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Wool supported manganese dioxide nano-scale dispersion: As a biopolymer based catalyst for the aerobic oxidation of the organic compounds

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Abstract

Wool supported manganese dioxide nano-scale dispersion (MnO_2@wool) were synthesized by soaking wool in a potassium permanganate solution and characterized by x-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The synthesized catalyst, MnO_2@wool complex, has been found to be able to catalyze the selectively aerobic oxidation of alkyl arenes, alcohols, oximes, and sulfides to their corresponding carbonyl and sulfoxide compounds in the absence of additional oxidizing reagent. The selectively conversion of thiols to disulfides was carried on by this biopolymer based supported catalyst, too.

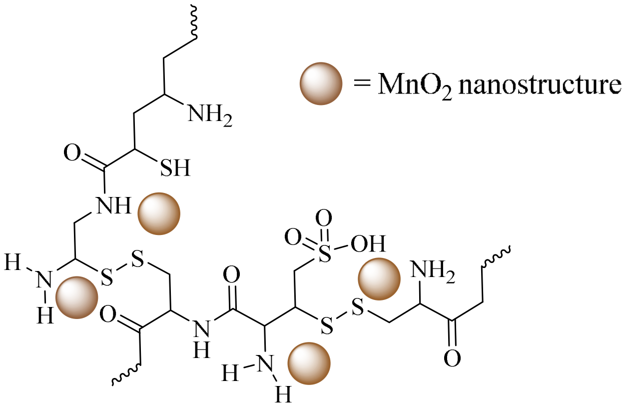
Introduction

Manganese dioxide occurs naturally as the mineral pyrolusite. This blackish or brown solid is a cheap, renewable, mild, easily handled, and low toxic reagent, which has been extensively used as catalyst for the oxidations of a variety of functional groups.[1-3] MnO_2 usually provides a relatively low surface area (10–80 m^2 g^{-1}) because of its aggregation which impresses its catalytic activities.[4] Producing of manganese dioxide nanostructures provides the large surface area of catalyst.[5] By using of supports for the distribution of MnO_2 nanostructures, aggregation of MnO_2 is prevented and high catalytic activity is accessible.[4, 6]

Industrial applications of MnO_2 have become more attractive environmentally by the introduction of a process for recycling MnO_2.[7] For this reason, it is important that at the end of the catalytic oxidation process, the MnO_2 is separable from supports. Although the procedure for separating MnO_2 from supports such as kieselguhr ,[8] aluminum silicate,[9] alumina,[10] or silica,[11] has not been described before, but in our previous work[6] it was suggested that it possible to separate the MnO_2 from a bio-support by burning or chemical decomposing of bio-support.

The oxidation of organic compounds to their corresponding oxygenated compounds by air as green oxidant using a bio-support catalyst is of main importance for both economic and environmental reasons.[12] Natural biopolymers such as cellulose,[5, 6] chitosan,[13] starch,[14] and protein[15] with emphasis on environmentally friendly, sustainable resources and reusable catalytic processes have been used as supports in various oxidation processes. However, to the best of our knowledge, the use of natural wool as attractive candidate to be solid support for oxidation reactions has not been explored until now.

Wool is a very cheap natural biopolymer of amino acids cross-linked by S–S bonds and its main component is keratin. The mentioned biopolymer contains numerous amino acids units with –NH–CO–, $–NH_2$, and –S–S– functional groups.[16] The metal uptake by wool fibers can be enhanced by chemically modifying the fibers with oxidation of –S–S– and –NH–CO– to $–SO_3H$, $–NH_3^+$ and$–CO_2^-$ groups that able to coordinate metals in the surface of the wool.[17] Furthermore, the loaded metal particles could be distributed evenly on the surface of the wool.[18] As mentioned the aggregation and agglomeration of MnO_2 particles into less active large particles and bulk MnO_2 during the reaction decreased its catalytic activities. To settle the matter, wool can be used as support for manganese dioxide nanostructures. Due to the structurally ordered amino acid chains, the aggregation of MnO_2 could be prevented. The structure of MnO_2@wool complex is shown in Scheme 1.



Scheme 1 The possible structure of MnO_2@wool

As part of our ongoing program related to developing new methods using heterogeneous catalysts for organic transformations,[19, 20] and based on our previous investigations on MnO_2,[6, 21, 22] and due to the importance of the using wool as a bio-support,[16-18] heterogeneous catalyst based on immobilization of MnO_2 nanoparticles on wool was synthesized and applied for selective aerobic oxidative transformations of alkyl arenes, alcohols, oximes, and sulfides into the corresponding carbonyl compounds and sulfoxides, in the absence of any other oxidizing reagent or initiator. Disulfides can also be prepared by aerobic oxidation of thiols using MnO_2@wool catalyst. It is important to note that these aerobic transformations did not proceed without air blowing.

Materials and methods

1 General

Natural white wool (sheep of Kangavar/Iran) was washed with NaOH solution, distilled water and methanol, and then cut into very short pieces. All reagents were obtained from Aldrich or Merck and used without further purification. Mn(IV) determination was carried out on an FAAS (Shimadzu model AA-680 flame atomic absorption spectrometer) with a Mn hollow cathode lamps 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 ºC min^{-1} in air. Products were analyzed using a Varian 3900 GC. 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). Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. All samples were sputtered with gold before observation.

2 Experimental: preparation of supported manganese dioxide nanostructures on wool

Natural white wool was washed with NaOH solution (0.01 M), distilled water and methanol and dried at 60 °C, then cut with scissors to very short pieces (about 20-500 μm, based on SEM images). To a magnetically stirred mixture of the wool pieces (1.00 g) in 200 mL of H_2O, a 0.01 M solution of $KMnO_4$ (130 mL) was added dropwise during 12 h at room temperature and stirring was continued at room temperature for 12 h. Then, the mixture was filtered and washed with $CHCl_3$ (3 × 7 mL) and EtOH (3 × 10 mL), successively and dried under vacuum at 60 °C for 12 h to give MnO_2@wool (as brown color, 1.1 g).

3 Analysis and results

The Mn(IV) content of the MnO_2@wool catalyst was determined using FAAS method and the amount of MnO_2 was determined 7.9% in this catalyst. The XRD patterns of wool fibers and MnO_2@wool were employed to investigate the structure of the synthetic catalyst. As shown in Fig. 1-I, two broad peaks of wool fibers are observed around 2θ of 9° and 21° that clearly these peaks exist in the diagram II of Fig.1. It can be seen from Fig. 1-II that all the diffraction peaks of MnO_2 nanostructures rather than the peak of wool fibers are extremely weak in intensity and four weak peaks at $2\theta = 13.90°, 24.28°, 34.60°$, and 65.26° can be ascribed to the MnO_2 nanostructures dispersed onto the surface of wool fibers.

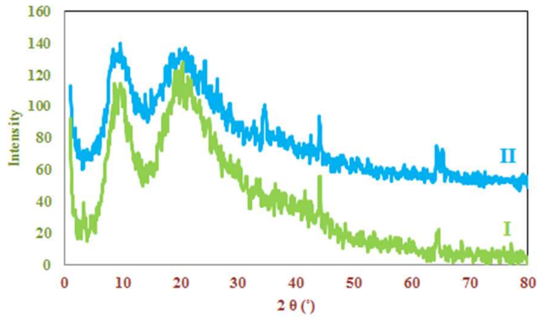


Fig. 1 XRD patterns of wool fibers (I) and MnO_2 nanoparticle coated wool fibers (II).

TGA demonstrated that wool was decomposed in three stages (Fig. 2-I): the removal of adsorbed water (stage 1) and decomposition of wool (stages 2 and 3). In fact, decomposition of wool was happened in two stages above 241 °C and 487 °C, which showed relatively high thermal stability of the wool fibers in air (Fig. 2-I). High thermal stability was observed for MnO_2@wool (Fig. 2-II), too. In the TGA curve of MnO_2@wool catalyst, three stages could be observed. In the low temperature range (up to 242 °C), the mass slowly decreased by 1.9% that should be related to the removal of adsorbed water on the surface in MnO_2@wool. In the range of 242-516 °C and 516-735 °C in two stages large weight loss for this catalyst was observed, which is attributed to the decomposition of wool.

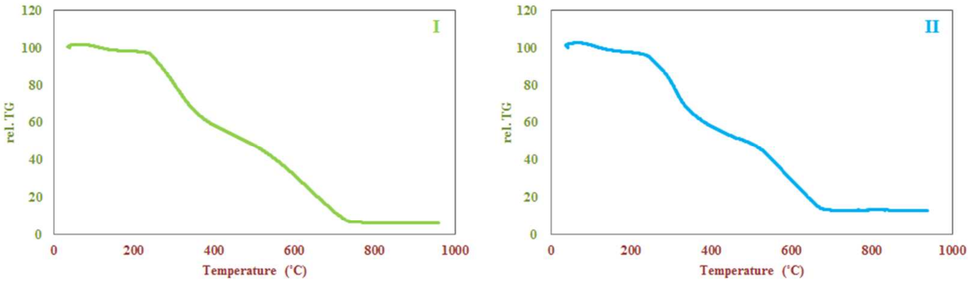


Fig. 2 TG curves of wool (I) and MnO_2 nanoparticle coated wool fibers (II) in air.

Fig. 3 reveals the surface morphology of the wool fibers and MnO_2@wool. Clearly, the wool fibers have a length of about 20-500 μm (Fig. 3a) and its surface has a wrinkled structure (Fig. 3b). The structure and morphology of the obtained MnO_2@wool composites were illustrated by SEM (Fig. 3c, d) and MnO_2 nanostructures could be observed on the wool fiber surface which nanoparticles are well dispersed on the wool fiber surface (Fig. 3d).

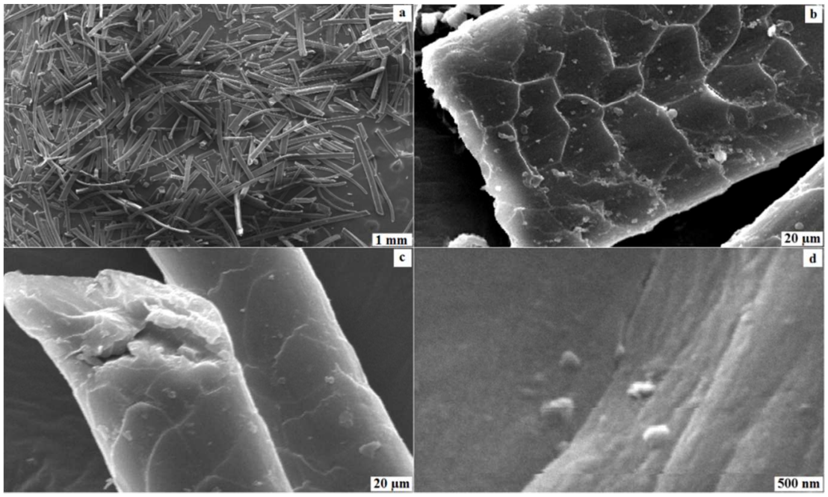


Fig. 3 SEM images of wool (a, b) and MnO_2@wool (c, d).

Additionally, for determination of the chemical composition of MnO_2@wool composite, the energy dispersive spectroscopy (EDS) analysis was employed that proves the presence of manganese in the MnO_2@wool composite (Fig. 4).

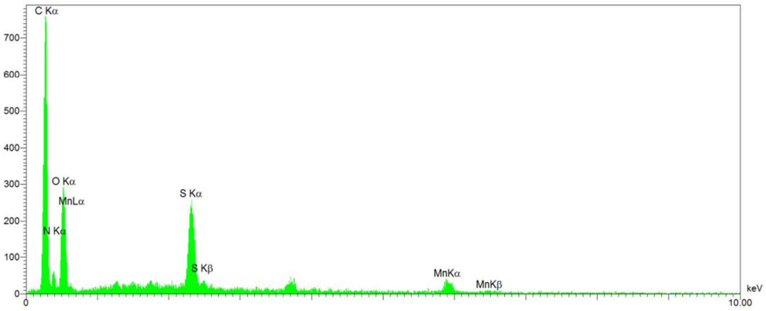


Fig. 4 SEM-EDS results for MnO_2@wool catalyst.

4 Oxidation of alkyl arenes; General procedure

In a typical reaction, an alkyl arene (1.00 mmol), MnO_2@wool (0.11 g, 10 mol% of MnO_2), and *o*-xylene (5.00 mL) were added to a two-necked flask. The mixture was stirred under reflux conditions and air blowing for the indicated time in Table 2. 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.

5 Oxidation of alcohols; General procedure

In a typical reaction, an alcohol (1.00 mmol) was added to a two-necked flask containing MnO_2@wool (0.11 g, 10 mol% of MnO_2), K_2CO_3 (0.50 mmol), and *o*-xylene (5.00 mL) and stirred under room temperature and air blowing for the indicated time in Table 4. The progress of the reaction was followed by TLC. After completion of reaction and then filtration, the filtrate was analyzed by GC method.

6 Oxidation of oximes; General procedure

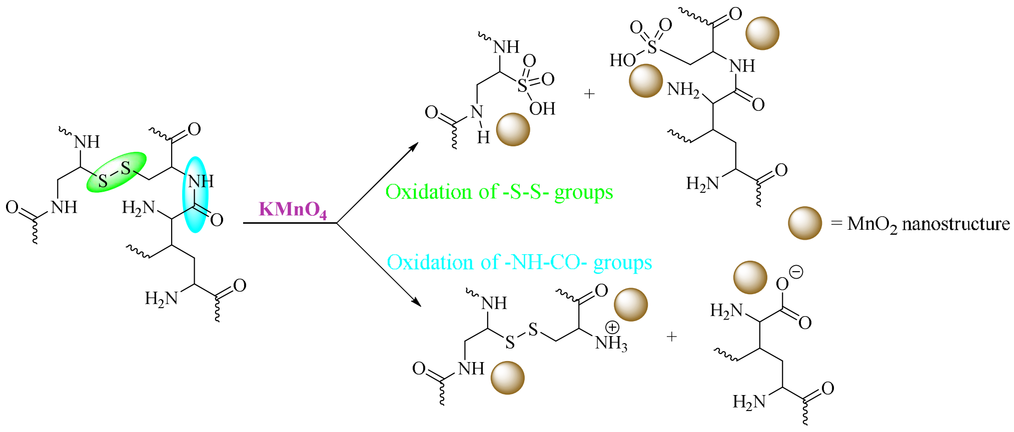
MnO_2@wool (0.11 g, 10 mol% of MnO_2) and an oxime (1.00 mmol) were well ground at room temperature using a pestle. The progress of the reaction was monitored by TLC. After the indicated time in Table 6 which the reaction was complete, the solid was washed with dichloromethane (3 × 5 mL). After the filtration of the reaction mixture, the filtrate were evaporated to give crude product. Analysis of the crude product has been done by GC method.

7 Oxidation of sulfides and thiols; General procedure

In a round bottom flask, to a solution of sulfide or thiol (1.00 mmol) in *o*-xylene (5.00 mL), MnO_2@wool catalyst (0.11 g, 10 mol% of MnO_2 for oxidation of sulfides and 0.22 g, 20 mol% of MnO_2 for oxidation of thiols) was added and the mixture was stirred magnetically at room temperature for the indicated time in Table 5. the progress of the reaction was monitored by TLC. After completion, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure to give the corresponding pure sulfoxide or disulfide. All of the products were characterized by melting points which were compared with those obtained from authentic samples.[23-25]

Results and discussion

The natural wool was treated by potassium permanganate. The $KMnO_4$ is able to oxidize and modify the surface of wool, and *in situ* was reduce to MnO_2 nanostructures as a catalyst. $KMnO_4$ molecules were adsorbed by the wool fibers and the maximum absorption of $KMnO_4$ is at the edge of scale layer. The $KMnO_4$ can attack the disulfides linkage and the peptide bonds of the wool fiber and reduced to MnO_2 covering on the surface of this fiber.[26] In fact, the wool fibers act not only as a reduction agent to produce MnO_2, but also has support role to impregnate MnO_2 nanostructures on its surface (Scheme 2).



Scheme 2 The preparation of MnO_2@wool catalyst.

After the successful production of catalytic systems in which wool plays dual role: as a *in situ* reducing agent of $KMnO_4$ to generate MnO_2 nanostructures and as the support to achieve a suitable catalytic system for aerobic oxidation, we examined MnO_2@wool catalyst in the reaction media. Aerobic oxidation of indane was selected as a model reaction. Indane (0.12 g, 1.00 mmol), MnO_2@wool, solvent (5.00 mL) were added to a two-necked flask equipped with a gas bubbling tube. Air that used as an environment friendly oxidant, was bubbled at a rate of 5 mL min^{-1}. After completion of reaction, as indicated by TLC or GC method, catalyst was filtered and washed with acetone (2 × 5 mL), and EtOH (2 × 5 mL). The analysis of the crude product using GC method showed that corresponding aldehydes and ketones was produced.

In order to find the best reaction conditions, optimization studies were performed in various solvents (Table 1, Entries 2-10). The efficiency of MnO_2@wool catalyst in *o*-xylene was higher than other solvents (Table 1, Entries 10). Therefore *o*-xylene was selected as the preferred solvent for the aerobic oxidation of indane.

From the data presented in the Table 1, it is clear that the prepared catalyst, MnO_2@wool, has better catalytic role than aggregated MnO_2 (Entries 1 and 10).

The comparison of the results related to the effect of various amounts of MnO_2@wool revealed that the 10 mol% of MnO_2 is providing the best result (Table 1, Entries 10-12).

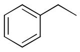
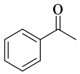
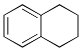
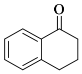
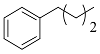
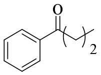
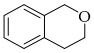
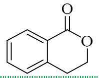
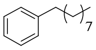
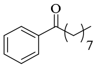
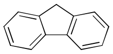
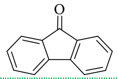
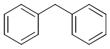
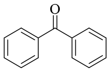
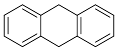
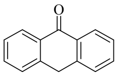
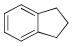
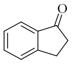
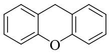
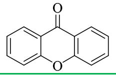
Table 1 Optimization of the reaction conditions for aerobic oxidation of alkyl arenes by MnO_2@wool catalyst[a]

Entry	Catalyst	Amount of catalyst (MnO_2 content/mol%)	Solvent	Yield (%)[b]
1	MnO_2	0.01 g (10)	*o*-xylene	24
2	MnO_2@wool	0.11 g (10)	n-hexane	61
3	MnO_2@wool	0.11 g (10)	CH_2Cl_2	49
4	MnO_2@wool	0.11 g (10)	CH_3CN	22
5	MnO_2@wool	0.11 g (10)	THF	19
6	MnO_2@wool	0.11 g (10)	MeOH	Trace
7	MnO_2@wool	0.11 g (10)	EtOH	Trace
8	MnO_2@wool	0.11 g (10)	DMF	25
9	MnO_2@wool	0.11 g (10)	toluene	83
10	**MnO_2@wool**	**0.11 g (10)**	***o*-xylene**	**99**
11	MnO_2@wool	0.09 g (8)	*o*-xylene	63
12	MnO_2@wool	0.07 g (6)	*o*-xylene	46

[a] Reaction conditions for MnO_2@wool catalyst: indane (1.00 mmol), solvent (5.00 mL), air as oxidant, reflux, 10 h.
[b] Yield determined by GC analysis.

Finally, the oxidation of the various alkyl arenes to related carbonyl compounds using MnO_2@wool catalyst in *o*-xylene as the preferred solvent under reflux conditions was studied. The oxidation of the alkyl arenes was proceeded effectively and selectively without any overoxidation to carboxylic acid during the reaction (Table 2).

Table 2 Aerobic oxidation of variuos alkyl arenes to corresponding ketones[a]

Entry	Alkyl arene	Product	Time (h)	Yeild (%)[b]	**Entry**	Alkyl arene	Product	Time (h)	Yeild (%)[b]
1			10	93	**6**			10	91
2			12	95	**7**			12	84
3			12	86	**8**			9	99
4			9	100	**9**			9	94
5			10	99	**10**			10	89

[a] Reaction conditions: alkyl arene (1.00 mmol), MnO_2@wool (0.11 g), *o*-xylene (5.00 mL), air as oxidant, reflux.
[b] Yield determined by GC analysis.

The oxidation of the alkyl arenes has been carried out successfully using the MnO_2@wool catalyst, therefore the usability of this catalytic system has been examined for the oxidation of the alcohols, as well. Optimization studies were performed with aerobic oxidation of 1-indanol, as a model substrate. As indicated in Table 3, the best result is related to the 10 mol% of of MnO_2, *o*-xylene as a preferred solvent, and K_2CO_3 as base (Entry 10).

Table 3 Optimization of the reaction conditions for aerobic oxidation of alcohols by MnO_2@wool catalyst[a]

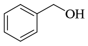
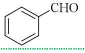
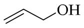
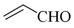
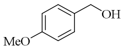
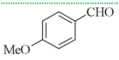
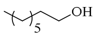
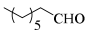
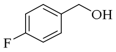
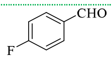
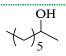
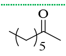
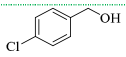
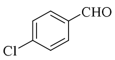
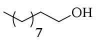
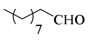
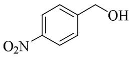
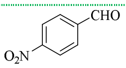
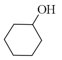
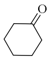
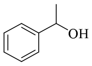
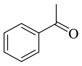
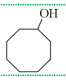
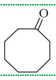
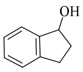
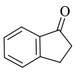
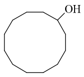
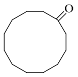
Entry	Catalyst	Amount of catalyst (MnO_2 content/mol%)	Solvent	Base (mmol)	Yield (%)[b]
1	MnO_2	0.01 g (10)	*o*-xylene	K_2CO_3 (0.5)	32
2	MnO_2@wool	0.11 g (10)	n-hexane	K_2CO_3 (0.5)	91
3	MnO_2@wool	0.11 g (10)	CH_2Cl_2	K_2CO_3 (0.5)	48
4	MnO_2@wool	0.11 g (10)	CH_3CN	K_2CO_3 (0.5)	19
5	MnO_2@wool	0.11 g (10)	THF	K_2CO_3 (0.5)	28
6	MnO_2@wool	0.11 g (10)	MeOH	K_2CO_3 (0.5)	trace
7	MnO_2@wool	0.10 g (10)	EtOH	K_2CO_3 (0.5)	trace
8	MnO_2@wool	0.09 g (10)	DMF	K_2CO_3 (0.5)	33
9	MnO_2@wool	0.11 g (10)	toluene	K_2CO_3 (0.5)	89
10	**MnO_2@wool**	**0.11 g (10)**	***o*-xylene**	**K_2CO_3 (0.5)**	**98**
11	MnO_2@wool	0.09 g (8)	*o*-xylene	K_2CO_3 (0.5)	69
12	MnO_2@wool	0.07 g (6)	*o*-xylene	K_2CO_3 (0.5)	44
13	MnO_2@wool	0.11 g (10)	*o*-xylene	KOH (0.5)	54
14	MnO_2@wool	0.08 g (10)	*o*-xylene	Na_2CO_3 (0.5)	36
15	MnO_2@wool	0.11 g (10)	*o*-xylene	-	27

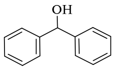
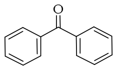
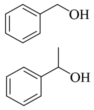
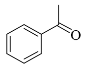
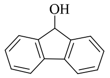
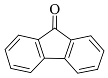
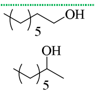
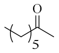
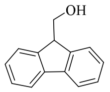
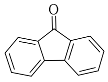
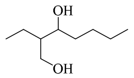
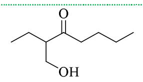
[a] Reaction conditions: 1-indanol (1.00 mmol), solvent (5.00 mL), air as oxidant, r.t., 8 h.

[b] Yield determined by GC analysis.

To extend the scope of the prepared catalyst, the oxidation of the alcohols to the related carbonyl compounds have been investigated. The results of the mentioned reactions have been presented in the Table 4. The reactions were done under air blowing at room temperature with good to high yields. Selectivity for the oxidation of the alcohols to the corresponding carbonyl compounds had been observed, too (Table 4).

Table 4 Selective aerobic oxidation of variuos alcohols to corresponding aldehydes and ketones[a]

Entry	Alcohol	Product	Time (h)	Yield (%)[b]	Entry	Alcohol	Product	Time (h)	Yield (%)[b]
1			8	98	**11**			12	96
2			8	93	**12**			14	89
3			8	92	**13**			13	90
4			8	93	**14**			14	85
5			8	95	**15**			13	93
6			7	98	**16**			13	88
7			8	98	**17**			13	86

8			6	99	**18**			6	94^{c}
9			6	97	**19**			13	87^{c}
10			9	87	**20**			13	89^{c}

[a] Reaction conditions: alcohol (1.00 mmol), MnO_2@wool (0.11 g), K_2CO_3 (0.50 mmol), o-xylene (5.00 mL), air as oxidant, r.t.

[b] Yield determined by GC analysis.

[c] The yield of only ketone product determined by GC analysis and the integrals of the ^{1}H NMR.

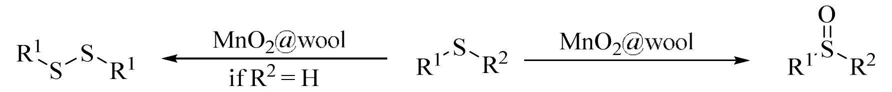
According to Table 4, MnO_2@wool catalyst showed high selectivity for the oxidation of the benzylic alcohols to the related carbonyl compound, and no carboxylic acid was produced (Entries 1-10). The prepared catalyst has same selectivity for the oxidation of allylic and aliphatic alcohols to corresponding aldehydes and ketones (Entries 11-17).

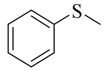
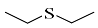
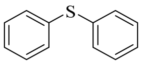
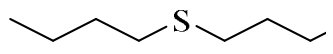
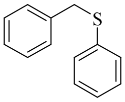
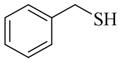
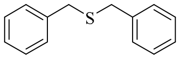
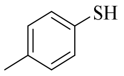
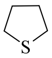
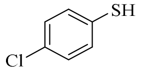
Variety of reagents are available to selectively oxidize a secondary alcohol in the presence of primary alcohol. The rate of these used reagents to oxidize secondary alcohols is slightly faster than primary alcohols but some of reagents have not been highly selective for oxidation of secondary alcohols because of the small magnitudes of rate differences. In fact, when the substrate structure is compatible with the reaction mechanism of the reagent, high selectivity is possible.[27] Between these reagents, MnO_2 acts highly selective for the oxidation of secondary aliphatic and benzylic alcohols in the presence of primary ones.[6] In our previous work, examples of inter- and intramolecular competition experiments and regioselective oxidations was shown basis on the evidence for secondary-primary selectivity of MnO_2 stable nano-scale dispersion.[6]

In this report, mixed primary and secondary benzyl alcohols (Entry 18) and alkylalcohols (Entry 19) as the reactants was used to investigate the selectivity of the MnO_2@wool catalytic system. The results showed that the oxidation of the secondary functional group is favored and only one of the reactants undergoes oxidation reaction. The oxidation of 2-ethylheptane-1,3-diol, a diol with both primary and secondary hydroxyl functional groups revealed that only product 3-(hydroxymethyl)octan-4-one was obtained (Entry 20). In both cases (inter- and intramolecular competition experiments), at first step the oxidation of the secondary functional group was done and in continue after the completion of this reaction, the transformation of the primary alcohol was started.

The production of sulfoxide containing compounds as important intermediates in organic chemistry, medicinal chemistry and drug metabolism are very important.[28] Since oxidation of sulfides with manganese dioxide is known to give only sulfoxides,[22] the oxidation of the sulfides to the related sulfoxides compounds using MnO_2@wool has been investigated as well. The obtained results (Table 5, Entries 1-7) showed that the oxidation of sulfides to sulfoxides has been carried out without any overoxidation to sulfones. Aerobic oxidation of thiols to the related disulfides using MnO_2@wool catalyst was done and the obtained data have been shown in the Table 5 (Entries 8-10).

Table 5 Selectively aerobic oxidation of variuos sulfides to corresponding sulfoxides[a]



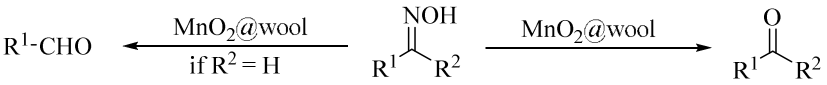
Entry	Sulfide or thiol	Time (h)	Yield (%)[b]	Entry	Sulfide or thiol	Time (h)	Yield (%)[b]
1		3	97	**6**		5	96
2		4	94	**7**		6	88
3		7	90	**8**		1	93
4		7	87	**9**		1.5	96
5		5	91	**10**		1.5	87

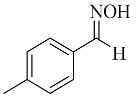
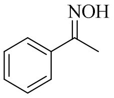
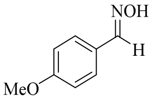
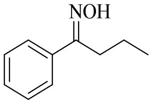
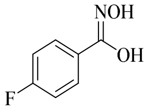
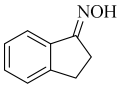
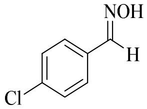
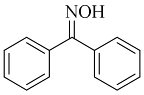
[a] Reaction conditions: sulfide or thiol (1.00 mmol), MnO_2@wool (0.11 g, 10 mol% of MnO_2 for oxidation of sulfides and 0.22 g, 20 mol% of MnO_2 for oxidation of thiols), *o*-xylene (5.00 mL), air as oxidant, r.t.
[b] Yield determined by GC analysis.

Imine derivatives of carbonyl compounds (such as oximes, semicarbazones and phenylhydrazones) are used extensively for the characterization, isolation, and purification of carbonyl compounds. Oximes are also used as carbonyl protectors of parent carbonyl compounds[29, 30] because of their hydrolytic stability and could be regenerated at the completion of a synthetic procedure. On the other side oximes can also be prepared from noncarbonyl compounds. The carbonyl generation from these compounds provides an alternative method for the preparation of aldehydes and ketones[31]. Many methods such as hydrolytic, reductive, and oxidative reactions and reagents have been reported for regeneration of carbonyl compounds from oxime derivatives. Using mild reagents and reaction conditions will cause the regeneration of the carbonyl compound to be done without modification to the rest of the molecule.

Thus, oxidation of oximes to the related carbonyl compounds has been studied under solvent-free conditions at room temperature with the yields between 87 and 99. The obtained results have been presented in the Table 6. It is important to note that with adding several drops of any solvent which can solve the oximes, and oxidation reactions were accelerated.

Table 6 Selectively oxidation of variuos oximes to corresponding aldehydes and ketones[a]



Entry	Alcohol	Time (min)	Yield (%)[b]	**Entry**	Alcohol	Time (min)	Yield (%)[b]
1		7	94	**5**		7	96
2		7	91	**6**		7	94
3		9	87	**7**		6	97
4		9	90	**8**		5	99

[a] Reaction conditions: oxime (1.00 mmol), MnO_2@wool (0.11 g), room temperature.
[b] Yield determined by GC analysis.

Recyclability of the MnO_2@wool catalyst was examined in the oxidation reaction of indane, 1-indanol, 2,3-dihydro-1H-inden-1-one oxime, and methyl phenyl sulfide. Catalyst was recovered from reaction media by filtration and reused for three repetitive cycles in the reaction. The results revealed that the activity of the MnO_2@wool was saved during successive uses (Fig. 5).

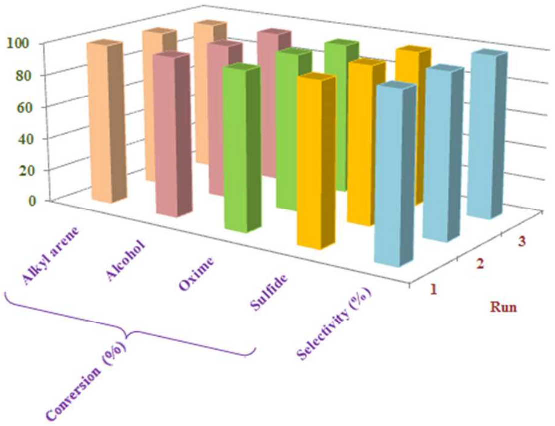


Fig. 5 Successive use of the prepared catalyst for the oxidation of indane, 1-indanol, 2,3-dihydro-1H-inden-1-one oxime, and methyl phenyl sulfide.

The results of our investigations have been compared to previous reports of MnO_2.[6, 8, 9, 11, 32-35] The results show that MnO_2 impregnated on wool is one of the best oxidant systems in reaction times and yield viewpoints (Table 7).

Table 7 Comparison of the results obtained from active MnO_2, MnO_2 on different supports and nano MnO_2 impregnated on wool for the oxidation of benzylalcohol

Entry	Catalyst	Conditions	Molar ratio substrate to MnO_2	Time (h)	Yield (%)	Ref.
1	active MnO_2	solvent free/ r.t.	1:0.08	48	77	[32]
2	active MnO_2	toluene/O_2/110 °C	1:0.80	4	85	[33]
3	MnO_2/Graphite	CH_2Cl_2/ref.	1:2.00	10	92	[34]
4	MnO_2/Kieselguhr	CH_2Cl_2/ref.	1:2.00	10	90	[35]
5	MnO_2/Kieselguhr	solvent free/50-55 °C/grind	1:2.00	3	95	[8]
6	MnO_2/Aluminum Silicate	CH_2Cl_2/ref.	1:3.00	12	96	[9]
7	MnO_2/Silica	solvent free/ref./Microwave irradiations	1:5.00	0.3	88	[11]
8	Nano MnO_2/Cellulose	*o*-xylene/air/r.t.	1:0.10	7	99	[6]
9	Nano MnO_2@wool	*o*-xylene/air/r.t.	1:0.10	8	98	This work

Conclusion

Manganese dioxide nanostructures supported on wool which composed of protein with repeated unit of amino acid, as bio-supported heterogeneous catalyst, were synthesized and used for the selective oxidation of a variety of functional groups. The distribution of MnO_2 on the surface of wool fibers gave an active catalytic system. The prepared catalyst showed high selectivity for the aerobic oxidation of the alkyl arenes, alcohols, and sulfides to the related carbonyl and sulfoxide compounds without any overoxidation. Use of air as oxidant (inexpensive oxidant), the absence of any co-promoter and additional oxidizing reagent, the recyclability of catalyst with no loss in its activity, excellent yield, and easy workup are several advantages of MnO_2@wool catalyst. This catalyst has high selectivity for the oxidation of oximes to related aldehydes and ketones.

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