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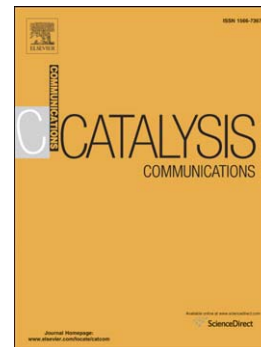
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# Heterogeneous synthesis of 1,4-enediones and 1,4-diketones with manganese oxide molecular sieves OMS-2 as a recyclable catalyst

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**Abstract:** An efficient manganese oxide octahedral molecular sieves OMS-2-catalyzed chemoselective synthesis of 1,4-enediones and 1,4-diketones from 1,3-dicarbonyls and  $\alpha$ -iodoacetophenones is described. The present catalytic system can be applied in one-pot, three-component reactions of methyl ketones, 1,3-dicarbonyls and iodine. Moreover, OMS-2 can be reused at least 5 times without loss of activity.

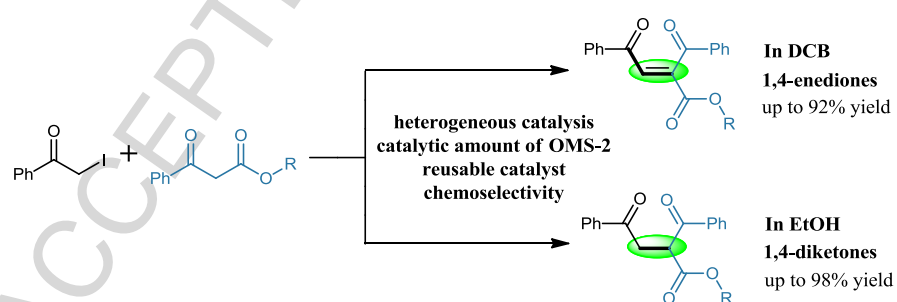
**Keywords:** heterogeneous catalysis, OMS-2, C-C bond formation, 1,4-enediones, 1,4-diketones

## 1. Introduction

Heterogeneous catalysis plays an important role in a wide range of applications, due to convenient catalyst handling, recyclability of catalyst and easy separation of catalyst from reaction medium [1-4]. As a mixed valent material, OMS-2 (cryptomelane-type manganese oxide-based octahedral molecular sieves,  $\text{KMn}_8\text{O}_{16}$ ) has captured broad attention and also been applied to catalysis, ion-exchange, battery materials and adsorption because it is crystalline and semi-conductive [5]. OMS-2 has a  $2 \times 2$  edge- and corner-shared  $\text{MnO}_6$  octahedral chain, which is corner connected to form a one-dimensional tunnel structure with a pore size of  $4.6\text{\AA}$ , and shows  $\sim 3.8$  as the average oxidation state [6, 7]. Previously, OMS-2 had been used as a heterogeneous catalyst in oxidation [8], cyanation [9], dehydrogenation [10], epoxidation [11], ring opening [12], as well as the synthesis of imines, amides, quinoxalines and 2-aminodiphenylamines [13-17].

1,4-Enediones are not only important structural motifs in natural products and pharmaceutical compounds [18], but also versatile building blocks for the synthesis of heterocycles [19]. Many synthetic routes have been established, including oxidation of furans and enones [20], rearrangement of 2-alkynyl alcohols [21], Stille coupling [22], Wittig reaction [23], nucleophilic addition of dibenzoylacetylenes and oxidative coupling [24]. Most recently, Wu's group reported an oxidative synthesis of 1,4-enediones from acetophenones and 1,3-dicarbonyls mediated by

stoichiometric amounts of CuO and I<sub>2</sub> [25]. However, these approaches are not eco-friendly and generally suffer from limited substrate scope. Therefore, there is an incentive to develop a convenient and straightforward approach for producing 1,4-enediones by environmentally friendly way with a recyclable catalyst. In continuation of our research towards heterogeneous catalysis [26-28], we would like to describe a heterogeneous OMS-2-catalyzed chemoselective synthesis of 1,4-enediones and 1,4-diketones from  $\alpha$ -iodoacetophenones and 1,3-dicarbonyls. This synthetic method avoids using stoichiometric amounts of metal reagents, which can be an alternative to previous methods (Scheme 1).



**Scheme 1.** OMS-2-catalyzed synthesis of 1,4-enediones and 1,4-diketones.

## 2. Experimental

### 2.1. Catalyst preparation [26]

5.89 g of KMnO<sub>4</sub> in 100 mL of water was added to a solution of 8.8 g of MnSO<sub>4</sub>·H<sub>2</sub>O in 30 mL of water and 3 mL concentrated HNO<sub>3</sub>. The solution was refluxed at 100 °C for 24 h, and the product was filtered,

washed, and dried at 120 °C for 8 h. Finally, the dry OMS-2 was calcined in a muffle furnace at 350 °C for 2 h. Then, the black powder OMS-2 was obtained. BET surface area: 158.4870 m<sup>2</sup>/g; Pore volume: 0.5249 cm<sup>3</sup>/g; Pore size: 127.058 Å.

## 2.2. Characterization

The specific surface areas ( $S_{\text{BET}}$ ) of the catalysts were measured from a multipoint Braunauer–Emmett–Teller (BET) analysis of the nitrogen adsorption isotherms at 77K recorded on a Quantachrome Autosorb-1 apparatus. The transmission electron microscopy (TEM) images of the catalysts were obtained on a JEM2010 microscope operated at 200 kV. The sample was dispersed into ethanol with ultrasonic treatment for 1 h, and drops of the suspension were placed on a copper grid for TEM observations. The X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO MPD powder diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm). The working voltage was 40 kV and the current was 40 mA. The intensity data were collected at 25 °C in a  $2\theta$  range from 10° to 90°, with a scanning speed of 0.7° s<sup>-1</sup> and a step of 0.03°.

## 2.3. General procedure for the synthesis of 1.4-enedione

OMS-2 (12 mg, 0.015 mmol, 5 mol%),  $\alpha$ -iodoacetophenone (0.3 mmol), 1,3-dicarbonyl compound (0.3 mmol), DCB (1 mL) were added to a flask with a stirring bar. The mixture was stirred at 100 °C for 12 h

under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography to yield corresponding product.

#### 2.4. General procedure for the synthesis of 1,4-diketones

OMS-2 (12 mg, 0.015 mmol, 5 mol%),  $\alpha$ -iodoacetophenone (0.3 mmol), 1,3-dicarbonyl compound (0.3 mmol), EtOH (1 mL) were added to a flask with a stirring bar. The mixture was stirred at 70 °C for 12 h under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography to yield corresponding product.

### 3. Results and discussion

In our initial study, the reaction between  $\alpha$ -iodoacetophenone **1a** and 1,3-dicarbonyl compound **2a** was chosen as a model reaction (Table 1 and S1). Firstly, the reaction did not proceed without a catalyst in DMSO (Table 1, entry 1). Using OMS-2 as a catalyst in DCB also failed the transformation (Table 1, entry 2). Interestingly, increasing reaction temperature to 100 °C enabled the formation of 1,4-enedione **3a** with E/Z mixture in 92% yield (Table 1, entry 3). Next, more experiments confirmed that increasing or decreasing OMS-2 loading did not enhance reactivity and the reaction did not occur without OMS-2 even at a higher

temperature (Table 1, entries 4-6). Using  $\text{MnSO}_4$  and  $\text{KMnO}_4$  that are precursors of OMS-2 as catalysts gave inferior results (Table 1, entries 7 and 8). Moreover,  $\text{MnO}_2$  was tested and it did not trigger the reaction at all (Table 1, entry 9). Surprisingly, the reaction offered 98% yield of 1,4-diketone **4a** [29] instead of **3a** in EtOH at 70 °C *via* nucleophilic substitution (Table 1, entry 10). Then, more experiments were conducted in EtOH to better the yield of **4a** and results showed that the reaction did not work without OMS-2, and decreasing reaction temperature slowed down the transformation (Table 1, entries 11-13). Finally, the formation of **4a** also worked efficiently under nitrogen (Table 1, entry 14).

**Table 1** Optimization of the reaction conditions.<sup>a</sup>

Entry	Catalyst	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>	
				<b>3a</b>	<b>4a</b>
1	-	DMSO	70	0	0
2	OMS-2	DCB	70	trace	0
3	OMS-2	DCB	100	92	0
4	OMS-2 (10 mol%)	DCB	100	90	0
5	OMS-2 (2 mol%)	DCB	100	72	0
6	-	DCB	100	0	0

7 <sup>c</sup>	MnSO <sub>4</sub>	DCB	100	10	0
8 <sup>c</sup>	KMnO <sub>4</sub>	DCB	100	15	0
9 <sup>c</sup>	MnO <sub>2</sub>	DCB	100	0	0
10	OMS-2	EtOH	70	0	98
11	-	EtOH	70	0	0
12	OMS-2	EtOH	r.t.	0	20
13	OMS-2	EtOH	40	0	23
14 <sup>d</sup>	OMS-2	EtOH	70	0	92

<sup>a</sup> Reaction conditions: catalyst (for OMS-2, 12 mg, 0.015 mmol, 5 mol%), **1a** (0.3 mmol), **2a** (0.3 mmol), solvent (1 mL), temperature, air, 12 h.

<sup>b</sup> Isolated yields.

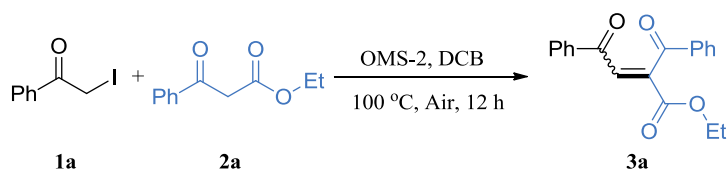
<sup>c</sup> 5 mol% of catalyst was used.

<sup>d</sup> Under N<sub>2</sub> atmosphere.

In order to prove that the observed catalysis is derived from the solid catalyst OMS-2 rather than the leached Mn species, the hot filtration experiment was conducted (see ESI, Figure S1) and the results suggested that the observed catalysis is heterogeneous. Then, the recyclability of OMS-2 on the synthesis of 1,4-enedione **3a** was investigated (Table 2). After each run, OMS-2 was separated by filtration and washed with deionized water and EtOH respectively, then dried at 110 °C for 4 h. It was found that OMS-2 can be reused at least 5 times without obvious loss of activity.

**Table 2** Reusability of OMS-2 on the synthesis of **3a**.<sup>a</sup>

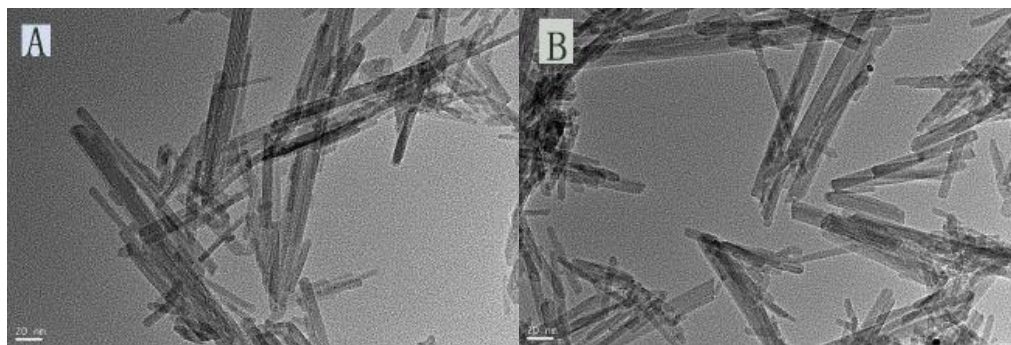




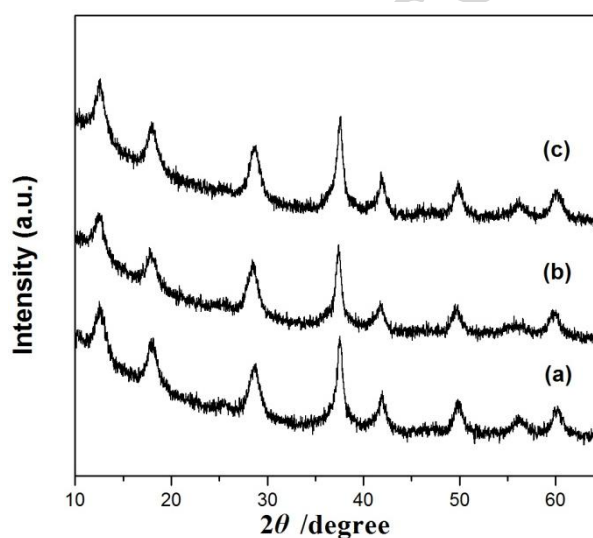
Cycle	1	2	3	4	5
Isolated yield of <b>3a</b> (%)	92	90	92	89	90

<sup>a</sup> Reaction conditions: OMS-2 (12 mg, 0.015 mmol, 5 mol%), **1a** (0.3 mmol), **2a** (0.3 mmol), DCB (1 mL), 100 °C, air, 12 h.

Then, transmission electron microscopy (TEM) and X-ray diffraction (XRD) were employed to characterize the fresh and retrieved OMS-2 (Figure 1 and 2). Specifically, the TEM image of OMS-2 demonstrated that the fresh catalyst was composed of short nanorods which were structurally single crystalline (Figure 1, A). Additionally, the TEM image showed retrieved OMS-2 which was used for 1 cycle maintained the morphology and lattice structure (Figure 1, B). The XRD pattern of OMS-2 showed peaks which can be indexed to the pure cryptomelane phase consistent with JCPDS file No. 29-1020. Reused OMS-2 was also characterized by XRD, which confirmed that the structure of it was not altered even after the fifth cycle (Figure 2). TEM and XRD revealed that OMS-2 has good structural stability.



**Figure 1.** TEM images of fresh OMS-2 (A) and OMS-2 after 1 cycle (B).

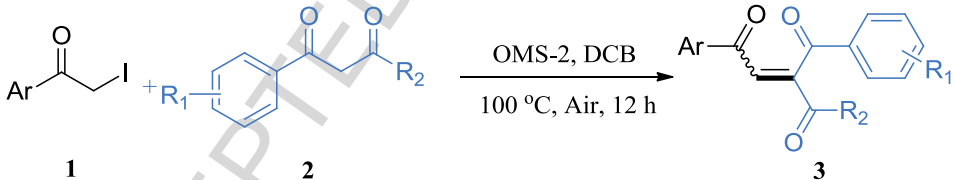


**Figure 2.** XRD pattern of OMS-2 (a), OMS-2 after 1 cycle (b) and OMS-2 after 5 cycles (c).

With the optimized reaction conditions in hand, we examined the scope of the C-C bond formation between  $\alpha$ -iodoacetophenones and 1,3-dicarbonyls using OMS-2 as the catalyst in DCB (Table 3). Gratifyingly, the reactions were tolerant of various substrates and gave moderate to good yields of corresponding 1,4-enediones with mixture of major thermodynamically stable *E*-isomers and minor *Z*-isomers. Electron-rich iodoacetophenones offered slightly higher yields of

1,4-enediones than electron-poor ones did (Table 3, **3b-3i**). Heterocyclic  $\alpha$ -iodoketone, 1-(furan-2-yl)-2-iodoethanone, also proceeded in a good yield (Table 3, **3j**). On the other hand, various 1,3-dicarbonyls participated in the reactions and good yields were obtained (Table 3, **3k-3o**). Unfortunately, aliphatic  $\alpha$ -iodoketones, such as 1-iodobutan-2-one and 1-iodopropan-2-one, did not participate in the reactions and aliphatic acetylacetone was not a suitable substrate for this catalytic system. And  $\alpha$ -bromo acetophenone did not react under the present reaction conditions.

**Table 3** OMS-2-catalyzed synthesis of 1,4-enediones.<sup>a</sup>



Product	Ar	R <sub>1</sub>	R <sub>2</sub>	Yield (%) <sup>b</sup>
<b>3b</b>	<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub>	H	OEt	90 ( <i>E:Z</i> = 88:12)
<b>3c</b>	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	H	OEt	91 ( <i>E:Z</i> = 87:13)
<b>3d</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	H	OEt	87 ( <i>E:Z</i> = 92:8)
<b>3e</b>	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	H	OEt	85 ( <i>E:Z</i> = 96:4)
<b>3f</b>	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	H	OEt	80 ( <i>E:Z</i> = 90:10)
<b>3g</b>	<i>p</i> -CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	OEt	82 ( <i>E:Z</i> = 93:7)
<b>3h</b>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	H	OEt	72 ( <i>E:Z</i> = 80:20)
<b>3i</b>	2-Naphthyl	H	OEt	88 ( <i>E:Z</i> = 89:11)

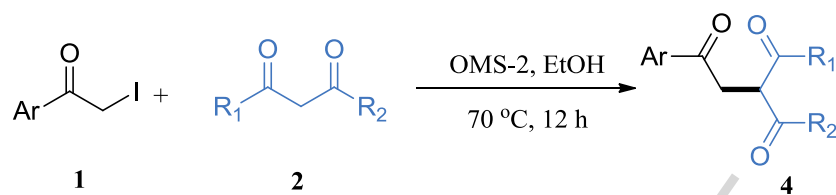
<b>3j</b>	Furan-2-yl	H	OEt	70 ( <i>E:Z</i> > 99:1)
<b>3k</b>	Ph	<i>p</i> -F	OEt	90 ( <i>E:Z</i> = 89:11)
<b>3l</b>	Ph	<i>p</i> -OMe	OEt	80 ( <i>E:Z</i> = 82:18)
<b>3m</b>	Ph	<i>p</i> -Cl	OMe	70 ( <i>E:Z</i> = 97:3)
<b>3n</b>	Ph	<i>p</i> -OMe	OMe	88 ( <i>E:Z</i> = 93:7)
<b>3o</b>	Ph	H	Ph	65

<sup>a</sup> Reaction conditions: OMS-2 (12 mg, 0.015 mmol, 5 mol%), **1** (0.3 mmol), **2** (0.3 mmol), DCB (1 mL), 100 °C, air, 12 h.

<sup>b</sup> Isolated yields, *E:Z* ratio determined by <sup>1</sup>H NMR.

Since the excellent chemoselectivity of this heterogeneous catalytic system, a number of 1,4-diketones were synthesized *via* OMS-2-catalyzed nucleophilic substitutions in EtOH (Table 4). In all cases, the desired 1,4-diketones were obtained chemoselectively. *Ortho*-substituted  $\alpha$ -iodoacetophenones gave low yields of 1,4-diketones, which indicates the reaction was affected by steric hindrance of the substrates (Table 4, **4b-4m**). 1,3-Dicarbonyls with substitutions underwent reactions to furnish desired products in excellent yields (Table 4, **4n** and **4o**). When aliphatic acetylacetone was employed as a substrate, the desired product **4p** was isolated in a low yield of 8%. However, the reactions of aliphatic  $\alpha$ -iodoketones, such as 1-iodobutan-2-one and 1-iodopropan-2-one, did not occur under the present reaction conditions.

**Table 4** OMS-2-catalyzed synthesis of 1,4-diketones.<sup>a</sup>



Product	Ar	R <sub>1</sub>	R <sub>2</sub>	Yield (%) <sup>b</sup>
<b>4b</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	92
<b>4c</b>	<i>m</i> -Cl-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	88
<b>4d</b>	<i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	65
<b>4e</b>	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	88
<b>4f</b>	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	84
<b>4g</b>	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	83
<b>4h</b>	<i>m</i> -Me-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	76
<b>4i</b>	<i>p</i> -OMe-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	82
<b>4j</b>	<i>m</i> -OMe-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	70
<b>4k</b>	<i>o</i> -OMe-C <sub>6</sub> H <sub>4</sub>	Ph	OEt	63
<b>4l</b>	2-Naphthyl	Ph	OEt	88
<b>4m</b>	Furan-2-yl	Ph	OEt	73
<b>4n</b>	Ph	<i>p</i> -OMe-C <sub>6</sub> H <sub>4</sub>	OEt	93
<b>4o</b>	Ph	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	OEt	95
<b>4p</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	Me	Me	8

<sup>a</sup> Reaction conditions: OMS-2 (12 mg, 0.015 mmol, 5 mol%), **1** (0.3 mmol), **2** (0.3 mmol), EtOH (1 mL), 70 °C, air, 12 h.

<sup>b</sup> Isolated yields.

Because  $\alpha$ -iodoacetophenones are easily formed from corresponding

acetophenones with iodine [26, 30, 31], the one-pot, three-component reactions of I<sub>2</sub>, acetophenones and 1,3-dicarbonyls catalyzed by OMS-2 to yield 1,4-enediones and 1,4-diketones were smoothly realized (see ESI, Scheme S1).

Based on the previous reports [25, 30, 31] and control experiments we performed (see ESI, Scheme S2),  $\alpha$ -ketoaldehyde **A** (Scheme S2) probably is an intermediate during the oxidative synthesis of 1,4-enedione. In the presence of OMS-2,  $\alpha$ -ketoaldehyde **A** that is formed from  $\alpha$ -iodoacetophenone under air reacts with 1,3-dicarbonyl *via* Knoevenagel condensation to afford the desired 1,4-enedione after loss of H<sub>2</sub>O [32]. In EtOH, 1,4-diketone is generated by OMS-2-assisted nucleophilic substitution between electrophilic  $\alpha$ -iodoacetophenone and nucleophilic 1,3-dicarbonyl compound.

#### 4. Conclusion

In summary, we have developed a heterogeneous OMS-2-catalyzed oxidative C-C bond formation between  $\alpha$ -iodoacetophenones and 1,3-dicarbonyls for the synthesis of 1,4-enediones. By changing the reaction solvent, the catalytic system can afford high yields of 1,4-diketones. This simple catalytic system tolerates a variety of substrates and can be performed in one-pot, three-component reaction of acetophenones, 1,3-dicarbonyls and I<sub>2</sub>. Furthermore, OMS-2 can be reused 5 times without loss of catalytic activity.

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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. OMS-2 acts as an efficient heterogeneous catalyst for C-C bond-forming.
2. The catalyst can be recycled for 5 times.
3. Chemoselectivity of reactions can be tuned by reaction solvents.
4. 1,4-enediones and 1,4-diketones can be prepared in one-pot manner.