Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

http://chemeng.hust.edu.vn/jca/

# Nickel nanoparticles supported on titanium oxides nanotubes as an efficient catalyst for hydrodechlorination of 3-chlorophenol

Thanh Thien Co[1,2*], Thanh Hai Do[1], Thanh My Nguyen[1], Dinh Tuan Anh Lu[1], Thi Duyen Diep[1], Duong Viet Tan Vo[1], Thi Yen Nhi Nguyen[1], Thuan Khiet Trinh Nguyen[1], Ngoc Thao Nguyen Du[1], Thien An Nguyen[1], Pham Anh Vu Ho[1,2], Thi Diem Huong Nguyen[1,2], Hue Ngan Dai[1,2], and Tan Phat Vu[1,2]

[1] *University of Science, Ho Chi Minh City, VIETNAM*
[2] *Vietnam National University, Ho Chi Minh City, VIETNAM*
**Email: ctthien@hcmus.edu.vn*

ARTICLE INFO

Received: 30/9/2021
Accepted: 12/12/2021
Published: 15/12/2021

*Keywords:*
Hydrodechlorination, nanocatalyst, nickel nanoparticles, titanium oxides nanotubes

ABSTRACT

Titanium oxides nanotubes (TNTs) were prepared by hydrothermal method and used as nano-support for nickel nanoparticles. Indeed, nickel nanoparticles supported TNTs (Ni-TNTs) were in situ synthesized from nickel salt and TNTs by chemical reduction method using sodium borohydride ($NaBH_4$) as reducing agent. The physio-chemical properties of Ni-TNTs nano-catalysts were fully characterized such as Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM), and X-ray diffraction (XRD). The results showed that nickel salt was completely reduced to $Ni^0$ metal with an average particle size of 12 nm. On the other hand, the catalytic activity is tested by the hydrodechlorination of chlorinated organic compounds. The hydrode-chlorinated conversion of 3-chlorophenol was obtained over 97%.

## Introduction

Recently, the environmental pollution caused by the organic contaminants has received especial attention from many scientists [1–3]. Especially, organic compounds derived from chlorinated starting meterials caused toxicity for environment and human health [4]. It is really necessary to develop the new technologies for the degradation of organic contaminants in the environment. Thus, numbers of researchers all over the world suggested to find the solution for this problem such as the oxidative degradation, biological decomposition, and hydrodechlorination, etc… Among these, hydrodechlorination method promises high efficiency and safety in industrial application [5–7].

One of the useful methods to hydrodechlorinate chlorine derivatives is using nanomaterials because of the low cost and easy to control the process. In fact, number of metal nanoparticles have been used such as platinum, palladium, nickel nanoparticles, etc…[8–11] . Among them, nickel is one of the bright candidates because of low cost compared to other metals [12]. On the other hand, immobilization of the metallic nanoparticles on solid materials has received a great interest because of their use in industrial application. Although nanocatalysts serve as an excellent heterogeneous catalyst, they usually need an additional support to obtain thermal stability as well as improve the catalytic activity [13] . Thus, varieties of materials such as zeolites, aluminum oxides, aluminosilicates, activated carbon, zinc oxides, etc. have been used as

https://doi.org/10.51316/jca.2021.078

supports for nanocatalysts [14–16]. However, TNTs and carbon nanotubes have not been widely used as supports for hydrodechlorination. For example, H. Liang and coworkers have used montmorillonite supported-nano titanium oxides as photocatalysts for the methylene blue (MB) degradation in which over 80% of MB was decomposed within 180 min at RT [17]. Likewise, C. Wang *et al*. carried out the degradation of methyl orange over carbon-formed loaded nano titanium oxides as efficient photocatalysts which exhibited the most desired efficiency reaching up to 83–87% conversion within 240 min [18]. Therefore, the exploitation of the TNTs uses in order to eliminate the chlorinated organic contaminants is one of the most important roles which is attracting of many scientists.

Herein, we focused on the preparation of Ni-TNTs and their catalytic activity to the hydrodechlorination of 3-chlorophenol in the presence of potassium hydroxide. All the results will be presented in this report.

## Experimental

All the chemicals were used as received without further purification. Reagent grade nickel chloride hexahydrate 98% ($NiCl_2.6H_2O$), sodium borohydride 98% ($NaBH_4$), ethylene glycol 99.5% (EG), 3-chlorophenol 98%, and titanium oxides 99% ($TiO_2$) were purchased from Acros (USA). Polyvinyl pyrrolidone K-30 (PVP) were purchased from Xilong (China). 2-Propanol (IPA) and ethanol were supplied by Chemsol (Vietnam).

Titanium oxides nanotubes were synthesized by the hydrothermal method [19,20] , in which 5.0 g of $TiO_2$ and NaOH 10 M were stirred at RT for 3h before adding to autoclave at 45 °C for 22h. After being cooled to RT, the mixture was decanted, washed several times and diluted with HCl 0.01 M for 2h. then it was washed again by distilled water (until pH 7) and dried at 100 °C for 3h. The powder of TNTs was obtained after being calcinated at 500 °C for another 3h.

Nickel nanoparticles supported on TNTs were prepared by in situ reduction of nickel salt in the mixture of TNTs and reducing agent ($NaBH_4$). To the 250 cc two-necked round bottom flask, PVP (0.4 g), TNTs (0.71 g) and 40 mL of ethanol were added. After stirring for 30 min at 80 °C, 0.81 g of $NiCl_2.6H_2O$ (3.4 mmol) were dissolved in the mixture. In another flask, ethylene glycol (5 mL, 88.6 mmol) and $NaBH_4$ (0.66 g, 1.7 mmol) in 50 mL of ethanol were prepared. Then, the solution of reducing agent was dropwise added to the mixture of nickel salt. The mixture was stirred for another 6h until the black solution was observed. The obtained catalysts were centrifuged and washed several times by distilled water before being dried at 60 °C under vacuum in 8h.

The morphologies of nickel catalysts were examined by scanning electron microscope (SEM, JEOL series JSM-7401F). Transmission electron microscopy (TEM) was done on a FEI Tecnai G2 F20 at 120 kV fitted with a Gatan Ultra Scan 4000 CCD camera. The powder X-ray diffraction (XRD) were recorded on a Bruker D8 powder X-Ray (Cu Kα). GC/MS were obtained by using an Agilent 7890A series model with an electron energy of 20 or 70 eV. All the catalytic experiments were performed on Multireactors Carousel 12 plus.

The catalytic activities of Ni-TNTs were investigated via the hydrodechlorination of 3-chlorophenol in the presence of potassium hydroxide. However, in order to eliminate the effect of adsorption of the substrate on the supports, a dozen experimental adsorption was carried out with a various concentration of the substrate. The adsorption/desorption equilibrium between the substrate solution and the catalysts was established within 60 min. After that the catalytic evaluation of Ni-TNTs was carried out in 20 mL multireactor with stirring at room temperature. In this process, 0.1 mmol of catalysts was used in the hydrodechlorination of 3-chlorophenol (5.0 mmol), IPA (5.0 mL) and 5.0 mL of 2% potassium hydroxide solution in ethanol. Hydrogen was directly connected through Schlenk lines to the reaction at atmosphere pressure. The influence of reaction temperature on process at 30, 50, and 70 °C were performed. The conversion of substrate and the selectivity of products were analyzed by GC and GC-MS (HP5 column 30 m x 0.25 mm, FID) after eliminating the effective adsorption. Reproducibility was checked by repeating the measurement several times and was found to be within acceptable limits.

## Results and discussion

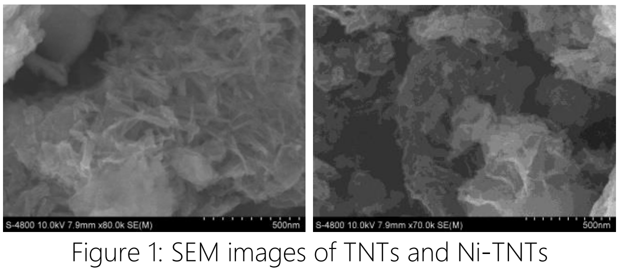
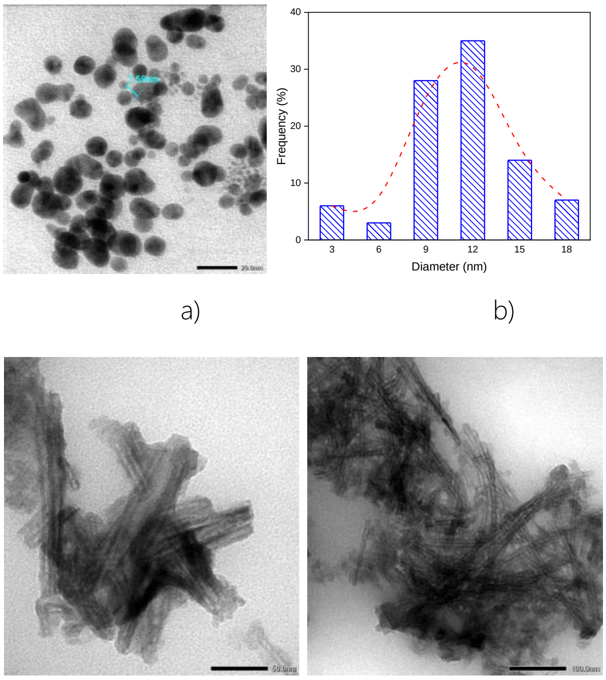


Figure 1: SEM images of TNTs and Ni-TNTs

https://doi.org/10.51316/jca.2021.078

Nickel nanoparticles were prepared as the same procedure as previous report [21]. However, the method was modified in order to enhance the particles size as well as the content of nickel on the TNTs support.

In fact, nickel salt was in situ reduced in the mixture of TNTs and sodium borohydride. In which, nickel nanoparticles size were easily controlled and anchored into the TNTs [22]. Therefore, it is expected that the dispersion of nickel nanoparticles inside TNTs could be enhanced by slowly addition of reducing agent mixture. Besides, TNTs were simply fabricated by the hydrothermal method after being calcinated at 500 °C for 3h. The TNTs characteristics such as high mobility and large surface area were observed and thus utilized in various applications [23].



a) b)

c) d)

Figure 2: TEM images of a) and b) Ni NPs and its average diameter; c) and d) Ni-TNTs taken at 50 nm and 100 nm

Thus, as shown in Figure 1, the surface morphology of TNTs is quite different from the $TiO_2$ powder. It is expected that nanotubes with higher porosity, consequently, with thinner walls and larger pores can permit a more metal concentration, indeed, according to atomic absorption spectroscopy (AAS) analysis, the amount of Ni nanoparticles in the sample of up to 13.50 wt% which could enhance the catalytic activity.

In addition, TEM images as shown in Figurs 2, further confirmed the successful deposition of the nickel into the nanotubes, the average size of nickel nanoparticles is around 9-12 nm (Fig 2b). It is smaller than the nickel prepared by the separated method [21].

Moreover, as illustrated in Fig 3, the XRD patterns clearly reveals that the crystallographic structure of the parent TNTs is in tetragonal anatase phase with a trace of combination phase, in reality, the corresponding diffraction peaks of TNTs located at the position of $2\theta$ = 25.03°; 37.59°; 48.05°; 54.06°, and 55.01°. Likewise, with high depositing of 13.28 wt% $Ni^0$ on TNTs resulted in significant nickel signals in the XRD patterns, in which the characteristic peaks of $Ni^0$ appeared at $2\theta$ of 44.55° and 51.78° [24]. This observation further confirmed that the in situ preparation method resulted in a well distribution of nickel particles in the meso-porous TNTs, as observed from TEM images.

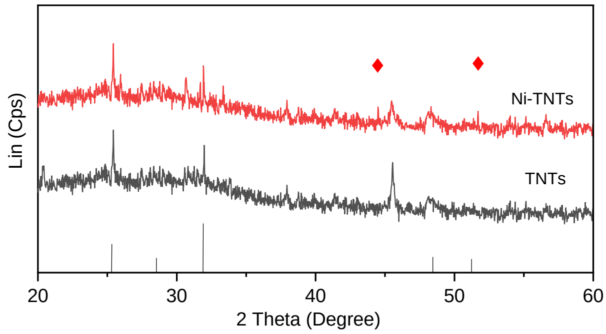


Figure 3: XRD patterns of TNTs and Ni-TNTs

On the other hand, before evaluating the catalytic activity of hydrodechlorination, the catalysts were saturated with the same 3-chlorophenol solution to eliminate the influence of catalysts adsorption and to reach adsorption/desorption equilibrium between the substrate solution and the catalysts. Thus, the adsorption test was carried out as the same condition reaction without the presence of hydrogen. All the results were summarized in Figure 4.

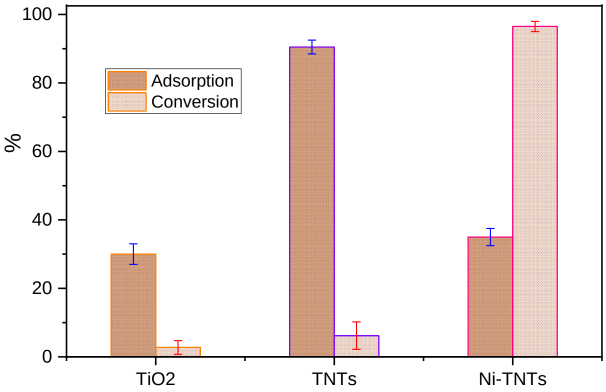


Figure 4: Adsorption and activity of catalysts

As we can see in Figure 4, the catalytic hydrodechlorination exhibited an excellent conversion of substrate in the presence of potassium hydroxide. In the case of $TiO_2$ and TNTs, only the adsorption was observed at 31% with $TiO_2$, in particular TNTs reached 90.5% adsorption. It could be explained that the large volume pores of TNTs could adsorpted significant amount of substrates. Whereas, as mentioned in the experimental section, Ni-TNTs was obtained by the in situ reduction method, in this case, nickel has significantly attached to TNTs pores leading to the decreasement of surface area and pores volume. It resulted in Ni-TNTs adsorption was very low (35% adsorption) compared to parent support's case.

In order to evaluate the hydrodechlorination activity of the Ni-TNTs catalysts. According to previous procedure [21], hydrodechlorination was performed in IPA with 2%mol of catalyst in the presence of potassium hydroxide within 90 min at RT. Unexpectedly, the conversion of 3-chlorophenol substrate was obtained of 96.5% over Ni-TNTs catalyst whereas the parent support and $TiO_2$ reaches adsorption/desorption equilibrium between the substrate solution and the catalysts without any catalytic activity (Fig 5). It could be explained in terms of the strong catalytic activity of nickel nanopartilces over hydrodechlorination of organic compounds [5]. Thus, TNTs only acted as adsorption-factor without showing any catalytic activity to the hydrodechlorination of 3-chlorophenol.

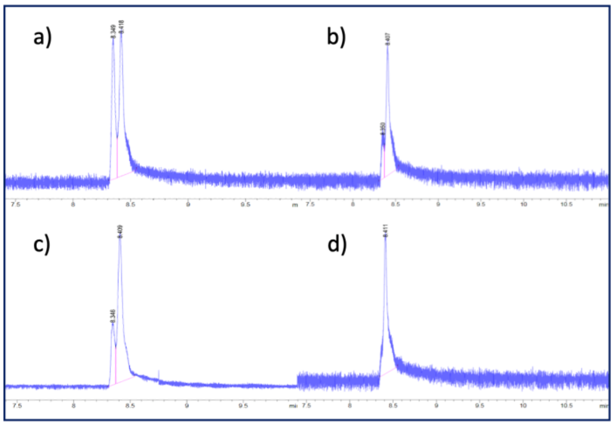


Figure 5: GC spectras of: a) 3-chlorophenol and STD50; and the mixture of hydrodechlorination with b) TNTs; c) $TiO_2$ powder; and d) Ni/TNTs catalyst including the adsorption

Besides, as described in Figure 6, the influence of temperature and catalyst concentration were performed, in which the higher temperature leads to the lower activity of the Ni-TNTs catalyst. Indeed, 96.5, 92.4, and 78.0% conversions of the substrate were observed at 30, 50, and 70 °C, respectively (Fig 6a). That could be explained that when the temperature increases leading to the desorption of the substrate, therefore, the catalytic activity was lower. Likewise, the influence of molar concentration of catalyst was carried out at 1.0, 2.0, 3.0, and 4.0% mol in the same reaction condition, 67.5, 96.5, 97.5, and 96.0% conversions of 3-chlorophenol were obtained, respectively. It means that the increase of the molar concentration could not significantly increase the catalytic acitivity. In sum, Ni-TNTs catalysts exhibited the excellent activity toward the hydrodechlorination of chlorinated substrate, meanwhile, TNTs only acted as adsorbents without showing any catalytic activity to hydrodechlorination of 3-chlorophenol. It is one of the most promising nanocatalysts which could be widely used in the field of environmental protection and water pollution treatment.

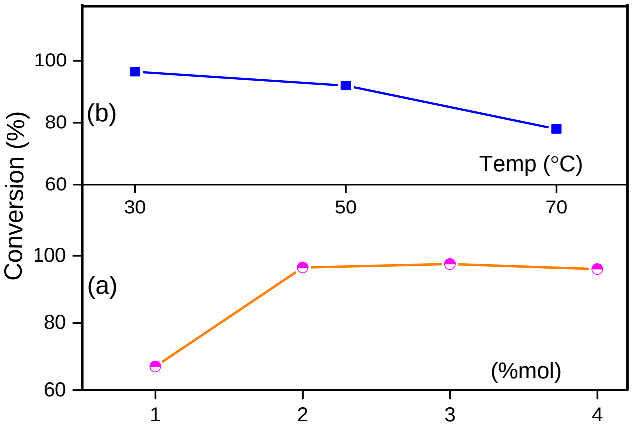


Figure 6: Catalytic activity of Ni-TNTs over hydrodechlorination of 3-chlorophenol; a) Influence of catalyst concentration; b) Temperature.

## Conclusion

In summary, the Ni-TNTs nano-catalysts were successfully synthesized and the physio-chemical characterization of this catalyst was presented in detail. In which, TEM images and XRD patterns illustrated that the average nickel-particles size was 12 nm with incorporated as $Ni^0$ inside TNTs. Furthermore, the catalytic test indicated that Ni-TNTs catalysts exhibited high catalytic activities in the hydrodechlorination of 3-chlorophenol of up to 97% conversion within 90 min.

## Acknowledgments

This research is funded by University of Science, VNU-HCM under grant number HH 2021-01. The authors would also like to thank APC Lab (University of Science, VNU-HCM) for technical supports.

## References

1. L. Gui, R. W. Gillham. ACS Div. Environ. Chem. Prepr. 41 (1), (2001) 1132–1137. http://doi.org/10.1021/bk-2002-0837.ch014

2. G. Chehade, N. Alrawahi, B. Yuzer, I. Dincer. Sci. Total Environ. 712 (2020) 136358. https://doi.org/10.1016/ j.scitotenv.2019.136358

3. T. Doan, A. Dang, D. Nguyen, T. H. Vuong, M. T. Le, H. P. Thanh. J. Chem. 5552187 (2021) 1-15. https://doi.org /10.1155/2021/5552187

4. R. A. Khaydarov, R. R. Khaydarov, O. Gapurova. J. Colloid Interface Sci. 406 (2013) 105–110. http://dx.doi. org/10.1016/j.jcis.2013.05.067

5. X. Ma, Y. Liu, X. Li, J. Xu, G. Gu, C. Xia. Appl. Catal. B Environ. 165 (2015) 351–359. http://dx.doi.org/10.1016/ j.apcatb.2014.10.035

6. S. Du, X. Wang, J. Shao, H. Yang, G. Xu, H. Chen. https://doi.org/10.1016/j.cej.2020.124185

12. K. Nakajima, K. Nansai, K. Matsubae, M. Tomita, W. Takayanagi, T. Nagasaka. Sci. Total Environ. 586 (2017) 730–737. http://dx.doi.org/10.1016/j.scitotenv.2017.02. 049

13. T. T. Co, N. M. Nguyen, L. D. K. Vo. Vietnam J. Chem. 59 (2), (2021) 192–197. http://doi.org/10.1002/vjch.202000 142

14. I. Khan, K. Saeed, I. Khan. Arabian Journal of Chemistry. 12 (2019) 908–931. http://doi.org/10.1016/j.arabjc. 2017.05.011

15. N. Neelakandeswari, G. Sangami, P. Emayavaramban, S. B. Ganesh, R. Karvembu, N. Dharmaraj. J. Mol. Catal. A Chem. 356 (2012) 90–99. http://doi.org/10.1016/ j.molcata.2011.12.029

16. M. Dusselier, M. E. Davis. Chem. Rev. 118 (11), (2018) 5265–5329. https://doi.org/10.1021/acs.chemrev. 7b00738

17. H. Liang, Z. Wang, L. Liao, L. Chen, Z. Li, J. Feng. Optik. 136 (2017) 44–51. http://dx.doi.org/10.1016/j.ijleo.2017. 02.018

18. C. Wang, Z. H. Shi, L. Peng, W. M. He, L. B. Liang, K.

Energy 74 (C), (2014) 295–300. http://dx.doi.org/10.1016/ j.energy.2014.01.012

7. T. T. Co, D. K. Le, V. D. Le, T. N. T. Doan. Sci. Technol Dev. J. 23 (4), (2020) 764–770. http://doi.org/10.32508/ stdj.v23i4.2451

8. K. Wiltschka, L. Neumann, M. Werheid, M. Bunge, R. A. Düring, K. Mackenzie, et al. Appl. Catal. B Environ. 275 (2020) 19100–19109. https://doi.org/10.1016/j.apcatb. 2020.119100

9. L. Xu, E. E. Stangland, A. L. Dumesic, M. Mavrikakis. ACS Catal. 11 (13), (2021) 7890–7895. http://doi.org/10.1021/ acscatal.1c00940

10. Y. Xu, J. Ma, Y. Xu, H. Li, P. Li, et al. Appl. Cata.l A Gen 413-414 (2012) 350–357. http://doi.org/10.1016/j.apcata. 2011.11.026

11. M. Balda, F. D. Kopinke. Chem. Eng. J. 338 (2020) 124185.

Z. Li.. Surfaces and Interfaces. 7 (2017) 116–124. http://doi.org/10.1016/j.surfin.2017.03.007

19. T. N. T. Le, B. T. Tran, T. H. T. Vu. Tạp chí khoa học ĐHSP Thành phố Hồ Chí Minh. 2 (67), (2015) 1–2. http://journal.hcmue.edu.vn/index.php/hcmuejos/article/download/451/443

20. V. S. Nguyen, T. D. T. Duong, T. P. Nguyen, T. S.N. Le. Sci. Tech. Dev. J. 18 (2015) 228–236. http://stdj.scienceandtechnology.com.vn/index.php/stdj/article/download/1188/1556/

21. T. T. Co, T. K. A. Tran, T. H. L. Doan, T. D. Diep. J. Chem. 8580754 (2021) 1–9. http://doi.org/10.1155/2021/8580754

22. L. G. Vernasqui, A. F. Sardinha, S. S. Oishi, N. G. Ferreira. J. Mater. Res. Technol. 12 (2021) 597–612. https://doi. org/10.1016/j.jmrt.2021.02.099

23. M. Tak, H. Tomar, R. G. Mote. Procedia CIRP. 95 (2020) 803–8. https://doi.org/10.1016/j.procir.2020.01.140

24. D. Li, S. Komarneni. J. Am. Ceram. Soc. 89 (5), (2006) 1510–1517. http://doi.org/10.1111/j.1551-2916.2006.00925.x