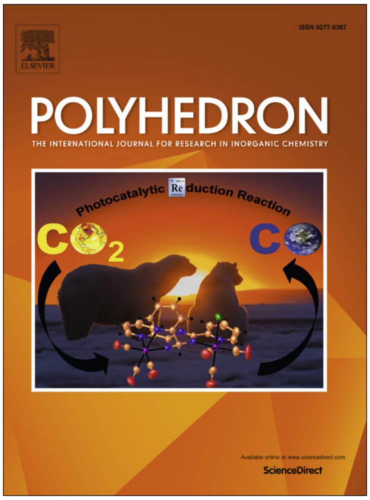


Natural Silk Supported Manganese Dioxide Nanostructures: Synthesis and Catalytic Activity in Aerobic Oxidation and One-Pot Tandem Oxidative Synthesis of Organic Compounds

Ahmad Shaabani, Zeinab Hezarkhani, Elham Badali

PII: S0277-5387(16)00033-4
DOI: http://dx.doi.org/10.1016/j.poly.2016.01.019
Reference: POLY 11781

To appear in: *Polyhedron*

Received Date: 17 December 2015
Accepted Date: 15 January 2016

Please cite this article as: A. Shaabani, Z. Hezarkhani, E. Badali, Natural Silk Supported Manganese Dioxide Nanostructures: Synthesis and Catalytic Activity in Aerobic Oxidation and One-Pot Tandem Oxidative Synthesis of Organic Compounds, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.01.019

Natural Silk Supported Manganese Dioxide Nanostructures: Synthesis and Catalytic Activity in Aerobic Oxidation and One-Pot Tandem Oxidative Synthesis of Organic Compounds

Ahmad Shaabani,* Zeinab Hezarkhani, and Elham Badali

Faculty of Chemistry, Shahid Beheshti University, G. C., P. O. Box 19396-4716, Tehran, Iran

Email: *a-shaabani@sbu.ac.ir*

Abstract

Manganese dioxide nanostructures were coated on natural silk (MnO_2@silk) by simple immersion of the silk fibers into a $KMnO_4$ aqueous solution. The silk was found to act as a *in situ* reducing agent and substrate in aqueous $KMnO_4$ solution for the heterogeneous production of MnO_2 nanostructures. The structure of synthesized catalyst was characterized by x-ray diffraction (XRD), flame atomic absorption spectroscopy (FAAS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) analysis. The catalytic activity of the MnO_2@silk was examined in the aerobic oxidation of alkyl arenes, alcohols, and oximes to their corresponding carbonyl compounds and a one-pot tandem oxidative two-component reaction of aromatic hydrocarbons of petroleum naphtha in the absence of any other oxidizing reagent or initiator.

Keywords

Silk; Manganese dioxide nanostructures; Aerobic oxidation; Tandem oxidative synthesis

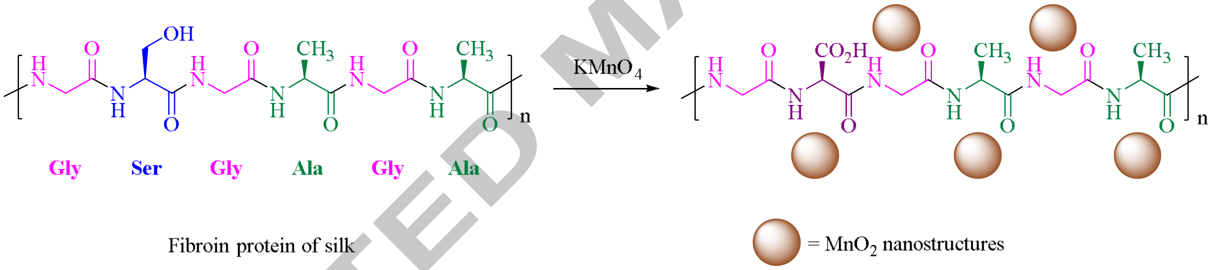
Introduction

Biopolymers, as common structural elements of biological systems, have highly specialized properties because of their complex three-dimensional structures. Natural polyamino acid biopolymers (polypeptides or proteins) in organisms are synthesized from combinations of amino acid (–NH–CHR–CO–) and imino acid (–NR^1–CHR^2–CO–) monomers linked *via* amide bonds (peptide bonds) [1]. Natural silk is a biopolymer that composed mainly of fibroin and is produced by certain insect larvae to form cocoons. Primary structure of fibroin protein mainly consists of the recurrent amino acid sequence $(\text{Gly-Ser-Gly-Ala-Gly-Ala})_n$ (Scheme 1) [2]. Due to the structurally ordered amino acid chains in the fibroin, silk proteins can form functional complexes with metals; therefore, silk protein-based materials have found application as solid supports for the immobilization of catalysts.

Catalytic oxidation processes play an important role in green organic transformations. The development of new catalytic materials based on green principles is of significant importance in organic chemistry. From both industrially and environmentally viewpoints, there is an important demand for greener approaches that employs aerobic catalytic oxidation processes with minimum amount of waste [3]. For this reason, various natural biopolymers have been employed as the solid support to produce green heterogeneous catalytic systems, such as cellulose [4], wool [5], alginate [6], gelatin [7], starch [8], and chitosan [9] derivatives. Among several renewable bio-supports, silk have unique properties and can be used as support for catalytic applications.

Manganese dioxide (MnO_2), as a cheap, renewable, mild, easily handled, and low toxic reagent, is one of the attractive materials due to its selective catalytic properties. MnO_2 has been extensively used as a selective catalyst for the oxidation of a variety of functional groups [3,10,11]. Unfortunately, MnO_2 usually has a relatively low surface area (10–80 $m^2\ g^{-1}$) because of its aggregation into less active large particles during the reaction. Since aggregation of the heterogeneous catalysts substantially affected and decreased their catalytic activity, to settle the matter, nanostructured manganese dioxide was prepared for providing a catalyst with a large surface area. Moreover, aggregation of MnO_2 nanostructures is prevented by its distribution on the supports and high catalytic activity is accessible [12]. In addition, industrial applications of MnO_2 have become more attractive environmentally by the recycling of MnO_2. For this reason, in our previous works it was suggested that it possible to separate the MnO_2 from a cellulose and wool biosupports by burning or chemical decomposition of biosupport [13,14].

As part of our ongoing program related to the developing new heterogeneous catalysts for organic transformations [15-18], and based on our previous investigations on MnO_2 [13, 14, 19-21], herein we report the synthesis of MnO_2 nanostructures on silk (MnO_2@silk) and investigated its catalytic activities in the selective aerobic oxidation of various of benzylic hydrocarbons, alcohols, and oximes into the corresponding aldehydes and ketones, and one-pot oxidative two-component reaction of aromatic hydrocarbons of petroleum naphtha in the absence of any other oxidizing reagent or initiator. We found the MnO_2 nanostructures are effectively immobilized on the surface of silk protein and prevented from its aggregation. In addition, there is the possibility of separation MnO_2 from silk support at the end of the catalytic process (Scheme 1).



Scheme 1 Structure of fibroin protein of silk and the possible structure of MnO_2@silk

Materials and methods

1 General

Natural white silk (silkworm cocoons of Gilan/Iran) was washed with NaOH solution, distilled water, and acetone, then cut with scissors to very short pieces (about 200 µm-1 mm, based on SEM images). All reagents were obtained from Aldrich or Merck and used without further purification. The elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL. X-ray diffraction (XRD) pattern of catalyst was recorded on a STOE STADI P with scintillation detector, secondary monochromator using Cu Kα radiation (λ = 0.1540 nm). Mn(IV) determination was carried out on an FAAS (Shimadzu model AA-680 flame atomic absorption spectrometer) with a Mn hollow cathode lamp at 279.5 nm, using an air-acetylene flame. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 °C min^{-1} in air. Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. All samples were sputtered with gold before observation. Products were analyzed using a Varian 3900 GC. Melting points were measured on an Electrothermal 9200 apparatus.

2 Experimental

2.1 Synthesis of MnO_2@silk

Natural white silk (silkworm cocoons of Gilan/Iran) was washed with NaOH solution (0.01 M), distilled water and acetone and dried at 60 °C, then cut with scissors to very short pieces (about 200 µm-1 mm, based on SEM images). For the synthesis of MnO_2@silk, a solution of $KMnO_4$ (0.01 M, 150 mL) was added dropwise to a magnetically stirred suspension of the natural silk pieces (1.0 g) in 200 mL of H_2O during 12 h at room temperature. The mixture was filtered to give brown MnO_2@silk. The prepared catalyst washed with H_2O (3× 10 mL) and EtOH (3 × 10 mL), successively and dried under vacuum at 80 °C for 12 h.

2.2 Oxidation of alkyl arenes; General procedure

In a typical reaction, an alkyl arene (1.0 mmol), MnO_2@silk (0.09 g, 10 mol% of MnO_2), and *o*-xylene (5.0 mL) were added to a two-necked flask. The mixture was stirred under reflux conditions and air blowing. The thin layer chromatography (TLC) method was used to investigate the progress of the reaction. Upon completion, analysis of the crude product has been done by GC method.

2.3 Oxidation of alcohols; General procedure

In a typical reaction, an alcohol (1.0 mmol) was added to a two-necked flask containing MnO_2@silk (0.09 g, 10 mol% of MnO_2), K_2CO_3 (0.50 mmol), and *o*-xylene (5.0 mL) and stirred under air blowing at room temperature. The progress of the reaction was followed by TLC and GC method. After completion of reaction and filtration of mixture, the filtrate was analyzed by GC method.

2.4 Oxidation of oximes; General procedure

An oxime (1.0 mmol) and MnO_2@silk (0.09 g, 10 mol% of MnO_2) were well ground using a pestle at room temperature. The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the solid was washed with dichloromethane. After the filtration of the reaction mixture, analysis of the filtrate has been done by GC method.

2.5 General procedure for the preparation of products 3a-d, 5a-d, and 7a-d

In a two-necked flask, to a solution of amine source (1.0 mmol) in toluene or xylene (5.0 mL), MnO_2@silk (the amount of catalyst was listed in Table 4) was added and the mixture was stirred magnetically under reflux conditions and air blowing for the indicated time in Table 4. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was filtered and washed with ethanol. After removing of the organic solvents, the crude product was separated on a silica gel column to give final product.

Analysis and results

The synthesized catalyst was characterized by FAAS, XRD, TGA, SEM, and EDS. The Mn(IV) contents of the MnO_2@silk catalyst was determined using FAAS method. The amount of MnO_2 in this catalyst was determined 9.67%.

The XRD patterns of silk fibers and MnO_2@silk catalyst was employed to investigate the structure of the synthetic catalyst. The diffraction peaks of silk fibers appear as two broad peaks at 2θ values of around 9.5° and 19.5°, which are its characteristic (Fig. 1-I). Because of the diffraction peaks of silk fibers are stronger than the diffraction peaks of MnO_2, the peaks related to the MnO_2 were not observed. Clearly, the characteristic peaks of silk were observed in the XRD pattern MnO_2@silk catalyst, meaning that the morphology of silk after immobilization of MnO_2 was retained (Fig. 1-II).

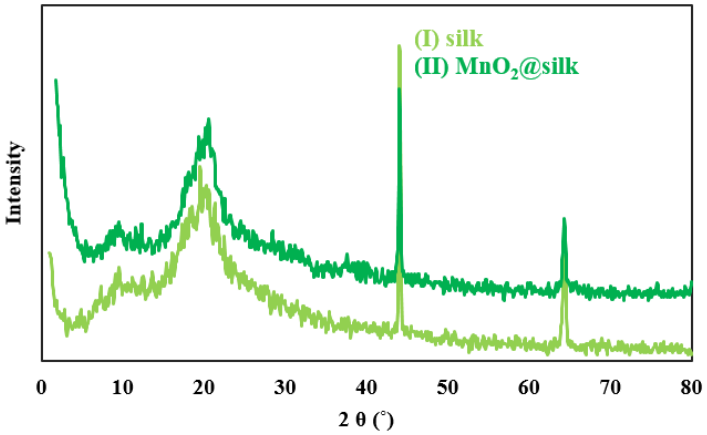


Fig. 1 XRD patterns of silk (I) and MnO_2@silk (II).

TGA demonstrated that silk was decomposed above 268 °C, which approved relatively high thermal stability of the silk fibers in air (Fig. 2-I). High thermal stability was observed for MnO_2@silk catalyst (Fig. 2-II), too. In the TGA curves of silk fibers and MnO_2@silk catalyst, three stages could be observed. In the low temperature range (up to 268 °C), the mass slowly decreased by 4.2% and 4.3% for silk and MnO_2@silk, respectively; it should be related to the removal of adsorbed water on the surface in the silk fibers and MnO_2@silk catalyst. In the range of 268-380 °C and 380-696 °C, a large weight loss for silk was observed in two stages, which is attributed to the decomposition of silk. Three stages in the TGA curve of MnO_2@silk catalyst should be related to: the removal of adsorbed water (stage 1), decomposition of silk (stage 2 and 3).

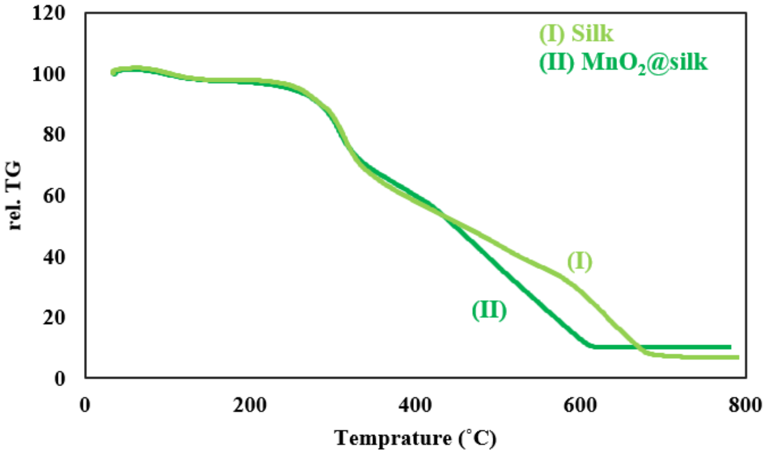


Fig. 2 TG curves of silk fibers (I) and MnO_2@silk (II) in air

The morphological characterization of silk and the obtained MnO_2@silk catalyst was conducted by scanning electron microscope (SEM). According to Fig. 3a, the silk fibers have a length of about 200 µm-1 mm. Comparing Fig. 3b that related to silk fibers, SEM image of MnO_2@silk (Fig. 3c) confirmed that the catalyst material is formed without a large change in its morphology. The structure and morphology of the obtained MnO_2@silk nanocomposite was illustrated by SEM (Fig. 3-c and d) and MnO_2 nanostructures could be observed on the silk fiber surface which nanostructures are well dispersed on the silk fiber surface (Fig. 3d).

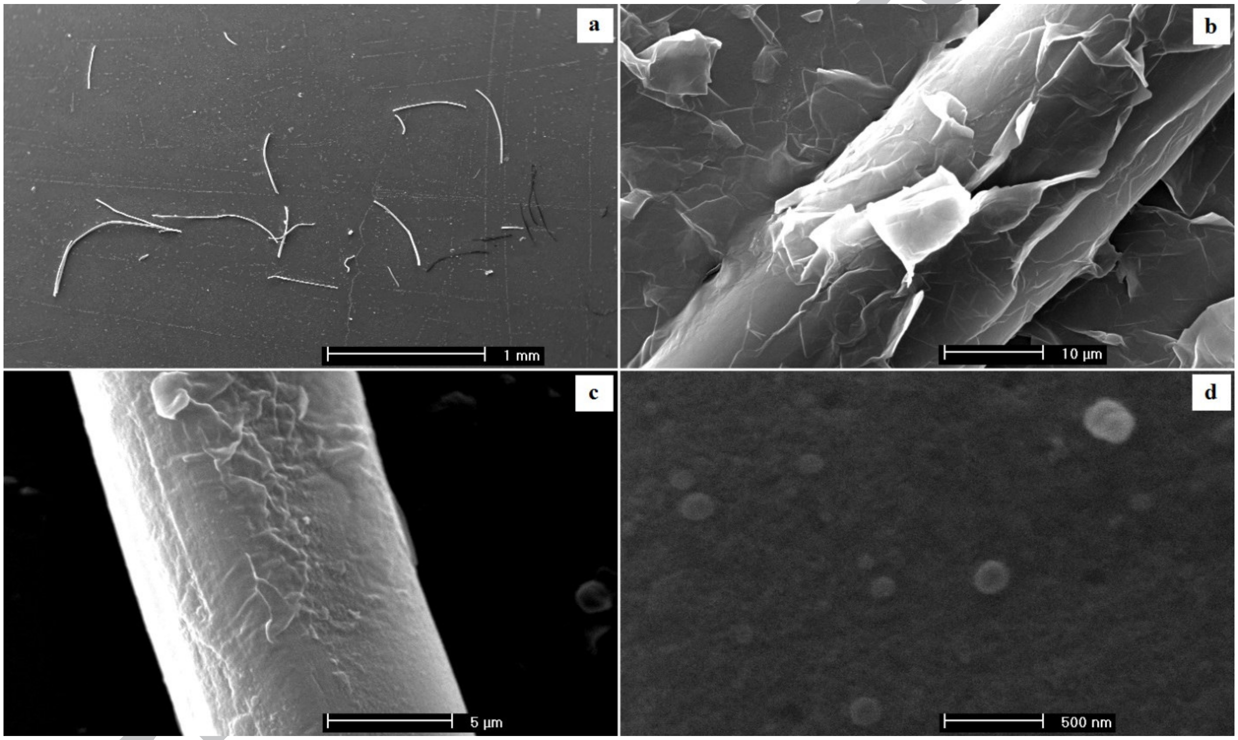


Fig. 3 SEM images of silk (a,b) and MnO_2@silk (c,d)

The EDS analysis was employed for determination of the chemical composition of MnO_2@silk nanocomposite (Fig. 4).

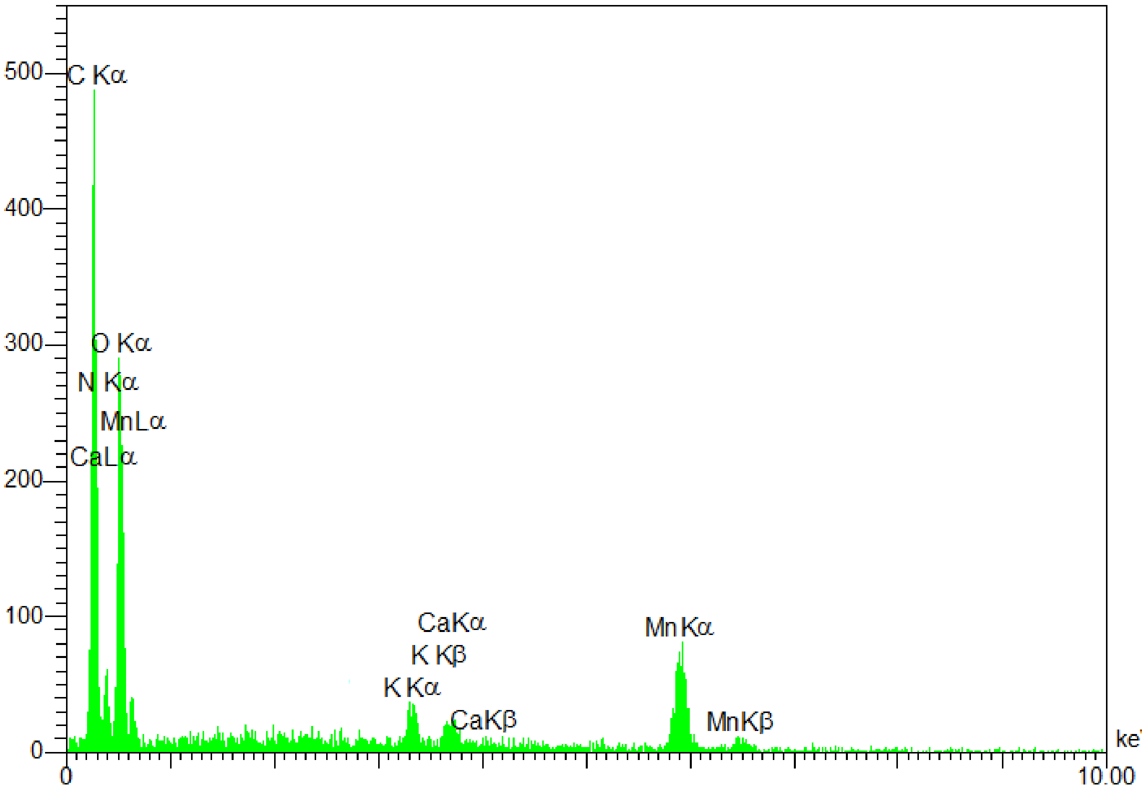


Fig. 4 SEM-EDS results for MnO_2@silk catalyst.

Results and discussion

To achieve a suitable catalytic system for the aerobic oxidation, we examined MnO_2@silk catalyst in the reaction media. Aerobic oxidation of indane, 1-indanol, and 2,3-dihydro-1*H*-inden-1-one oxime were selected as model reactions for transformation of alkyl arenes, alcohols, and oximes, respectively. The results show that the entries 5, 12, and 15 have provided the best conditions, respectively (Table 1).

Table 1 Optimization of the reaction conditions for the aerobic oxidation of alkyl arenes, alcohols, and oximes by MnO_2@silk catalyst^{a,b,c}

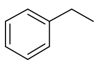
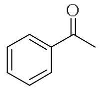
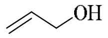
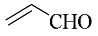
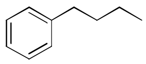
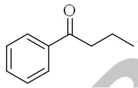
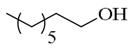
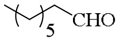
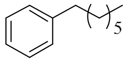
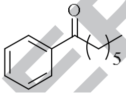
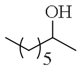
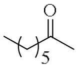
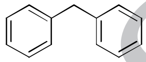
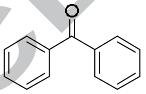
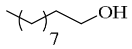
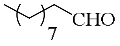
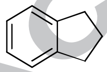
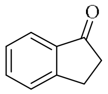
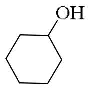
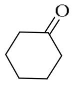
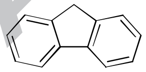
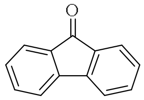
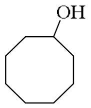
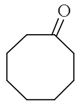
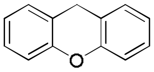
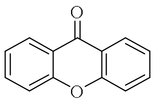
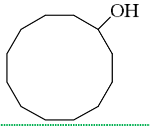
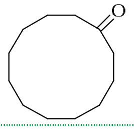
Entry	Substrate	Amount of catalyst (MnO_2 mol%)	Solvent	Base (mmol)	Time	Temperature (°C)	Conversion (%)^d
1	Indane	0.09 g (10)	*n*-Hexane	-	9 h	Reflux	7
2		0.09 g (10)	CH_2Cl_2	-	9 h	Reflux	14
3		0.09 g (10)	CH_3CN	-	9 h	Reflux	35
4		0.09 g (10)	Toluene	-	9 h	Reflux	57
5		**0.09 g (10)**	***o*-Xylene**	**-**	**9 h**	**Reflux**	**89**

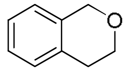
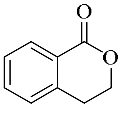
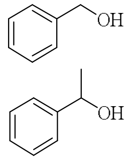
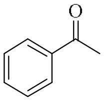
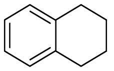
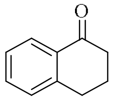
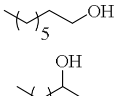
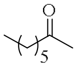
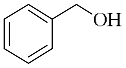
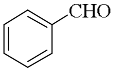
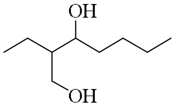
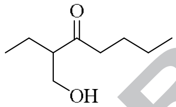
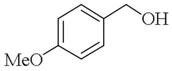
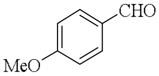
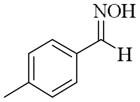
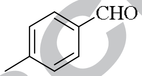
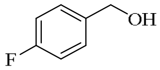
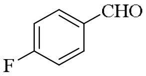
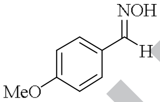
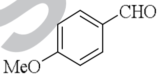
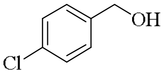
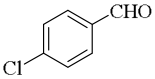
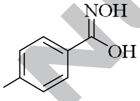
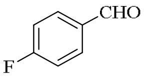
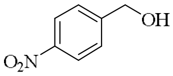
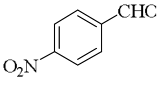
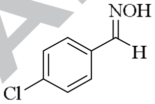
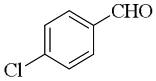
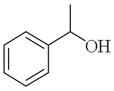
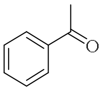
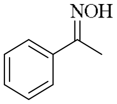
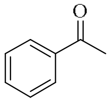
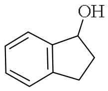
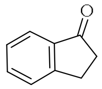
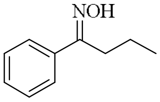
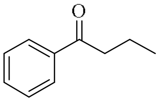
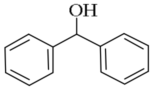
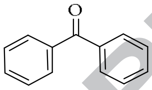
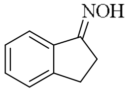
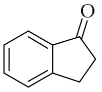
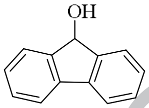
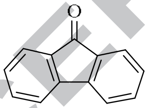
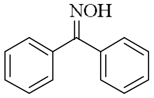
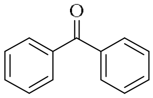
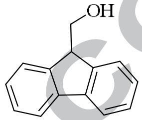
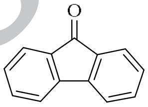
6		0.07 g (8)	*o*-Xylene	-	9 h	Reflux	57
7		0.05 g (6)	*o*-Xylene	-	9 h	Reflux	48
8		0.09 g (10)	*n*-Hexane	K_2CO_3 (0.5)	8 h	r.t.	16
9		0.09 g (10)	CH_2Cl_2	K_2CO_3 (0.5)	8 h	r.t.	14
10		0.09 g (10)	CH_3CN	K_2CO_3 (0.5)	8 h	r.t.	23
11	1-Indanol	0.09 g (10)	Toluene	K_2CO_3 (0.5)	8 h	r.t.	58
12		**0.09 g (10)**	***o*-Xylene**	**K_2CO_3 (0.5)**	**8 h**	**r.t.**	**92**
13		0.07 g (8)	*o*-Xylene	K_2CO_3 (0.5)	8 h	r.t.	53
14		0.05 g (6)	*o*-Xylene	K_2CO_3 (0.5)	8 h	r.t.	40
15	2,3-Dihydro-1*H*-inden-1-one oxime	**0.09 g (10)**	-	-	**5 min**	**r.t.**	**98**
16		0.07 g (8)	-	-	5 min	r.t.	71
17		0.05 g (6)	-	-	5 min	r.t.	57

[a] Reaction conditions for oxidation of alkyl arenes: indane (1.0 mmol), solvent (5.0 mL), air as oxidant.
[b] Reaction conditions for oxidation of alcohols: 1-indanol (1.0 mmol), solvent (5.0 mL), air as oxidant.
[c] Reaction conditions for oxidation of oximes: 2,3-Dihydro-1*H*-inden-1-one oxime (1.0 mmol).
[d] Conversion determined by GC analysis.

Finally, the aerobic oxidation of the various alkyl arenes and alcohols to related aldehydes and ketones was carried out in *o*-xylene as the preferred solvent. Also, oxidation of oximes to the related carbonyl compounds has been done under solvent-free conditions at room temperature (Table 2).

Table 2 Aerobic oxidation of various alkyl arenes, alcohols, and oximes to corresponding aldehydes and ketones[a,b,c]

Entry	Substrate	Product	Time	Conversion (%)[d]	Entry	Substrate	Product	Time	Conversion (%)[d]
1			10 h	85	**20**			14 h	86
2			10 h	84	**21**			16 h	85
3			12 h	89	**22**			16 h	89
4			9 h	91	**23**			16 h	87
5			9 h	89	**24**			16 h	87
6			10 h	96	**25**			16 h	85
7			12 h	94	**26**			18 h	79

8			13 h	89	**27**[e]			7 h	66
9			12 h	90	**28**[e]			13 h	59
10			9 h	91	**29**			15 h	70
11			9 h	92	**30**			5 min	92
12			9 h	87	**31**			5 min	93
13			9 h	90	**32**			5 min	90
14			9 h	89	**33**			5 min	96
15			9 h	91	**34**			5 min	97
16			8 h	92	**35**			5 min	97
17			8 h	96	**36**			5 min	98
18			8 h	94	**37**			5 min	98
19			14 h	88					

---

[a] Reaction conditions for oxidation of alkyl arenes: alkyl arene (1.0 mmol), MnO_2@silk (0.09 g), *o*-xylene (5.0 mL), air as oxidant, reflux.

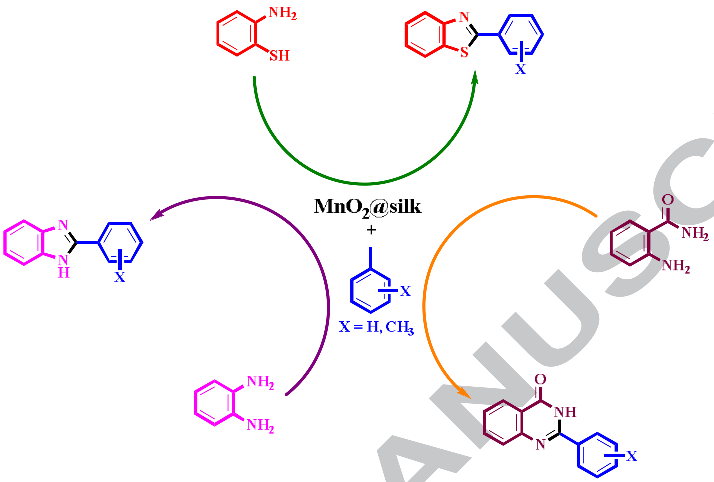
[b] Reaction conditions for oxidation of alcohols: alcohol (1.0 mmol), MnO_2@silk (0.09 g), *o*-xylene (5.0 mL), K_2CO_3 (0.5 mmol), air as oxidant, r.t.

[c] Reaction conditions for oxidation of oximes: oxime (1.0 mmol), MnO_2@silk (0.09 g), r.t.

[d] Conversion determined by GC analysis.

[e] Mixed primary and secondary benzyl alcohols (Entry 27) and alkyl alcohols (Entry 28) as the reactants was used to investigate the selectivity of the MnO_2@silk catalytic system.

Because of the oxidation of the alkyl arenes has been carried out successfully using the prepared catalyst, therefore the usability of this catalytic system has been examined for the one-pot oxidative two-component reaction of aromatic hydrocarbons of petroleum naphtha (Scheme 2).



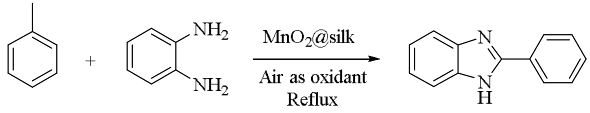
Scheme 2 The oxidative synthesis of 2-aryl-1*H*-benzo[*d*]imidazole, 2-arylbenzo[*d*]thiazole, and 2-aryl-4-quinazolinone derivatives.

Between the BTX family members (the benzene, toluene, and three isomers of xylene), as very important materials in the petroleum refining and petrochemical industries, toluene and xylenes usually are modified by chemical procedures. The products of the mentioned chemical reactions can be used as precursors in synthetic processes.

One of the important reactants in synthetic chemistry is carbonyl compounds which unfortunately this limits the diversity of these reactions. To solving this issue, one-pot oxidative protocol can be done by transforming an inert substance (such as toluene and xylenes) into a reactive substrate of the synthetic processes.

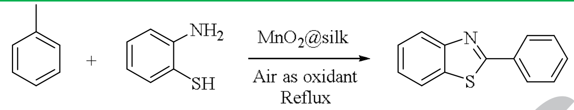
At first the MnO_2@silk catalytic system has been investigated in the oxidative synthesis of 2-phenyl-1*H*-benzo[*d*]imidazole (**3a**), 2-phenylbenzo[*d*]thiazole (**5a**), and 2-phenyl-4-quinazolinone (**7a**) as model reactions. The results of optimization studies were listed in Table 3. The results show that the entries 1, 4, and 7 have provided the best results for the synthesis of **3a**, **5a**, and **7a**, respectively.

Table 3 Optimization of the reaction conditions for the oxidative synthesis of 2-phenyl-1*H*-benzo[*d*]imidazole (**3a**), 2-phenylbenzo[*d*]thiazole (**5a**), 2-phenyl-4-quinazolinone (**7a**) compounds by silk supported MnO_2 nanocatalyst[a,b,c]



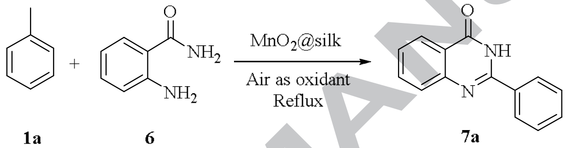
1a **2** **3a**

Entry	Amount of catalyst (mol% of MnO_2)	t (h)	Yield (%)[d]
1	**0.09 g (10)**	**10**	**69**
2	0.08 g (9)	10	50
3	0.07 g (8)	10	39



1a **4** **5a**

Entry	Amount of catalyst (mol% of MnO_2)	t (h)	Yield (%)[d]
4	**0.09 g (10)**	**9**	**75**
5	0.08 g (9)	9	52
6	0.07 g (8)	9	40



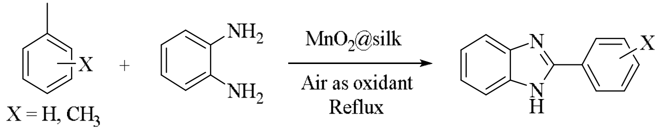
1a **6** **7a**

Entry	Amount of catalyst (mol% of MnO_2)	t (h)	Yield (%)[d]
7	**0.11 g (12)**	**16**	**86**
8	0.09 g (10)	16	59
9	0.07 g (8)	16	38

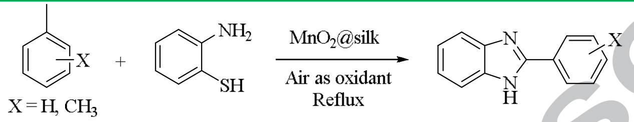
[a] Reaction conditions for the synthesis of **3a**: toluene (5.0 mL), *o*-phenylenediamine (1.0 mmol), air as oxidant, reflux.
[b] Reaction conditions for the synthesis of **5a**: toluene (5.0 mL), 2-aminobenzenethiol (1.0 mmol), air as oxidant, reflux.
[c] Reaction conditions for the synthesis of **7a**: toluene (5.0 mL), 2-aminobenzamide (1.0 mmol), air as oxidant, reflux.
[d] Isolated yield.

The MnO_2@silk catalyst has showed high capability for the oxidation of the toluene and then the synthesis of **3a**, **5a**, and **7a**. To extend the scope of the prepared catalyst, the oxidative synthesis of the **3**, **5**, and **7** compounds with xylenes have been studied. The reactions were done under air blowing and reflux conditions. The obtained results of the mentioned reactions have been presented in the Table 4.

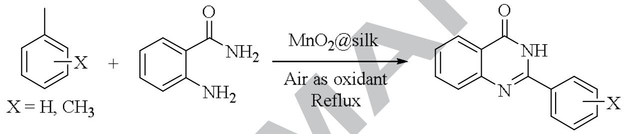
Table 4 The oxidative synthesis of 2-aryl-1*H*-benzo[*d*]imidazole (**3**), 2-arylbenzo[*d*]thiazole (**5**), and 2-aryl-4-quinazolinone (**7**) derivatives by silk supported MnO_2 nanocatalyst[a]



Entry	Arene	Product	t (h)	Yield (%)[b]	Mp (°C)	
					Found	Reported
1	toluene	**3a**	10	69	289-292	292-293 [22]
2	*o*-xylene	**3b**	10	64	221-223	223-224 [22]
3	*m*-xylene	**3c**	10	38	229-232	231-232 [22]
4	*p*-xylene	**3d**	10	78	273-275	275-276 [22]



Entry	Arenes	Product	t (h)	Yield (%)[b]	Mp (°C)	
					Found	Reported
5	toluene	**5a**	9	75	111-113	110-112 [23]
6	*o*-xylene	**5b**	9	68	56-58	55-57 [24]
7	*m*-xylene	**5c**	9	36	68-70	67-68 [23]
8	*p*-xylene	**5d**	9	82	87-89	86 [23]



Entry	Arenes	Product	t (h)	Yield (%)[b]	Mp (°C)	
					Found	Reported
9	toluene	**7a**	16	86	230-231	232-235 [25]
10	*o*-xylene	**7b**	16	78	210-212	212-215 [25]
11	*m*-xylene	**7c**	16	41	211-212	210-211 [26]
12	*p*-xylene	**7d**	16	90	230-232	231-234 [25]

[a] Reaction conditions: arene (5.0 mL), *o*-phenylenediamine (Entries 1-4, 1.00 mmol), 2-aminobenzenethiol (Entries 5-8, 1.0 mmol), 2-aminobenzamide (Entries 9-12, 1.0 mmol), MnO_2@silk (Entries 1-8, 0.09 g), MnO_2@silk (Entries 9-12, 0.11 g).
[b] Isolated yield.

Recyclability of the MnO_2@silk was examined in the oxidation of indane, 1-indanol, and 2,3-dihydro-1*H*-inden-1-one oxime and oxidative synthesis of **3a** compound. Catalyst was recovered from reaction media by filtration, washed with EtOH, dried and then reused for five repetitive cycles in the reaction. The results showed that the activity of the catalyst was saved during successive uses in a considerable amount (Fig. 5).

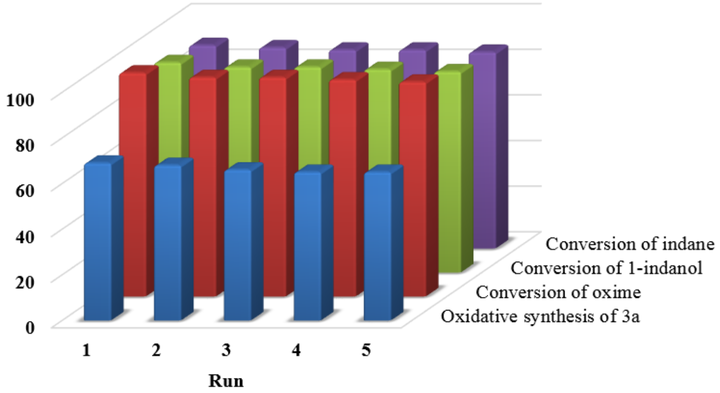


Fig. 5 Successive use of the MnO_2@silk catalyst for the oxidation of indane, 1-indanol, and 2,3-dihydro-1*H*-inden-1-one oxime and oxidative synthesis of **3a** compound.

Conclusion

In conclusion, we have developed a straightforward procedure for the aerobic oxidation and tandem oxidative synthesis of organic compounds using new biopolymer supported MnO_2 nanostructures catalyst, MnO_2@silk. The distribution of MnO_2 on the surface of silk fibers gave a biopolymer based catalytic system, which has high catalytic activity and selectivity in the aerobic oxidation of the alkyl arenes, alcohols, and oximes to the corresponding aldehydes and ketones without any overoxidation. As well, the one-pot tandem aerobic oxidative two-component reactions (O-2CRs) of aromatic hydrocarbons of petroleum naphtha, for the synthesis of 2-aryl-1*H*-benzo[*d*]imidazole, 2-arylbenzo[*d*]thiazole, and 2-aryl-4-quinazolinone derivatives, was done using MnO_2@silk. Use of air as oxidant (inexpensive oxidant) in the absence of additional oxidizing reagent, renewability, biodegradability, good yield, easy workup, the recyclability of catalyst (with no loss in its activity) are some of advantages of the MnO_2@silk catalyst.

Acknowledgements

We gratefully acknowledge financial support from the Iran National Science Foundation (INSF) and Research Council of Shahid Beheshti University.

References

[1] J.G. Hardy, L.M. Römer, T.R. Scheibel, Polymer, 49 (2008) 4309–4327.

[2] R.E. Marsh, R.B. Corey, L. Pauling, Biochim. Biophys. Acta. 16 (1955) 1–34.

[3] R.J.K. Taylor, M. Reid, J. Foot, S.A. Raw, Acc. Chem. Res. 38 (2005) 851–869.

[4] M. Kaushik, K. Basu, C. Benoit, C.M. Cirtiu, H. Vali, A. Moores, J. Am. Chem. Soc. 137 (2015) 6124–7.

[5] B. Jia, X. Yang, M.-Y. Huang, Y.-Y. Jiang, React. Funct. Polym. 57 (2003) 163–168.

[6] W.-L. Wei, H.-Y. Zhu, C.-L. Zhao, M.-Y. Huang, Y.-Y. Jiang, React. Funct. Polym. 59 (2004) 33–39.

[7] C. Crecchio, P. Ruggiero, M.D. Pizzigallo, Biotechnol. Bioeng. 48 (1995) 585–91.

[8] K. Huang, L. Xue, Y.-C. Hu, M.-Y. Huang, Y.-Y. Jiang, React. Funct. Polym. 50 (2002) 199–203.

[9] E. Guibal, Prog. Polym. Sci. 30 (2005) 71–109.

[10] J. Mei, L. Zhang, RSC Adv. 5 (2015) 14843–14850.

[11] S. Kumari, A. Shekhar, D.D. Pathak, RSC Adv. 4 (2014) 61187–61192.

[12] R. Nie, J. Shi, S. Xia, L. Shen, P. Chen, Z. Hou, et al., J. Mater. Chem. 22 (2012) 18115–18118.

[13] A. Shaabani, Z. Hezarkhani, S. Shaabani, RSC Adv. 4 (2014) 64419–64428.

[14] A. Shaabani, Z. Hezarkhani, E. Badali, RSC Adv. 5 (2015) 61759–61767.

[15] H. Mofakham, Z. Hezarkhani, A. Shaabani, J. Mol. Catal. A Chem. 360 (2012) 26–34.

[16] M. Mahyari, A. Shaabani, Y. Bide, RSC Adv. 3 (2013) 22509–22517.

[17] M. Mahyari, M.S. Laeini, A. Shaabani, Chem. Commun. 50 (2014) 7855–7857.

[18] A. Shaabani, Z. Hezarkhani, Cellulose. 22 (2015) 3027–3046.

[19] A. Shaabani, P. Mirzaei, S. Naderi, D.G. Lee, Tetrahedron. 60 (2004) 11415–11420.

[20] A. Shaabani, P. Mirzaei, D.G. Lee, Catal. Letters. 97 (2004) 119–123.

[21] A. Shaabani, Z. Hezarkhani, E. Badali, RSC Adv. 5 (2015) 91966–91973.

[22] D. Mahesh, P. Sadhu, T. Punniyamurthy, J. Org. Chem. 80 (2015) 1644–1650.

[23] Q. Song, Q. Feng, M. Zhou, Org. Lett. 15 (2013) 5990–5993.

[24] M. Bala, P.K. Verma, U. Sharma, N. Kumar, B. Singh, Green Chem. 15 (2013) 1687.

[25] H. Hikawa, Y. Ino, H. Suzuki, Y. Yokoyama, J. Org. Chem. 77 (2012) 7046–7051.

[26] J. Zhou, J. Fang, J. Org. Chem. 76 (2011) 7730–7736.

Natural Silk Supported Manganese Dioxide Nanostructures: Synthesis and Catalytic Activity in Aerobic Oxidation and One-Pot Tandem Oxidative Synthesis of Organic Compounds

Ahmad Shaabani,* Zeinab Hezarkhani, and Elham Badali

Faculty of Chemistry, Shahid Beheshti University, G. C., P. O. Box 19396-4716, Tehran, Iran

Email: *a-shaabani@sbu.ac.ir*

Silk supported MnO_2 nanostructures as a heterogeneous catalyst was synthesized and used in the aerobic oxidation of alkyl arenes, alcohols, and oximes to their corresponding carbonyl compounds and a one-pot tandem oxidative two-component reaction of aromatic hydrocarbons of petroleum naphtha in the absence of any other oxidizing reagent or initiator.