

## Manganese tetraoxide supported on nanocrystalline cellulose as catalyst for synthesis of acetophenone

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**Abstract:** The catalytic activity and selectivity of manganese tetraoxide ( $Mn_3O_4$ ) supported on nanocrystalline cellulose (NCC) for the oxidation of ethylbenzene to acetophenone have been studied. The catalyst was prepared by sol-gel method in presence of solid nanocrystalline cellulose dispersed in aqueous medium. Characterisation of  $Mn_3O_4/NCC$  was made using XRD patterns, FT-IR spectroscopy, TGA and ICP-MS. The effects of solvent, reaction time, reactants content and the amount of catalyst in liquid-phase oxidation reaction of aromatic hydrocarbon were carefully investigated. In the oxidation of ethylbenzene, the catalyst  $Mn_3O_4/NCC$  provides extremely high selectivity of acetophenone (>90%) and good conversions at temperature of 70°C with the presence of tert-butyl hydroperoxide. The catalyst absolutely satisfied green chemical principles such as low-toxicity, eco-friendly synthesis, low-cost and reusability.

**Keywords:** Manganese Tetraoxide, Nanocrystalline Cellulose, Acetophenone, Ethylbenzene, Tert-Butyl Hydroperoxide

### 1. Introduction:

Oxidation of hydrocarbons, especially ethylbenzene (EB), is one of the most important processes in petrochemical industry which is paid much attention both in liquid phase and vapour phase reactions. A huge of catalysts have been applied for these processes to improve the conversions and the selectivity of acetophenone. Neili et al supported copper on SBA-15 and used it as catalyst for liquid phase oxidation of ethylbenzene without solvent at 90°C. TBHP was used as oxidant. After 5 hours, 94 % conversion of ethylbenzene and 99% selectivity of acetophenone were achieved [1]. In another research, Habibi prepared nanoparticles Fe supported  $SiO_2/Al_2O_3$  and applied as heterogeneous catalyst for oxidation of ethylbenzene with TBHP as oxidant. 84% ethylbenzene was selectively oxidized. The selectivity of acetophenone was 89% beside the presence of by-products such as benzaldehyde and benzoic acid [2]. Cavalerio et al utilized MnTDCPP and  $Mn(\mu-NO_2 TDCPP)Cl$  as catalysts for ethylbenzene oxidation with  $H_2O_2$  as oxidant at 65°C. After 10 hours, 66% ethylbenzene was converted, and 75% of products was acetophenone. There was the presence of benzaldehyde (20%) [3]. Catalysts based on Manganese were attracted much attention because of high selectivity for acetophenone and good conversion of ethylbenzene. Manganese tetraoxide ( $Mn_3O_4$ ) in nanoscale would be a good catalyst for oxidation, for instant, decomposition of  $NO_x$ , epoxidation of alkenes, degradation of dyes and oxidation of organic compounds. In 21st century - the era of nanomaterials, nanocatalysts are appreciated as good catalysts due to their special characteristics and high catalytic activities in nano-scale. However, the highly developed specific surface and the small size make nanocatalysts be less stable and difficult to separate. A support is necessary to prevent the aggregation and produce the heterogeneous catalyst systems which are easier to isolate. Bio-supports are preponderant candidates because of the low toxicity

and renewability. Among the bio-supports such as chitosan, starch,... nanocrystalline cellulose (NCC) has unique properties, for instant, the good dispersity in water, the inertness in organic solvents and the presence of OH groups on surface. Wu et al used nanocrystalline cellulose as the green support for Au nanoparticles and studied catalytic behaviour of this material [4]. In the work, we prepared  $Mn_3O_4$  nanoparticles supported on nanocrystalline cellulose ( $Mn_3O_4/NCC$ ) and studied its catalytic activity for selective oxidation of ethylbenzene to acetophenone. Various parameters including solvent, temperature and amount of catalyst were investigated.

### 2. Materials and Methods:

#### 2.1. Materials and instrumentation

All chemicals being of analytical grade were used without further purification. Sodium hydroxide 96%, manganese sulfate monohydrate 99%, hydrogen peroxide 30%, oxalic acid 99%, acetonitrile, ethylbenzene were products of Xilong Chemical, China. Tert-butyl hydroperoxide was purchased from Merck, Germany. Water hyacinth plants (*Eichhornia crassipes*), cellulose precursor, were collected in the Saigon river, washed and cut off the leaves and roots. Their stems were dried under sunlight in air from 3 to 5 days. After being completely removed water, the raw material were well grinded into tiny pieces of 0.5x0.5 mm.

X-ray diffraction (XRD) patterns were obtained at D8 BRUCKER ADVANCE power diffractometer with  $Cu K_{\alpha}$  radiation ( $\lambda=0.1542$  nm) at a voltage of 40 kV and a 40mA power. The angle  $2\theta$  increased 0.0300 per 0.7 second from 10.000 to 80.000 degrees. Fourier transform infrared spectra (FT-IR) was recorded with TENSOR37 Spectrometer. The sample was treated with KBr. Thermal Gravimetric Analyses were performed on TGA Q500 V20.10 Build 36 with the heating rate of 20°C/min, from 25 to 800°C in air. Transmission Electron Microscopy

(TEM) images were obtained with JEOL-JEM 1400 at accelerating voltage of 100 kV and magnification of 30000. Gas chromatography was carried out with Varian 4300 using flame ionization detector FID and mass spectrometry (MS) and FactorFour™ Capillary Column VF-1ms.

## 2.2. Synthesis of Mn<sub>3</sub>O<sub>4</sub>/NCC

For the preparation of NCC, the alkali pretreatment of cellulose precursor was carried out with 1M sodium hydroxide solution at temperature of 70°C for 10 hours. Products of this step were filtered by using a vacuum filter and washed with deionized water to pH=7. Solid products of filtering were decolorized by using 10% hydrogen peroxide solution for 14 hours. After the decolorization and filtering, these solid products were hydrolyzed with 0.4M oxalic acid solution at 90°C for 24 hours and were followed by sonication for 45 minutes in ultrasound cleaner. The final product (nanocrystalline cellulose) was collected by a vacuum filter, washed with distillation water to pH=7 and dried in air for 2 days.

For the synthesis of Mn<sub>3</sub>O<sub>4</sub>/NCC, nanocrystalline cellulose was dispersed in distillation water for 2 hours under vigorous stirring. 0.05 mol of MnSO<sub>4</sub>·H<sub>2</sub>O was added into the nanocrystalline cellulose suspension. Then, 50 ml of 1M NaOH was added drop-wise under continuous stirring. Thereafter, 18 ml of 10% H<sub>2</sub>O<sub>2</sub> was added instantly. Brown-black precipitates were formed. The mixture was kept on stirring vigorously at 90°C for 24 hours for aging process. After this process, the mixture was treated with sonication for 45 minutes. The resultant compound was collected by using a vacuum filter, washed three times with distillation water and anhydrous ethanol for once and dried at 100°C for 24 hours.

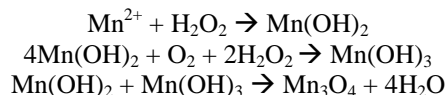
## 2.3. Catalytic reaction and recycling study

To investigate the catalytic activity, reaction tests were carried out in 22ml vial covered tightly by rubber septum with a magnetic stirrer. In a typical run, determined amount of catalyst was added to vial, followed by addition of 1 mmol of ethylbenzene, 2.5 mL of acetonitrile and determined amount of TBHP as the oxidant. The mixture was heated to 70°C under vigorous stirring. After the reaction time, liquid in the vial was removed of solid catalyst by using filter. The products of the reaction were identified by mass spectrometry (MS) and analysed by gas chromatography. A monochlorobenzene was used as the internal standard. The solid catalyst was collected after the reaction and measured the concentration of manganese with ICP-MS to detect the leach of manganese. After the first run, the solid catalyst was washed three times with ethanol and acetone, dried at temperature of 100°C in air oven and used for recycling study.

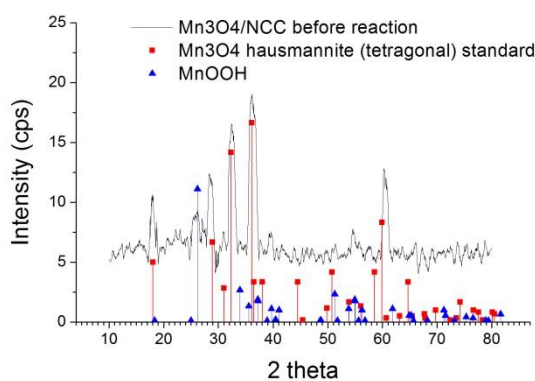
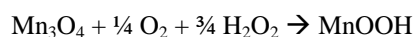
## 3. Results and Discussion:

### 3.1. Characterization of catalyst

Mn<sub>3</sub>O<sub>4</sub>/NCC was synthesized by the oxidation of salt MnSO<sub>4</sub> using hydroperoxide in the presence of nanocrystalline cellulose as support. The reaction used to prepare the catalyst can be summarized below [5]:



XRD pattern of catalyst is displayed in the Fig.1 which shows peaks assigned to manganese tetraoxide (Mn<sub>3</sub>O<sub>4</sub>) hausmannite (tetragonal). Moreover, there are the existence of peaks of manganese oxy hydroperoxide (MnOOH or Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O) in this figure. This is the result of the oxidation of Mn<sub>3</sub>O<sub>4</sub> to MnOOH in the appearance of oxygen and water [5].



**Figure 1.** XRD pattern of Mn<sub>3</sub>O<sub>4</sub>/NCC before reaction (square: Mn<sub>3</sub>O<sub>4</sub> standard peaks, triangle: MnOOH standard peaks)

According to ICP-MS result, the concentration of manganese in Mn<sub>3</sub>O<sub>4</sub>/NCC sample was 42.1 % (7mmol Mn/g).

Figure 2 is FT-IR Spectrum of Mn<sub>3</sub>O<sub>4</sub>/NCC sample. The peaks at 520 cm<sup>-1</sup> and 592 cm<sup>-1</sup> are assigned to the coupling mode between Mn-O stretching of tetrahedral and octahedral sites of Mn<sub>3</sub>O<sub>4</sub>. Moreover, the peaks at 1076, 1110 and 1154 cm<sup>-1</sup> illustrated the vibrations of the out-of-plane bending modes of OH and the in-plane bending modes of OH of MnOOH and nanocrystalline cellulose. In addition, the peaks at 1316 cm<sup>-1</sup>, 1370 cm<sup>-1</sup>, 1427 cm<sup>-1</sup>, 1030 cm<sup>-1</sup> and 2853 cm<sup>-1</sup> are qualitative ones of cellulose nanocrystals. The peak at 1627 cm<sup>-1</sup> performs the presence of water absorbed. The peaks at 2041 and 2667 cm<sup>-1</sup> is assigned to the vibrations of C=O stretch and C-H stretch of H-C=O groups which are formed by the oxidation of some CH<sub>2</sub>OH groups of nanocrystalline cellulose in the presence of hydrogen peroxide and Mn<sub>3</sub>O<sub>4</sub> nanoparticles.

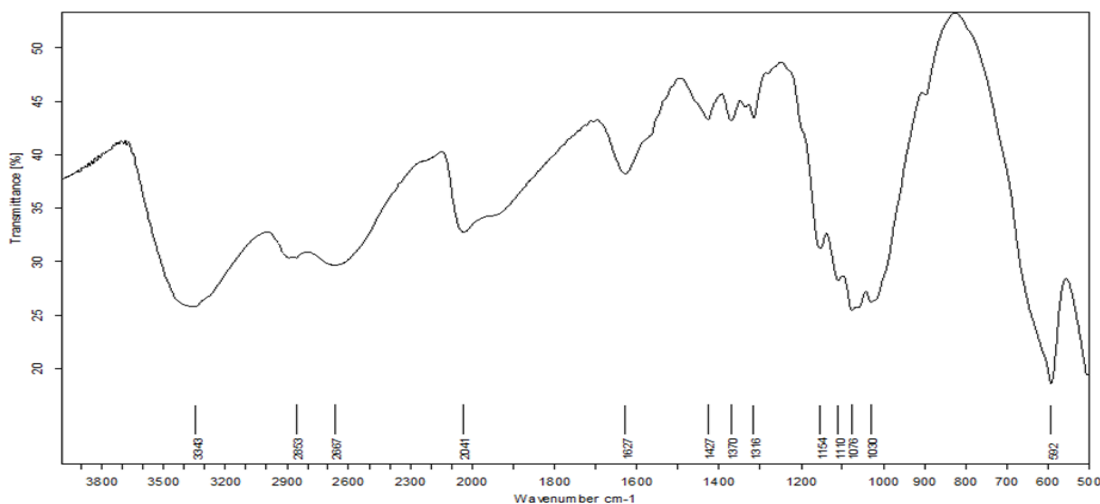


Figure 2. FT-IR Spectrum of  $Mn_3O_4/NCC$  sample

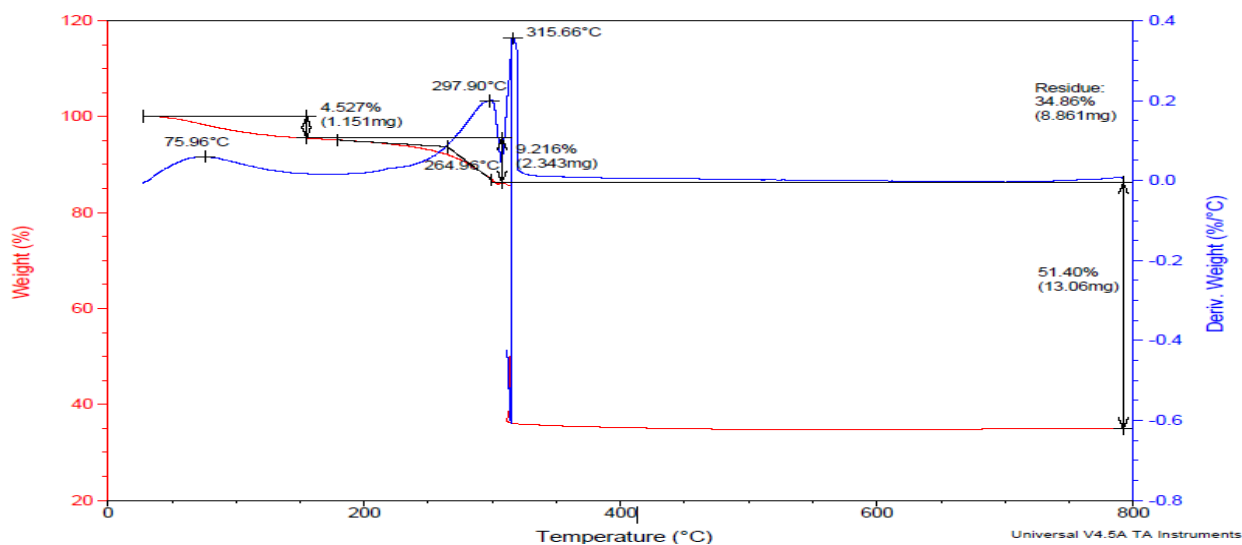


Figure 3. TGA and DTG curves of  $Mn_3O_4/NCC$

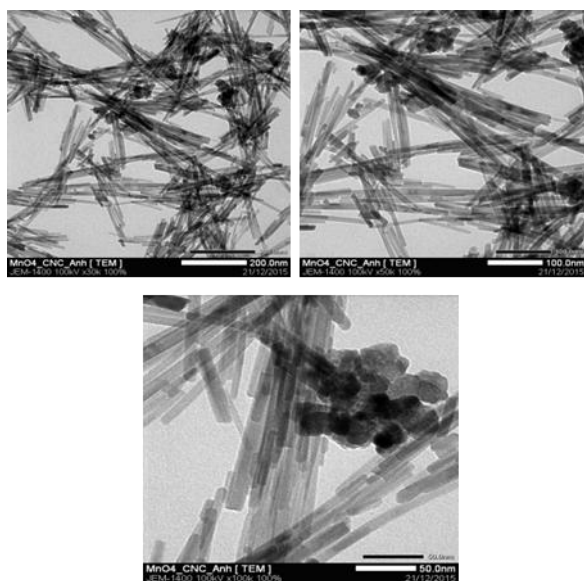


Figure 4. TEM images of  $Mn_3O_4/NCC$  sample (scale in images a. 200nm, b.100nm, c.50nm)

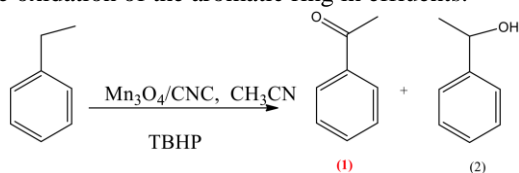
The TGA profile of  $Mn_3O_4/NCC$  sample (Figure 3) has two endothermic effects at 297.90°C assigned to the decomposition of cellulose and 315.66°C attributed to the decomposition of both cellulose and  $MnOOH$  particles. When the temperature increased from 28°C to 150°C, the weight decreased due to the vaporization of water molecules on the surface of cellulose nanocrystals

Based on TEM images (Figure 4), the diameter of cellulose nanofibrils was about 10÷20nm, and their length was approximately from 100 to 400 nm. The  $Mn_3O_4$  and  $MnOOH$  nanoparticles had the diameter from 20 to 25 nm. The aggregation of particles is also performed on the images. The shapes of cellulose nanocrystals likes rod.

### 3.2. Catalytic reaction and recycling study

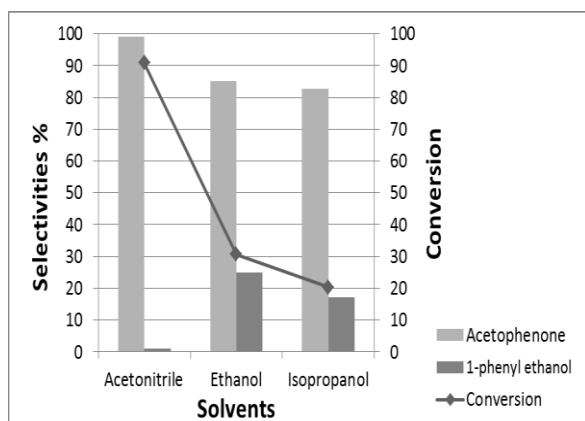
The optimization of the selective oxidation of ethylbenzene (EB) was studied by investigating various parameters such as solvent, temperature, oxidant, the reaction time, amount of catalyst and ratio of oxidant to reagent. In the reaction, main

products are acetophenone, 1-phenylethanol. The GC and GC-MS analysis did not show any products of the oxidation of the aromatic ring in effluents.



**Figure 5.** Possible products obtained from the oxidation of EB

In studying effect of solvent on the selectivity of acetophenone and the conversion of ethylbenzene, acetonitrile, ethanol and isopropanol were examined at temperature of  $70^\circ\text{C}$  for 20 hours. The conversion of ethylbenzene decreased on different solvents in the following order: 90.85% (acetonitrile) > 30.7% (ethanol) > 20.28% (isopropanol). Although acetophenone was major product, the selectivity of acetophenone declined in the following order: 99% (acetonitrile) > 85% (ethanol) > 82.72% (isopropanol). The change of solvent from aprotic one (acetonitrile) to protic ones (ethanol and isopropanol) was extremely effective on oxidation of EB. (Figure 6)

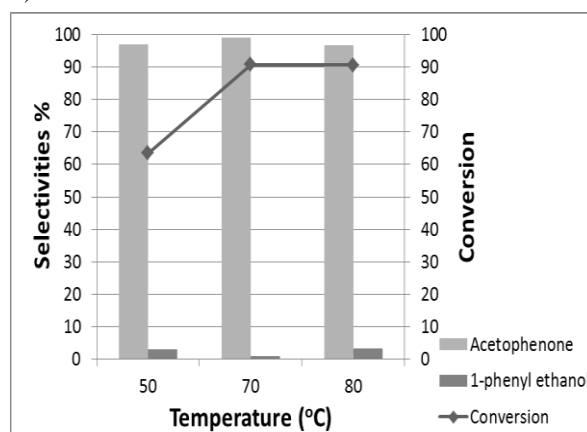


**Figure 6.** Effect of solvents. Conditions: 0.025g cat, EB 0.1 ml, TBHP 0.7 ml, 20h,  $70^\circ\text{C}$

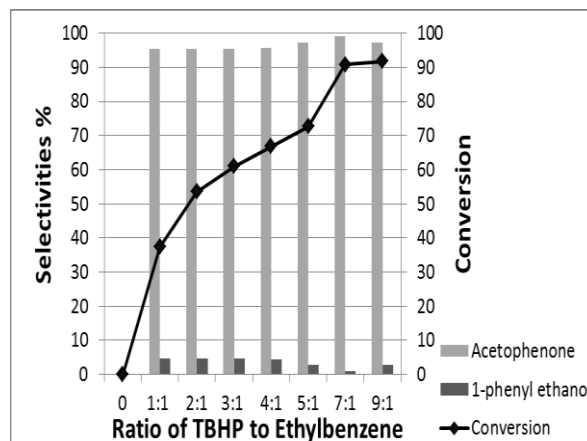
In order to investigate the effect of temperature on the oxidation of ethylbenzene, the temperature of the reaction was increased from  $50^\circ\text{C}$  to  $80^\circ\text{C}$  ( $50^\circ\text{C}$ ,  $70^\circ\text{C}$  and  $80^\circ\text{C}$ ). The increase of temperature was apparently effective on the conversion of ethylbenzene. The temperature effect was monitored on the oxidation of ethylbenzene at the ratio of TBHP:EB = 7:1 after 20 hours with the presence of catalyst. When the temperature increased from  $50^\circ\text{C}$  to  $70^\circ\text{C}$ , the conversion of EB developed 27 % (from 63.46% to 90.85%). The rise of temperature from  $70^\circ\text{C}$  to  $80^\circ\text{C}$  caused the negligible change of EB conversion (90.85% and 90.7%). The increase of temperature resulted in the faster movement and the more frequent collision of molecules. Therefore, the conversion of EB developed. The temperature of the reaction should not be higher than  $80^\circ\text{C}$  because of

the vaporization of solvents (acetonitrile and ethanol). (Figure 7)

The ratio of oxidant (TBHP) to reagent (EB) played an essential role in oxidation of EB. Using acetonitrile as solvent, the effect of ratio TBHP:EB was investigated at  $70^\circ\text{C}$  for 20 hours in the presence of catalyst. The different volume ratios of TBHP:EB were applied (1:1, 2:1, 3:1, 4:1, 5:1, 7:1 and 9:1). In most of experiments, the acetophenone was the major product (>95%). The best catalytic activity was obtained at the TBHP:EB ratio of 7:1. The increase of the ratio from 7:1 to 9:1 causes the negligible change of EB conversion (90.85% to 91.7%). (Figure 8)



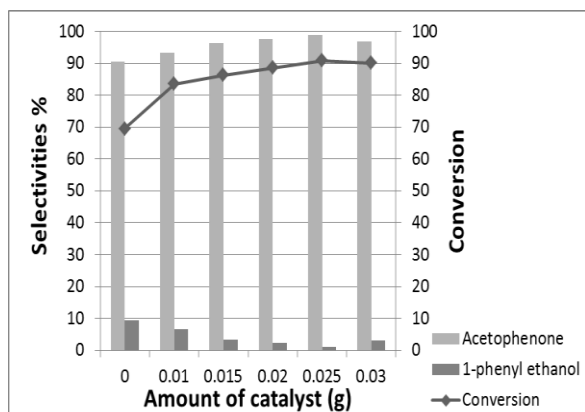
**Figure 7.** Effect of temperature. Conditions: 0.025g cat, EB 0.1ml, TBHP 0.7 ml, 20 h,  $\text{CH}_3\text{CN}$



**Figure 8.** The influence of ratio of TBHP to EB. Conditions: 0.025g cat, EB 0.1 ml, 20h,  $70^\circ\text{C}$ ,  $\text{CH}_3\text{CN}$

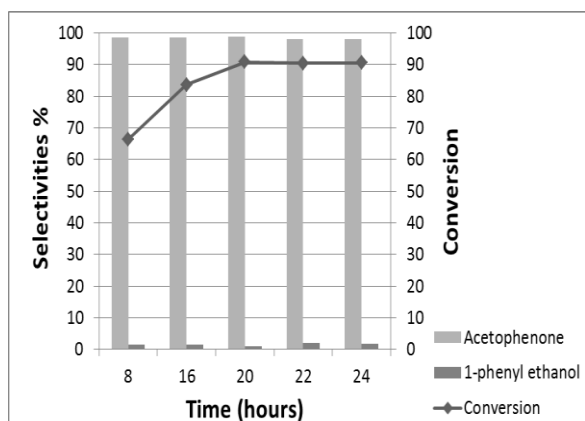
To evaluate the effect of amount of catalyst on the conversion of EB and the selectivity of acetophenone in acetonitrile, the reactions were carried out with different amounts of catalyst (0, 0.010g, 0.015g, 0.020g, 0.025g, 0.030g) at TBHP:EB ratio of 7:1 at temperature of  $70^\circ\text{C}$  for 20 hours. The use of catalyst improved the conversion of EB from 69.57% to 90.85 % and the selectivity of acetophenone from 90.65% to 99%. When amount of catalyst increased from 0.010 g to 0.025 g, the conversion of EB and

the selectivity of acetophenone increased. However, the conversion was negligibly different between amount of catalyst of 0.025g and 0.030g. (Figure 9) Moreover, in order to estimate the effect of the reaction time, the reactions were carried out with 0.025g catalyst at TBHP:EB ratio of 7:1 at temperature of 70°C for determined periods of time (8, 16, 20, 22, 24 hours). The equilibrium of the oxidation of EB in acetonitrile was reached after 20 hours. (Figure 10)

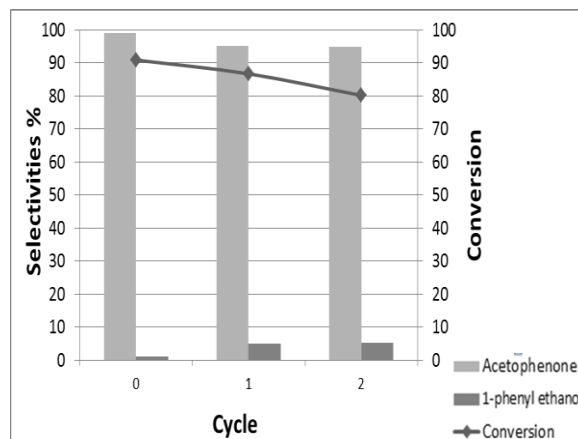


**Figure 9.** The influence of amount of catalyst. Conditions: EB 0.1 ml, TBHP 0.7 ml, 20h, 70°C, CH<sub>3</sub>CN

To study the reusability of catalyst, after the first run, the catalyst were reused two times. The conversion of EB and the selectivity of acetophenone reduced in each cycle of reusing (from 90.85% to 80.15%). The losses of catalytic activity and the selectivity maybe resulted from the aggregation and the loss of metal oxide nanoparticles in washing and drying. In spite of being reused two times, the existence of catalyst provided the reaction the higher conversion of EB and the better selectivity of acetophenone than the disappearance of one. (Figure 11)

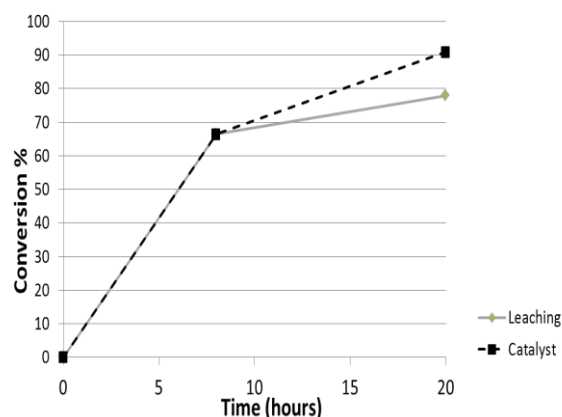


**Figure 10.** The effect of reaction time. Conditions: 0.025 g cat, EB 0.1 ml, TBHP 0.7 ml, 70°C, CH<sub>3</sub>CN



**Figure 11.** Reusability of catalyst. Conditions: 0.025 g cat, EB 0.1 ml, TBHP 0.7 ml, 70°C, 20h, CH<sub>3</sub>CN

Finally, the heterogeneity of the catalyst was tested by leaching test. This test had two phase and occurred for 20 hours. In the first phase, the oxidation of EB occurred in the presence of catalyst for 8 hours and provided the conversion of EB of 66.42% and the selectivity of acetophenone of 98.6%. In the second phase, the catalyst was removed, and the oxidation continued occurring without catalyst. After 12 hours, the reaction reached the conversion of EB of 77.69% and the selectivity of acetophenone of 94.65%. This indicated that the disappearance of catalyst reduced the conversion of EB 13% when comparing with the one of the oxidation occurring with catalyst for 20 hours. Moreover, amount of ethylbenzene converted in leaching test was 8% higher than one of the oxidation of EB without catalyst. This was the result of the improvement the conversion in the presence of catalyst for initial 8 hours. Although catalyst was removed, the oxidation of EB could occur. Thereafter, the conversion of EB increased from 66.42% to 77.69% in phase 2. (Figure 12)

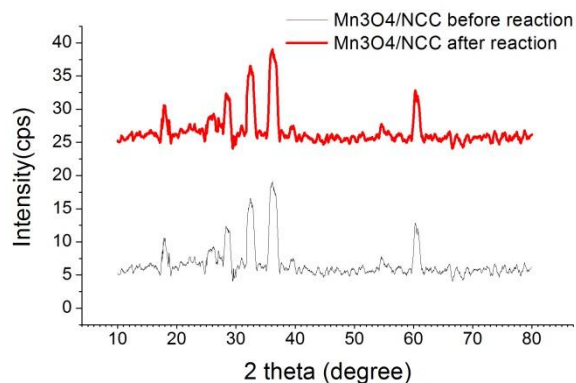


**Figure 12.** Leaching test

**Table 1.** The comparison of literature catalysts and our catalyst system for selective oxidation of EB

Entry	Catalyst system	Reaction conditions	Ethylbenzene conversion	Selectivity	
				Acetophenone	Other
1	Kumar et al [6]	0.2g Mn-SBA, TBHP, solvent free, 80°C, 8h	25	37	63
2	Vetrivel et al [7]	0.3g Mn-MCM41, TBHP, solvent free, 80°C, 24h	60	39	61
3	Bhoware and Singh [8]	0.05g Co-MCM41, TBHP, solvent free, 80°C, 24h	26	85	15
4	Cavalerio et al [3]	3μg Mn(TDCPP)Cl, H <sub>2</sub> O <sub>2</sub> , 5,5h, room temperature	64	75	25
5	Parida [9]	0.05g Mn-MCM41, TBHP, CH <sub>3</sub> CN, 80°C, 6h	57,7	82	18
6	D.Habibi, A.R Faraji [10]	0.05g SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> -APIMS-BPK-Mn, solvent free, 100°C, 24h	87	96	4
7	Imran et al [11]	100mg MnTUD, TBHP, CH <sub>3</sub> CN, 80°C, 8h	19,8	60,8	39,2
8	This work	0.025g Mn <sub>3</sub> O <sub>4</sub> /NCC (7 mmol Mn/g), TBHP, CH <sub>3</sub> CN, 70°C, 24h	90.85	99	1

Recycled catalyst was characterized by XRD, and the concentration of manganese of Mn<sub>3</sub>O<sub>4</sub>/NCC was measured by ICP-MS. There are no novel peak in the XRD pattern of catalyst sample after reaction (Figure 13). Therefore, no new compound was formed during reaction time in catalyst sample. According to ICP-MS results, the concentration of manganese of catalyst sample after reaction is 41.8% (~7mmol Mn/g) which is approximately same the one of catalyst sample before reaction. We can conclude that Mn<sub>3</sub>O<sub>4</sub>/NCC is a catalyst with the high heterogeneity.

**Figure 13.** XRD patterns of fresh Mn<sub>3</sub>O<sub>4</sub>/NCC and reused Mn<sub>3</sub>O<sub>4</sub>/NCC.

#### 4. Conclusion:

In this research, a new catalyst Mn<sub>3</sub>O<sub>4</sub>/NCC which is renewable, low-toxic and inexpensive has been successfully synthesized. This catalyst has been applied in the oxidation of ethylbenzene to investigate the catalytic activity. The high selectivity of acetophenone (> 90%) and the good conversion of EB have been achieved. In the optimal condition, 91% ethylbenzene was converted, and the selectivity of acetophenone was 99%.

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