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MnOx/catechol/H₂O: a cooperative catalytic system for aerobic oxidative dehydrogenation of N-heterocycles at room temperature

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Keywords: manganese oxide, recyclable catalyst, oxidative dehydrogenation, cooperative catalysis



Graphic abstract:

Abstract: Amorphous manganese oxide doped by Na⁺ ion (Na-AMO) was successfully prepared and found to be an efficient heterogeneous catalyst in aerobic oxidative dehydrogenation of N-heterocycles, cooperate with catachol. Na-AMO was fully characterized by XRD, XPS

BET H_2 -TPR, CO₂-TPD FT-IR, TEM, SEM and had rich amounts of surface absorbed active oxygen species which are responsible for superior catalytic performance. The synergistic interaction between Na-AMO and catechol makes catalytic system efficient and tolerant, which offers various N-heterocycles in good to excellent yields under mild conditions.

1. Introduction

Unsaturated N-containing heterocycles are key structural motifs in many pharmaceutical and bioactive compounds.[1] Besides, they are important intermediates in organic synthesis for providing late-stage functionalized products.[2] Many processes have been developed for the synthesis of N-heterocycles liking quinoline, quinazoline, indole, pyridine and cridine, mainly include intermolecular cyclization and intramolecular dehydrogenation.[3-7] Gradually, oxidative dehydrogenation of these N-heterocycles has developed as an important and efficient pathway. In recent years, homogeneous catalysts and heterogeneous catalysts both were developed, while photoredox catalysis and electrochemical process were proved to be successful means. [8-18] Especially, Beller and Stahl with their co-workers respectively prepared novel iron- and cobalt-based catalysts for aerobic oxidative dehydrogenation of nitrogen heterocycles with good yields.[19] Very recently, Shi's group synthesized a metal-free single-active site heterogeneous catalyst via oxidative polymerization of derivatives for maleimide selective oxidation of N-containing heterocycles. [20] Although these catalytic systems show merits of heterogeneous catalysis, toxic organic solvents, high reaction temperature. Therefore, employing catalytic systems non-noble recyclable metal catalyst, green reaction media and mild reaction conditions are desirable. Amorphous manganese oxide (AMO) composed by disordered [MnO₆] units has been applied in electrocatalysis, environmental catalysis and clean organic synthesis because of its relatively large surface area, increased numbers of active sites and rich amounts of surface oxygen species compared with crystalline MnO₂. [21-24] So far, aerobic oxidative dehydrogenation of N-heterocycles catalyzed by Mn-based materials is less explored. For instance, Suib's group reported a mesoporous MnOx-catalyzed oxidative dehydrogenation of N-heterocycles in DMF and they found that AMO was less efficient for the oxidative dehydrogenation. [25] From the viewpoint of a green

and environmental perspective, design and development of MnOx-based catalytic system being able to proceed oxidative dehydrogenation of N-heterocycles under mild conditions in green solvent are highly desirable.

According to the work from Stahl, Kobayashi and Doris, bioinspired metalloenzyme-like cooperative systems involving a transition metal and a suited catechol derivative could generate a synergistic effect which conducted oxidative dehydrogenation of N-heterocycles under ambient conditions. [26-29] It was reported that catechol molecules or oxidized counterparts (o-quinone) played a role as redox-active organic catalysts and transition-metal-based materials promoted the in-situ reoxidation of hydroquinones to finish the catalytic cycle. Interestingly, we recently found that Na-modified AMO (designated as Na-AMO) could efficiently catalyze catechol Q-2 to quinone Q-22 (table1,Q-22) since we demonstrated manganese oxide octahedral molecular sieve (OMS-2) had catalytic activity for the oxidation of catechols for the synthesis of benzoxazoles.[30] These results indicated there was a possibility that AMO-based material and a suitable catechol compound could make up a cooperative co-catalytic system for oxidative dehydrogenation of N-heterocycles under mild conditions.

In continuation of our previous research for application of MnOx-based materials in oxidative catalytic system, [31] we would like to report a cooperative catalytic system comprised by Na-doped AMO and 4-tert-butylcatechol for oxidative dehydrogenation of N-heterocycles. The co-catalytic process tolerated a wide range of N-heterocycles and could carry out the reactions in H_2O as the solvent at room temperature.

2. Experimental

2.1 Catalyst Preparation

Na-AMO. Firstly, KMnO₄ (5.89 g, 37.27mmol) was dissolved into 100 mL of deionized water and the solution was stirred until KMnO₄ was fully dissolved at slightly elevated temperature less than 50 °C if necessary. Then, MnSO₄ · H₂O (8.8 g, 52.06mmol) and NaNO₃ (1.55 g, 18.23mmol) were dissolved into 30 mL of deionized water. The KMnO₄ solution was dropwise added into MnSO₄ solution at room temperature

and the resulted mixed solution was kept stirring for another 10 minutes. Finally, the black suspension liquid was filtrated and washed. The filter cake was dried at 150° C under air for 12 h. Eventually, black power was obtained as the target catalyst Na-AMO.

2.2 The general procedure of oxidative dehydrogenation

N-heterocycle substrate (0.2 mmol), Na-AMO (20 mg, 10 mol%), catechol Q-2 (3.3 mg, 0.02 mmol) was added into a reaction tube. The reaction tube was filled and protected with oxygen using a O₂ balloon, then H₂O was added into the reaction tube with a syringe. The reaction was allowed to react at room temperature for 20 hours. After completion of reaction, the resulting mixture was filtered, washed with EtOAc and extracted by EtOAc. The organic phases were combined, washed with brine and dried with Na₂SO₄. Next, organic solution was concentrated under reduced vacuum to give the crude product. Finally, the product was purified by silica gel chromatography to yield the pure product_o

3. Results and discussion

We combined substituted catechols or quinone compounds (Q-1 to Q-6,Q-22) and MnO_x to test the catalytic activity. As expected, AMO with Q-1 showed a little catalytic activity in the reaction in EtOH when air was used as the oxidant (Table 1, entry 1). According the examination of substituted catechols Q-1 to Q-5 and 1,10-phenanthroline-5,6-dione Q-6, it was found that the co-catalysts affected the reaction obviously and Q-2 was proved to be the most suitable one in the cooperative catalytic system (Table 1, entries 1-6). After that, manganese oxide-based materials were investigated to further improve the reaction, which showed that manganese oxide octahedral molecular sieves (OMS-2), its H-modified counterpart (H-OMS-2) and commercial bulk MnO₂ all did not offer better results of the reactions (Table 1, entries 7-9). Interestingly, Na-doped AMO using NaNO₃ as the dopant provided 76% yield of 2a (Table 1, entry 10). Furthermore, it was found that both oxygen and hydrogen peroxide as the green oxidant could improve the yield of **2a** to 95%, (Table 1, entries **11** and **12**). Compared to O_2 , H_2O_2 has the disadvantage of handing hazard, so we chose molecular oxygen as environmentally acceptable oxidant. At the same time, the reaction was

proved to be aerobic because the poor result was obtained when the reaction was carried out under N_2 (table1 entry 11). Subsequently, many solvents including biomass-derived dimethyl carbonate (DMC), DMF, dichloromethane (DCM), toluene and the greenest water, were tested in the reaction and the results showed that the reaction could occur smoothly in H_2O with complete conversion and nearly quantitative yield (Table 1, entries **13-17**).

Further optimization demonstrated that decreasing the reaction time slightly lowered the yields of the reaction (table1 entry18). Then we changed the ratio of Na-AMO/Q-2 and found that the yields was susceptible to the amount of Q-2(table1 entry 13, 19 and 20,23). in addition, the changes in Na-AMO had slightly impact to the yields (table1 13, 21 and 22,23). Na-AMO (10mol%) and Q-22(5mol%) seemed best condition(table1 19), but a poor yield was attained in gram scale reaction (table1 entry 24). So we chose entry 13 (table1) as optimal reaction condition. As a result, the environmentally-friendly catalytic system for the oxidative dehydrogenation of 1a was established as following: Na-AMO as the catalyst, catechol Q-2 as the co-catalyst, O_2 as the oxidant and H_2O as the reaction media.

Table 1 optimization of reaction condition



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2	AMO	Q-2	EtOH	air	67		
3	AMO	Q-3	EtOH	air	31		
4	AMO	Q-4	EtOH	air	8		
5	AMO	Q-5	EtOH	air	56		
6	AMO	Q-6	EtOH	air	14		
7	OMS-2	Q-2	EtOH	air	58		
8	H-OMS-2	Q-2	EtOH	air	41		
9	a-MnO ₂	Q-2	EtOH	air	57		
10	Na-AMO	Q-2	EtOH	air	76		
11	Na-AMO	Q-2	EtOH	O ₂	95 (35°)		
12 ^d	Na-AMO	Q-2	EtOH	H_2O_2	95		
13	Na-AMO	Q-2	DCM	O ₂	95		
14	Na-AMO	Q-2	DMC	O ₂	34		
15	Na-AMO	Q-2	DMF	O ₂	35		
16	Na-AMO	Q-2	PhMe	O_2	87		
17	Na-AMO	Q-2	H ₂ O	O ₂	98		
18 ^e	Na-AMO	Q-2	H_2O	O_2	85		
19	Na-AMO	Q-2(5)	H_2O	O ₂	95		
20	Na-AMO	Q-2(12.5)	H_2O	O ₂	83		
21	Na-AMO(10)	Q-2	H_2O	O ₂	94		
22	Na-AMO(30)	Q-2	H_2O	O ₂	95		
23	Na-AMO(10)	Q-2(5)	H_2O	O ₂	85		
$24^{\rm f}$	Na-AMO	Q-2(5)	H_2O	O ₂	70		
25 26 27 28 29 30	- - Na-AMO (20) Na-AMO (100) Na-AMO (20)	Q-2(10) Q-2(100) - Q-22 (10)	$\begin{array}{c} {\rm H_2O} \\ {\rm H_2O} \end{array}$	$\begin{array}{c} O_2\\ O_2\\ O_2\\ O_2\\ O_2\\ O_2\\ O_2\\ O_2\end{array}$	N.R. 5 8 8 56 95		

a.Reaction conditios: 1a (0.2 mmol), MnOx (20 mg, 10 mol%), co-catalyst (10 mol%), solvent (1 mL), 20 h, oxidant, room temperature.

b.Yields were determined by ¹HNMR using dibromomethane as theinternal standard.

c. Under N₂.

d. 10 uL of H_2O_2 (30 wt%) was used.

e. For 10 h.

f: reaction was magnified by 100 times; Q-2 (5 mol%)

Na-AMO was proved as best heterogeneous catalyst, which was characterized by XRD, XPS, BET, SEM, TEM, FT-IR, H₂-TPR, CO₂-TPD. First of all, XRD patterns shows that Na-AMO has the same crystal phase to pristine AMO featured typical amorphous structure, composed by disordered [MnO₆] units as (**Fig. 1**). ICP-MS results of Na-AMO indicate that K⁺ ion of Na-AMO was replaced partially by Na⁺ ion, which means Na⁺ doping was successful. Subsequently, the morphologies of the catalysts were probed by scanning electron microscope and transmission electron microscope.(**Fig. S4, S5**)



Figure 1. XRD patters of original AMO, Na-AMO and used Na-AMO.

For getting more information of surface chemical properties of the catalysts, X-ray photoelectron spectroscopy was carried out. As expected, O 1s of pristine AMO could be deconvoluted into two peaks that are surface adsorbed oxygen species (531.6eV) with low coordination and lattice oxygen (529.8eV) for maintaining the catalyst structure, which is agreement with the results of the reference.[24] For O1s of Na-AMO, three kinds of oxygen species (532.9eV, 531.2eV, 529.5eV) These results exhibit that Na-AMO has more amounts of surface oxygen vacancies than AMO does, because surface active oxygen species generally adsorb on the oxygen vacancies (Fig. 2 and Table S1). Accordingly, more abundant of oxygen vacancies of Na-AMO possibly result into superior catalytic activity. On the other hand, Mn 2p of AMO and Na-AMO was analyzed by XPS and they show similar results with three oxidation stage (Mn²⁺,Mn³⁺,Mn⁴⁺) (Fig. S3 and Table S2). To further examine the catalyst composition, FT-IR was used to characterize Na-AMO, as showed in Fig 3. The peaks at 550 cm⁻¹ and 720 cm⁻¹ were attributed to Mn-O and Mn-O-Mn stretching vibration. The peaks during 3200-3500 cm⁻¹ were assigned to stretching vibration of H₂O and OH⁻ and the peak of 1600 cm⁻¹ aroused from bending vibration of H₂O and OH⁻. Abundant surface OH⁻ and H₂O may derive from the break of Mn-O-Mn chain of Na-AMO.[32]





Redox characterization of matarial is crucial For our redox reaction, so we carried out H₂-TPR exeperiment **Fig 4(a)**, there are two peaks located in 294 °C and 380 °C respectively, which means two change of oxidation state may exist in our reaction. The peak of 294 °C could attribute to the trasformation of MnO₂ to Mn₂O₃, and the peak of 380 °C could assign to Mn₂O₃ to MnO.[32] Additionally, the alkalinity of catalyst is helpful to dehydrogenation, so we used CO₂-TPR to evaluate the Alkaline site as showed in **Fig 4(b)** which included two wide peaks located at 360 °C and 460 °C, and a narrow peak in 546 °C. CO₂-TPR means Na-AMO is fulled with Alkaline site which may resulted from introduction of Na⁺.



Figure 4. H₂-TPR spectrum of Na-AMO (a); CO₂-TPD spectrum of Na-AMO (b);

We conducted hot filtration experiment to ensure the true catalyst is Na-AMO itself rather than leached Na⁺ and Mn^{x+} ion. we performed the reaction with tetrahydroquinolines as substrate, Under stardand condition. After one hour, the catalyst was filtrated, and the NMR yield of quinolines was 63%. At the same time, the filtrate was kept reacting for another 19 hour, and no further improvement in yield was detected. Meanwhile, no ion leached was observed when the filtrate analyzed by ICP-MS, which means Na-AMO is completely heterogeneous. Recycling test shows Na-AMO could be reused for at least 8 consecutive times with slightly decreasing yields and the yield was stable at around 87% eventually as show in **Fig. 5**.



With the cooperative catalytic system containing as-synthesized Na-AMO and 4-tert-butylcatechol **Q-2** in hand, a number of N-containing substrates were examined. As shown in Table 2, substituted

tetrahydroquinolines could be tolerated in H₂O and good to excellent yields of corresponding quinolines were obtained under the present reaction conditions (Table2, 2a-2i). Importantly, bio-active 2,3-dihydro-1H-cyclopenta[c]quinoline 2i can be catalyzed by the cooperative Na-AMO/catechol system, which enhances the practicality of the catalytic system. Moreover, substituted quinazolines were obtained in good yields ranging from 60% to 80% by Na-AMO/Q-2 through oxidative dehydrogenation of tetrahydroquinazolines in water (Table 2, 2j-2p). Tetrahydroquinazolines with heteroatom-containing substitute and aliphatic substitute both proceeded very well under the standard conditions. Subsequently, various indolines and 2,3-dihydro-7-azaindole were tested in the reactions (Table 2). Indole and 2-methyl-indole(table2 2r, 2t) were obtained in moderate yields, while 7-azaindole and 80% 2-carboxyindole were isolated in and 90% yields respectively.(table2 2q 2s) More complex tetrahydro- β -carbolines which contain indoline as the main structure also carried out the reactions smoothly, although the yields of desired products were slightly low (Table 2, 2u,2v). In the case of oxidative dehydrogenation of Hantzsch ester compounds, it was found that the reactions hardly occurred at room temperature in pure water. Delightedly, the reactions could work in mixed solvent of EtOH and H₂O (v/v = 1/10) when the reaction temperature was increased to 40 °C, and moderate to excellent yields of desired substituted pyridines were offered (Table 2w-2y). Eventually, polycyclic compound 2z was obtained, which is the key building block for the synthesis of a number of biologically active molecules, such as antiprotozoal agent and phase II topoisomerase inhibitor TAS-103 (Table 2, 2z).[33-34] For tetrahydroisoquinoline, it was found that the elevated temperature was needed and an incomplete dehydrogenation product was provided chemoselectively (Table 2, 2za). And, 9,10-dihedroacridine could participate in water at room temperature and acridine was isolated in 90% yield (Table 2, 2zb)

Table 2The scope of substrate



b.40℃

c. EtOH/H2O(v/v)=1/10.40°C

To gain insight into the reaction mechanism, some control experiments were performed. Firstly, the oxidative dehydrogenation of 1a did not occur at all without manganese oxide and catechol Q-2 (Table 1, entry 25). Then, it was found that trace amounts of desired product 2a were observed when 0.1 equiv. or 1.0 equiv. of Q-2 was used in the absence of manganese oxide (Table 1, entries 26-27). On the other hand, the blank experiments proved that the reaction hardly occurred without Q-2 and O₂ cannot efficiently re-oxidize the reacted Na-AMO that oxidizes 1a at room temperature (Table 1, entry 28). And, the moderate yield of 2a was detected using 100 mg of Na-AMO without Q-2 (Table 1, entry 29). These findings tell that the catalytic specie is manganese oxide and catechol does not play a role as the catalyst for the oxidative dehydrogenation of **1a** in our catalytic system. Moreover, the same yield of 2a was offered when Q-2 was replaced by its oxidation state Q-22 under the standard conditions (Table1, entry 30). Considering results from Table 1, we proposed that catechol Q-2 re-oxidizes reductive Na-AMO and cooperates with Na-AMO as a redox couple.

4. Conclusion

In summary, we have developed an environmentally-friendly catalytic system by the use of Na-doped AMO as heterogeneous catalyst, catechol as co-catalyst, O₂ as terminal oxidant and H₂O as reaction medium for oxidative dehydrogenation of various N-heterocycles. The highly efficient catalytic system that works via the cooperative Na-AMO/catechol redox couple tolerates wild range of substrates and performs the reactions at room temperature. Employing the greenest solution, mild reaction conditions and recyclable catalyst makes this scalable catalytic method potential for industrial application, and we are promoted to apply it in other clean synthesis processes.

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Graphic abstract:



Highlights

1. Heterogeneous oxidative dehydrogenation of N-heterocycles was achieved in water.

2. Na-doped AMO combined with catechol was found to be an efficient catalytic system.

3. A broad of N-heterocycles can be tolerated under the catalytic system.

4. The catalytic system shows merits of green chemistry

The authors declare no competing financial interest