successfully utilized in hydrogen-borrowing reactions and for the synthesis of *tert*-butyl esters.

Results and discussion

Characterization of the Ag@MnO, nanorod

The supported $Ag@MnO_2$ nanorods were synthesized by a hydrothermal method³⁹ 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 α -MnO₂ nanorods. The morphologies and structural characteristics of the Ag@MnO₂ nanorods could be observed diametrically by SEM and TEM. As shown in Figure 2, it is clearly observed that the surface of the MnO₂ 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 MnO₂ nanorods (Figure 3).

Figure 4 shows the X-ray diffraction patterns of the synthetic α -MnO₂ and Ag@MnO₂. By comparing to previous wok,^{40–42} the XRD pattern of Ag@MnO₂ revealed the presence of α -MnO₂ (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 -MnO₂. 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 -MnO₂ 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



Figure 4. XRD pattern of Ag@ MnO2.

peaks located at 368.1 eV for Ag 3d3/2 and 374.2 eV for Ag 3d5/2, 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@MnO₂ 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@MnO₂ 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-benzylaniline (3a) is obtained in a higher yield by replacing Na₂CO₂ with NaOH as the base (Table 1, entries 9–13). It seems that



Figure 5. (a) XPS wide-scan spectrum of $Ag@MnO_2$ and (b) high-resolution spectrum of Ag.

Table 1. Optimization of reaction conditions.^{a,b}

\bigcirc	ОН +	∠NH₂ Ag@MnC solv	02, base	N H
1a	2a		-	3a
Entry	Solvent	Base	T (°C)	Yield (%)⁵
1	Toluene	Na ₂ CO ₃	rt	13
2	EtOAc	Na ₂ CO ₃	rt	<5
3	DCM	Na_2CO_3	rt	<5
4	MeOH	Na_2CO_3	rt	<5
5	Et ₂ O	Na_2CO_3	rt	<5
6	DMF	Na ₂ CO ₃	rt	<5
7	DCE	Na_2CO_3	rt	<5
8	Toluene	Na_2CO_3	60	21
9	Toluene	Na ₂ CO ₃	110	56
10	Toluene	NaOH	110	88
11	Toluene	Cs ₂ CO ₃	110	81
12	Toluene	K ₂ CO ₃	110	67
13	Toluene	NaOAc	110	73

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

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

^bIsolated yields.

the stronger the alkalinity is, the higher the isolated yield of *N*-benzylaniline (**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 (-OCH₃), 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, 31) gave a lower yield than examples with an electrondonating group such as methyl (-CH₃) and methoxy (-OCH₃) (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, 30) and alky 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 arylacetonitrile 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 60, 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@ MnO_2 nanorod catalyzed reactions as a radical scavenger, and the experiments revealed that nearly the same yields of



^aConditions: I (0.50 mmol), **2** (0.75 mmol), Ag@MnO₂ (10 mg), NaOH (0.75 mmol), toluene (3.0 mL), 12 h, and 110 °C. ^bIsolated yields.

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.

As for the reaction of the arylcyanide with TBHP, we inferred from the control experiment that it proceeded via a

radical pathway. Although the exact mechanism is still unclear, based on the literature^{33,34} and the control experiments, we have proposed a tentative mechanism (Scheme 3). According to the previous work,³⁵ it is possible to generate *tert*-butoxyl and *tert*-butylperoxy radicals in this system. Intermediate radical I might then be generated, which is able to form the intermediate II by trapping TBHP. Intermediate 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 $Ag@MnO_2$ nanorods was explored by repeating the hydrogen-borrowing reaction of benzyl alcohol (1a) and aniline (2a). The $Ag@MnO_2$ nanorods were separated conveniently by centrifugation, followed by



Table 3. Expansion of the substrate scope of arylcyanides with hydroperoxides.^{a,b}.

^aConditions: **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. ^bIsolated yields.





Scheme I. Control experiments.

Scheme 2. The proposed reaction pathway.

washing with EtOH and H_2O , 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_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@MnO₂ 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



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



Figure 6. Recyclability of the Ag@MnO $_2$ nanorods in hydrogen-borrowing reactions.

moderate-to-high yields. Further investigation on the application of this catalyst in other reactions systems is in progress.

Experimental

Synthesis of Ag@MnO₂

The α -MnO₂ nanorods were synthesized by hydrothermal method according to the reported procedure.³⁹ Next, 400 mg of α -MnO₂ nanowires and 130 mg of PVP (polyvinyl 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.

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, 127.3, 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



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

1.5h and then cooled to room temperature. After removing the solvent, the resulting reside 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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ORCID iD

Dawei Wang (D) https://orcid.org/0000-0001-9327-7487

Supplemental Material

Supplemental material for this article is available online.

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