

**Catalytic Aerobic Oxidation System via Terephthalic Acid Production
Using Economic and Readily Available Nanocatalyst**

Nadia G. kandile^a, A. M. Badawi^b, Sanaa M. Solyman^{b,c}, Mohamed A. Betiha^{b,d} and Ahmed S. Afify^b

^a *Chemistry Dep., Faculty of women for Arts, Science and Education, Ain Shams University, Cairo, Egypt*

^b *Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt.*

^c *AL-Ghad International College for Applied Medical Science, Kingdom of Saudi Arabia.*

^d *Egypt nanotechnology center (EGNC) Cairo university, El-Shiekh Zayed, 12588, Egypt.*

Abstract

One of the most important commercial industrial processes is liquid phase catalytic oxidation of *p*-xylene by oxygen for terephthalic acid (TPA) production. A recent catalytic system used environmentally benign N-hydroxyamide as a free radical promoter rather than more hazardous bromine molecules. An economical and easily prepared heterogeneous oxidation catalyst, nanorods manganese dioxide, was synthesized by ultrasonic technique. The crystal structure and morphology of the MnO₂ were confirmed by HRTEM, XRD, and N₂-adsorption-desorption isotherms. The prepared MnO₂ nanorods had a high aspect ratio and surface area of 300 m² g⁻¹. The catalytic oxidation of *p*-toluic acid (PTA) to terephthalic acid using MnO₂ nanorods was studied under the different conditions (reaction time, catalyst dosages, reaction solvent and varied pressures and temperatures) to control the yield and selectivity toward TPA synthesis. The obtained results showed that the high yield (88.9%) and conversion (90.1%) in ethyl acetate with fixed oxygen pressure (20 atm) at 150°C.

Keywords:

MnO₂; nanorods; catalytic oxidation; terephthalic acid (TPA)

Corresponding author: ahmedsamayas@hotmail.com

1. Introduction

The catalytic oxidation of *p*-xylene is a major industrial process for the production of terephthalic acid, which is an essential monomer and widely used for polyesters production. The polymer is a high melting and its crystalline material forming very strong fibers. The commercial production of terephthalic acid is based on the liquid phase catalytic oxidation of *p*-xylene by air or oxygen in the presence of manganese acetate and cobalt acetate as homogeneous catalyst and bromine or HBr as a promoter in acetic acid as a solvent. This oxidation occurs at a temperature of 175–225 °C and pressures of 15 - 30 atm and reaction time of 8–24 h. However, acetic acid and bromine cause severe corrosions in equipment when used especially at high temperatures. Also, acetic acid gives different unwanted reaction by-products due to the partial combustion of acetic acid. Furthermore, bromine is very harmful to the human body, and cause serious environmental pollution [Illes, K. E. and Dickinson, D. A. 2017; Plant, J. A. et al. 2012].

An interesting aerobic oxidation of organic compounds catalyzed by N-hydroxyimides, such as N-hydroxyphthalimide (NHPI) and transition metal salts, was developed mainly by Ishii and coworkers [Ishii, Y. and Sakaguchi, S. 2006a; Ishii, Y. et al. 2005; Hirai, N. et al. 2006; Sakaguchi, S. et al. 2002]. This method of selective catalytic oxidation of alkylbenzenes with oxygen is a very important reaction for the production of bulk and fine chemicals such as benzoic acid and terephthalic acid [Clennan, E. L. 2016]. Practically, the oxidation of toluene is carried out by Ishii and coworkers [Ishii, Y. and Sakaguchi, S. 2006a; Ishii, Y. et al. 2005; Hirai, N. et al. 2006; Aoki, Y. et al. 2005; Aoki, Y. et al. 2006; Kamae, K. et al. 2009] under normal oxygen pressure at room temperature by the use of a combined catalyst of NHPI and Co(II) species and oxidation of *p*-xylene to 85% yield of *p*-toluic acid (not terephthalic acid) for 20 h at room temperature (Fig. 1).

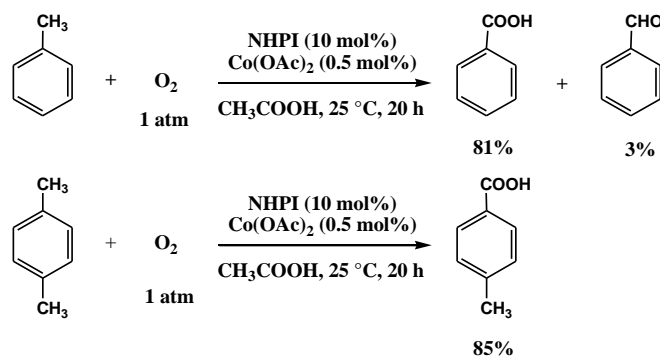


Fig. 1. Oxidation of alkylbenzenes with NHPI by oxygen.

Various studies were reported including different transition metal ions like (Co(II), Mn(II), V(III) and Ce(IV), etc) as homogenous catalysts. For example, the oxidation of *p*-xylene with oxygen gas (1 atm) in the presence of NHPI (20 mol%) and Co(OAc)₂ (0.5 mol%) as catalysts in acetic acid as solvent at 100 °C for 14 h produced TPA in 67% yield and PTA (15%) together with small amounts of (4-carboxybenzyl alcohol), 1,4-diacetoxymethylbenzene and 4-acetoxymethylbenzoic acid as well as several unidentified compounds in 1–2% yields, respectively, at over 99% conversion. The yield of TPA is improved to 82% when Mn(OAc)₂ (0.5 mol%) is added to the NHPI/Co(OAc)₂ system. The synergistic effect of Co and Mn salts in the aerobic oxidation of alkylbenzenes has been well documented [Partenheimer, W. 2004; Partenheimer, W. 2003; Tashiro, Y. et al. 2001]. From a practical point of view, it is important that the aerobic oxidation of *p*-xylene under air (30 atm) by the NHPI/Co/Mn system is completed within 3 h at 150 °C to form TPA in 84% yield [Gomes, J. F. 2013; Ishii, Y. and Sakaguchi, S. 2006b] (Fig. 2).

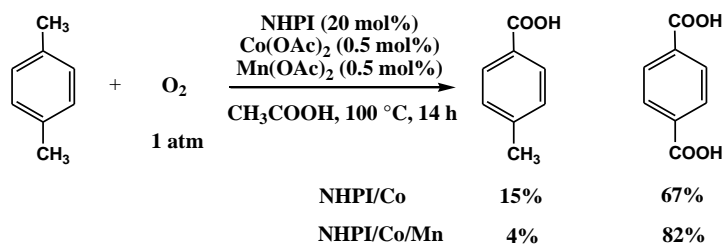


Fig. 2. Oxidation of PX by O₂ with NHPI/Mn(OAc)₂/Co(OAc)₂

This method has many advantages such as using environmentally benign *n*-hydroxysuccinimide as a free radical promoter rather than more hazardous bromine compounds, besides using cheap and easily obtained oxidizing agent, oxygen gas. But this

method is based on acetic acid as a reaction solvent. From an economical point of view, this process needs a cheap and easily prepared heterogeneous nanocatalyst with high surface area instead of soluble transition metal salts to overcome the separation and recycling disability problems.

In this paper, one of the most promising metal oxides is manganese dioxide (MnO_2) that is more economical, non-toxic, readily available catalyst could play a great role as a good catalyst for *p*-xylene aerobic oxidation in the presence of *n*-hydroxysuccinimide as a promoter. Consequently, MnO_2 -nanorods is prepared by facile synthesis, characterized by different techniques and studied for the methyl groups of *p*-xylene oxidation with oxygen to give the corresponding carboxylic groups. Different conditions (reaction time, catalyst dosages, reaction solvent and varied pressures and temperatures) were also studied to explore its catalytic role towards terephthalic acid synthesis.

2. Experimental

2.1. Materials

All chemicals and solvents were purchased and used without any further purification. *p*-toluic acid, *N*-Hydroxysuccinimide, cobalt(II) acetate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), manganese(II) acetate ($\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), potassium permanganate (KMnO_4) were purchased from Sigma-Aldrich. All solvents like acetonitrile, glacial acetic acid, and ethyl acetate were obtained from Merck Chemical Co.

2.2. Preparation of manganese dioxide (MnO_2) nanorods catalyst

KMnO_4 (6.5 gm) was charged into 150-ml round flask filled with 150 ml water/ethanol (1:1/V:V). After complete dissolution, the flask is transferred to ultrasonic bath operated at 35 kHz for 3 h. Then, 1 ml of H_2O_2 (30v/v) was added to complete the precipitation. The black precipitate of manganese oxide was collected by filtration and washed thoroughly several times with water to remove any residual of K^+ ions from the solid product, vacuum dried overnight in at 60°C and calcined at 400°C for 2 h [Kannan, R. et al. 2011].

2.3. Characterization

Wide-angle X-ray diffraction pattern was recorded on a XPERT X-ray diffractometer in the angular range from 10 to 70° (2 θ). The BET surface area, average pore diameter, and pore volume were measured at -196 °C on a NOVA 3200 system (USA). The catalysts were outgassed for 3 h at 300 °C under vacuum in the degassing port of the adsorption analyzer. The specific surface area was calculated using the BET model. The pore size distributions were obtained from the desorption branch of the nitrogen isotherms using Barrett-Joyner-Halenda (BJH) method. High-resolution transmission electron microscope (HRTEM) images were obtained using a JEOL JEM-2100 (Japan) operating at 200 kV.

2.3. Catalytic test

The catalytic activity was screened at atmospheric pressure, and then the catalytic reaction is carried out at the optimum condition at a different pressure.

2.3.1. Atmospheric pressure

The oxidation of *p*-toluic acid was performed in a 3-neck flask equipped with a magnetic stirrer and a septum for withdrawing samples at intervals of 1 h. The system was also equipped with a condenser to ensure complete condensation and recycling of the evaporated compounds. In a typical run, 80 mmol of *p*-toluic acid, 16 mmol of N-hydroxysuccinimide, 0.4 mmol of Co(OAc)₂, 0.4 mmol of Mn(OAc)₂ and 250 ml of selected solvent were mixed in a glass batch flask. An appropriate weight of selected metal/mixed metal oxide catalyst was added, and the stirring speed was set at 600 rpm. When the mixture was refluxed at 85 °C, pure oxygen was continuously bubbled into the solution mixture.

2.3.2. High pressure (high-pressure reactor, autoclave)

The high-pressure reactor is a 450 ml inconel autoclave. The system is also equipped with a condenser, a gas–liquid separator and a liquid recycle tank to ensure complete condensation and recycling of the evaporated compounds. The liquid-phase is continuously stirred at 193 rpm. The reactor temperature is regulated by an electric heating jacket with a thermocouple within ± 0.2 °C, and a regulating valve controlled the reactor pressure.

In a typical experimental run, the reactor was charged with mixtures of 80 mmol of *p*-toluic acid, 16 mmol of N-hydroxysuccinimide, 0.4 mmol of Co(OAc)₂, 0.4 mmol of Mn(OAc)₂ and 250 ml of selected solvent and required weight of manganese dioxide catalyst. Before heating the reactor, pure oxygen was introduced into the autoclave until required pressure is obtained, and agitation was started at the specific temperature for certain time.

In atmospheric and pressurized reaction, sampling in the previously scheduled times, the solid and mother liquor were separated by filtration. The clear liquid containing organic substrate intermediates, and products were analyzed using an HPLC with an Ultraviolet detector with a suitable analytical method to calculate the yield, conversion, and selectivity of all compounds.

3. Results and Discussion

3.1. Characterization of manganese dioxide nanorods catalyst

3.1.1. X-ray diffraction analysis (XRD)

The XRD pattern of MnO₂ showed the characteristic peaks at 12.5°, 18.07°, 28.65°, 37.3°, 41.95°, 49.85°, 59.74° and 65.15°, which matched well the diffraction peaks (1 1 0), (2 0 0), (3 1 0), (2 1 1), (3 0 1), (4 1 1), (6 0 0) and (5 2 1) reflection plane of MnO₂ (JCPDS card PDF # 00-044-0141), and the lattice parameters of caddice-clew-like MnO₂ are a = 9.7875 and c = 2.8600, which are highly identical to the standard values (JCPDS card PDF file no. 44-0141, a = 9.7847, c = 2.863) (**Fig. 3**).

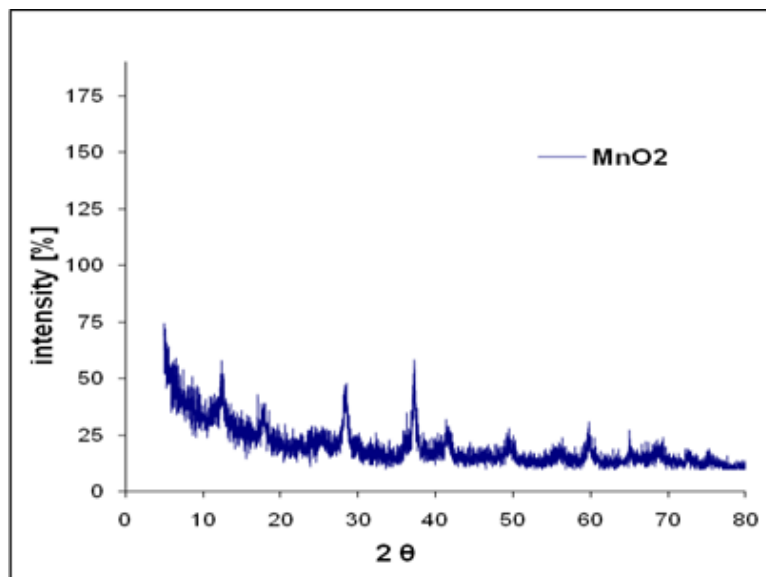


Fig. 3. XRD pattern of prepared MnO₂ nanocatalyst

3.1.2. Surface area analysis (BET) of MnO₂ nanorods catalyst

Fig. 4 shows the corresponding N₂-isotherm, and BJH pore size distributions, which reveals that the MnO₂ exhibits Type IV isotherm with the H1 hysteresis loop, which is a characteristic of open cylindrical pores. BJH analysis on the desorption branch of the isotherm confirms the MnO₂ nanorods possesses well-defined mesopore diameter. It should be noted that the hysteresis loop for MnO₂ is narrower due to the influence of mesopore interconnectivity on N₂ vaporization. The surface area of MnO₂ was calculated to be 300 m²/g using the BET method. The total pore volume was estimated to be 0.35 cm³/g.

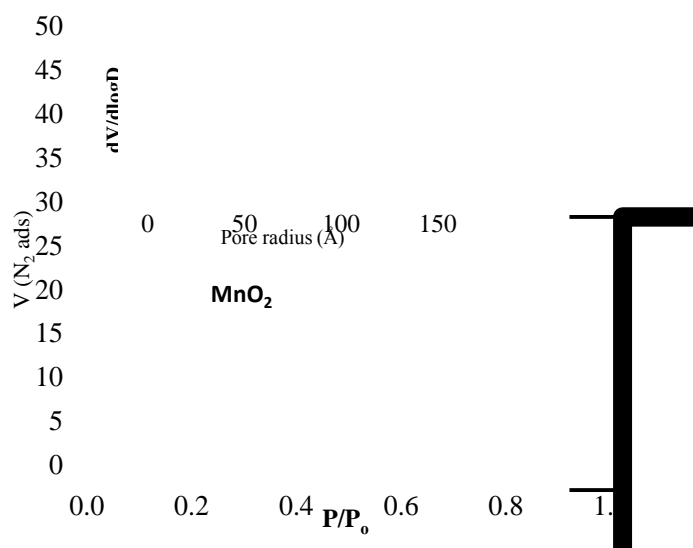


Fig. 4: N₂- adsorption: (a) isotherms and (b) pore size distributions of MnO₂ nanocatalyst

3.1.3. HRTEM of MnO₂ nanorods metal oxide nanocatalyst

High-resolution transmission electron microscopy analysis (HRTEM) is a widely used technique in catalysis research field for collecting information about small metal particle sizes and its morphology. The HRTEM analysis of nano MnO₂ catalyst is shown in **Fig. 5**. It reveals the formation of uniform rod-like morphology, which may be with hollow nature. Moreover, it shows low agglomeration of MnO₂ particles. The average dimensions calculated from the HRTEM micrographs ranged from $\approx 11 \pm 3$ nm widths and $\approx 58 \pm 8$ nm lengths. The high crystallinity of MnO₂ particles may be due to the using of ultrasonication during preparation [Li, C. et al. 2014; Wang, P. et al. 2014]

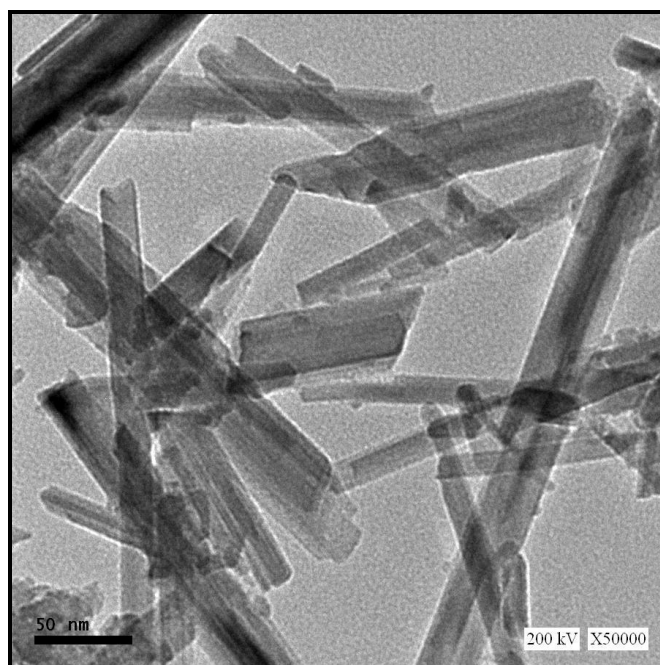


Fig. 5: HRTEM photo of MnO₂ nanocatalyst.

3.2 The catalytic activity of MnO₂ nanorods:

To evaluate the effectiveness of prepared metal oxide (MnO₂) as a heterogeneous catalyst, the liquid phase oxidation reaction of *p*-toluic acid (PTA) was also conducted in the presence of *n*-hydroxysuccinimide as a promoter in acetonitrile. The major products of catalyzed

PTA oxidation are 4-carboxybenzaldehyde (4-CBA) and terephthalic acid (TPA). So, various conditions were used for maximizing yield and conversion of the *p*-toluic acid to terephthalic acid as the following:

3.2.1. Effect of reaction time

To follow up the catalyst performance towards the reaction products by one hour interval time for 12 h at atmospheric pressure with the constant weight of catalyst (0.2 gram) and *n*-hydroxysuccinimide in acetonitrile. **Fig. 6** shows a diagram of *p*-toluic acid conversion, terephthalic acid and 4-carboxybenzaldehyde yield with time.

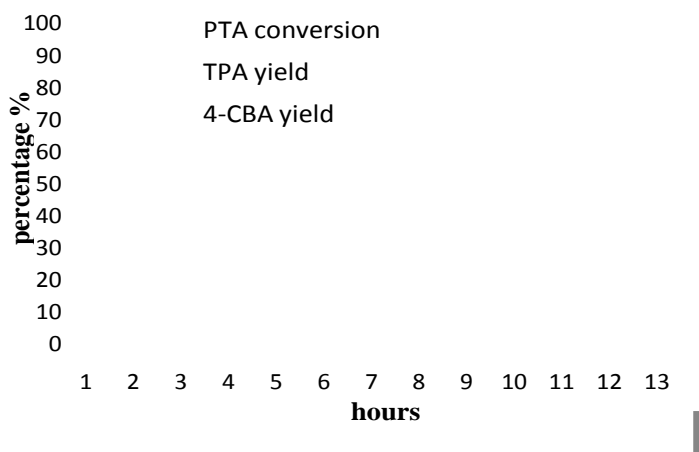


Fig. 6: Catalytic activity of using MnO₂ nanorods catalyst with reaction time

For 12 h, MnO₂ nanocatalyst achieves moderate yield of terephthalic acid to about 40% at atmospheric pressure and reflux conditions. The oxidation reaction was initiated after passing 4 h, which clearly appeared through continued increase in the conversion of *p*-toluic acid. Obviously, it started by forming the intermediate product, 4-CBA, was formed at the 4th hour and continued in a fixed manner from 6th hour within yield value (10%) then followed by formation of terephthalic acid after 5 h of reaction. The fast growing rate of *p*-toluic acid conversion reveals the role of MnO₂ nanorods catalyst throughout oxidation reaction. It is interesting to note that, the intermediate (4-CBA) is proportional to the yield of TPA, in which

the most active catalyst yielded high intermediate and vice-versa. This means that the intermediate may be adsorbed on the catalyst surface, poisoning the catalyst and hence no available active site is present.

Despite the previous work of [Partenheimer, W. 2004; Partenheimer, W. 2003; Tashiro, Y. et al. 2001] obtained 92% terephthalic acid yield by using oxygen gas at atmospheric pressure in the presence of NHPI (10 mol %), $\text{Co}(\text{OAc})_2$ (0.5 mol %), and $\text{Mn}(\text{OAc})_2$ (0.5 mol %) as homogenous catalysts which is double-yield that our work. So, it still using the industrially unfavourable solvent, acetic acid, at higher temperature for longer time, where the author doesn't consider the recyclability and environmental issues for his aim.

3.2.2. Effect of catalyst weight

To estimate the optimum catalyst weight for achieving maximum yield of terephthalic acid, **Fig. 7** displays a comparison between MnO_2 nanorods catalyst weights (0.15, 0.2 and 0.4 gram) for oxidation of *p*-toluic acid at atmospheric pressure by refluxing in acetonitrile for reaction time 12 h.

It illustrates that the conversion of *p*-toluic acid increases with increasing the MnO_2 nanorods catalyst weight but nearly the same with 0.2 and 0.4 gram (52.2% and 52.6%). Also, the yield of terephthalic acid has the same behavior (35.5% and 34.1%) respectively. While 4-CBA exhibited the same percentages with all selected catalyst weights. This may be due to a part of product and intermediate could block some of active sites by adsorption on catalyst surface. Accordingly, it is clearly concluded that no significant effect was appeared when catalyst weights more than 0.2 gram were used.

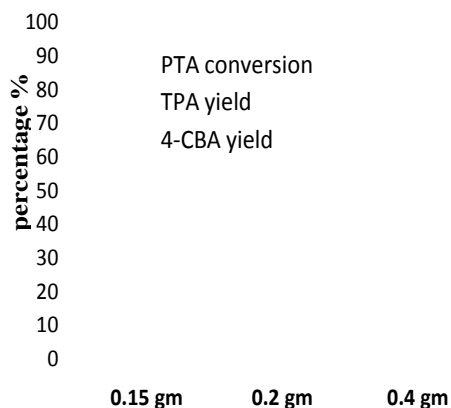


Fig. 7: Effect of catalyst weights of MnO₂ nanorods catalyst on oxidation of p-toluic acid

3.2.3. Effect of solvent

Solvent is one of the most factors affecting on the catalytic oxidation process. The selection of solvent actually based on that the reactants should be soluble sufficiently in the reaction medium in order to not retard the reaction. In industrial process, acetic acid and bromine cause corrossions in equipments when used at high temperatures. Therefore, expensive special corrosion resistant equipment was required. In addition to, acetic acid gives different reaction by-products including methanol, methyl acetate and methyl bromide also, carbon oxides are produced by partial combustion of the solvent and the aromatic compounds [Dunn, J. B. and Savage, P. E. 2002]. The p-toluic acid oxidation using prepared catalysts was carried out using different solvents like acetonitrile (polar), ethyl acetate (nonpolar), and mixture of acetonitrile / acetic acid 9:1 (acidic). The last mixture was used to confirm the definite role of acidic medium in target reaction. The solvent was changed with 0.2 gram of MnO₂ nanorods catalyst (the optimum weight obtained from subsection 3.2.2).

At atmospheric pressure by refluxing for reaction time 12 h while the other conditions were remained the same. As shown in **Fig. 8**, the maximum conversion of p-toluic acid was achieved by using acetonitrile (52.2%) rather than ethyl acetate (25.4%). besides, terephthalic acid and 4-CBA yield with acetonitrile was greater than that of ethyl acetate. In contrast, mixture of acetonitrile / acetic acid 9:1 has the lowest one. This illustrates that acetonitrile is the best of choice for targeted oxidation reaction which may be due to highly polar solvents like

acetonitrile may facilitate formation of active oxygen species and thereby enhance the catalytic activity [Mahdavi, V. and Mardani, M. 2015]. However, the acidic mixture of acetonitrile / acetic acid 9:1 as a reaction solvent didn't introduce satisfied results in the direction of terephthalic acid yield, may be due to the solubility power of this mixture.

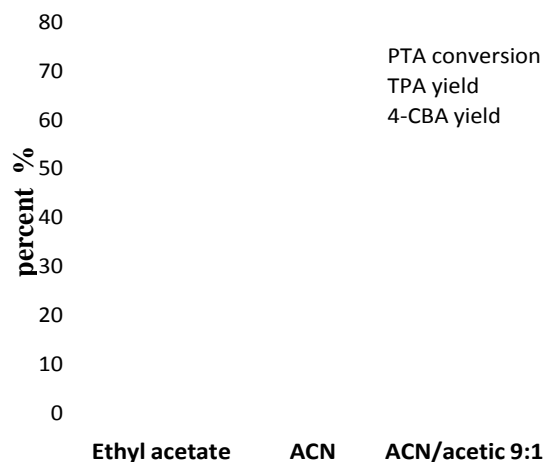


Fig. 8: Effect of solvent on oxidation of p-toluic acid with MnO₂ nanorods in atm. pressure.

3.2.4. Effect of oxygen pressure

The oxidation of p-toluic acid was studied by performing the reaction in high pressure reactor at (10 atm, 15 atm and 20 atm) by using more efficient solvents acetonitrile or ethyl acetate at different temperatures (110 °C and 150 °C). All runs were done for reaction time 12 h in addition to the other conditions were remained constant. The catalytic activity of MnO₂ nanorods were studied by changing the oxygen pressure (10, 15 and 20 atm) of target reaction at 110 °C. **Fig. 9** shows that the p-toluic conversion raised when applying (10, 15 and 20 atm) oxygen pressures to 74.6%, 78.6% and 79.4%, respectively. Furthermore, the yield of terephthalic acid increased gradually with increasing the oxygen pressure to 64.0%, 66.0% and 70.5% with the same manner. Fortunately, 4-CBA yield was very negligible when applying higher oxygen pressures.

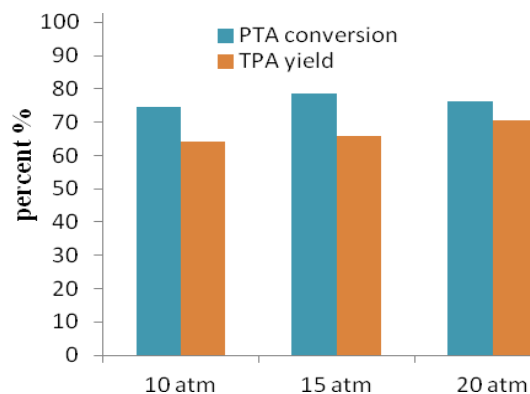


Fig. 9: Effect of pressure on oxidation of p-toluic acid with MnO₂ nanorods in acetonitrile

Fig. 10 explains the role of temperature in oxidation of p-toluic acid when applying fixed pressure (20 atm) in acetonitrile. At temperature (110°C and 150°C), the conversion of p-toluic acid increased by 10.5% at 150°C while terephthalic acid yield with MnO₂ nanorods catalyst raised to 75.8% only for reaction time 12 h.

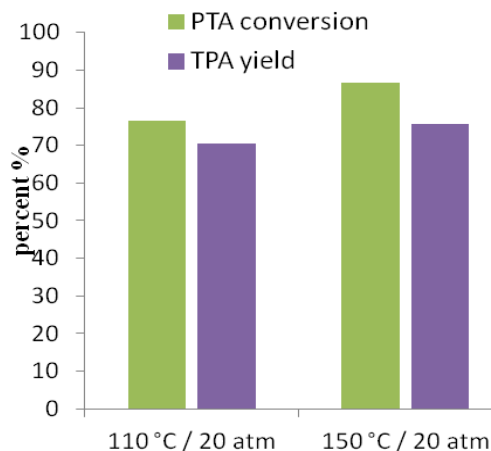


Fig. 10: Effect of temperature on oxidation of p-toluic acid with 20 atm. pressure in acetonitrile

As shown in **Fig. 11**, when ethyl acetate was used as solvent, the p-toluic acid conversion reached 88.6% and 90.1% at 110°C and 150°C respectively, furthermore, the great improvement was obtained in the yield of terephthalic acid that achieved 88.9% at 150°C rather than the conversion of p-toluic acid with low effect by 1.5% only.

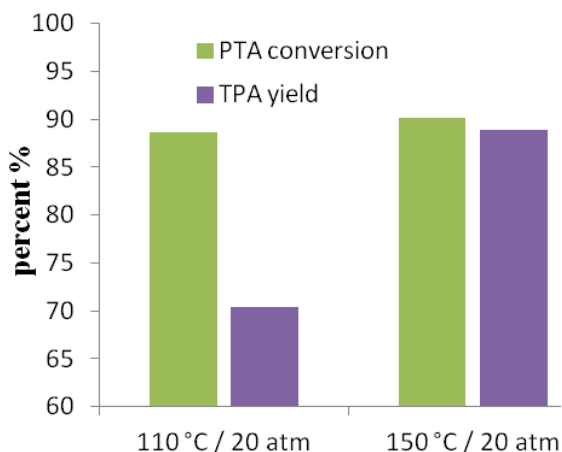


Fig. 11: Effect of temperature on oxidation of p-toluic acid with 20 atm. pressure in ethyl acetate

An essential step of this catalysis appears that the phthalimide N-oxyl (PINO) radical generated in situ from the reaction of O_2 and NHPI can abstract a hydrogen atom from C–H bonds of a target organic substrate. The newly formed carbon radical then rapidly reacts with O_2 to give ultimately oxygenated products (**Fig. 12**) as predicted by Ishii et al. [Partenheimer, W. 2004; Partenheimer, W. 2003; Tashiro, Y. et al. 2001].

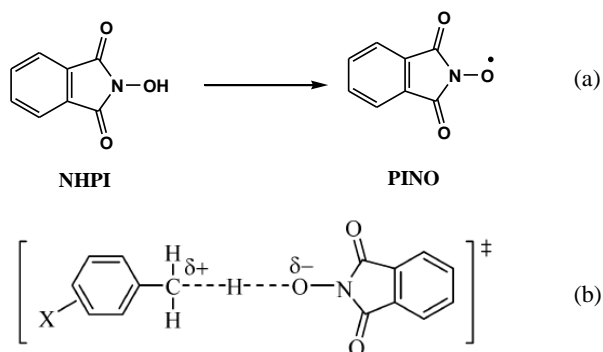


Fig. 12: (a) Formation of phthalimide N-oxyl (PINO) radical from NHPI
(b) PINO-alkyl hydrogen intermediate complex.

4. Conclusion

MnO_2 nanorods metal oxide was synthesized by smart method using ultrasonication for obtaining uniform rod-like morphology. It is used as an economical heterogeneous oxidation catalyst for terephthalic acid production from p-toluic acid by oxygen gas. A recent catalytic

system used environmentally benign N-hydroxysuccinimide as a free radical promoter rather than more hazardous bromine molecules. The crystal structure and morphology of the MnO₂ were confirmed by HRTEM, XRD, and N₂-adsorption-desorption isotherms. The catalytic oxidation of p-toluic acid to terephthalic acid using MnO₂ nanorods was studied under the different conditions to control the yield and selectivity toward terephthalic acid synthesis. The obtained results showed that the high yield (88.9%) and conversion (90.1%) in ethyl acetate with fixed oxygen pressure (20 atm) at 150°C.

5. References

Aoki, Y.; Hirai, N.; Sakaguchi, S., Ishii, Y., "Aerobic oxidation of 1,3,5-triisopropylbenzene using N-hydroxyphthalimide (NHPI) as key catalyst"; *Tetrahedron* 61:10995-10999. (2005).

Aoki, Y.; Sakaguchi, S., Ishii, Y., "Synthesis of aromatic aldehydes by aerobic oxidation of hydroaromatic compounds and diarylalkanes using N-hydroxyphthalimide (NHPI) as a key catalyst"; *Tetrahedron* 62:2497-2500. (2006).

Clennan, E. L., "Overview of the Chemical Reactions of Singlet Oxygen"; *Singlet Oxygen: Applications in Biosciences and Nanosciences Volume 1*:353. (2016).

Dunn, J. B., Savage, P. E., "Terephthalic acid synthesis in high-temperature liquid water"; *Industrial & engineering chemistry research* 41:4460-4465. (2002).

Gomes, J. F., "Gomes, JFP, Bordado, J., Tomás, R., p-Xylene oxidation to terephthalic acid. A literature review oriented toward process optimization and development", *Chemical Reviews*; *Chemical Reviews*. (2013).

Hirai, N.; Tatsukawa, Y.; Kameda, M.; Sakaguchi, S., Ishii, Y., "Aerobic oxidation of trimethylbenzenes catalyzed by N,N',N''-trihydroxyisocyanuric acid (THICA) as a key catalyst"; *Tetrahedron* 62:6695-6699. (2006).

Iles, K. E., Dickinson, D. A. "Carcinogens, Environmental"; *International Encyclopedia of Public Health (Second Edition)*, p 422-437, Academic Press, Oxford, (2017)
<https://doi.org/10.1016/B978-0-12-803678-5.00053-9>.

Ishii, Y., Sakaguchi, S., "Recent progress in aerobic oxidation of hydrocarbons by N-hydroxyimides"; *Catalysis Today* 117:105-113. (2006).

Ishii, Y.; Sakaguchi, S., Obora, Y. "Aerobic Oxidations and Related Reactions Catalyzed by N-Hydroxyphthalimide", p 187-240, *Modern Oxidation Methods* doi:10.1002/9783527632039.ch6. Wiley-VCH, (2005).

Kamae, K.;Obora, Y., Ishii, Y., "Baeyer-villiger oxidation of cycloalkanones with in situ generated hydrogen peroxide from alcohols and molecular oxygen using NHPI as a key catalyst"; Bulletin of the Chemical Society of Japan 82:891-895. (2009).

Kannan, R.;Jegan, A.;Ramasubbu, A.;Karunakaran, K., Vasanthkumar, S., "Synthesis and catalytic studies of layered and oms type nano manganese oxide material"; Dig J Nanomat Biostruct 6:755-760. (2011).

Li, C.;Chan, D., Yu, J. "Ultrasound-Assisted Synthesis of Metal Oxide Nanomaterials", p 89-118, Cavitation doi:doi:10.1201/b15669-510.1201/b15669-5. Pan Stanford Publishing, (2014).

Mahdavi, V., Mardani, M., "Preparation of manganese oxide immobilized on SBA-15 by atomic layer deposition as an efficient and reusable catalyst for selective oxidation of benzyl alcohol in the liquid phase"; Materials Chemistry and Physics 155:136-146. (2015).

Partenheimer, W., "The effect of zirconium in metal/bromide catalysts during the autoxidation of p-xylene: Part I. activation and changes in benzaldehyde intermediate formation"; Journal of Molecular Catalysis A: Chemical 206:105-119. (2003).

Partenheimer, W., "The Unusual Characteristics of the Aerobic Oxidation of 3, 4-Dimethoxytoluene with Metal/Bromide Catalysts"; Advanced Synthesis & Catalysis 346:1495-1500. (2004).

Plant, J. A.;Voulvoulis, N., Ragnarsdottir, K. V. "Pollutants, human health and the environment: a risk based approach". John Wiley & Sons (2012).

Sakaguchi, S.;Hirabayashi, T., Ishii, Y., "First Ritter-type reaction of alkylbenzenes using N-hydroxyphthalimide as a key catalyst"; Chemical Communications:516-517. (2002).

Tashiro, Y.;Iwahama, T.;Sakaguchi, S., Ishii, Y., "A New Strategy for the Preparation of Terephthalic Acid by the Aerobic Oxidation of p-Xylene using N-Hydroxyphthalimide as a Catalyst"; Advanced Synthesis & Catalysis 343:220-225. (2001).

Wang, P.;Zhao, Y.-J.;Wen, L.-X.;Chen, J.-F., Lei, Z.-G., "Ultrasound–microwave-assisted synthesis of MnO₂ supercapacitor electrode materials"; Industrial & Engineering Chemistry Research 53:20116-20123. (2014).

الملخص العربي

تعتبر عملية الأكسدة الحفزية للبارازيلين باستخدام الاكسجين واحدة من أهم العمليات الصناعية التي تتم لإنتاج حمض التيرفيثالك. يوجد طريقة حفزية حديثة تعتمد على منشط حفزي ذو شق حر صديق للبيئة هو ن-هيدروكسي أميد بديلا عن مركبات البروم الخطرة. تم تحضير أعواد اكسيد المنجنيز النانوية كحفاز غير متجانس سهل التحضير و اقتصادي بأستخدام تقنية الموجات فوق الصوتية. تم تأكيد التركيب البلوري و الشكل الخارجي لأكسيد المنجنيز النانوية بأستخدام الميكروسكوب الالكتروني الانتقالي و حيود أشعة X و حساب فرق امتزاز و طرد النيتروجين لقياسات السطح. اثبتت أعواد اكسيد المنجنيز النانوية المحضرة مساحة سطح عالية حوالي 300 م²/جرام. و بذلك تم دراسة الأكسدة الحفزية لحمض الباراتولويك لأنتاج حمض التريفثاليك بأستخدام أعواد اكسيد المنجنيز النانوية تحت ظروف مختلفة (زمن التفاعل، جرعات الحفاز، المذيب المستخدم في التفاعل والضغط ودرجات الحرارة المتنوعة) للتحكم في الإنتاجية والانتقائية نحو تخليق حمض التريفثاليك. وأظهرت النتائج التي تم الحصول عليها أن الإنتاجية العالية (88.9%) والتحويل (90.1%) في مذيب أسيتات الإيثيل مع ضغط الأكسجين ثابت (20 ضغط جوي) عند 150 درجة مئوية.

**Catalytic Aerobic Oxidation System via Terephthalic Acid Production
Using Economic and Readily Available Nanocatalyst**

طريقة الاكسدة الحفزية لإنتاج حمض التريفثاليك باستخدام حفاز نانوي أقتصادي و سهل الاتاحة

أحمد سامي عفيفي شعبان

باحث مساعد بقسم البتروكيماويات بمعهد بحوث البترول

جهة التسجيل: كلية البنات للأداب والعلوم والتربية – جامعة عين شمس
قسم الكيمياء

السادة المشتركين في البحث:

- | | |
|----------------------------|--|
| أ.د. نادية غريب قنديل | أستاذ الكيمياء العضوية بقسم الكيمياء بكلية البنات – جامعة عين شمس |
| أ.د. عبد الفتاح محسن بدوى | أستاذ الكيمياء العضوية التطبيقية – معهد بحوث البترول |
| أ.م.د. ثناء محمود سليمان | أستاذ مساعد الكيمياء العضوية – معهد بحوث البترول |
| أ.م.د. محمد احمد حسن بطيحة | أستاذ مساعد كيمياء عضوية تطبيقية – قسم التكرير – معهد بحوث البترول |
| ب.م. أحمد سامي عفيفي | باحث مساعد بقسم البتروكيماويات بمعهد بحوث البترول |

الأسماء المقترحة للسادة المحكمين:

- | | |
|--------------------------|---|
| أ.د. محمد السكري | أستاذ الكيمياء العضوية التطبيقية – معهد بحوث البترول |
| أ.د. منصوره أحمد اسماعيل | أستاذ الكيمياء العضوية بقسم الكيمياء بكلية البنات – جامعة عين شمس |
| أ.د. سيد عبد القادر أحمد | أستاذ الكيمياء العضوية بقسم الكيمياء - كلية العلوم – جامعة بني سويف |
| أ.د. نبيل عبد المنعم نجم | أستاذ الكيمياء العضوية التطبيقية – معهد بحوث البترول |

أستاذ الكيمياء العضوية – كلية العلوم – جامعة عين شمس

أ.د. جلال حسني سيد