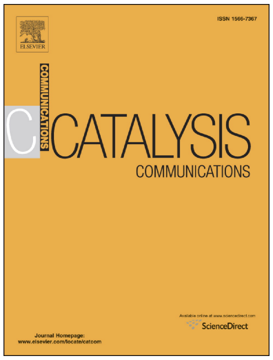

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Base-free synthesis of 1,3,5-triazines via aerobic oxidation of alcohols and benzamidine over a recyclable OMS-2 catalyst

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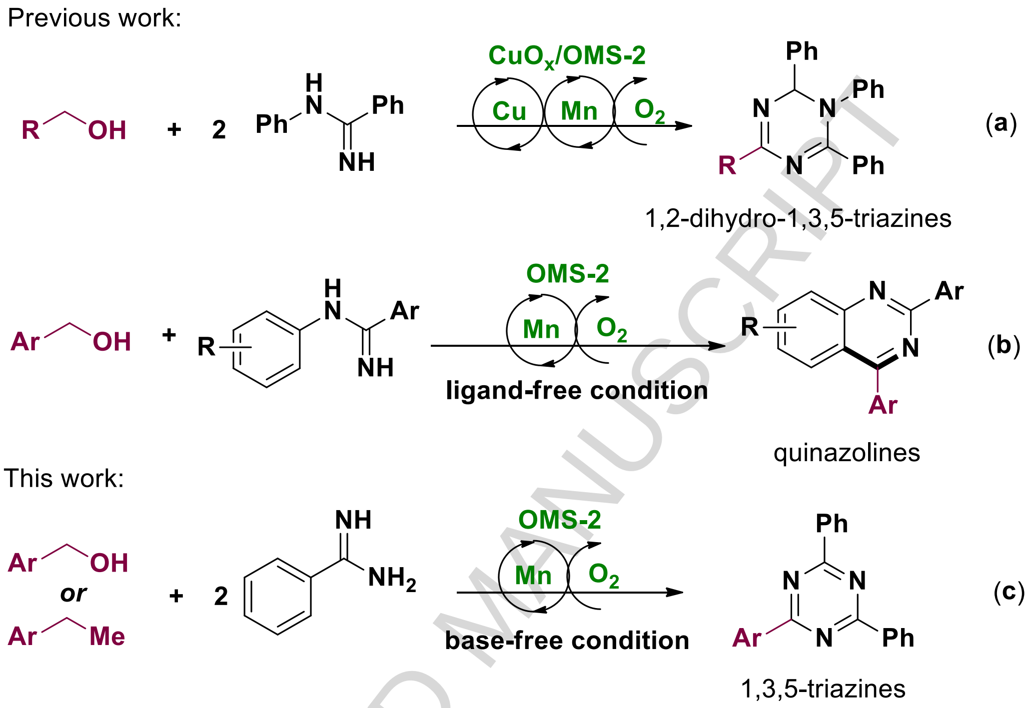
Abstract: By using $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ as a reductant, manganese oxide octahedral molecular sieve (OMS-2) with enhanced surface area and mixed valence was prepared successfully. OMS-2 showed excellent catalytic ability towards aerobic oxidative synthesis of 1,3,5-triazines from benzyl alcohols and benzamidine. Methyl benzenes, DMF and DMSO could also be employed as substrates to react with benzamidine offering triazines under the heterogeneous conditions. The catalytic system features base-free conditions, broad substrate scope, high chemoselectivity, operational simplicity, catalyst recyclability and utilization of O_2 as the green oxidant.

Key word: heterogeneous catalysis, oxidative cyclization, OMS-2, triazine, benzamidine

1. Introduction

1,3,5-triazines, as key skeletons of many important bioactive heterocyclic compounds, frequently present in insecticides, fungicides, herbicides, antimalarial, antitumor and antivirals.[1-3] Meanwhile, due to their chemical properties, they are used in organic dyes, chelating ligands for synthesis of organometallic materials, liquid crystals, electroluminescent materials and fluorescent brighteners.[4-6] Generally, synthesis of 1,3,5-triazines involves cyclotrimerization of nitriles, coupling of halogenated triazines over transition-metal catalysts and specific multicomponent reactions.[7-9] In recent years, amidines were found to be efficient substrates to react with alcohols, aldehydes, amines, DMF, DMSO or toluene for synthesis of 1,3,5-triazines via oxidative pathway.[10-15] However, from the perspective of clean synthesis, very limited reports have been found on the applications of non-noble metals as recyclable catalysts in 1,3,5-triazines synthesis under base- and ligand-free conditions.

Manganese oxide octahedral molecular sieve (OMS-2) containing 2X2 and 1D tunnel structure with a pore size of 0.46 nm is composed by edge- and corner-shared MnO_6 octahedra.[16] Because of its excellent properties, like catalysis, adsorption and semiconductivity, OMS-2 has been applied in organic synthesis, environmental catalysis, separation and batteries.[17-21] Especially, it generally exhibits mixed-valence of Mn (Mn^{4+}, Mn^{3+} and Mn^{2+}), which makes it superior heterogeneous catalyst and support in many aerobic oxidations through tuning the ratio of mixed-valent manganese to accelerate electron transfer during redox process.[22-26] Our group recently developed methods for preparation of OMS-2 to further prepare supported catalyst or directly use it as the catalyst in N-containing heterocycles synthesis under ligand- and additive-free conditions. And, chemoselective synthesis of 1,2-dihydro-1,3,5-triazine and quinazolines from alcohols and N-arylamidines via establishment of certain catalytic systems was realized (Scheme 1, a and b).[27,28] Very recently, we prepared OMS-2 successfully using $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ as a reductant via reduction of $KMnO_4$ (denoted as OMS-2-SH-A). Synthesized OMS-2-SH-A which exhibited obviously enhanced surface area and amounts of Mn^{2+} compared with OMS-2 prepared by conventional reflux method was found to be a highly efficient catalyst for oxidation of benzyl alcohols. As shown in Scheme S1 (see ESI), the catalytic system could tolerate various substrates and excellent conversions and yields were obtained when the reactions were carried out in toluene at 110 ^{o}C under O_2.



Scheme 1. OMS-2-based catalytic systems for the oxidative synthesis of heterocycles using amidines as substrates.

With our continuous research interest in clean synthesis of heterocycles over MnO_x-based catalysts,[29-31] we would like to describe a procedure for synthesis of OMS-2 material using relatively safe and stable H_2O_2 trapped reagent, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, as the reductant via reduction of $KMnO_4$. After full characterization, obtained OMS-2 catalyst shows larger surface area and more amounts of Mn^{2+} than OMS-2 synthesized by conventional procedure. Importantly, as-synthesized material is an efficient recyclable catalyst for the aerobic oxidative synthesis of 1,3,5-triazines from benzamidine and alcohols via in-situ formed aldehydes. Furthermore, toluene and its derivatives were directly employed as substrates replacing alcohols to yield desired products over the synthesized catalyst (Scheme 1, c).

2. Experimental

2.1. Catalyst preparation

OMS-2-SH material was synthesized by the reduction of $KMnO_4$. Firstly, a mixture of KOAc (2.5 g, 25 mmol), acetic acid (2.5 mL) and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ was stirred at room temperature to generate a buffer solution. The solution of $KMnO_4$ (3.25 g, 20 mmol) was added dropwisely into the buffer solution with stirring at room temperature. Subsequently, the brown mixture was kept stirring at 100 ºC for 24 h under air. The reaction mixture was cooled down and filtrated followed by washing with deionized water. Lastly, the obtained solid material was dried at 120 ºC for overnight to yield the OMS-2-SH catalyst. The obtained OMS-2-SH catalysts were named OMS-2-SH-A, OMS-2-SH-B, OMS-2-SH-C and OMS-2-SH-D, when $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ was added in 7, 5, 3.5 and 1.75 g respectively into the buffer solution.

2.2. Typical procedure for the synthesis of 1,3,5-triazine 3a

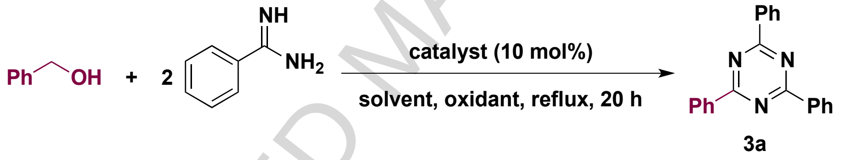
OMS-2-SH-B (20 mg, 10 mol%), benzyl alcohol (0.3 mmol) and benzamidine (0.5 mmol) were added into a Schlenk tube. Then, air was removed and toluene (1 mL) was added by a syringe under O_2 atmosphere. If substituted benzyl alcohol was liquid, it was added with toluene under O_2 balloon protection. If methyl benzene was used as substrate instead of benzyl alcohol, it was added as solvent (1 mL) into the reaction tube by syringe under O_2 atmosphere. The mixture was stirred for required time at certain temperature for 20 hours. The resulting mixture was cooled down, filtered and washed with EtOAc, and concentrated under reduced pressure to give the crude product. Finally, the product was purified by silica gel chromatography to yield the pure product.

3. Results and discussion

Due to the excellent catalytic performance of OMS-2-SH-A in oxidation of benzyl alcohol (Scheme S1, in ESI), we firstly used it as the catalyst to optimize the reaction between benzyl alcohol and benzamidine in toluene under reflux conditions (Table 1). Initially, the reaction results prove that OMS-2-Re made by conventional method and its supported catalyst Cu/OMS-2-Re both failed the reaction by the use of air as the oxidant (Table

1, entries 1 and 2). Delightedly, 45% yield of **3a** was isolated when OMS-2-SH-A was used as the catalyst (Table 1, entry 3). According to changing the oxidant, O_2 was the best green oxidant and 85% yield of **3a** was obtained (Table 1, entries 3-5). These results imply that the method for preparation of catalyst has significant influence. In addition, it was found that decreasing the reaction temperature was deleterious to the reaction. The precursors of OMS-2 were also tested in the reaction under the standard conditions, while the reactions did not occur at all (Table 1, entries 6 and 7). Subsequently, different solvents were used in the reaction at their reflux temperatures and only dimethyl carbonate (DMC), PhCl and $MeNO_2$ yielded **3a** more or less (Table 1, entries 8-15). Therefore, non-proton and non-polar solvents and reaction temperature were important factors for the success of the oxidative cyclization. Hence, the optimized reaction condition is as shown in Table 1, entry 4.

Table 1. Optimization of reaction conditions[a]



Entry	Catalyst	Solvent	Oxidant	Yield of **3a** (%)[b]
1	OMS-2-Re	toluene	air	0
2	Cu/OMS-2-Re	toluene	air	0
3	OMS-2-SH-A	toluene	air	45
4	OMS-2-SH-A	toluene	O_2	85 (48[c])
5	OMS-2-SH-A	toluene	H_2O_2	0
6	$KMnO_4$	toluene	O_2	0
7	$MnSO_4$	toluene	O_2	0
8	OMS-2-SH-A	DMC	O_2	28

9	OMS-2-SH-A	EtOH	O_2	0
10	OMS-2-SH-A	DEC	O_2	0
11	OMS-2-SH-A	2-Me-THF	O_2	0
12	OMS-2-SH-A	DMSO	O_2	0
13	OMS-2-SH-A	chlorobenzene	O_2	15
14	OMS-2-SH-A	dioxane	O_2	0
15	OMS-2-SH-A	$MeNO_2$	O_2	40

[a] Reaction conditions: benzyl alcohol (0.3 mmol), phenyl amidine (0.5 mmol), catalyst (10 mol%; for OMS-2-based catalyst, 20 mg was used), solvent (1 mL), 20 h, under air or O_2 balloon. [b] Isolated yields. [c] At 90 ^{o}C.

To further optimize the catalytic reaction, the catalysts synthesized using different amounts of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ were investigated (Figure 1). It was found that OMS-2-SH-B showed the best catalytic ability (95% yield of **3a**) and it exhibited the second largest surface area (114 m^2/g). However, OMS-2-SH-D with the highest surface area (220 m^2/g) only offered 15% yield of 1,3,5-triazine **3a** under the optimal conditions. Characterization of catalysts via X-ray diffraction (XRD) demonstrates that OMS-2-SH-A, OMS-2-SH-B, and OMS-2-SH-C all possessed typical and pure cryptomelane phase (JCPDS 29-1020) while OMS-2-SH-D possessed birnessite phase (JCPDS 80–1098, Scheme S2, in ESI). So, the results from XRD imply that too less amounts of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ was not enough to reduce $KMnO_4$ and ordered cryptomelane phase and MnO_6 units cannot form, which makes OMS-2-SH-D the largest surface area. The added loadings of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ not only affected the surface areas, but also crystallinity of the final catalysts, such as OMS-2-SH-B has the largest surface area and relatively weaker crystallinity. Compared with OMS-2-Re (surface area is 67 m^2/g), catalysts prepared involving $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ all show much larger surface area and stronger crystallinity (Table S1, in ESI). From our experimental results of **3a** synthesis (Figure 1), it is believed that large surface area usually means more exposed surface reactive sites which are critical in catalysis and different crystal phases of solid catalysts always influence the catalytic activity.[32]

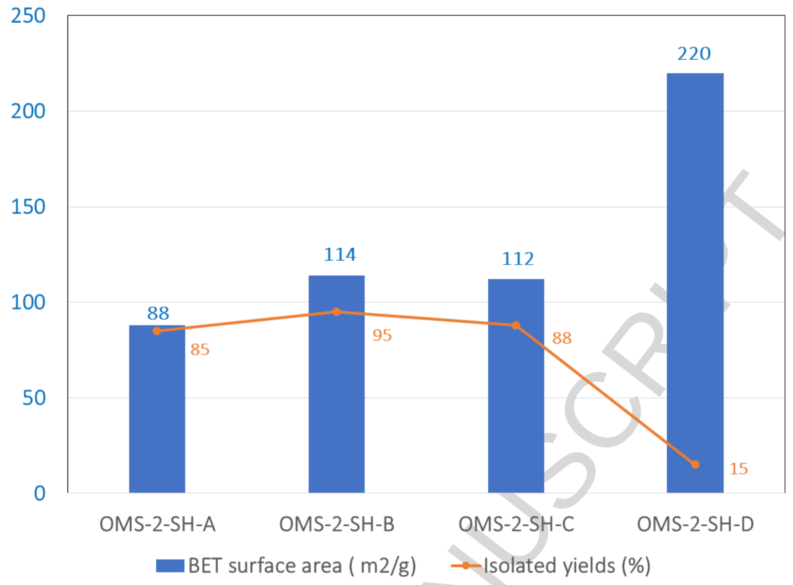


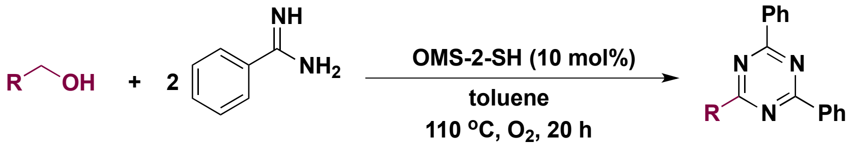
Figure 1. The influence of surface area of the catalysts on the catalytic performance.

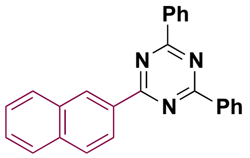
Characterization of as-synthesized catalysts was also performed by SEM and TEM. From the SEM images, we found that added loadings of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ could significantly affect the morphologies of catalysts. Obviously, OMS-2-SH-B shows longer, thinner and more uniform, while OMS-2-SH-A is thicker and OMS-2-SH-C is shorter (Scheme S3, in ESI). In addition, compared with OMS-2-Re possessing short rod-like morphology, OMS-2-SH-B possesses long fiber-like morphology (Scheme S5, in ESI). Especially, OMS-2-SH-D does not have fiber-like morphology and is composed by small flakes (Scheme S3 and S12, in ESI). Similarly, difference of morphologies of as-synthesized catalysts was confirmed by TEM images (Scheme S4, in ESI). From the analysis of EDX, there are not Na ions existed in catalysts prepared by $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ and only K ions are detected clearly, which indicates that manganese oxide was formed by MnO_6 unites with K ions in tunnel to stabilize the structure (Scheme S6, in ESI). These results from morphologies are in agreement with the information of XRD very well.

Subsequently, the surface chemistry of obtained catalysts was studied by X-ray photoelectron spectroscopy (XPS). The catalysts synthesized with $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ possess very similar oxygen species from analysis of O 1s (Scheme S8 and Table S3, in ESI). On the other hand, all catalysts synthesized with $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ show mixed-valence of Mn as the same as OMS-2-Re (Scheme S7, in ESI). It is obvious to find out that the method of catalyst preparation and the added loadings of $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ affect the ratio of mixed-valence of manganese. Specifically, OMS-2 catalysts prepared with $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ all possess lower amounts of Mn^{4+} than OMS-2-Re does. Among as-synthesized OMS-2 in this study, OMS-2-SH-B possesses the lowest amounts of Mn^{4+} and highest amounts of Mn^{2+} (Table S2, in ESI). Low amounts of Mn^{4+} in OMS-2 materials generally imply high concentration of oxygen vacancy defects which can adsorb, active and desorb the substrates in the reaction.[33] Therefore, low amounts of Mn^{4+} and high concentration of oxygen vacancy defects of OMS-2-SH-B might be important factors in catalytic performance.

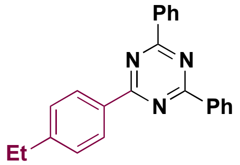
With the optimal catalyst (OMS-2-SH-B) in hand, a series of substituted benzyl alcohols were employed to react with benzamidine to examine the tolerance of the catalytic system (Table 2). Generally, electronic effect did not affect the reactions, while steric effect influenced the reaction significantly (Table 2, **3g**). Benzyl alcohols which can be oxidized to corresponding aldehydes all participated in the reaction smoothly and led to 1,2,3-triazines in good to excellent yields under the optimal conditions. Moreover, cinnamyl alcohol and the less-reactive heterocyclic alcohols could be tolerated successfully and gave corresponding functional 1,3,5-triazines in high yields (Table 2, **3n**, **3o** and **3p**). Cyano-substituted benzyl alcohol that has two reactive functional groups was reported to react with benzamidine yielding 1,2,4-triazole with an aldehyde group through copper-catalyzed oxidative cyclization.[34,35] Interestingly, under our Mn-based catalytic system, desired 1,3,5-triazine with an untouchable cyano was obtained in excellent yields, which implies that the present reaction conditions have superior chemoselevtivity (Scheme 2).

Table 2. Scope of the reaction[a]

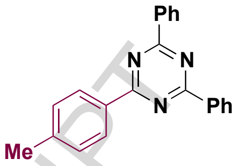




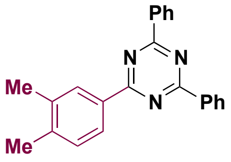
3b, 88%



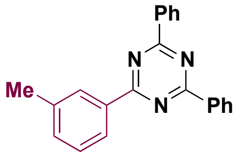
3c, 89%



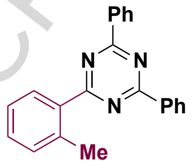
3d, 88%



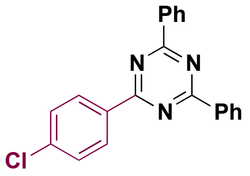
3e, 90%



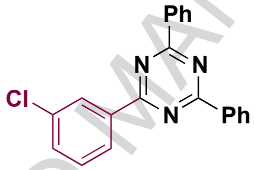
3f, 91%



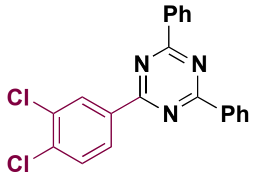
3g, 55%



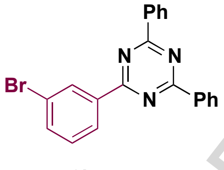
3h, 95%



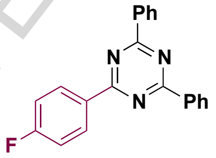
3i, 93%



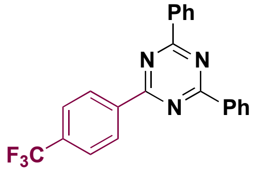
3j, 90%



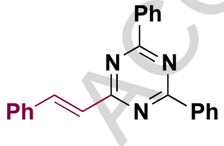
3k, 90%



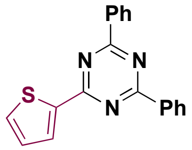
3l, 92%



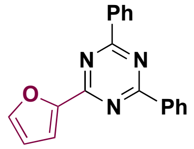
3m, 90%



3n, 91%



3o, 83%



3p, 78%

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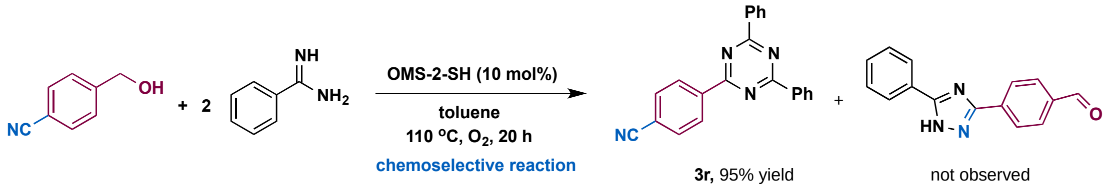
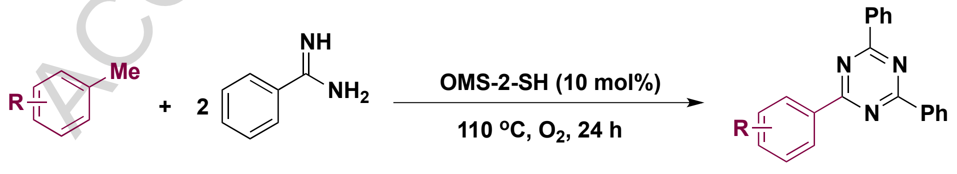
[a] Reaction conditions: OMS-2-SH-B (20 mg, 10 mol%), alcohol (0.3 mmol), phenyl amidine (0.5 mmol), toluene (1 mL), 110 °C, 20 h, O_2 balloon, isolated yields.



Scheme 2. The chemoselectivity of the catalytic system between two functional groups of benzyl alcohol under the optimized reaction conditions.

For further expanding the scope of the reaction, aliphatic alcohols were tried in the reaction. However, corresponding cyclic alkanes substituted 1,3,5-triazines were not observed at all and triphenyl-substituted 1,3,5-triazines were isolated in good yields under the optimal conditions (Scheme S9). Additionally, aliphatic alcohols, like cyclohexanemethanol and cyclohexenemethanol, did not react with OMS-2-SH-B and all alcohols were recovered after the reactions. These experimental facts indicate that toluene which was oxidized by OMS-2-SH-B proceeded into the reaction. In this way, some simple methyl benzenes were selected to directly react with benzamidine under the optimal conditions. As expected, electron-rich or electron-neutral toluenes proceeded the reactions very well and corresponding 1,3,5-triazines were obtained in good yields (Table 3, entries 1-4). However, electron-poor toluenes were difficult to oxidize over OMS-2-SH-B and very poor yields of final products were obtained (Table 3, entries 5 and 6).

Table 3. The scope of the reaction directly using substituted toluene as the substrates.



Entry	R =	Compound	Isolated yield %
1	H	**3a**	82
2	4-Me	**3d**	71

3	4-Et	**3c**	70
4	3,4-diMe	**3e**	75
5	4-Cl	**3h**	35
6	3-Cl	**3i**	38

[a] Reaction conditions: OMS-2-SH-B (20 mg, 10 mol%), substituted toluene (1 mL), phenyl amidine (0.5 mmol), 110 °C, 24 h, O_2 balloon, isolated yields.

Finally, inspired by the results of Jiang`s and Zhang`s work,[11,13] one-carbon suppliers, such as DMF and DMSO, were used in the reactions to form biphenyl-substituted 1,3,5-triazines **3q** (Scheme S10). The reactions using DMF or DMSO replacing alcohols proceeded smoothly and provided desired products in good yields, which offers a simple and straightforward pathway on synthesis.

In order to investigate the stability of the optimal catalyst (OMS-2-SH-B), it was recycled and reused for 5 consecutive times with the reaction of benzyl alcohol and benzamidine under the optimized conditions. As shown in Figure 2, the catalyst shows very stable activity and could be reused for many times. After the first run, the reaction solution after removal of solid catalyst was analyzed by ICP-MS and the results imply that Mn and K were below 10 ug/L respectively. In addition, XRD patterns show that the catalyst retrieved after five recycles maintains cryptomelane phase very well (Scheme S11, in ESI).

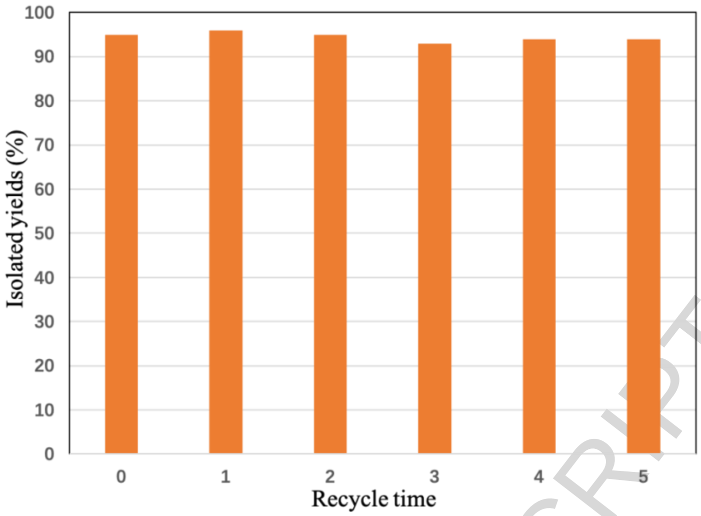


Figure 2. The recycling experiments.

4. Conclusion

In summary, we developed a mixed-valent OMS-2 catalyst with enhanced surface area and high concentration of oxygen vacancy defects. The obtained catalyst exhibits excellent oxidative ability for oxidation of benzyl alcohols and catalytic performance in aerobic oxidative synthesis of 1,3,5-triazines. A broad array of benzyl alcohols and electron-rich toluenes were both tolerated in the reactions and offered 1,3,5-triazines in good to excellent yields. The catalytic system which is chemoselective, recyclable and base-/ligand-free provides a sustainable, simple and straightforward way to synthesize N-containing heterocycles.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://

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Highlights

1. Heterogeneous synthesis of triazines was achieved using OMS-2 as the catalyst.
2. Various substituted toluenes can be employed directly as the substrates.
3. A broad of starting materials can be tolerated under the catalytic system.
4. The catalytic system shows good chemoselectivity.

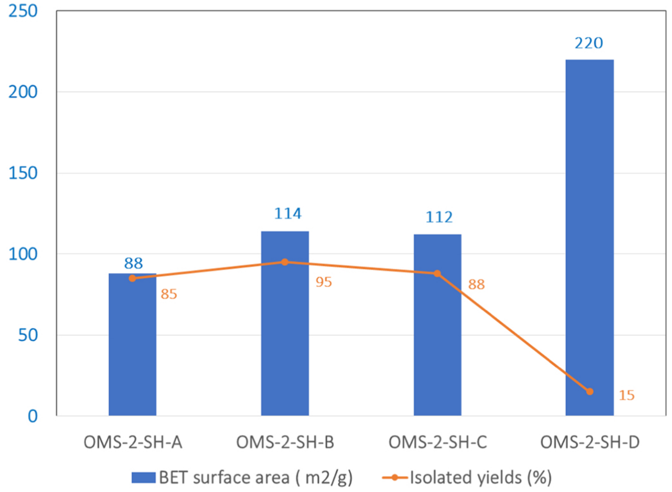
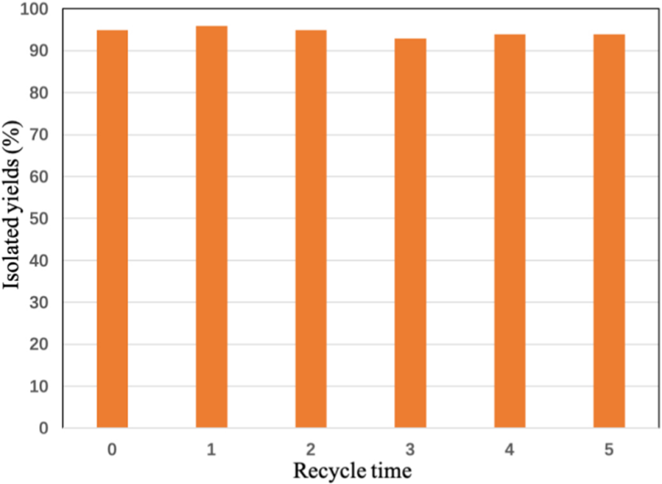

250
200
150
100
50
0
88
114
112
220
85
95
88
15
OMS-2-SH-A
OMS-2-SH-B
OMS-2-SH-C
OMS-2-SH-D
BET surface area (m2/g)
Isolated yields (%)

Figure 1



100
90
80
70
60
50
40
30
20
10
0
Isolated yields (%)
0
1
2
3
4
5
Recycle time

Figure 2