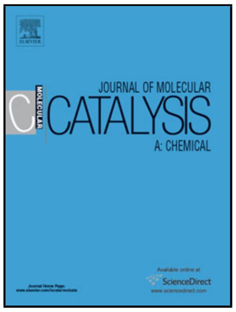

Title: Manganese catalyst and N-hydroxyphthalimide as an efficient catalytic system for selective oxidation of ethylbenzene, cyclohexene and oximes under aerobic condition

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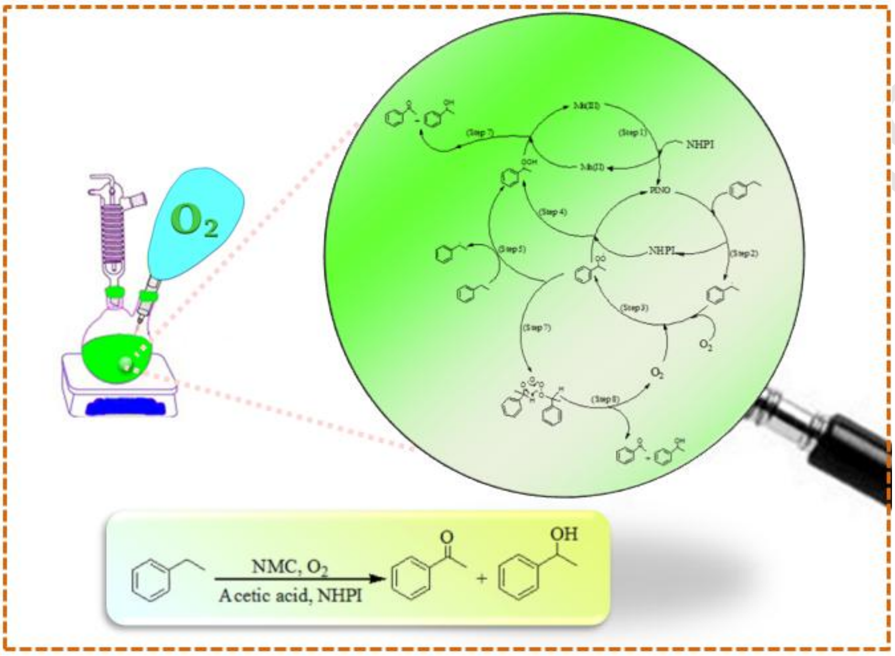
Efficient catalytic systems based on manganese for oxidation of ethylbenzene, cyclohexene and oximes in the presence of N-hydroxyphthalimide



Highlights

Mn supported on SiO_2-Al_2O_3 used as catalysts using N-hydroxyphthalimide.

Mn catalysts were studied in the oxidation of ethylbenzene to acetophenone.

Mn catalysts were studied in the oxidation of cyclohexene to 2-cyclohexene-1-one.

Conversions reached to 95 and 99%, and selectivities of 99%.

Mn catalysts for the oxidative deprotection of oximes to carbonyl compounds.

Manganese catalyst and N-hydroxyphthalimide as an efficient catalytic system for selective oxidation of ethylbenzene, cyclohexene and oximes under aerobic condition

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Abstract

The catalytic activity of the nano-manganese-catalyst in the aerobic oxidation of ethylbenzene, cyclohexene and oximes were evaluated without the need of any reducing agent, using N-hydroxyphthalimide (2-Hydroxy-1H-isoindole-1,3-dione;NHPI) under oxygen pressure. The oxidation of ethylbenzene and cyclohexene to acetophenone and 2-cyclohexene-1-one using N-hydroxyphthalimide (2-Hydroxy-1H-isoindole-1,3-dione;NHPI) under oxygen atmosphere in the presence of a SiO_2/Al_2O_3-supported manganese catalyst occurs with conversions of 95 and 99% and selectivities of 99%. The supported manganese is also a suitable and efficient catalyst for the oxidative deprotection of oximes to the corresponding carbonyl compounds. A mild and efficient method has been optimized for manganese catalysts by considering the effect of various parameters such as the reaction time and the amount of catalyst, the temperature and the

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reusability of the catalyst after several runs without modification. Moreover, some possible mechanisms for the oxidation of ethylbenzene, cyclohexene and oximes have been proposed.

Keywords: Manganese supported catalyst; Oxidation; Ethylbenzene; Cyclohexene; Oxime.

1. Introduction

Selective oxyfunctionalization of substrates to give oxygen containing compounds is a fundamental reaction in organic chemistry for fundamental research and industrial manufacturing. Direct oxidation of the abundant and cheapness hydrocarbons containing benzylic and allylic carbon-hydrogen bonds into corresponding ketones are of major important transformations in organic synthesis, since the oxidation products are essential intermediates for the generation of the useful primary, special chemicals and high economic value fine chemicals, agrochemicals, pharmaceutical and perfumes industry [1]. Selective oxidation of organic substrates with eco-friendly and readily available oxidants instead of hazardous oxidant such as peroxides, permanganate sodium hypochlorite, iodosobenzene and dichromate have received recently considerable attention [2,3]. In the last few years, due to apparent advantages of using O_2 as oxidant, considerable attempt has been invested to improve efficient catalytic system for the aerobic oxidation of organic compounds. The dominant position of O_2 as the oxidant for bulk chemical oxygenations is due to the fact that it is the only economically and environmentally feasible oxidant for large scale processing. The success of these oxy-functionalizations always depends largely on the development of catalysts to promote productivity, the rate of reaction, as the selectivity of products. The heterogenisation of metal complexes with catalytic activity within inorganic matrixes (such as SiO_2, clay, MCM-41, SBA-15, mesoporous materials, zeolite, etc) is a field that has progressed in last decades due to the combination of high reactivity and chemical selectivity with facile separation of the catalyst from the reaction mixture. Due to its properties, particular attention has been paid to reusability, thermal stability and low cost of the catalysts.

In recent years, there has been an increased interest in the aerobic oxidation of allylic and benzylic carbon-hydrogen bonds using transition metal Schiff base complexes immobilized on several solid supports. Schiff base complexes are excellent chemical and thermal stability, easily accessibility and synthesized [4,5]. These wide ranges of applications of metal complexes of Schiff base in homogeneous and heterogeneous catalysis have generated a great deal of interest in the synthesis of new metal complexes. Investigation related to the new solid oxidation catalysts is one of the most significant current topics, connected with both industrial and fundamental researches, because the traditional techniques involve the use of large amounts of highly toxic oxidation state of Os, Mn, and Co reagents [6]. In fact, as the traditional metal compounds used in this process are in catalytic amounts, the reaction conditions are harsh; the product selectivity is low and often corrosive promoters are used along with the traditional catalyst. However, the separation of the catalyst from the reaction mixture is very difficult, the catalyst cannot be reused, low conversion and selectivity and also a lot of waste is produced [1,7,8]. These disadvantages were minimized if homogeneous complexes were immobilized on the surface of solid supports. Much effort has been made to activate molecular oxygen by several catalysts or transition metal complexes, in particular the Schiff base ones, for the catalytic oxidation of organic substrate under mild condition. In past decade, N-hydroxyphtalimide (NHPI) has considerable interest as a novel organo-catalyst and co-catalyst for a wide variety of free radical out oxidant [9]. With this oxidation system, in oxidation of organic substrates containing reactive carbon-hydrogen bonds, e.g. alkylbenzene [10] and alkyl aromatic compounds containing benzylic functions [11-13], oxidation reactions catalyzed by NHPI in the presence of transition metal as a co-catalyst [14-22] have been studied. In the proposed mechanisms, the phthalimide-N-oxyl radical (PINO) is formed by abstracting H atoms from the NHPI, then PINO can in turn abstract H atoms from the substrate [23-38]. In the present investigation, we report a simple procedure for preparation of a type Mn catalyst immobilized the Schiff base ligands (Scheme 1), and apply this catalyst with homogeneous NHPI for direct aerobic oxidation of ethylbenzene and cyclohexene. When concerning their catalytic performances for the oxidation of ethylbenzene, cyclohexene and oximes under mild conditions with excellent conversion and high selectivity, the catalyst show promising activities for the reactions as expected.

2. Experimental

2.1. Materials and characterization techniques

All reagents were purchased from the Merck and Fluka chemical companies. Reagents were used without extra purification, but solvents were purified with standard methods. All compounds were known and identified by comparison of their physical and spectroscopic data with those of authentic samples. Inductively coupled plasma (ICP) measurements for manganese content evaluation were performed using a Perkin-Elmer ICP/6500. Infrared was collected on KBr pellets using a JASCO FT/IR (680 plus) spectrometer. Diffuse reflectance spectra were registered on a JASCO-550 UV-Vis spectrophotometer that was equipped with a Diffuse reflectance attachment in which $BaSO_4$ was as the reference. XPS (small area X-ray photoelectron spectroscopy) data were recorded with the PHI-5702 Multi-Technique System.

The thermal analysis was recorded on a Perkin-Elmer TG-DTA 6300 instrument at a heating rate of 15˚C.min^{-1} and for elemental analysis a CHN-Rapid Heraeus elemental analyzer (Wellesley MA) was used. Before carrying out the nitrogen (99.999 %) adsorption experiments, the sample was outgassed at 393 K for 14 h, then the experiment have been carried out at 77 K using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). The specific surface areas were calculated using the BET method. The images of scanning electron micrograph (SEM) and transmission electron microscopy (TEM) were taken using a Philips 501 microscope and a Tecnai F30TEM operating at 300 kV, respectively. In addition, energy dispersive X-ray analysis was conducted on each sample. Size distribution was measured in order to number of nanoparticles in reverse microemulsion by Zetasizer Nano-ZS-90 (ZEN 3600, MALVERN instruments). The reaction products of aerobic oxidation were determined and analyzed by a HP 6890/5973 GC/MS instrument and analyzed by a Shimadzu GC-16A gas chromatograph (GL-16A gas chromatograph with a 5m×3mm OV-17 column, 60–220 ˚C (10 ˚C/min), Inj. 230 ˚C, Det. 240 ˚C).The products were determined by comparing with the standard mass spectrometry of organic compounds and fragmentation pattern.

2.2. Preparation of organometallic-SiO_2/Al_2O_3

SiO_2/Al_2O_3 was used as the support prepared by the sol-gel method. First, some defined value of Tetra-Ethyl-Ortho-Silicate (TEOS) and Aluminium butyrate in n-butanol were dissolved. The final mixture has a standard mole ratio of $Si(-OC_2H_5)_4$–$Al(-OC_4H_9)_3$–C_4H_9OH in the range of $15(Si(-OC_2H_5)_4)$ – $10(Al(-OC_4H_9)_3)$ –15 (C_4H_9OH). The obtain solution was heated up to 70 ºC and the components were entirely mixed. Then it was cold down to the room temperature. 2,4-Pentandione (H-acac) as the complacing agent was added to it. In this way, the apparent solution was obtained. After that by adding deionized water (12.0 mol H_2O/mol alkoxide) to the obtained solution, the solution was hydrolyzed and the apparent gel was produced. Then for removing the solvent and water from the gel, it was dehydrated up to 100 ºC. Also for eliminating of organic compounds, it was calcined at 550 ºC for 5 h. So, the synthesized solid SiO_2/Al_2O_3 was being used as the support in synthesis of the catalyst [34]. At first, 3.5 g of SiO_2/Al_2O_3 was activated at 500 ºC for 5 h under air and then was refluxed with 4.3 cm^3 of trimethoxysilylpropylamine (APTMS) in dry toluene (50 cm^3) for 24 h. The solid achieved during this process was filtered and washed off with dry methanol at 100 ºC under vacuum for 5 h. Then, bipyridylketone (BPK) was added to a suspended solution of SiO_2/Al_2O_3-APTMS in dry methanol. To synthesize of SiO_2/Al_2O_3-APTMS-BPK-Mn, 2.0 g SiO_2/Al_2O_3-APTMS-BPK was suspended in 50 cm^3 of ethanol in a round bottom flask followed by adding of 3.0 mmol $Mn(OAc)_2 \cdot 4H_2O$. The mixture was refluxed during 24 h under magnetically stirring.

2.3. General procedure for oxidation of ethylbenzene and cyclohexene

A suspension of the heterogeneous catalyst (0.1 g), solvent (5 cm^3 of acetic acid/ benzonitrile), 2 mmol substrate and N-hydroxyphthalimide (NHPI) (15 mol %) were mixed in a three necked round bottom flask which was fitted with a equipped water condenser through a balloon filled with O_2. The liquid phase oxidation reactions were carried out at desired temperature with vigorous stirring. After filtration and washing with solvent, the type and quantity of the resulting products from oxidation were determined by GC-MS instrument. Besides, a comparative experiment with various conditions was carried out.

2.4. General procedure for oxidation of oximes

In this procedure, a suspension of the heterogeneous catalyst (0.07 g), solvent (5 cm^3 of toluene), oxime (2 mmol) and benzaldehyde (6 mol) were mixed in a three necked round bottom flask which was fitted with a equipped water condenser with a balloon filled of O_2. The liquid phase oxidation reactions were carried out at desired temperature with vigorous stirring. After completing the reaction, the catalyst has been separated through filtering and the products and the amounts of them have been quantified by GC-MS and GC. Finally, a suitable reaction condition has been optimized.

3. Results and discussion

3.1. Synthesis of manganese-supported catalyst

Using BPK and $Mn(OAc)_2 \cdot 4H_2O$ through the covalently immobilization, the heterogeneous manganese catalyst was synthesized on the SiO_2/Al_2O_3 mixed oxides, as illustrated in Scheme 1. The formation of manganese catalyst on the SiO_2/Al_2O_3 was verified using CHN analysis, FT-IR, UV–vis, Scanning Electron Microscope (SEM), Transmission

Electron Microscope (TEM), X–ray photoelectron spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDX), Dynamic light scattering (DLS), Inductively coupled plasma (ICP),TGA-DTA and nitrogen adsorption. The elemental analysis report along with summary of measured and calculated values for C, H and N is presented in Table 1. Analysis of the results indicated the fact that the CHN content increased with the organic chain size because of immobilization of organic groups in the inorganic matrix. The loading of manganese in the heterogeneous manganese catalyst was characterized by elemental analyses. The final metal content was 0.35 mmol/g, indicating that 74.4 % of the immobilized ligands were complexed with manganese ions.

Analysis of the specific surface area was performed by standard Brunauer-Emmett-Teller technique (BET) for analysis of gas adsorption using nitrogen. Nitrogen adsorption experiments were performed using 1 g of the SiO_2/Al_2O_3. The specific surface area, pore size and pore volume of the modified support were significantly decreased compared to the parent SiO_2/Al_2O_3. This behaviour indicates the decrease in interaction between molecular nitrogen as an adsorbate and the parent SiO_2/Al_2O_3 surface after modification with organic groups. Furthermore, the isotherm for support is type I, which is characteristic for microporous materials. The micropores have a size of 0.60 nm and a rather broad pore size distribution (see Table 1).

The FT-IR spectra of SiO_2/Al_2O_3-APTMS, SiO_2/Al_2O_3-APTMS-BPK, and SiO_2/Al_2O_3-APTMS-BPK-Mna are shown in Figure 1. The strong absorption bands related to Si-O-Si stretching vibrations are observed in the spectrum of SiO_2/Al_2O_3 at 798 and 1010-1290 cm^{-1}. The FT-IR spectrum of SiO_2/Al_2O_3-APTMS shows several signals originating from amino propyl groups, which are related to C-H stretching modes of the propyl, appeared in the area of 1450-1560 cm^{-1} and 2860-2935 cm^{-1}. By observing the FTIR results it could be concluded that the SiO_2/Al_2O_3 was successfully modified by amine spacer groups. The N-H deformation peak at 1540-1560 cm^{-1} confirms the successful functionalization of the Si/Al mixed oxide with 3-APTMS. The C=N imine vibration signal was observed at 1630 cm^{-1}, which shows the condensation reaction between BPK with organo-functionalized SiO_2/Al_2O_3 (see Figure 1-B). The peaks in the 3020-3066 cm^{-1} ranges and the peaks at 1434-1437 cm^{-1} are attributed to the C-H stretching vibrations of pyridine groups and C=C stretching vibration of pyridine groups. Furthermore, after complexing of manganese with immobilized BPK over modified SiO_2/Al_2O_3, the weak absorption peak at 413 cm^{-1} was appeared that is attributed to the Mn-N bands [39,40].

The UV-Vis spectrum of the SiO_2/Al_2O_3 had a side-band adsorption near 249 nm. In the SiO_2/Al_2O_3-APTMS-BPK transitions $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ of the ligands caused strong adsorption in the 255-320 nm (see Figure 2). After the reaction of SiO_2/Al_2O_3-APTMS-BPK with $Mn(OAc)_2{\cdot}4H_2O$, the color of the reaction mixture was changed from yellow to deep brown. Consequently, UV-visible spectra of the immobilized Mn(III) species indicated the appearance of several new metal d–d migration bands around 490 nm upon complexation.

A selected image of scanning electron microscope (SEM) and transmition electron microscope (TEM) of catalyst is shown in Figure 3, from which it can be seen that the nanoparticles appearance and size of them were similar, demonstrating that the particles of SiO_2-Al_2O_3 have good mechanical stability and they have not been destroyed during the whole modification. However, the average particle size in reverse micro emulsion solution of the catalyst was around 31 nm. According to the small nanoparticle size and ligand capping as an obstacle in agglomeration, the Mn-catalyst could be used as a suitable catalyst for oxidation of several substrates such as ethylbenzene, and cyclohexene. The energy dispersive spectrum (EDS) of Mn-catalyst was shown in Figure 3. In the EDS spectrum of the cobalt catalyst, signals related to Si, Al, O and Mn were observed. The existence of Mn signal in the spectrum resulted from the Mn complexation with active sites of the organic functional groups (-C=N) that increased the catalytic activity of the synthesized catalyst in comparison with the unmodified support.

Thermal stability of the synthesize materials were studied with TGA (thermo gravimetric analysis) and DTG (derivative thermogravimetric) in Ar atmospheres in the range of 25-1200 °C with a rate of heating of 10 °C/min (see Figure 4) [32]. Thermal analysis of nanoscale SiO_2/Al_2O_3 showed two stages of weight loss, stage I (25-115 ºC) corresponds to the desorption of physically held water (2.6 wt.%), on the surface of SiO_2/Al_2O_3, and Stage II (120-1200 ºC) is due to the condensation of Al-OH and Si-OH (13.4 wt.%), present in the structure of support (for example; $2Si\text{-}OH \rightarrow Si\text{-}O\text{-}Si + H_2O$). However, Mn catalyst showed four distinct steps: at 25-89, 89-291, 291-556 and 556-1200 ºC (see Figure 4). Stages II and III (89-556 ºC) are due to desorption of water molecules from the pores of SiO_2/Al_2O_3 and also decomposition of the immobilized organic functional groups (-*pr*-NH_2). The additional weight losses in stage IV could be observed due to the several phenomena; the calcination of coke, the loss of the new generated Al-OH and Si-OH groups and decomposition of the immobilized Mn complex groups. From thermogram analysis of samples, it could be concluded that thermal stability of SiO_2/Al_2O_3 in Mn catalyst improved rather than unmodified SiO_2/Al_2O_3 and the weight losses of the modified SiO_2/Al_2O_3 with Mn complex groups in the temperature range of dehydration are less than that for unmodified SiO_2/Al_2O_3.

The XP spectroscopic analysis of the heterogeneous catalyst was used to study for the characterization of oxidation state of the active sites of immobilized manganese complexes on the surface of SiO_2/Al_2O_3. This technique has previously been shown to provide valuable information regarding the chemical state of the catalytically active sites in various catalysts [41-44]. The XPS spectrum of Mn catalyst produced a Mn $2p_{3/2}$ and a Mn $2p_{1/2}$ peak at 643.01 eV and 654.61 eV, and is depicted in Figure 5. These results indicated that most of the Mn ions on the surface of the heterogeneous catalyst were in +3 oxidation state (due to the binding energy (BE) 643.01 eV which are attributed to Mn(III) state of manganese), and they are in accordance with earlier literature data [41-43].

3. 2. Oxidation of ethylbenzene

The oxidation of ethylbenzene with oxygen by the new catalytic system using a heterogeneous transition metal in the presence of NHPI was investigated. The reaction products were identified by comparison with authentic products and GC-MS. For ethylbenzene oxidation, acetophenone (AcPO) and α-phenylethanol (PEA) were determiated. The effects of various operating parameters, such as the amount of the catalyst to NHPI, the temperature, and the reaction time, on the performance of the heterogeneous manganese-catalyst was investigated in the oxidation of ethylbenzene by O_2 in the presence of the acetic acid as solvent. In fact, due to its polar nature, NHPI has a low solubility in ethylbenzene at the mild temperature employed in our protocol. Thus, the use of acetic acid is mandatory in order to dissolve the quantities of NHPI necessary for observing a good catalytic activity. Acetophenone and α-phenyl ethanol (Scheme 2) were the major reaction products obtained. The GC analysis did not show any oxidation products of the aromatic ring in effluents.

Several solvents were examined in the present aerobic oxidation. The aerobic oxidations of ethylbenzene must be carried out in an appropriate solvent such as acetic acid or acetonitrile due to the lower solubility of NHPI in nonpolar solvents such as hydrocarbons. Among the various solvents, acetic acid was found to be the optimum solvent [35-38]. In order to assess the effect of catalyst to oxidant molar ratio on the catalytic activity and selectivity in acetic acid under oxygen, the reactions were studied at various amounts of catalyst:NHPI (see Table 2). It was observed that catalytic activity and selectivity is strongly affected by increasing amount of catalyst to NHPI. The most promising observation is that acetophenone was found to be the major product in most of the catalytic reactions. The temperature and time dependences of ethylbenzene oxidation, employing Mn(III)/NHPI as the catalytic system, are presented in Table 2. Ethylbenzene was oxidized at 25 °C and the conversion was 19%. When the temperature was increased to 100 °C, the conversion of ethylbenzene was significantly improved to 53%. The results indicated that the temperature is another key factor in the selective oxidation of ethylbenzene. Therefore, the appropriate temperature for oxygenation catalyzed by Mn(III)/NHPI system should be 100–120 °C. In all EB oxidation reaction conditions, conversion and selectivity to acetophenone increased with reaction time.

Table 2 shows the conversion and selectivity do rise with rising concentration of manganese catalyst to EB and NHPI, when the reaction temperature is fixed, that is, due to the presence of excess of active sites on the catalyst. The optimized conditions were found to be as follows: ethyl benzene (2 mmol), catalyst (0.1 g), NHPI (15 % of substrate) and acetic acid (5 ml) under pressure of oxygen at 120 °C. The oxidation of ethylbenzene in the absence of catalyst gives low conversion and selectivity to acetophenone under oxygen pressure at 25 °C (see Table 2, entry 1).

NHPI has been demonstrated to be a free radical oxidation catalyst [11,12]. In contrast to transition metals, NHPI does not accelerate the hydroperoxide decomposition reaction; therefore, the catalytic activity of NHPI results from phthalimido-N-oxyl radical (PINO) formation in the propagation step of the oxidation process. PINO radical is highly electrophilic species and can efficiently promote hydrocarbon oxyfunctionalization with molecular oxygen.

In fact, transition metals, such as cobalt and manganese, are typically used as catalysts in these oxidation processes, that is, their catalytic effect lowers the activation energy of the decomposition reaction of the hydroperoxide. A plausible reaction pathway for the aerobic oxidation of ethylbenzene by the combined use of NHPI and manganese catalyst is proposed in Scheme 3, at first step, NHPI was easily converted into reactive PINO radicals under reaction conditions, and promoted radical transfer and chain rupture the benzylic hydrogen atom of ethylbenzene. Futheremore, Mn(III) ions supported on the catalyst were able to accelerate NHPI to form PINO radicals [45-48]. Furthermore, for demonstrating the role of the Mn-catalyst pyridine molecule was added into the system which resulted in decreasing the catalytic activity of manganese complex quickly, in fact, the nitrogen of pyridine molecule easily occupies the active sites of the catalyst. In the second step, NHPI in situ could be converted to PINO by the reaction of NHPI with the catalyst-oxygen complex that would be the most important step in the present oxidation [38]. The BDE (Bond Dissociation Energy) value of the O-H bond for NHPI is > 86 kcal/mol by means of ESR spectroscopy [49,50]. The BDE of the benzylic C-H bond in ethylbenzene is estimated to be about 87 kcal/mol. This suggests that PINO could abstract the benzylic hydrogen atom of ethylbenzene; therefore, at third step, PINO abstracts the hydrogen of a C-H bond in ethylbenzene to produce carbon-centered radicals, and then propagates the autoxidation. However capturing the obtaining ethylbenzyl radicals by dioxygen molecules provides alkylperoxy radicals, which are eventually converted into oxygenated compounds through 1-phenylethyl hydroperoxide (PEHP) (step 3). This intermediate can produce AcPO and PEA in two paths (steps 4 and 6), at step 5, alkylproxy radical can abstract hydrogen from NHPI and at step 6, two alkylproxy radicals combine to form a tetroxide intermediate, which further decomposes through a 6-membered ring transition state rearrange to a molecule of oxygen, an acethophenone and phenylalcohol; well-known as Russell termination. It is expected from this mechanism that the ratio of these products are 1.0. During the first 2 h of the reaction, ketone and alcohol formation takes place only via Russell termination but at higher conversions it is clear that other mechanisms play an important role [11,12,38]. Mn(II) were reoxidized to ones with higher valences during the course of the oxidation. The oxidants for low-valence Mn species were suggested to be the intermediate alkyl hydroperoxide and molecular oxygen [49]. The concentration of alkyl hydroperoxide decreased quickly, because it was catalytically decomposed by the manganese complex. It has been reported that the acidity of catalyst plays an important role for dehydration of PEHP to AcPO [51]. Therefore, the selectivity of hydroperoxide in acetic acid decreased after the increase in reaction time or temperature. Therefore in the next step, the PEHP was catalytically decomposed by the Mn(II) complex, so, the selectivity of PEHP decreases after the increase of reaction time. The selectivity of AcPO increases with the catalyst amount (entry 5 and 9, table 2). This observation indicated that as the amount of the Mn complex increases, the decomposition of PEHP becomes more rapid [35,38].

In relation with the above discussion, it could be concluded that both reduction and reoxidation of manganese species of the catalyst occurred together to construct the redox cycle in the oxidation. However, in the presence of acetic acid, the rate of this reaction increased and the selectivity of PEHP decreased, that is, the proton of solvent can prompt decomposition of PEHP, and eventually this step becomes more rapid [35,38]. The PEHP in the next steps further converts to acetophenone and 1-phenylethanol (steps 7 and 8).

The high selectivity to acetophenone and the absence of 2-phenylacetaldehyde can be rationalized from the following discussion. The methyl group carries more number of hydrogen than the methylene group that was not oxidized. However, the methyl group might be rotating more rapidly than the methylene group and hence its hydrogen was not abstracted by activated oxygen as shown in Scheme 3. The existence of a barrier to rotation about C_{sp^2}-C_{sp^3} was already reported [52,53]. Therefore, the hydrogen of methylene group was more readily available for oxidation than that of methyl group. The distant chemisorbed oxygen abstracts the hydrogen from the methylene group of ethylbenzene and fashions phenyl ethyl radical and metal hydroperoxide. The free radical rapidly reacts with metal hydroperoxide to form PEA. The local magnetic field of active sites of heterogeneous catalyst (Mn ions) could be thought to retain the paramagnetic phenyl ethyl radical until it is hydroxylated. The obtaining PEA is rapidly acted upon by the chemisorbed oxygen on the metal active site or PINO to form the product radical as shown in the reaction (Scheme 3). The oxidation of PEA might be more rapid than ethylbenzene, as the rotation of -CHOH group is slower than the -CH_2- group. Furthermore, the polar nature of transition state model between PINO and benzylic hydrogen confirmed the high reactivity of PEA compared to ethylbenzene. In fact, the benzylic OH-group of PEA stabilizes the partial positive charge on the benzylic carbon atom by resonance, and therefore favors further oxidation to AcPO. Consequently, the hydrogen atom which reacted with active sites of Mn-supported catalyst was ejected by radical in order to form H_2O and AcPO.

Besides coordination to a Schiff base ligand, the Mn ions may also interact with the surface Si–OH and Al–OH groups of the SiO_2/Al_2O_3. Thus, the materials of blank SiO_2/Al_2O_3 that adsorbed Mn acetate were also used for oxidation experiment. It turned out that the conversion of ethylbenzene was almost 8.5% (similar to the result of blank experiments, Table 2, entry 1). Therefore, in the oxidation of ethylbenzene with NHPI and oxygen under acetic acid, the manganese ions absorbed on the surface of the support did not contribute in the oxidation reaction. The above observations suggest that the oxidation occurs due to the catalytic nature of the chemically immobilized of Mn catalysts onto the Schiff base ligands.

To assess the reusability, the catalyst was separated by filtration after the first run, washed with ether and dried at 120 °C under vacuum and then used for the next runs under the same conditions (see Fig. 6). No significant loss of activity and selectivity was observed, confirming that the Mn-supported catalyst has high stability during the oxidation process. To further proof that the reaction was catalyzed by the manganese sample, we added extra ethylbenzene to the filtrate after the removal of the catalyst and no more products were produced under the same conditions. Based on the above, we reasoned that manganese catalyst and NHPI could couple to be an effective catalytic system for ethylbenzene oxidation.

3.3. Oxidation of cyclohexene

To extend the present method, the oxidation catalytic activity of the manganese catalyst has been examined using NHPI and oxygen under benzonitrile as solvent at several temperatures. After the reaction, the products were identified and quantified by GC-MS. The products of the reaction were cyclohexene oxide, 2-cyclohexene-1-one and 2-cyclohexene-1-ol (see Scheme 4).

Several results of the cyclohexene conversion and the selectivity of the products are summarized in Table 3. The oxidation of CH using NHPI proceeded even at 25 ºC to give 2-cyclohexene-1-one in higher selectivity after 24 h (76.6 %). As the reaction time were raised from 2 to 10 h the CH conversion and the selectivity to 2-cyclohexene-1-one increased from 66 to 84 and 93 to 99 %, respectively, while the selectivity to cyclohexene oxide and 2-cyclohexene-1-ol were decreased at 120 ºC. In the oxidation of cyclohexene, all the reaction conditions showed excellent selectivity for the ketone with only trace amounts (in total < 1.0 %) of by-products after 16 h at 100 ºC.

The oxidation of CH in the absence of catalyst gives low conversion and selectivity to 2-cyclohexene-1-one at 25 °C (entry 1). Furthermore, no reaction was observed in the absence of NHPI because no radical formations from manganese centers occur under the conditions selected in this work [12]. Reaction carried out to some extent in the absence of the catalyst, but the activity is lower (4 %) than when this compound is present. NHPI oxidizes CH slowly, and selectivity to 2-cyclohexene-1-one was not high after 24 h (58.9 %). This result is in accord to the previously reported reaction mechanisms [12,35], where NHPI are responsible for radical formation and the heterogeneous manganese is the co-catalyst that enhance the activity of the NHPI. Therefore, these could be demonstrated again from the results that under the mentioned reaction conditions, the allylic hydrogen is more reactive than the C=C double bond. However, the abstraction of hydrogen from the allylic carbon leads to allylic radical, which requires lower activation energy than the reaction at double bond.

Reusability of the immobilized manganese catalyst onto the SiO_2/Al_2O_3 was confirmed by performing a series of consecutive experiments in which the used catalyst was filtered, washed with fresh solvent, and employed without any further treatment in another run. The results shown in Fig. 7 clearly prove that a slight decline of activity and selectivity occurs after fifth run. Consequently, the results clearly suggest that the manganese catalyst efficiently catalyze conversion of cyclohexene (84 %) with ca. 99 % selectivity to 2-cyclohexene-1-one under NHPI and oxygen in benzonitrile as solvent. In order to confirm the heterogeneous nature of the manganese catalyst, a series of experiments were conducted in which the catalyst was filtrated after 2, 4 and 6 h and the reactions were continued with the filtrate. Under these conditions the reaction did not proceed at all, the data indicated that there was no leaching of the manganese ions from the catalyst, therefore establishing the really heterogeneous nature of the catalyst.

3. 3. Oxidation of oximes

In this protocol, a novel useful procedure for the facile deoximation system by reusable Mn supported catalyst and molecular oxygen as oxidant were studied (see Scheme 5). The experiments were designed with acetophenone oxime as a model substrate. For optimizing the conditions in oxidation of oximes, several factors have been investigated such as the amount of catalyst, the effect of temperature, the amount of benzaldehyde and the effect of solvent. In this reaction, the main product for oximes with electron-donating groups is carbonyl compounds. In order to examine the effect of catalyst on deoximation reaction; the reaction was carried out in the presence of various amounts of catalyst. The observations indicated that in the case of absence of catalyst, the reaction is carried out slowly while in the presence of the optimum amounts of the catalyst, the reaction is performed considerably. The maximum selectivity of carbonyl compound was obtained with 0.15 g of catalyst. The conversion of the acetophenone from 7% in the absence of the catalyst, to higher than 99% in the presence of the catalyst indicates that the catalyst has an efficient and effective role in this reaction.

For examining the role and effect of the solvent in the reaction, various solvents which are suitable for radical reactions have been used [54]. Therefore, acetonitrile, benzene, toluene, and cyclohexane solvents and water have been used. The results showed that in various solvents the selectivity was 100 % and the maximum conversion decreased in the following order: toluene (99.0) > acetonitrile (90.0) > benzene (83.0) > cyclohexane (15.0) > and water (0.0). The reaction at the presence of coordinating solvents such as water made no reaction. It seems that the donor electrons of this solvent had more ability to occupy the vacant space around the existed metal in the catalyst, so this prevents coordinating from oxygen molecules [52]. In this work, toluene provided the highest conversion and selectivity to acetophenone. Therefore, toluene as a solvent plays an effective role in oxidation of oximes, because toluene was reluctant to undergo free radical addition [53,54].

In oxidation of oximes, the presence of several amounts of benzaldehyde can also have a determining role. Observations indicated that in the absence of benzaldehyde, the reaction has a little progress even in a long time period, but in the presence of benzaldehyde a great conversion was observed. This observation indicated that benzaldehyde was used as the oxygen transfer agent in this oxidation reaction. In addition, when isobutyraldehyde was used as the only oxygen transfer agent, great conversion was not observed (see Figure 8).

To estimate the reusability of the manganese supported catalyst, after the first performance the catalyst was filtrated and washed with ether and dried at 120 ºC under vacuum and then used for the next performances under the same conditions. No apparent loss of activity and selectivity was observed after 6th runs, confirming that the manganese catalyst has high stability during the process. To further proofs that the reaction was catalyzed by the heterogeneous Mn-catalyst, we added extra acetophenone oxime to the filtrate after the removal of the catalyst and found that no more products were produced under the same conditions. In addition, the Mn ions absorbed on the surface of the support did not contribute in the deoximation reaction. This observation indicated that this reaction occurs due to the catalytic nature of the chemically immobilized of Mn catalysts onto the Schiff base ligands. To further explore the utility of this catalytic system, oxidation of several oximes (aldoximes and ketoximes) were also studied (see Table 4). Aldehydes were obtained with excellent yields and the overoxidation to carboxcylicacid and Beckmann rearrangement were not observed, which was another advantage of the proposed system. Furthermore, steric structure almost has no effect on conversion and selectivity of oxime (entry 14). The hydroxyl group in the ortho position of oximes (entry 12 and 13) exerts only an partly inductive effect, but hydrogen bonding between the OH and the nitrogen atom in imine will decrease the electron density of the carbon atom in the C=N. This factor probably influences the reactivity of oxime. Consequently, the yield of this oxime against with other oximes is slightly decreased, and the reaction time is longer[55].

In order to verify the kind of mechanism,2,6-di-tert-butyl-4-methylphenol(BHT), as a scavenger of chemical radical was used. The reaction appeared to be radical processes since it was totally inhibited in the presences of BHT (5 mol %). It seems that oximes with different groups (electron-donating and electron-drawing) go in various paths in the oxidation reaction with oxygen over the catalyst .To further elucidate the reaction mechanism, series of experiments were conducted, when the oxidation of acetophenoneoxime was conducted in the presence of dioxygen and benzaldehyde, in the absence of manganese catalyst, the conversion of acetophenone could only reach 9%. However, the conversion was remarkably increased by adding 70 mg of manganese catalyst to the mixture (Table 5, 99%, entry 11). The results indicate that manganese catalyst is crucial for the deoximation reaction. According to the proposed mechanism, at the first Mn(III) ions and benzaldehyde generate an acyl radical (ph-CO$^{\cdot}$) , so the radical formed is quickly trapped by dioxygen to give an acylperoxy radical (ph-COO$^{\cdot}$). The acylperoxy radical acts as a carrier in a chain mechanism by reaction with another benzaldehyde molecule to give the peroxybenzoic acid, and generating another acyl radical as well (equation 3) [56-61]. The peroxybenzoic acid is assumed to play important roles, where peroxybenzoic reacts with another Mn(III) catalyst molecule to generate high-valent cobalt intermediate (equation 4). The color of the reaction mixture changed to tinge green which also indicated valence change of Mn(III) to Mn(IV) [58-62]. Then, the intermediate attacks to the imine group of oxime through a nucleophilic attack [61], thereby, the reaction of an oxo-catalyst radical and oximes, which is proposed to generate a nitroso oxy radical species eventually loses NO to generate an aldehyde and ketone. Via this process, oxime will be converted to its corresponding carbonyl compound.

Although, the oxidation efficiency was not affected by electrondenoting group of substrate, the presence of electron-drawing groups in oxime (like nitro group;entry 15 and 16) will change the path of reaction (equation 6) so as the speed of protonation of hydroxyl group in oxime will be more than the speed of oxo-catalyst attack to imine bond, consequently, it produces nitrile by the elimination of water, the same result was observed in the literature [63-69] (see Scheme 6).

Mn and Co complexes are extensively used in oxidation of organic compounds as both a catalyst and co-catalyst because of their oxidation–reduction property and ability to demonstrate several valencies (Co: (II), (III); Mn: (II), (III), (IV) and (VII)) with easy electron transfer between these states [70-72]. Recently, we reported the direct aerobic oxidation of ethylbenzene, cyclohexene and various oximes to acetophenone, 2-cyclohexene-1-one and corresponding carbonyl compounds using SiO_2/Al_2O_3-supported cobalt catalyst in the presence of NHPI [73]. Manganese and cobalt spices in heterogeneous catalysts are typically main role in these oxidation processes, wherein their catalytic effect lowers the activation energy of the decomposition reaction of the alkylhydroperoxide. The synergistic effect of Co and Mn spices in the aerobic oxidation of alkylbenzenes has been well documented [74]. The behaviours of the Co(II) and Mn(III) ions may be a result of their different redox potentials and, in association with this, their different behaviours in catalyzing hydroperoxide decomposition [75,76].Comparison between performance of manganese and cobalt catalysts are shown in Table 5.

4. Conclusions

A catalyst was developed based on the immobilization of manganese on SiO_2/Al_2O_3 to efficiently promote the aerobic oxidation of ethylbenzene, cyclohexene and oximes to acetophenone, 2-cyclohexene-1-one and carbonyl compounds, under oxygen atmosphere. Oxidation of alkyl aromatic and allylic site was resulted with the oxidant of NHPI and O_2 without the use of any reductant. The catalytic performance was remarkably high in the oxidation reaction. The effect of the catalyst amount, reaction time, reaction temperature and effect of various solvents on the oxidation of ethylbenzene and cyclohexene were investigated. The results indicated that Mn/NHPI facilitated the generation of the active species phtalimido-N-oxyl (PINO) radical which further catalyzed the oxidation of ethylbenzene and cyclohexene. Furthermore, we have reported a new and efficient methodology for the regeneration of aldehydes and ketones from oximes. The extension of the method to other catalysts is currently under investigation.

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Captions

Scheme 1. Schematic representation of the preparation process for SiO_2/Al_2O_3-APTMS-BPK-Mn.

Scheme 2. Products of the oxidation of ethylbenzene.

Scheme 3. Reaction mechanism for the aerobic oxidation of ethylbenzene catalyzed by Mn /NHPI.

Scheme 4. Reaction products of catalytic oxidation of cyclohexene with SiO_2/Al_2O_3-APTMS-BPK-Mn.

Scheme 5. Reaction products of the catalytic oxidation of oximes with SiO_2/Al_2O_3-APTMS-BPK-Mn.

Scheme 6. Mechanism for the oxidation of oximes in the presence of molecular oxygen.

Table 1. Chemical composition and physicochemical properties of the organometallic functionalized SiO_2/Al_2O_3 mixed oxide.

Table 2. Effect of temperature and amount of catalyst on the conversion and selectivity of the catalytic oxidation of ethylbenzene by Mn-supported catalyst.

Table 3. Effect of the temperature and the reaction time on the conversion and selectivity of the catalytic oxidation of cyclohexene by Mn-supported catalyst.

Table 4. Aerobic oxidations of oximes by using Mn-supported as catalyst.

Table 5. Comparison of Co(II)/NHPI and Mn(III)/NHPI catalytic system for direct aerobic

oxidation of ethylbenzene, cyclohexen and oximes.

Figure 1. FTIR spectra of: (A) SiO_2/Al_2O_3-APTMS; (B) SiO_2/Al_2O_3-APTMS-BPK; (C) SiO_2/Al_2O_3-APTMS-BPK-Mn.

Figure 2. UV-vis spectra of: (A) SiO_2/Al_2O_3; (B) SiO_2/Al_2O_3-APTMS; (C) SiO_2/Al_2O_3-APTMS-BPK; (D) SiO_2/Al_2O_3-APTMS-BPK-Mn.

Figure 3. SEM and TEM images corresponding to SiO_2/Al_2O_3-APTMS-BPK-Mn sample.

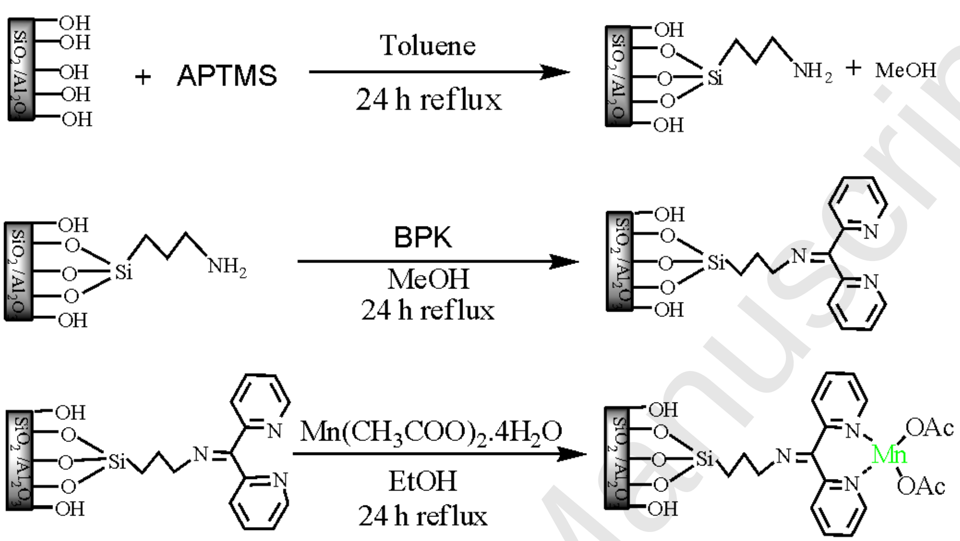
Figure 4. TGA curves of the SiO_2/Al_2O_3 and SiO_2/Al_2O_3-APTMS-BPK-Mn catalyst.

Figure 5. XPS image of the SiO_2/Al_2O_3-APTMS-BPK-Mn catalyst.

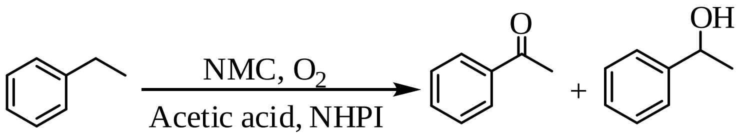
Figure 6. Reusability of the manganese-supported catalyst on the oxidation of ethylbenzene and selectivity to acetophenone. Conditions: ethylbenzene: 2 mmol; amount of catalyst: 0.1 g; NHPI, 15 %; acetic acid, 5 cm^3; T = 120 ºC.

Figure 7. Reusability of the manganese-supported catalyst on the oxidation of cyclohexene and selectivity to 2-cyclohexene-1-one. Conditions: cyclohexene, 2 mmol; amount of catalyst, 0.1 g; NHPI, 15 %; benzonitrile, 5 cm^3; T = 120 ºC.

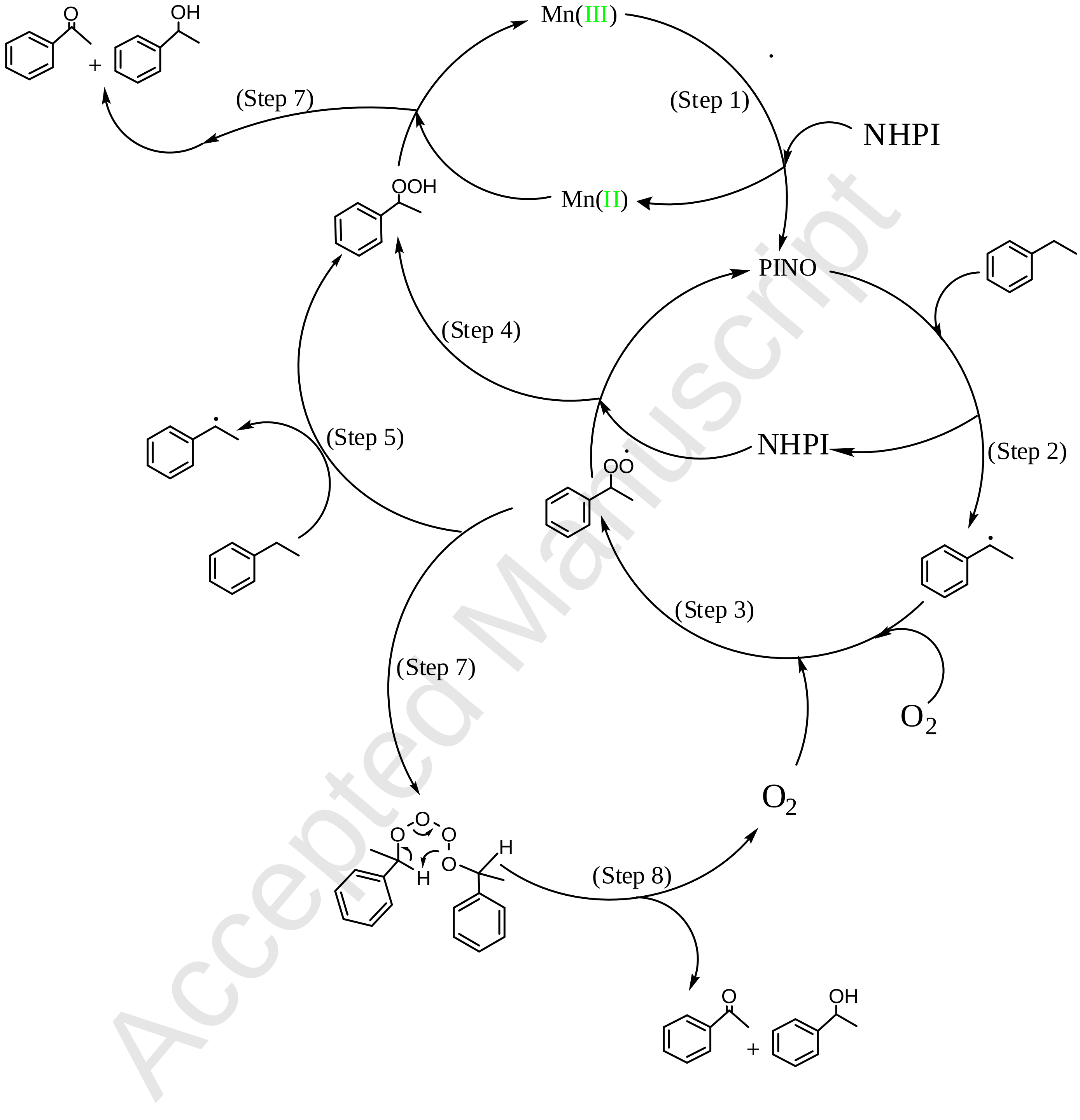
Figure 8. Effect of the amount of benzaldehyde on the acetophenone oxime oxidation to acetophenone by the manganese catalyst. Conditions: acetophenone oxime, 2 mmol; amount of catalyst, 0.15 g; NHPI, 15 %; toluene, 5 cm^3; T = 60 ºC.



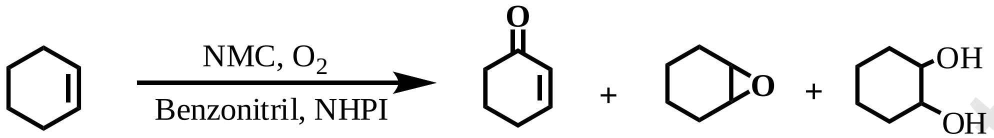
Scheme 1. Schematic representation of the preparation process for SiO_2/Al_2O_3-APTMS-BPK-Mn.



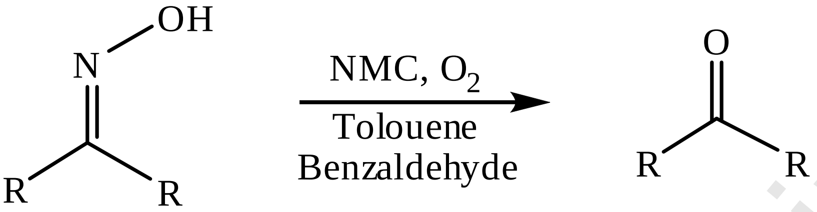
Scheme 2. Products of the oxidation of ethylbenzene.



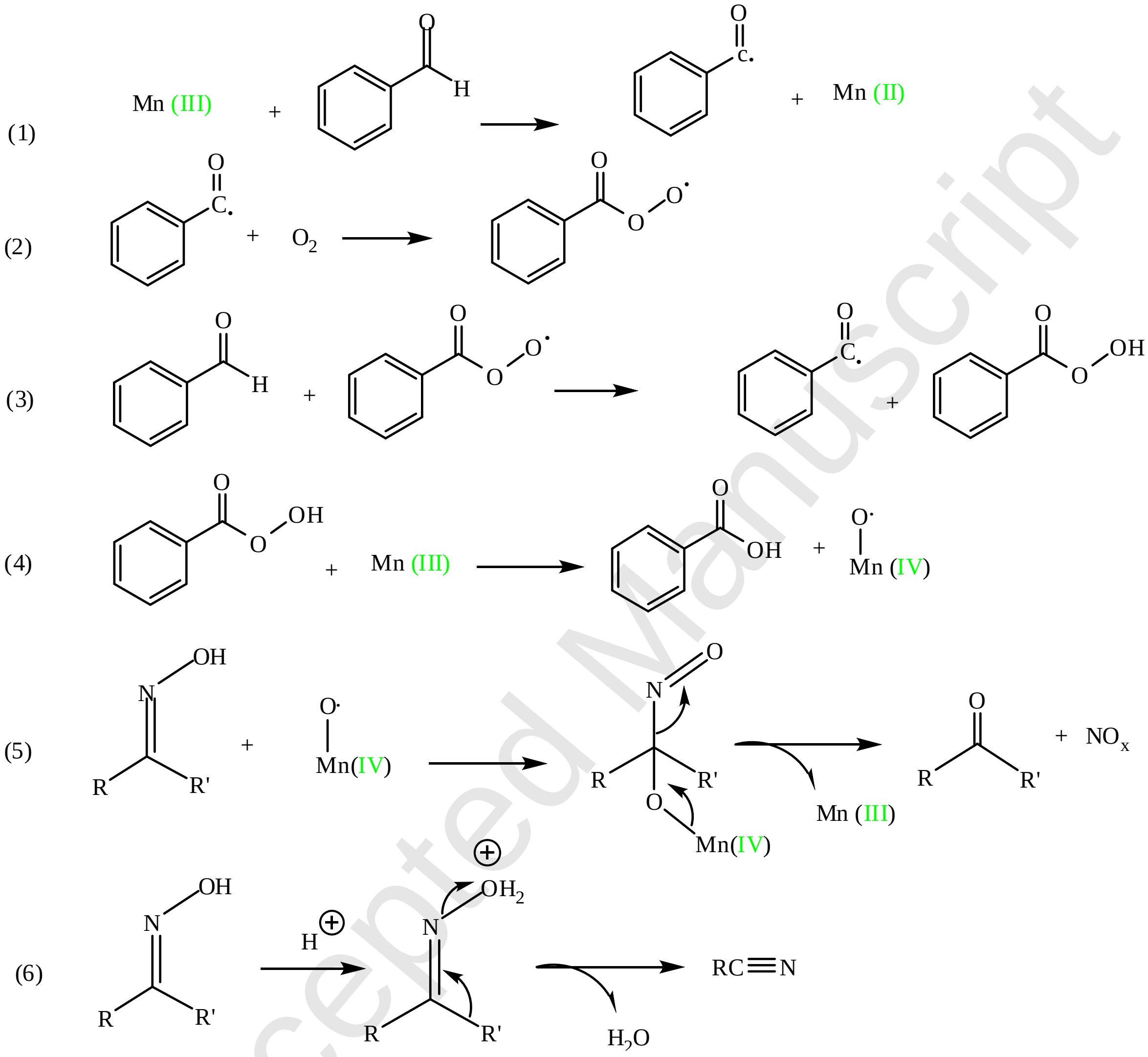
Scheme 3. Reaction mechanism for the aerobic oxidation of ethylbenzene catalyzed by Mn /NHPI.



Scheme 4. Reaction products of catalytic oxidation of cyclohexene with SiO_2/Al_2O_3-APTMS-BPK-Mn.



Scheme 5. Reaction products of the catalytic oxidation of oximes with SiO_2/Al_2O_3-APTMS-BPK-Mn.



Scheme 6. Mechanism for the oxidation of oximes in the presence of molecular oxygen.

Table 1. Chemical composition and physicochemical properties of the organometallic functionalized SiO_2/Al_2O_3 mixed oxide.

Sample	Elemental analysis (wt%)[b]			Organic functional group (mmol/g mixed odide)[c]	Immobilized Mn-Schiff base-complex (mmol/g mixed oxide)[d]	%Coordinated Schiff base groups to Mn ions	Structural parameters[e]		
	C	N	Mn				Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
SiO_2/Al_2O_3 [a]	-	-	-	-	-	-	498	0.045	36
SiO_2/Al_2O_3 - APTMS	8.13	3.75	-	2.67	-	-	378	0.031	25
SiO_2/Al_2O_3 - APTMS-BPK	10.9	4.92	-	3.51	-	-	320	0.026	20
NMC	9.49	2.04	1.94	1.46	0.35	74.4	274	0.018	17

[a] Molar ratio of SiO_2/Al_2O_3 was 60:40, determined from EDX analysis.
[b] Nitrogen was estimated from the elemental analyses. Mn content determined from EDX analysis.
[c] Determined from the N-contents.
[d] Determined from the Mn-content, assume that manganese ions coordinated with Schiff base ligands.
[e] From N_2 adsorption experiments.

Table 2. Effect of temperature and amount of catalyst on the conversion and selectivity of the catalytic oxidation of ethylbenzene by Mn-supported catalyst.

Entry	Catalyst (g)	Time (h)	T (°C)	Conversion[a] (mol %)	TON[b]	Selectivity (mol %)	
						AcPO	PEA
1	-	10	25	8	-	31	69
2	0.02	10	25	10.2	29.14	36	64
3	0.03	10	25	11.7	22.28	42	58
4	0.05	10	25	15	17.14	58	42
5	0.05	8	100	46	52.57	69	31
6	0.1	2	25	6.9	3.94	34	66
7	0.1	10	25	14	8.0	46	54
8	0.15	10	25	19	7.23	50	50
9	0.1	8	100	53	30.28	74	26

[a] Reaction conditions: Ethylbenzene, 2 mmol; Acetic acid, 5 cm^3; NHPI (15% mol).

[b] TON, turn over number, moles of ethylbenzene converted per mole of metal.

Table 3. Effect of the temperature and the reaction time on the conversion and selectivity of the catalytic oxidation of cyclohexene by Mn-supported catalyst.

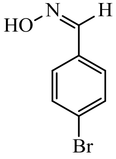
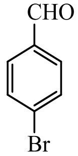
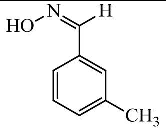
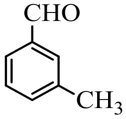
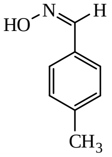
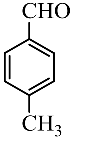
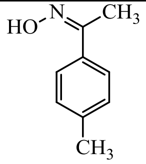
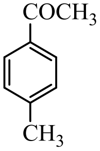
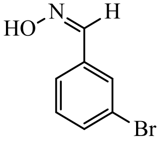
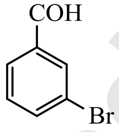
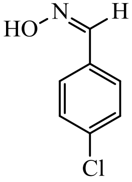
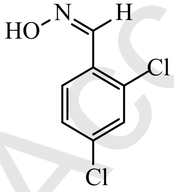
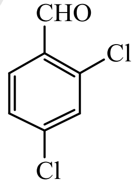
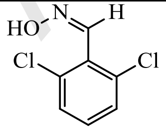
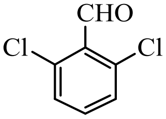
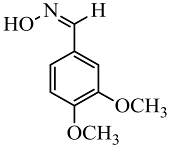
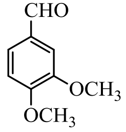
Entry	Time (h)	T (^{o}C)	Conversion[a] (mol %)	TON[b]	Selectivity (mol %)		
					Enol	Enone	Oxide
1	24	25[c]	4	-	23.6	58.9	17.5
2	2	25	5.3		48	36	16
3	6	25	11		35	49	16
4	8	25	12.6		33	54	13
5	10	25	15		26	59	15
6	12	25	16		21	63	16
7	16	25	21		16	67	17
8	18	25	24		14	72	14
9	24	25	27.5	15.71	11	76.6	13.4
10	2	60	26.4		30	64	6
11	6	60	32.9		19	78	3
12	8	60	38		16	80	4
13	10	60	43		12	85	3
14	12	60	49		10	86	4
15	16	60	57		6.8	89	4.2
16	18	60	61		4.7	93	2.3
17	24	60	66.4	37.94	3	95.1	2.9
18	2	80	37		16.5	81	2.5
19	6	80	48.9		6.8	90	3.2
20	8	80	54		5	92	3
21	10	80	59		4.7	93.6	2.7
22	12	80	62		3.7	95	2.3
23	16	80	70		2	97	2
24	18	80	72.5		1.5	97.3	1.2
25	24	80	84.2	48.11	1.1	97.8	0.2
26	2	100	50		8.6	89	2.4
27	6	100	58		4.7	94.7	0.6
28	8	100	62		3	96	1
29	10	100	68		2.3	96.4	1.3
30	12	100	71		2	97.5	0.5
31	16	100	77.5		1.4	98.3	0.3
32	18	100	80		0.8	99	0.2
33	24	100	86	49.14	0.4	99.3	0.3
34	6	120	74		2	97	1
35	8	120	79		1.3	98.6	trace
36	10	120	84		0.7	99	0.3
37	12	120	87		0.4	99.2	0.4
38	16	120	93		-	99.9	0.1
39	18	120	94		-	99.9	0.1
40	24	120	97	55.42	-	99.9	trace

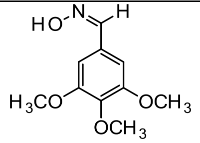
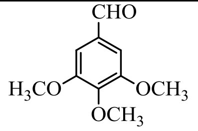
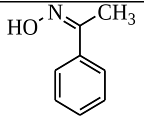
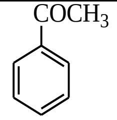
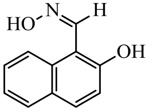
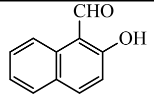
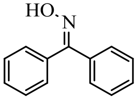
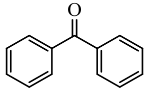
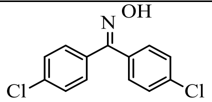
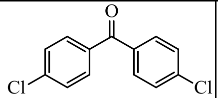
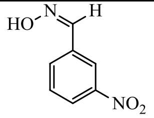
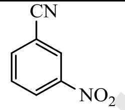
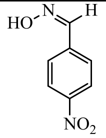
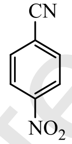
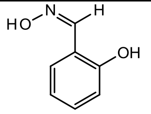
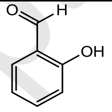
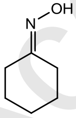
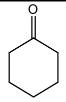
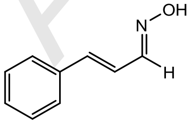
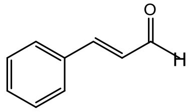
[a] Reaction conditions: Cyclohexene, 2 mmol; Benzonitril, 5 cm^3; NHPI (15% mol).

[b] TON, turn over number, moles of cyclohexene converted per mole of metal.

[C] Blank

Table 4. Aerobic oxidations of oximes by using NMC as catalyst.

Entry	Substrate	Product[a]	Time (min)	Conversion (%)	TON[b]	TOF (min^{-1}) [c]
1			70	95	77.55	1.108
2			90	>99	80.82	0.8980
3			95	>99	80.82	0.8507
4			75	98	80.00	1.067
5			90	98	80.00	0.8889
6			75	97	79.18	1.056
7			100	93	75.92	0.7591
8			120	97	79.18	0.6600
9			130	95	77.55	0.5965

10			155	>99	80.82	0.5214
11			80	>99	80.82	1.010
12			140	>99	80.82	0.5773
13			180	98	80.00	0.4450
14			165	>99	80.82	0.4900
15			155	37	30.20	0.1950
16			110	45	36.73	0.3340
17			200	94	76.73	0.3837
18			150	96	78.37	0.5224
19			240	92	75.10	3130

[a] Reaction condition: Oxime, 2 mmol; Toluene, 5 cm^3; Benzaldehyde, 6 mmol.

[b] TON, turn over number, moles of oximes converted per mole of metal.

[c] TOF, turn over frequencies.

Table 5. Screening data (aerobic oxidation of ethylbenzene, cyclohexene and various oximes).

Substrate	Catalysts	T (ºC)	Time (h)	Product	Conversion (%)	Selectivity (%)	TON[f]
Ethylbanzene[a]	Cat.1[d]	100	8	Acethophenone	53	74	30.28
	Cat.2[e]	100	8		81	98	82.26
Cyclohexene[b]	Cat.1	120	24	2-Cyclohexen-1-one	97	99.9	55.42
	Cat.2	100	24		93	99.9	97.89
Acetophenone oxime[c]	Cat.1	60	1.3	Acethophenone	99	100	80.82
	Cat.2	50	1.5		99	100	68.39
Benzophenone oxime[c]	Cat.1	60	3	Benzophenone	98	100	80.00
	Cat.2	50	3.33		97	100	67.01
4-Bromobezaldehyde[c]	Cat.1	60	1.1	4-Bromo benzaldehyde	95	100	77.55
	Cat.2	50	1.4		94	100	64.93
3,4,5-Trimethoxy benzaldehyde oxime[c]	Cat.1	60	2.5	3,4,5-Trimethoxy benzaldehyde	99	100	80.82
	Cat.2	50	2.8		97	100	67.02
2-Hydroxy naphthaldehyde oxime[c]	Cat.1	60	2.3	2-Hydroxy naphthaldehyde	99	100	80.82
	Cat.2	50	4.4		99	100	68.39

[a] Reaction condition: ethylbenzene; 2 mmol; 15 mol% NHPI; acetic acid, 5 cm^3.

[b] Reaction conditions: cyclohexene, 2 mmol; NHPI, 15%; benzonitrile, 5 cm^3.

[c] Reaction condition: oxime, 2 mmol; benzaldehyde, 10 mmol; toluene, 5 cm^3.

[d] SiO_2/Al_2O_3-APTMS-BPK-Mn(III).

[e] SiO_2/Al_2O_3-APTMS-BPK-Co(II).

[f] TON, turn over number, moles of substrate converted per mole of metal.

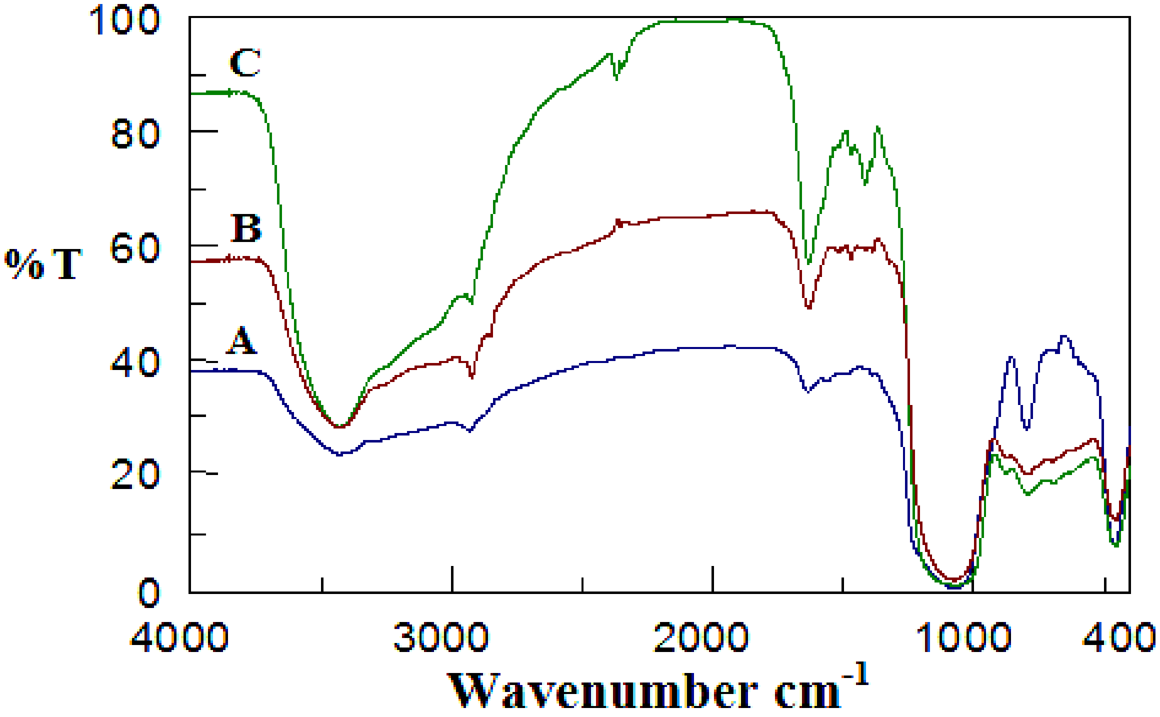


Figure 1. FTIR spectra of: (A) SiO_2/Al_2O_3-APTMS; (B) SiO_2/Al_2O_3-APTMS-BPK; (C) SiO_2/Al_2O_3-APTMS-BPK-Mn.

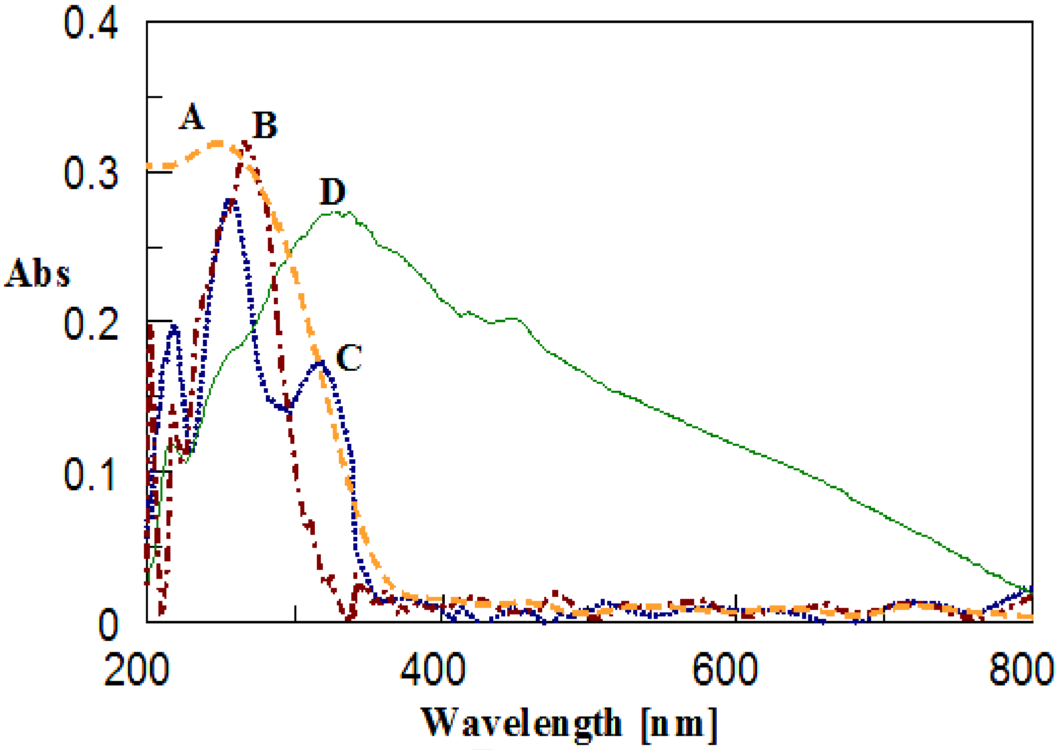


Figure 2. UV-vis spectra of: (A) SiO_2/Al_2O_3; (B) SiO_2/Al_2O_3-APTMS; (C) SiO_2/Al_2O_3-APTMS-BPK; (D) SiO_2/Al_2O_3-APTMS-BPK-Mn.

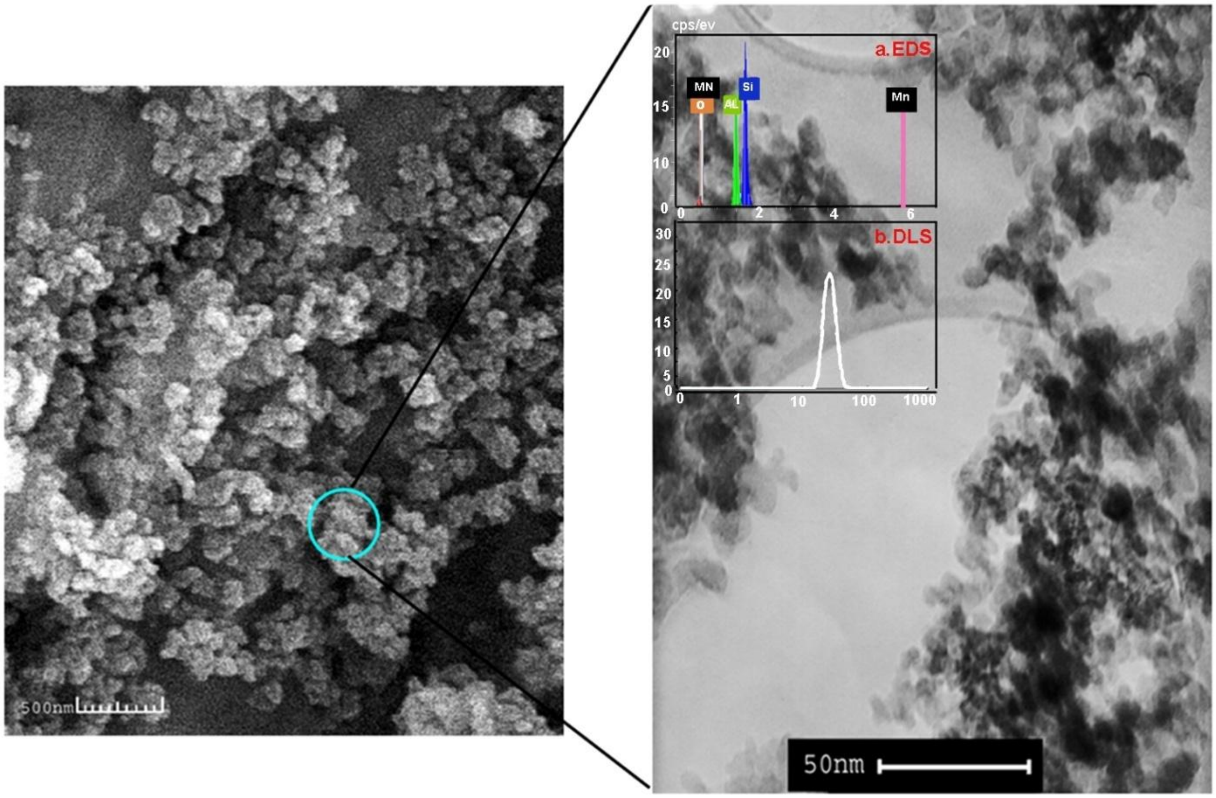


Figure 3. SEM and TEM images corresponding to SiO_2/Al_2O_3-APTMS-BPK-Mn sample.

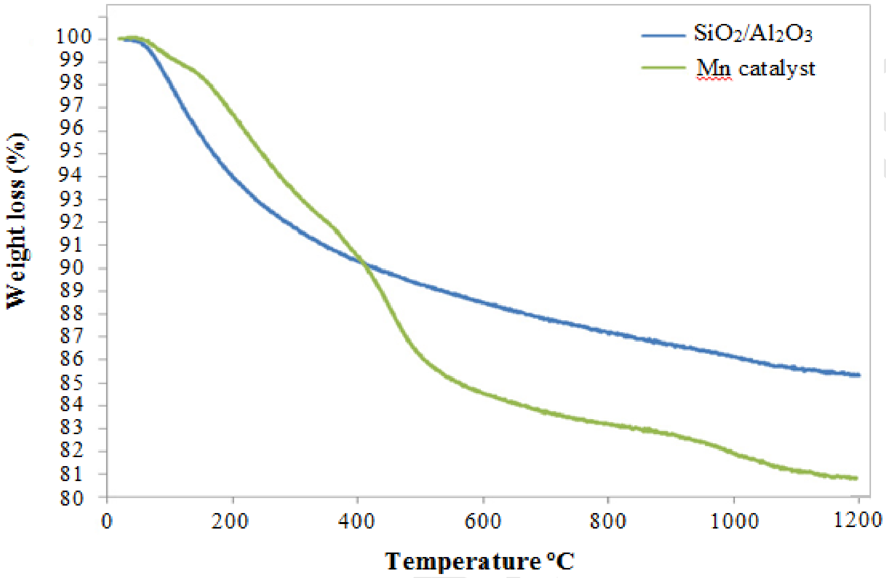


Figure 4. TGA curves of the SiO_2/Al_2O_3 and SiO_2/Al_2O_3-APTMS-BPK-Mn catalyst.

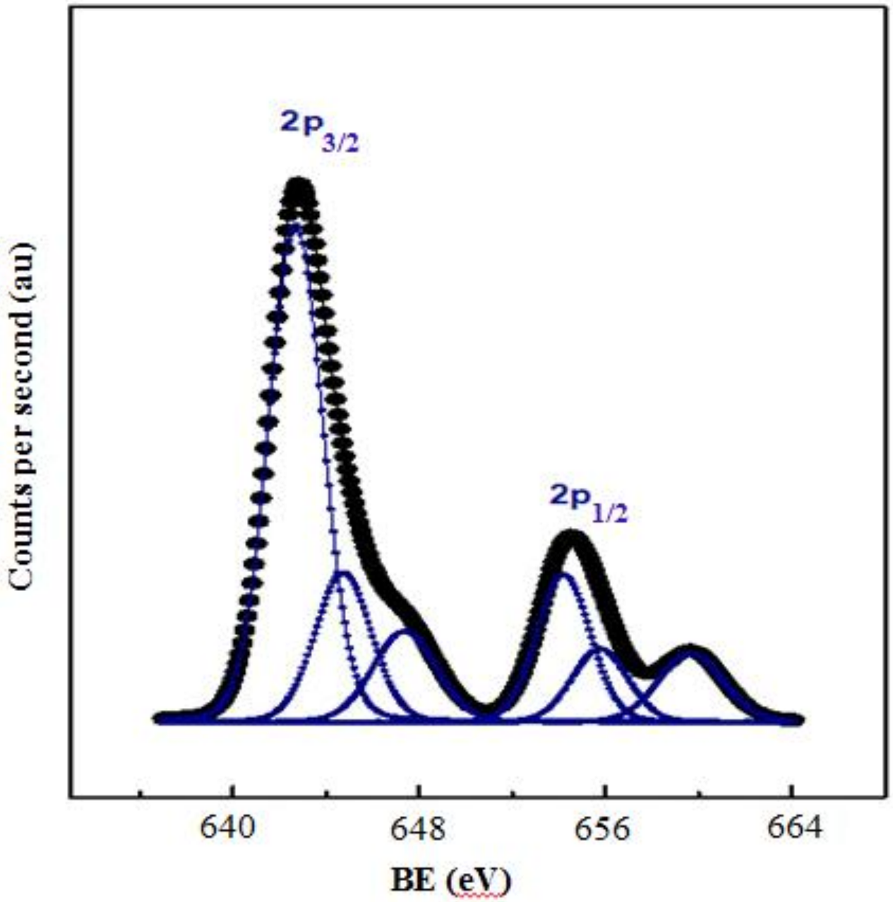


Figure 5. XPS image of the SiO_2/Al_2O_3-APTMS-BPK-Mn catalyst.

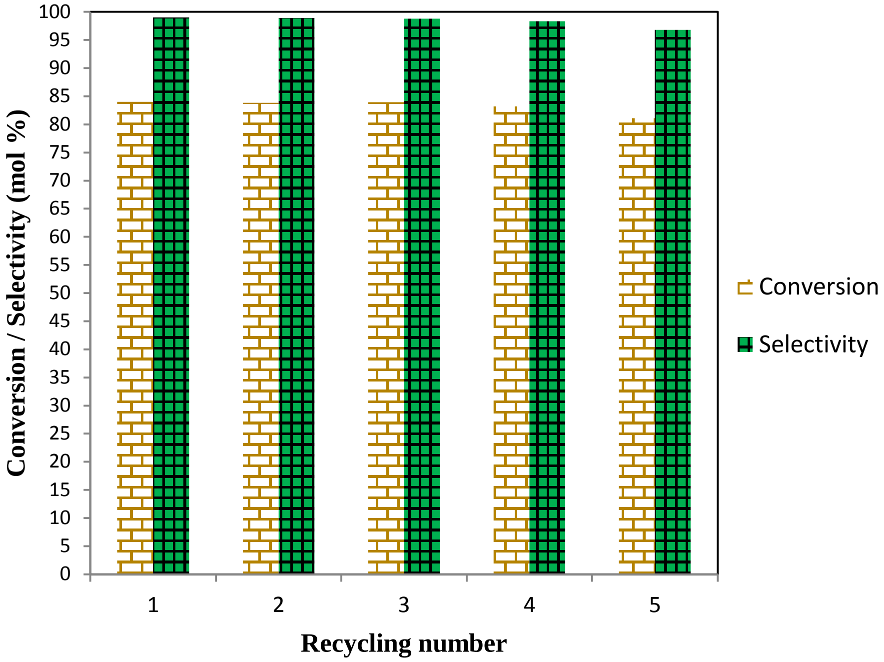


Figure 6. Reusability of the manganese-supported catalyst on the oxidation of ethylbenzene and selectivity to acetophenone. Conditions: ethylbenzene: 2 mmol; amount of catalyst: 0.1 g; NHPI, 15 %; acetic acid, 5 cm^3; T = 120 ºC.

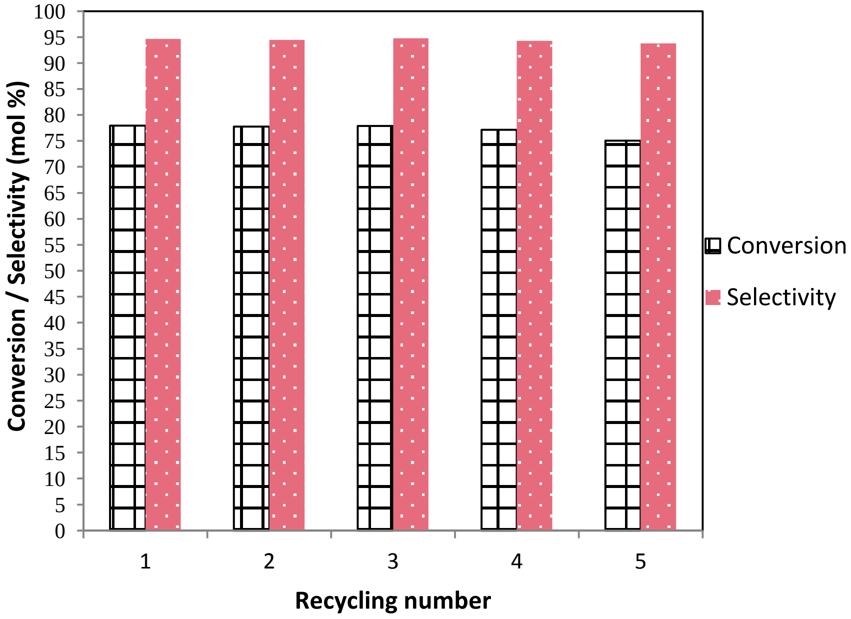


Figure 7. Reusability of the manganese-supported catalyst on the oxidation of cyclohexene and selectivity to 2-cyclohexene-1-one. Conditions: cyclohexene, 2 mmol; amount of catalyst, 0.1 g; NHPI, 15 %; benzonitrile, 5 cm^3; T = 120 ºC.

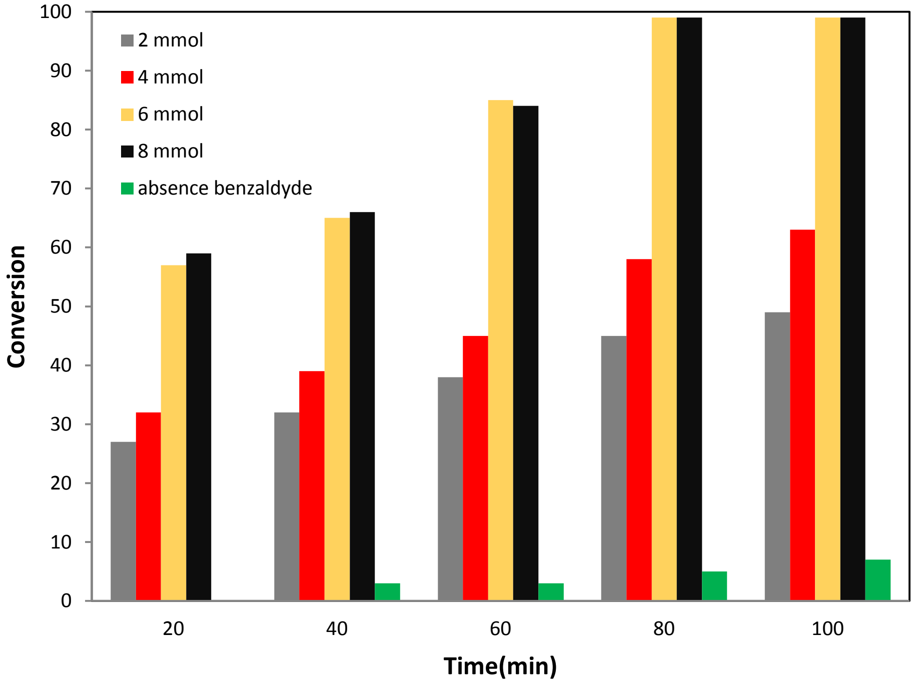


Figure 8. Effect of the amount of benzaldehyde on the acetophenone oxime oxidation to acetophenone by the manganese catalyst. Conditions: acetophenone oxime, 2 mmol; amount of catalyst, 0.07 g; NHPI, 15 %; toluene, 5 cm^3; T = 60 ºC.