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Cellulose Supported Manganese Dioxide Nanosheets Catalyzed Aerobic Oxidation of Organic Compounds

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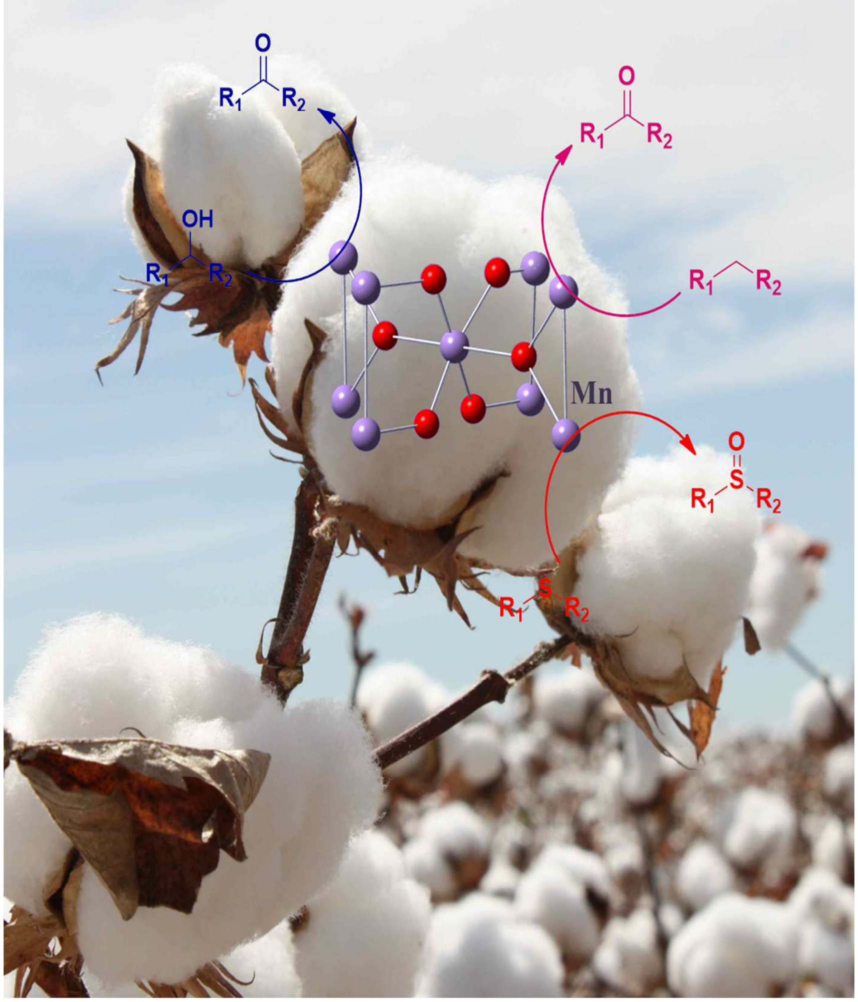

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Abstract

Cellulose supported manganese dioxide nanosheets, as a heterogeneous bio-supported and green catalyst, were synthesized by soaking porous cellulose in potassium permanganate solution. The prepared catalyst was used effectively for the oxidation of various types of alkyl arenes, alcohols and sulfides to their corresponding carbonyl and sulfoxide compounds, respectively in high yields by air as oxidant at ambient pressure. The catalyst can be recycled and reused for five runs without any significant loss of efficiency. Mild reaction conditions for the oxidation of alcohols and sulfides, high yields, recyclability of the catalyst, and very easy workup procedure are other advantageous of this catalyst.

1 Introduction

Oxidation reactions are among the most important transformations in synthetic chemistry, providing key methodologies to introduce and modify functional groups. The aerobic oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds is of significant importance in organic chemistry, both for fundamental research and industrial manufacturing.[1] Reactions related to the production of sulfoxide containing compounds in organic chemistry, medicinal chemistry and drug metabolism are very important, too.[2]

Oxidation reactions have been traditionally performed using stoichiometric inorganic oxidants, which are relatively expensive, toxic, environmentally polluting. Also, they generate large amounts of by-products.[3] Consequently, introducing green, biodegradable, recyclable, selective, and efficient aerobic oxidation systems for alkyl arenes, alcohols, and sulfides are of great importance for both economic and environmental reasons. Because of these reasons, different oxidation systems have been introduced; among them, manganese dioxide[4] and

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manganese dioxide nanosheets[5] are useful selective oxidizing reagents that are available for oxidation of organic compounds.

From both environmental and economic viewpoints, heterogeneous catalysts have attracted considerable interest for catalytic systems. Various materials have been employed as the support to produce heterogeneous catalytic systems, such as mesoporous silica,[6] activated carbon,[7] (bio)polymer[8] and biomass.[9] Recently, the direction of science and technology has been shifted to emphasis on environmentally friendly, sustainable resources and reusable catalytic processes. In this regard, natural biopolymers such as alginate,[10] gelatin,[11] starch,[12] and chitosan[13] derivatives are attractive candidates to be used as solid support for the catalysts. Among several heterogeneous bio-supports, cellulose and its derivatives, as a renewable resource, have unique properties, which make them attractive supports for catalytic applications.[14]

Manganese dioxide is a cheap, mild, low toxic, and selective reagent for the oxidation of a variety of functional groups, especially for the transformation of primary and secondary alcohols and alkyl arenes to the corresponding aldehydes and ketones. This catalyst has found an important place among the oxidants used in organic chemistry.[4] MnO_2, itself, is an aggregated heterogeneous catalyst whose catalytic activities have been underestimated because of a relatively low surface area (10–80 $m^2\ g^{-1}$). Manganese dioxide nanostructures have large surface area and high catalytic activity.[15] Using of cellulose as a support for MnO_2 nanostructures produces the well distributed MnO_2 on the surface of the cellulose with good dispersity;[5] the obtained catalyst has better catalytic role than aggregated MnO_2.

It is important to note, in the previous descriptions of MnO_2 supported catalysts, procedure for separating manganese dioxide from solid supports such as kieselguhr,[16] aluminum silicate,[17] alumina,[18] or silica,[19] have not been reported. Our experiences with these reagants suggest that separation of the MnO_2 from support, to reuse it, will not be easily achieved. We have, consequently, begun to investigate other strategies.[20]

The combination of MnO_2 with cellulose produces a catalyst which effectively catalyses the aerobic oxidation of variety organic compounds. At the end of the catalytic oxidation process, the MnO_2 is separable from cellulose by burning or chemical decomposing methods. Then, manganese dioxide can be

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used to regenerated potassium permanganate in a two stage process; involving air oxidation of MnO_2 to potassium manganate(VI) in a concentrated potassium hydroxide solution followed by electrochemical oxidation.[20a]

In view of our general interest in aerobic oxidation reactions,[21] cellulose-supported catalysts[22] and $KMnO_4$,[23] herein we report a simple and convenient method for the aerobic oxidation of various types of primary and secondary benzylic hydrocarbons, alcohols and sulfides. The reaction condition is mild and the catalytic system includes MnO_2 nanosheets on cellulose fibers (MnO_2/Cellulose) as a heterogeneous bio-supported catalyst. The introduced catalytic system is efficient, biodegradable, reusable, and uses the air at ambient pressure as the oxidant.

2 Materials and methods

2.1 General

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 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 ºC min^{-1} in air. Products were analyzed using a Varian 3900 GC. X-ray diffraction (XRD) pattern of product 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.

2.2 Preparation of MnO_2/Cellulose

Five different procedures have been used to grow nanostructured MnO_2 on the natural cellulose fibers:

*2.2.1 Preparation of MnO_2/Cellulose **1** (Method 1)*

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To a magnetically stirred suspention of cellulose (1.00 g) in 20 mL of H_2O, a 0.01 M solution of $KMnO_4$ (120 mL) was added dropwise during 12 h at room temperature. The stirring was continued at room temperature for 72 h; 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/Cellulose.

*2.2.2 Preparation of MnO_2/Cellulose **2** (Method 2)*

Cellulose (1.00 g) was added to 120 mL of solution of $KMnO_4$ (0.01 M) during 12 h at room temperature. The mixture was stirred at room temperature for 72 h. Finally, the product was filtered and washed with $CHCl_3$ (3 × 7 mL) and EtOH (3 × 10 mL), and dried under vacuum at 60 °C.

*2.2.3 Preparation of MnO_2/Cellulose **3** (Method 3)*

Manganese dioxide nanosheets on cellulose fiber was prepared from $KMnO_4$ solution according to the report by Zhou and coworkers.[5]

*2.2.4 Preparation of MnO_2/Cellulose **4** (Method 4)*

In this procedure, first, a preheated solution of $MnCl_2$ (0.02 M, 60 mL, 70 °C) was dropwise added to the solution of $KMnO_4$ (0.01 M, 80.0 mL) at 60 °C to obtain active MnO_2. After that, the mixture was filtered, washed with $CHCl_3$ (3 × 7 mL) and EtOH (3 × 10 mL) and dried at 60 °C. Finally active MnO_2 (0.11 g) was mixed with cellulose (1.00 g) by simple stirring to produce the desired MnO_2/Cellulose.

*2.2.5 Preparation of MnO_2/Cellulose **5** (Method 5)*

A mixture of cellulose (1.00 g) in 20 mL of H_2O at 60 °C, a solution of $KMnO_4$ (0.01 M, 80.0 mL) at 60 °C, and a solution of $MnCl_2$ (0.02 M, 60 mL) at 70 °C were prepared, separately. In continue, the solutions of KMnO4 and MnCl2 were added dropwise to the mixture of cellulose for 12 h at 60 °C. The mixture was stirred at room temperature; after 24 h, it was filtered, and the residue washed successively with $CHCl_3$ (3 × 7 mL) and EtOH (3 × 10 mL) and dried under vacuum at 60 °C.

The Mn(IV) content of the produced catalysts was determined using FAAS method. The amount of MnO_2 in the MnO_2/cellulose catalysts **1-5** was determined 6.19%, 7.03%, 8.59%, 9.01%, and 8.48%, respectively.

Thermogravimetric analysis (TGA) was used to analyze the contents of MnO_2 in above mentioned MnO_2/cellulose composites. In all of the TGA curves three stages could be observed. First stage occurred in the low temperature range (up to 200 °C). In this stage, the mass slowly decreased by 3.3%, 1.6%, 7.2%, 1.7% and 1.8% for MnO_2/cellulose **1-5**, respectively; it was related to the removal of adsorbed water on the surface in MnO_2/cellulose **1-5** and part of the adsorbed oleic acid in MnO_2/cellulose **5**.[5] In second stage, in the range of 200-400 °C, a large weight loss was observed which correspond to the decomposition of cellulose fibers and release of water from manganese oxide crystallites[5,24] in MnO_2/cellulose **1-5** and the complete removal of adsorbed oleic acid[5,25] in MnO_2/cellulose **5**. In the third stage, in the range of 400-900 °C, the weight loss of about 0.8-3.9% for MnO_2/cellulose **1-5** was observed, which is probably attributed to lattice oxygen.[5,24,26] The amount of MnO_2 in the MnO_2/cellulose fiber composites is suggested to be 6.4%, 7.2%, 8.7%, 9.3%, and 8.6%, in MnO_2/cellulose **1-5**, respectively (Fig.1), that corroborates the amount of MnO_2 in the MnO_2/cellulose catalysts **1-5** determined using FAAS method.

TGA demonstrated that MnO2/Cellulose was decomposed above 300 °C, which showed the relatively high thermal stability of this catalyst in air (Fig.1, f-a). Also, MnO_2/Cellulose recovered from the reaction has good thermal stability and was decomposed above 296 °C (Fig.1, f-b).

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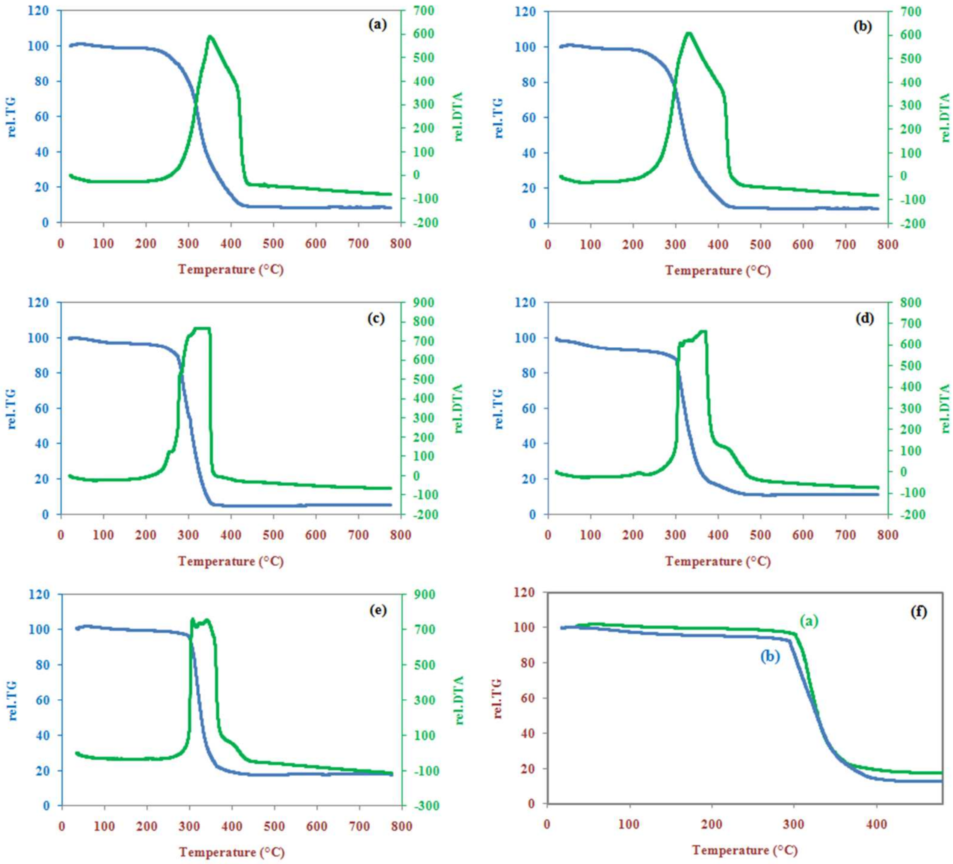

Fig. 1 TG-DTA curves of MnO_2 nanoparticle coated cellulose fibers (MnO_2/Cellulose **1** (a), MnO_2/Cellulose **2** (b), MnO_2/Cellulose **3** (c), MnO_2/Cellulose **4** (d), MnO_2/Cellulose **5** (e) and MnO_2/Cellulose **5** (f-a) and recovered MnO_2/Cellulose **5** (f-b)) in air

In addition to TGA, XRD pattern of cellulose fibers and MnO_2/cellulose **5** was also employed to investigate the structure of the catalyst. Fig. 2 shows the XRD pattern of cellulose fibers and MnO_2/cellulose fibers **5**. A strong peak at $2\theta = 22.56°$ and two weak peaks at 2θ of 5.01° and 15.07° can be ascribed to the cellulose.[5,27] Four weak peaks at 2θ of 11.18°, 25.77°, 34.57°, and 64.44°are also observed that corresponded to manganese oxide nanosheets.[5]

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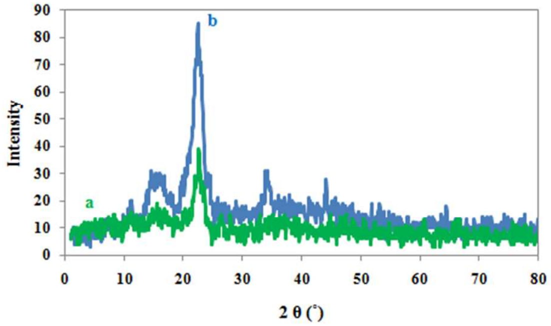

Fig. 2 XRD patterns of cellulose fibers (a) and MnO_2 nanoparticle coated cellulose fibers obtained from method **5** (b)

The SEM analyses have been used to study the structure and morphology of the prepared MnO_2 nanostructures coated on cellulose fibers (Fig. 3). The SEMs show good dispersity of MnO_2 nanoparticles on cellulose fibers (Fig. 3a-f). Additionally, the energy dispersive spectroscopy (EDS) analysis, that determined the chemical composition of MnO_2/Cellulose composite, proves the presence of manganese in the MnO_2/cellulose composite **5** (Fig. 3g).

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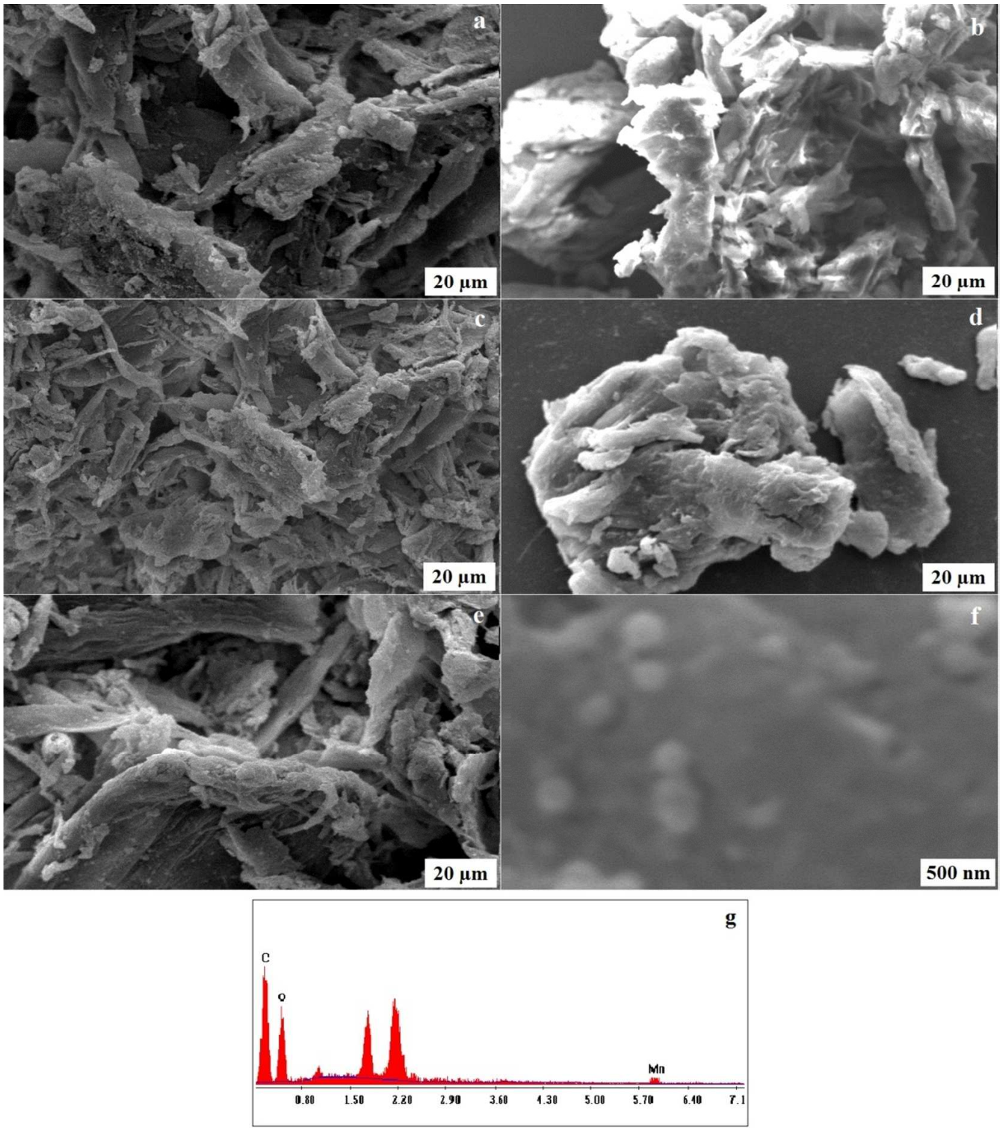

Fig. 3 SEM images of cellulose/MnO_2 composites prepared from method 1 (a), 2 (b), 3 (c), 4 (d), and 5 (e-f) and EDS result for MnO_2/Cellulose **5** (g).

In the following section, the utility of the prepared catalysts has been examined, for aerobic oxidation of various organic compounds including alkyl arenes, alcohols, and sulfides.

2.3 Oxidation of alkyl arenes; General procedure

An alkyl arene (1 mmol) and MnO_2/Cellulose **5** (0.1 g, 10 mol%) were stirred in *o*-xylene (5 mL) under air blowing for several hours at 120 °C. The TLC method was used to investigate the progress of the reaction. After the

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filtration of the reaction mixture, analysis of the crude product has been done by GC method.

2.4 Oxidation of alcohols; General procedure

In a typical reaction, an alcohol (1 mmol) was added to a two-necked flask containing MnO_2/Cellulose **5** (0.1 g, 10 mol%), K_2CO_3 (0.5 mmol), and *o*-xylene (5 mL). The reaction mixture was stirred under air blowing for several hours at room temperature. The progress of the reaction was followed by thin layer chromatography (TLC). Upon completion, the reaction mixture was filtered and the filtrate was analyzed by GC method.

2.5 Oxidation of sulfides; General procedure

In a typical reaction, a sulfide (1 mmol), MnO_2/Cellulose **5** (0.1 g, 10 mol%), K_2CO_3 (0.5 mmol), and *o*-xylene (5 mL) have been stirred in a two-necked flask under air blowing. The reaction mixture was stirred at room temperature for several hours and the progress of the reaction was followed by GC method. Upon completion, the reaction mixture was filtered and the crude product analyzed by GC method. The yields were determined from the integrals of the GC analysis.

3 Results and discussion

To achieve a suitable catalytic system for aerobic oxidation, we examined various MnO_2/Cellulose catalysts **1-5** in the presence of K_2CO_3 as a base. Aerobic oxidation of benzylalcohol was selected as a model reaction. Benzylalcohol (0.1 g, 1.0 mmol), MnO_2/Cellulose (0.1 g), K_2CO_3 (0.07 g, 0.5 mmol) and *o*-xylene (5 mL) were added to a two-necked flask equipped with a air bubbling tube. Air was bubbled into the reaction mixture at a rate of 5 $mLmin^{-1}$. After compeletion of the reaction, as indicated by TLC method, MnO_2/Cellulose catalyst was separated by filtration and washed with acetone (2 × 5 mL), and EtOH (2 × 5 mL). The analysis of the crude product using GC method showed that only the aldehyde was produced selectivly, and no acid product was observed.

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The comparison of the results related to the use of catalyst prepared with the mentioned methods **1-5** revealed that the efficiency of MnO_2/Cellulose perepared by method **5** was higher than other MnO_2/Cellulose catalysts; the reaction yield was 99% after 7h at room temperature. The order of activity of different MnO_2/Cellulose catalysts have been shown in Table 1 (Entries 2-6).

It is important to note that the aerobic oxidation of benzylalcohol did not proceed efficiently without air blowing and the benzaldehyde was produced only about 6% after 12 h stirring at room temperature.

In order to find the best reaction conditions, optimization studies were performed with aerobic oxidation of benzylalcohol, as a model substrate, in the presence of various amounts of MnO_2/Cellulose using K_2CO_3 in *o*-xylene as a solvent at room temperature. As indicated in Table 1, the present catalysts (MnO_2 nanostructures on cellulose) have better catalytic role than aggregated active MnO_2 (Entries 1-6). Percentage of MnO_2 loading on cellulose affected the catalytic activity of MnO_2/cellulose.[5] The optimal MnO_2 loading is 8.48% that related to MnO_2/Cellulose **5** (Table 1, Entries 2-6). Effect of various solvents was examined on the reaction yields, as well. Based on these experiments *o*-xylene was found as the prefered solvent (Table 1, Entries 6, 14-21). Also, different amount of the base was used to obtain the prefered amount of it. As it is clear from the Table 1 (Entries 6, 10, 11) the 0.5 mol% of the base is providing the best result.

Table 1 Optimization of the reaction conditions for aerobic oxidation of alcohols

Entry	Catalyst	Amount of catalyst (MnO_2 content/mol%)	Solvent	Base (mmol)	Yield (%)[a]
1	Active MnO_2	0.009 g (10)	*o*-xylene	K_2CO_3 (0.5)	18
2	MnO_2/Cellulose **1**	0.140 g (10)	*o*-xylene	K_2CO_3 (0.5)	95
3	MnO_2/Cellulose **2**	0.120 g (10)	*o*-xylene	K_2CO_3 (0.5)	90
4	MnO_2/Cellulose **3**	0.100 g (10)	*o*-xylene	K_2CO_3 (0.5)	97
5	MnO_2/Cellulose **4**	0.100 g (10)	*o*-xylene	K_2CO_3 (0.5)	83
6	MnO_2/Cellulose **5**	**0.100 g (10)**	***o*-xylene**	**K_2CO_3 (0.5)**	**99**
7	MnO_2/Cellulose **5**	0.070 g (7.0)	*o*-xylene	K_2CO_3 (0.5)	86
8	MnO_2/Cellulose **5**	0.050 g (5.0)	*o*-xylene	K_2CO_3 (0.5)	54
9	MnO_2/Cellulose **5**	0.020 g (2.0)	*o*-xylene	K_2CO_3 (0.5)	31
10	MnO_2/Cellulose **5**	0.100 g (10)	*o*-xylene	K_2CO_3 (0.4)	91
11	MnO_2/Cellulose **5**	0.100 g (10)	*o*-xylene	K_2CO_3 (0.3)	84
12	MnO_2/Cellulose **5**	0.100 g (10)	*o*-xylene	KOH (0.5)	51
13	MnO_2/Cellulose **5**	0.100 g (10)	*o*-xylene	-	16
14	MnO_2/Cellulose **5**	0.100 g (10)	*n*-hexane	K_2CO_3 (0.5)	93
15	MnO_2/Cellulose **5**	0.100 g (10)	toluene	K_2CO_3 (0.5)	89
16	MnO_2/Cellulose **5**	0.100 g (10)	H_2O	K_2CO_3 (0.5)	7
17	MnO_2/Cellulose **5**	0.100 g (10)	MeOH	K_2CO_3 (0.5)	5
18	MnO_2/Cellulose **5**	0.100 g (10)	EtOH	K_2CO_3 (0.5)	5

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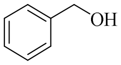
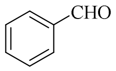
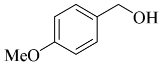
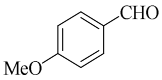
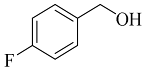
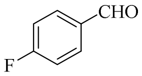
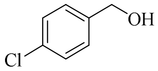
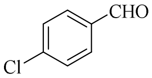
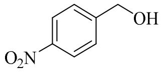
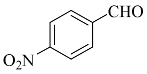
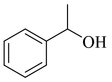
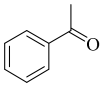
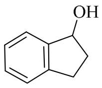
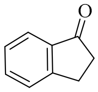
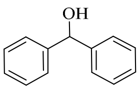
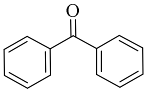
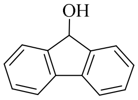
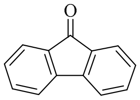
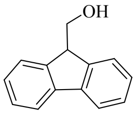
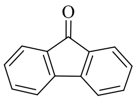
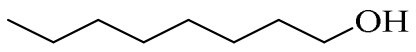
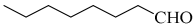
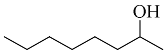
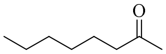
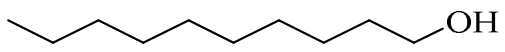
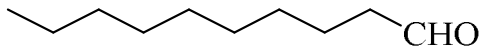
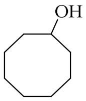
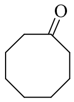
19	MnO_2/Cellulose **5**	0.100 g (10)	CH_2Cl_2	K_2CO_3 (0.5)	47
20	MnO_2/Cellulose **5**	0.100 g (10)	THF	K_2CO_3 (0.5)	14
21	MnO_2/Cellulose **5**	0.100 g (10)	CH_3CN	K_2CO_3 (0.5)	18

Reaction conditions: benzylalcohol (1.0 mmol), solvent (5 mL), air oxidant, room temperature, 7 h.
[a] Yield determined by GC analysis.

As mentioned before, the efficiency of MnO_2/Cellulose 5 was higher than other MnO_2/Cellulose catalysts, therefore the selective oxidation of various alcohols to the corresponding aldehydes and ketones in the presence of MnO_2/Cellulose 5, as a catalyst, and K_2CO_3, as a base, in *o*-xylene at room temperature was studied (Table 2).

Table 2 Selective aerobic oxidation of variuos alcohols to corresponding aldehydes and ketones

Entry	Alcohol	Product	Time (h)	Yield (%)[a]
1			7	99
2			7	90
3			7	86
4			7	91
5			7	96
6			7	98
7			8	98
8			6	96
9			8	92
10			8	89
11			15	77
12			15	79
13			15	75
14			15	78

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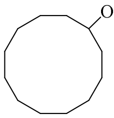
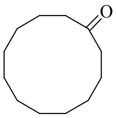
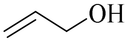
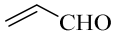
15			15	74
16			15	75

Reaction conditions: alcohol (1.0 mmol), MnO$_2$/Cellulose (0.1 g), K$_2$CO$_3$ (0.5 mmol), *o*-xylene (5 mL), air oxidant, room temperature.
[a] Yield determined by GC analysis.

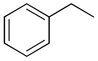
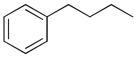
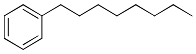
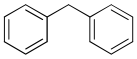
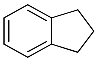
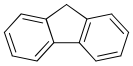
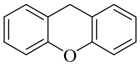
In the next step, the oxidation of the alkyl arenes to related carbonyl compounds was studied. The results of the mentioned reaction is provided in the Table 3. The reaction was done at 120 °C under air blowing with good to high yields. In this case, such as the oxidation of the alcohols, the oxidation was procedeed selectivly and no carboxylic acid product was produced during the reaction.

Table 3

1. Optimization of the reaction conditions for aerobic oxidation of arenes[a]

Entry	Catalyst	Amount of catalyst (MnO$_2$ content/mol%)	Solvent	Base (mmol)	Yield (%)[b]
1	Active MnO$_2$	0.009 g (10)	*o*-xylene	-	31
2	MnO$_2$/Cellulose **1**	0.140 g (10)	*o*-xylene	-	81
3	MnO$_2$/Cellulose **2**	0.120 g (10)	*o*-xylene	-	78
4	MnO$_2$/Cellulose **3**	0.100 g (10)	*o*-xylene	-	85
5	MnO$_2$/Cellulose **4**	0.100 g (10)	*o*-xylene	-	70
6	MnO$_2$/Cellulose **5**	**0.100 g (10)**	***o*-xylene**	-	**89**
7	MnO$_2$/Cellulose **5**	0.100 g (10)	*n*-hexane	-	61
8	MnO$_2$/Cellulose **5**	0.100 g (10)	toluene	-	80
9	MnO$_2$/Cellulose **5**	0.100 g (10)	H$_2$O	-	4
10	MnO$_2$/Cellulose **5**	0.100 g (10)	MeOH	-	9
11	MnO$_2$/Cellulose **5**	0.100 g (10)	EtOH	-	6
12	MnO$_2$/Cellulose **5**	0.100 g (10)	CH$_2$Cl$_2$	-	13
13	MnO$_2$/Cellulose **5**	0.100 g (10)	THF	-	18
14	MnO$_2$/Cellulose **5**	0.100 g (10)	CH$_3$CN	-	21
15	MnO$_2$/Cellulose **5**	0.100 g (10)	*o*-xylene	K$_2$CO$_3$ (0.5)	56
16	MnO$_2$/Cellulose **5**	0.100 g (10)	*o*-xylene	KOH (0.5)	42

2. Aerobic oxidation of variuos alkyl arenes to corresponding ketones[c]

Entry	Alkyl arene	Time (h)	Solvent	Yield of ketone (%)[b]
17		10	*o*-xylene	91
18		10	*o*-xylene	89
19		15	*o*-xylene	81
20		13	*o*-xylene	82
21		13	*o*-xylene	87
22		13	*o*-xylene	89
23		13	*o*-xylene	94

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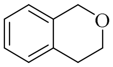
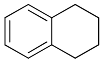
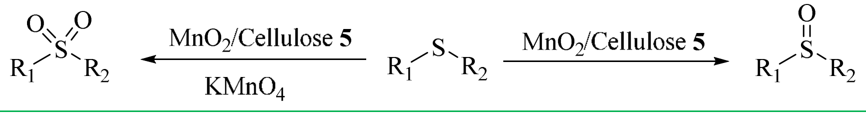
24		13	*o*-xylene	87
25		14	*o*-xylene	88

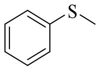
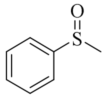
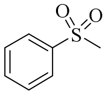
[a] Reaction conditions: indane (1.0 mmol), solvent (5 mL), air oxidant, ref., 13 h.
[b] Yield determined by GC analysis.
[c] Reaction conditions: alkyl arene (1.0 mmol), MnO_2/Cellulose (0.1 g), solvent (15 mL), air oxidant, 120 °C.

To extend the scope of the prepared catalysts, the oxidation of the sulfides to the related oxygenated compounds has been studied as well. In this study, the MnO_2/Cellulose **5** catalyst was used. The obtained results have been presented in the Table 4. The reaction was proceed smoothly with good to high yields. Oxidation of sulfides with manganese dioxide is known to give only sulfoxides.[20a] This procedure used for the oxidation of sulfides to sulfoxides without any overoxidation to sulfones.

Both sulfoxides and sulfones are important intermediates in the synthesis of organic compounds.[2a] Based on the previous reports, the oxidation of the sulfides in the presence of potassium permanganate lead to the sulfone derivatives.[20a] Therefore, we used potassium permanganate and the prepared MnO_2/Cellulose **5** catalyst. The examination of the catalyst in the oxidation reaction of the sulfides showed that the desired product was obtained in good yields. To obtain the sulfone product, sulfide reactant in the presence of $KMnO_4$ (0.4 g), and the catalytic amount of the MnO_2/Cellulose **5** (0.1 g, 10 mol%), was stirred at room temperature for 2-12 h, while bubbling the air into the reaction media. The reaction was proceeded effectively and selectively for the oxidation of sulfides to sulfones[20a] (Table 4).

Table 4 Selectively aerobic oxidation of variuos sulfides to corresponding sulfoxides and sulfones



Entry	Sulfide	Product	Catalyst	Time (h)	Yield (%)[a]
1			MnO_2/Cellulose **5**	4	95
			MnO_2/Cellulose **5** $KMnO_4$	2	94

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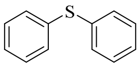
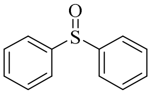
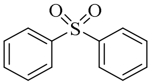
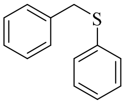
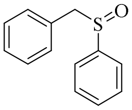
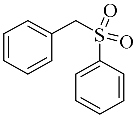
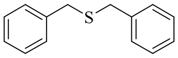
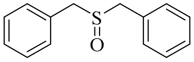
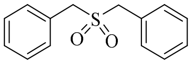
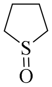
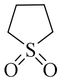
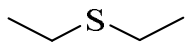
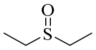
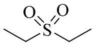
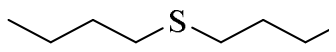
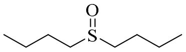
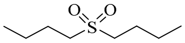
2			MnO_2/Cellulose **5**	7	91
			MnO_2/Cellulose **5** $KMnO_4$	5	92
3			MnO_2/Cellulose **5**	12	87
			MnO_2/Cellulose **5** $KMnO_4$	11	80
4			MnO_2/Cellulose **5**	15	85
			MnO_2/Cellulose **5** $KMnO_4$	12	76
5			MnO_2/Cellulose **5**	4.5	92
			MnO_2/Cellulose **5** $KMnO_4$	3	89
6			MnO_2/Cellulose **5**	5.5	90
			MnO_2/Cellulose **5** $KMnO_4$	2	88
7			MnO_2/Cellulose **5**	6	87
			MnO_2/Cellulose **5** $KMnO_4$	2.5	93

Reaction conditions: sulfide (1.0 mmol), MnO_2/Cellulose (0.1 g), $KMnO_4$ (0.4 g), *o*-xylene (5 mL), air oxidant, room temperature.
[a] Yield determined by GC analysis.

In order to investigate the selectivity of aerobic oxidation of variuos organic compounds to the related products, we used mixed primary and secondary benzylalcohols (Table 5, Entry 1) and alkylalcohols (Table 5, Entry 2) as the reactants. The reaction has been done in the presence of MnO_2/Cellulose **5** as a solid catalyst at room temperature during 7 and 15 h, respectively. The results have been presented in the Table 5. The analysis of the results revealed that at first step only one of the reactants undergoes oxidation reaction. The oxidation of the secondary functional group is favored based on the observed results. In both of the mentioned cases, after the completion of the oxidation of the reactant containing the secondary functional group, the oxidation of the primary alcohol was started. Using 2-ethylheptane-1,3-diol, a diol with both primary and secondary hydroxyl functional groups, only product 3-

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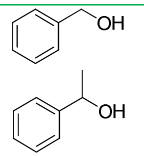
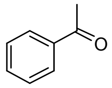
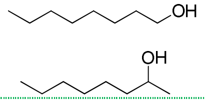
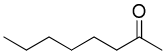
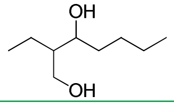
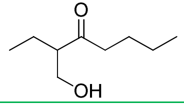
(hydroxymethyl)octan-4-one was obtained (Table 5, Entry 3). In this case, after 15 h, aldehyde formation was started, as well.

Table 5 Selectivity of aerobic oxidation of variuos alcohols

Entry	Alcohol	Product	Time (h)	Yield (%)[a]
1			7	96
2			15	75
3			15	81

Reaction conditions: any alcohol (1.0 mmol), MnO_2/Cellulose (0.1 g), K_2CO_3 (0.5 mmol), *o*-xylene (5 mL), air oxidant, room temperature.
[a] Yield determined by GC analysis and the integrals of the ^{1}HNMR.

Recyclability of the MnO_2/Cellulose was examined in the oxidation reaction of benzylalcohol. For this reason, catalyst which was recovered from reaction by filteration was reused in the reaction after drying under vacuum at 60 °C. This procedure was carried out for five repetitive cycles; The same analysis was used for the oxidation of the arenes and sulfides. The results showed that only minor decreases in the reaction yields were observed (Fig. 4) and the activity of the catalyst was saved during successive uses.

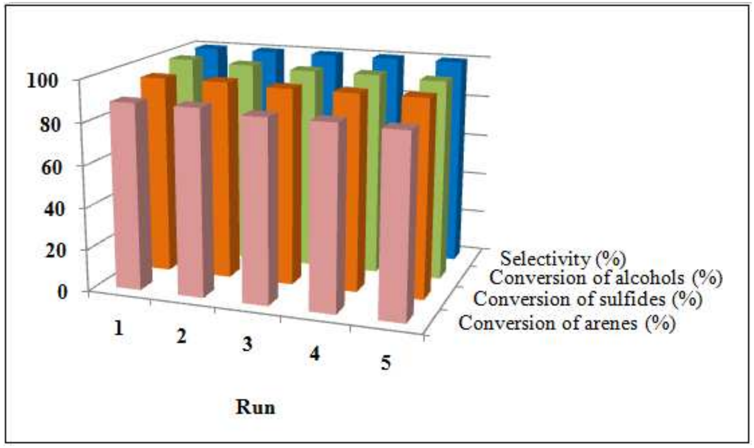


Fig. 4 Recycle of the catalyst for the oxidation of the alcohols, sulfides, and arenes. The catalyst was used in five successive runs after recycling.

The results of our investigation are compared with previous reports of oxidation by MnO_2[16,17,19,28-30] from yields and the reaction times viewpoints

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(Table 6). The results show that MnO_2 impregnated on cellulose is the best oxidant reagent.

Table 6 Comparison of the results obtained from active MnO_2, MnO_2 on different supports and nano MnO_2 impregnated on cellulose 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	[28]
2	active MnO_2	toluene/O_2/110 °C	1:0.8	4	85	[29]
3	MnO_2/Graphite	CH_2Cl_2/ref.	1:2	10	92	[30]
4	MnO_2/Kieselguhr	CH_2Cl_2/ref.	1:2	10	90	[16a]
5	MnO_2/Kieselguhr	solvent free/50-55 °C/grind	1:2	3	95	[16b]
6	MnO_2/Aluminum silicate	CH_2Cl_2/ref.	1:3	12	96	[17]
7	MnO_2/Silica	solvent free/ref./ Microwave irradiations	1:5	0.3	88	[19]
8	Nano MnO_2-Cellulose **5**	*o*-xylene/air/r.t.	1:0.1	7	99	This work

4 Conclusion

Coordination of MnO_2 nanosheets to cellulose fibers easily provides its immobilization. The distribution of MnO_2 on the surface of cellulose fibers gave an active catalytic system with 8.48% loading of MnO_2. Using MnO_2/Cellulose composite as a bio-supported heterogeneous catalyst, in the selective oxidation of various primary and secondary alcohols, alkyl arenes, and sulfides have several advantages such as excellent yield, easy workup procedure, recycability of catalyst with no loss in its activity, use of inexpensive catalyst, and mild reaction conditions without using any expensive oxidants. The prepared catalyst showed high selectivity in the oxidation of the alcohols to the related aldehydes or ketones and no carboxylic acid was produced. Similar selectivity for the oxidation of alkyl arenes was also observable, which increases the utility of the prepared catalyst in complex systems. In addition, this same catalyst can be used for the oxidation of sulfides to sulfoxides without any overoxidation to sulfones.

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