



Efficient microwave enhanced degradation of 4-nitrophenol in water over coupled nickel oxide and solid acid catalysts



Chih-Wei Tang^a, Te-Cheng Liu^b, Ruei-Ci Wu^b, Youn-Yuen Shu^{c,*}, Chen-Bin Wang^{b,*}

^a Department of General Education, Army Academy ROC, Chungli, Taoyuan 32092, Taiwan, ROC

^b Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan 33509, Taiwan, ROC

^c Environmental Analysis Laboratory, Department of Chemistry, National Kaohsiung Normal University, Kaohsiung 802, Taiwan, ROC

ARTICLE INFO

Keywords:

Solid acid
Nickel oxide
Degradation
4-Nitrophenol

ABSTRACT

An efficient and controllable abatement of 4-nitrophenol based on series of catalysts and auxiliary reagents, the as-prepared nickel oxide and solid acid tabloid, was reported as resulting by microwave degradation. In regard to the effects of microwave power, various kinds of nickel oxide and solid acid, at auxiliary reagent dosage, and in various concentrations were evaluated in relation to their removal efficiency. The results showed that the addition of solid acid can delicately tune the reaction pH and enhance the degradation of 4-nitrophenol over nickel oxide. The performance was apparently affected according to the kinds of solid acid and the as-prepared nickel oxide. The reducibility and amount of high valence of Ni³⁺ over the as-prepared NiO_x can influence the resultant reaction. The lower reduction temperature and higher N_{H2}/N_{Ni} ratio can weaken the bond strength of NiO_x and readily releases partial oxygen to assist with the degradation of 4-NP within a microwave system. Both 300 and 500 ppm 4-nitrophenol can be completely degraded within 25 min under low power of 7 W over 0.12 g of as-prepared nickel oxide coupled with 0.24 g zirconium sulfate tabloid to adjust the reaction pH below 3 via the combined effect of nickel oxide and solid acid.

1. Introduction

Phenolic compounds have been broadly used as widespread raw materials or intermediates in the manufacture of agrochemicals, dyes, drugs, organic chemicals (Oturán and Peiroten, 2000; Harrison and Barra, 2005; Lai and Zhang, 2014a), etc. They are among the hardest contaminants to dispose due to their high toxicity, stability, accumulation, low biodegradability, and potential risk to human health. They can severely damage the liver, kidneys, blood, and central nervous system of humans even at low concentration (Keith and Telliard, 1979; Bukowska and Michalowicz, 2007; Fan and Lu, 2010; Lai and Zhang, 2014b). Therefore, diminishing these pollutants and environmental problems from industrial wastewater before they are discharged into the environment is a priority. Currently, many treatment technologies based on physical and chemical processes for removing phenolic compounds exhibit great potential in the remediation of discharged water, such as capture with adsorbents (Dąbrowski et al., 2005; Kumar et al., 2007), separation with membrane (Conidi et al., 2017; Zagklis et al., 2015), biological degradation (Martínková et al., 2016; Sahoo et al., 2011), photo-Fenton and photo-catalytic degradation (Campo et al., 2014; Zhao et al., 2007), an advanced oxidation process (Ayed et al.,

2017), and catalytic oxidation (Ayrál et al., 2010; Hernández et al., 2012). Although these methods have attracted the attention of many researchers, they still have some drawbacks, such as longer operating time, high price and low efficiency in degrading highly concentrated wastewater. From economic and environmental points of view, an effective and energy-saving method needs to be developed.

Microwave (MW) is a kind of universal electromagnetic wave with frequency ranging from 300 MHz to 300 GHz. Using MW as a tool to remediate contaminated water and soil has been confirmed as a time saving, cost-effective, and environmental friendly method (Huang et al., 2011; Robinson et al., 2012; Mei et al., 2004; Ai et al., 2005). However, microwave energy is often incapable of cleaving the chemical bonds of phenol and its derivatives. Appropriate MW imbibed by the catalysts over coupled MW with catalysts, i.e. carbon materials, metals and metal oxides can enhance promising catalytic performance and efficiency (Zhou et al., 2012; Qiu et al., 2016; Yin et al., 2016). The 4-nitrophenol (4-NP) and other derivatives can usually be detected in contaminated soil and water; they will cause serious environmental problems. Many studies focus on the metal oxides, i.e. Mn, Cu, Fe and Ni in exploring the effects on the degradation of 4-NP in wastewater (Yin et al., 2016; Zhou et al., 2016; Bo et al., 2008; Liu et al., 2010) to minimize the deleterious

* Corresponding authors.

E-mail addresses: shuyy@nknuc.nknu.edu.tw (Y.-Y. Shu), chenbinwang@gmail.com (C.-B. Wang).

effects. In our previous studies, we have achieved the abatement of 200 ppm phenol, 4-chlorophenol (4-CP) and 4-NP with a microwave-enhanced catalytic degradation (MECD) process within 30 min (Lai et al., 2006, 2008a, 2008b, 2011). The performance of degradation is assessed quantitatively by high pressure liquid chromatography (HPLC). These results indicate that various factors can affect the activity, such as the pH, temperature and the kinds of catalyst employed. The performance increases with the decreasing of pH; the degradation of 4-NP becomes ineffective as the pH approaches neutral and basic solutions (Lai et al., 2011). However, the pretreatment of strong acids, such as H_2SO_4 and HCl , must be cautioned due to safety concerns in handling, damaging the body and plants by way of its corrosion and procedural difficulty through the use of quenching and separation stages, which create large amounts of toxic and corrosive wastes discharged into rivers.

Compared with liquid mineral acids, solid acids (SAs) possess obvious advantages in environmental friendliness, easy separation, shelf-life and recycling (Gupta and Paul, 2014). Zirconia is an appropriate material whose surface can be derived with sulfated functional group to get “sulfated zirconia” which is a fascinating and beneficial solid acid (Tanabe and Yamaguchi, 1994; Yadav and Nair, 1999). Unlike the above-mentioned study (Lai et al., 2011) the main objective of this study is to design a portable SA tabloid from metal sulfates to be employed as an auxiliary reagent for adjusting the reaction pH, combined with the microwave-irradiated method to assist in the degradation of 4-NP over a nickel oxide catalyst.

2. Experimental

2.1. Preparation of nickel oxide

Both high valence nickel oxides (NiO_x) were prepared via two methods (precipitation-oxidation and ultrasonic-assisted precipitation-oxidation) in an aqueous solution described previously (Lai et al., 2006, 2011; Yu et al., 2014). All reagents and chemicals in this study are analytically pure and used without further purification. The process was carried out at 70 °C with 100 mL of 3.2 M NaOH solution drop-by-drop added to the 50 mL of 0.6 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to obtain $\text{Ni}(\text{OH})_2$. Then, 100 mL of 12 wt% NaOCl was added in a dropwise manner with stirring maintained. The final obtained sediment was assigned as PO. The same condition was conducted as PO, but simultaneous irradiation with 480 W ultrasonic-assisted in beaker at RT for 6 h was performed. The final sediment was assigned as POU.

2.2. Preparation of solid acid

Three kinds of metal sulfates were chosen as the precursors: nickel sulfate (assigned as SNH), iron sulfate (assigned as SFH) and zirconium sulfate (assigned as SZH) which were calcined to obtain the SAs; another SA was directly impregnated by sulfuric acid on zirconium oxide (assigned as SZ), and then calcined. According to the thermogravimetric curves (Fig. S1) of the SNH, SFH, SZH and SZ precursors, each sample was calcined at 350, 550, 400 and 600 °C, respectively (assigned as SNHC350, SFHC550, SZHC400, SZHC600 and SZC600). The SA tabloid was fabricated by adopting 0.24 g calcined solid acid which was pressed with a pressure of 8 t.

2.3. Characterization of nickel oxide and solid acid

X-ray diffraction (XRD) analysis was carried out on a MAC Science MXP18 diffractometer with Cu K_1 radiation ($\lambda = 1.5405 \text{ \AA}$). The specific surface area and porosity were characterized by N_2 adsorption/desorption isotherms with Micromeritics ASAP 2010 at $-196 \text{ }^\circ\text{C}$. Temperature-programmed desorption of ammonia (NH_3 -TPD) was used to determine the total acidity of the catalysts. The reductive property of

nickel oxide was studied by temperature-programmed reduction (TPR). The sample ($\sim 50 \text{ mg}$) underwent temperature-controlled heating in a flow of 10% H_2/N_2 gas under a flow rate of 10 mL min^{-1} and $7 \text{ }^\circ\text{C min}^{-1}$ heating rate from ambient temperature to 600 °C. Thermogravimetric analysis (Perkinmer Pyris 6 TGA) was performed on 3–5 mg of samples in flowing nitrogen with a 70 mL min^{-1} flow rate. The experiment was conducted from 30° to 800 °C at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$.

2.4. Degradation of 4-nitrophenol

Evaluation of the efficiency on the degradation of 4-NP proceeded in a thermostatic microwave apparatus (CEM. Discover, USA) in which the microwave power, reaction time, and temperature can be controlled (Lai et al., 2011). 60 mL of aqueous 4-NP solution was placed in a flask of a refluxing device for each experimental run and the temperature was controlled under 70 °C by using low power (7 W) microwave irradiating. The microwave was irradiated successively until reaching the set temperature; therefore, the microwave effect enhanced the catalytic degradation that resulted. Upon arriving at the regulated temperature, only the thermal effect in the device resulted. A fit amount of catalyst and SA tabloid were suspended in solution and continuously bubbled air during the run. Catalyst dosage, loading of SA tabloid, power of microwave, reaction time, and concentration of 4-NP were in the ranges of 0.12 g, 0.12–0.36 g, 3–100 W, 0–25 min and 200–1000 ppm, respectively. The reaction system rose to 70 °C in about 20 min under 7 W microwave irradiating and then remained without any change. The concentration of 4-NP in each stage was evaluated by high-performance liquid chromatograph (HPLC) (Agilent 1100 series) equipped with an UV detector at 326 nm wavelength. Identification of intermediate was performed using gas chromatography (DB-5 column was used) coupled to a mass spectrometer (GC-MS, Shimadzu Corporation, Japan, Shimadzu-QP2010 Plus). In the analysis of GC-MS, the collected species after 15 min exposure were extracted thrice to 10 mL of CH_2Cl_2 and dried with anhydrous MgSO_4 for complete removal of water.

3. Results and discussion

3.1. Characterization of nickel oxides

The XRD patterns of prepared PO and POU are shown in Fig. 1. Two wide diffraction peaks around at 18.4° and 37.3° , illustrate that the species can be indexed to the (001) and (100) plane of nickel oxyhydroxide (JCPDS 06-0141) (Lai et al., 2011). All diffraction patterns for both PO and POU are broad, indicating the better dispersion and less crystallinity of the prepared catalysts. Based on the full-width half-maximum (FWHM) line width of the prominent (001) peak, an average

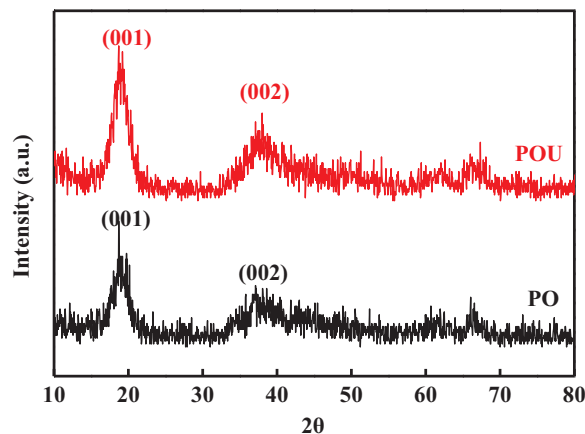


Fig. 1. XRD patterns of the prepared high valence state nickel oxides: PO and POU.

Download English Version:

<https://daneshyari.com/en/article/8862580>

Download Persian Version:

<https://daneshyari.com/article/8862580>

[Daneshyari.com](https://daneshyari.com)