



High efficiency degradation of 4-nitrophenol by microwave-enhanced catalytic method

Teh-Long Lai^a, Kim-Fui Yong^a, Jen-Wei Yu^a, Jung-Hui Chen^a, Youn-Yuen Shu^{a,*}, Chen-Bin Wang^{b,*}

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

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

ARTICLE INFO

Article history:

Received 28 January 2010

Received in revised form

11 September 2010

Accepted 13 September 2010

Available online 17 September 2010

Keywords:

Nickel oxide

Microwave-enhance catalytic degradation (MECD)

4-Nitrophenol

ABSTRACT

Application of the microwave-enhanced catalytic degradation (MECD) method on the abatement of 4-nitrophenol (4-NP) using nickel oxide was studied. A mix-valenced nickel oxide was prepared from nickel nitrate aqueous solution through a precipitation with sodium hydroxide and an oxidation by sodium hypochlorite with/without microwave-assisted heating. They were characterized by X-ray (XRD), infrared spectroscopy (IR), temperature programmed reduction (TPR), and transmission electron micrographs (TEM). Their catalytic activities towards the degradation of 4-NP were investigated through continuous bubbling of air during the liquid phase and evaluated quantitatively with high pressure liquid chromatography (HPLC). Also, the effect of the kinds of catalyst, temperature, pH, initial concentration, and dosage of catalyst on the efficiency of 4-NP degradation was investigated. The results showed that the 4-NP was completely degraded using the high efficiency MECD method within 15 min under $[H^+] = 1.0\text{ M}$, $T = 40\text{ }^\circ\text{C}$, and $C = 200\text{ ppm}$ over nickel oxide.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The degradation of organic pollutants, such as phenolic polycyclic aromatic hydrocarbons (PAHs), azo dye, and nitrobenzenes, has attracted considerable attention due to worldwide concern over their hazardous toxicity. Specifically, wastewaters containing phenolic compounds present a serious environmental problem. Aromatic pollutants, in particular phenol chlorophenol compounds and phenolic derivatives, have been on the EPA's priority pollutants list since 1976 [1]. These compounds are considered hazardous pollutants because of their potential to harm humans. As such, it is necessary to eliminate these pollutants from industrial wastewater before it is discharged. Various technologies are used, i.e., ultrasonic degradation [2–4], photocatalytic degradation [5–7], photo-Fenton degradation [8], photoelectrocatalytic degradation [9], advanced oxidation process with UV/H₂O₂ (AOP) [10,11], catalytic oxidation [12], and microwave enhanced advanced oxidation processes [13–16]. Notably, one of the most promising technologies uses a microwave-enhanced catalytic for the degradation of 4-chlorophenol (4-CP) [17]. Regarding the abatement of 4-nitrophenol in the context of wastewater, there are three key factors that affect green chemistry: (i) choice of energy, (ii) the

oxidizing agent employed, and (iii) the catalyst used. The use of microwaves as a source of energy is rapidly growing because of both its economical advantages and also its advantages in terms of convenience. This technology has already been applied to industrial, residential, the field of medical science, and environmental pollution scrubbing for polycyclic aromatic hydrocarbons (PAHs) [18–20] and polychlorinated biphenyls (PCBs) [21], etc.

4-Nitrophenol (4-NP) is an important organic compound that is widely used in the production of pesticides, insecticides, herbicides, and synthetic dyes [22]. The nitroaromatic compounds can also be used in the production of explosives. Therefore, the 4-NP and its derivatives are commonly detected in surface water and wastewater that have been the cause of serious environmental problems and many efforts have been made to minimize the deleterious effects. The photodegradation of 4-NP in TiO₂ suspensions has been studied by many investigators [23–28,22,29–31]. The results indicate that it takes a long time for 4-NP to decompose completely. Fenton's reagent could enhance the degradation of 4-NP through photo irradiation [32]. In both photo-Fenton processes, these acids were found as short-lived intermediate during the degradation process and were almost completely eliminated from the aqueous media. Bo et al. [33] found that a microwave-assisted oxidation process is capable of degrading 4-NP in aqueous solution and under atmospheric pressure, thereby reducing the operating risk resulting from high pressure and high temperatures within wet air oxidation (WAO) or catalytic wet air oxidation (CWAO). The process was operated in a continuous flow mode. Air

* Corresponding author. Fax: +886 33 891519.

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

was applied for oxygen supply. Granular activated carbon acted as a microwave energy absorption material as well as the catalyst for 4-NP degradation. Under 4-NP concentration of 1330 ppm, power of 500 W microwave and air flow of 100 mL/min conditions, the 4-NP was removed 90% during 180 min. The sonolysis process has proven to be effective in the degradation of 4-NP [34]. The finding suggests that thermolysis products (at pH 4), such as phenol, nitrate, and various gaseous products, notably CO, CO₂ and H₂, are formed in considerable yield in the aqueous phase. At pH 10, under these conditions, one practically only deals with decomposition reactions initiated by OH radicals and H atoms in the aqueous phase. There is a strong hydrophobic enrichment at the liquid–gas interface of the cavitation bubble, which is the case with 4-nitrophenol at pH < 7. A novel heterogeneous metallophthalocyanine catalyst which catalytic oxidation of 4-NP in 2-propanol is unlikely to involve predominant free hydroxyl radicals. In addition, the removal of total organic carbon of 4-NP accounted for about 90% in 300 min of reaction [35]. Notably, catalytic oxidation reactions could provide complete mineralization of organic substances while being environmental friendly.

For many years, nickel has been considered as the most suitable metal in hydrogenation, hydrotreating, and steam-reforming reactions. Nickel is cheap, sufficiently active, and allows suitable catalysts to be economically produced. In previous publications [36] we investigated a higher nickel oxide system, prepared by the precipitation-oxidation method, which contained an over stoichiometric amount of oxygen and nickel ions in a high oxidation state. It has been found that the obtained NiO_x catalyst has a high catalytic activity towards the degradation of phenol taking place in aqueous phase.

The key-advantage of energy input by microwave irradiation over conventional heating methods is the way in which energy is introduced via radiation instead of heat transfer and convection. Thus, a fast penetration of microwave transparent materials (insulators) is enabled. Ideally, the conversion of energy into heat takes place simultaneously and evenly across the entire volume of the microwave absorbing heat exchanger, heating load, or catalyst, which subsequently [37]. Thermal and non-thermal effects govern microwave assisted reactions when a system is subjected to a microwave radiation field. A typical thermal microwave effect is reported by Stuerge et al. using the sulfonation of naphthalene as an example [37]. Another thermal microwave effect is the formation of so call “hot spots”. Hot spots are areas that have higher temperatures than their surroundings due to their greater interaction with the microwave field and their poor heat transfer properties. The increased number of •OH radicals and changes in the hydrophilic/hydrophobic characteristics were attributed to the non-thermal effects of the microwave radiation [38].

In our previous work, we have succeeded in the degradation of 200 ppm phenol and 4-CP using a microwave-enhanced catalytic degradation (MECD) method under 30 min [36,39,40]. However, various factors can influence activity, such as the pH of 4-NP, and temperature and types of catalysts. Therefore, the main objective of this study is to adopt nickel oxide as the active component and combine it with microwave irradiation technology to promote the degradation of 4-NP.

2. Experimental

2.1. Preparation of nickel oxide

The as-prepared nickel oxide with high valence state of nickel was synthesized by the precipitation-oxidation and microwave method in an aqueous solution. The synthesis of the individual nickel oxide had been described in previous papers [17,36].

The process was carried out at 70 °C with dropwisely added 100 mL of 3.2 mol L⁻¹ NaOH solution to the 50 mL of 0.6 mol L⁻¹ Ni(NO₃)₂·6H₂O solution to obtain as-prepared Ni(OH)₂. Further, a 100 mL of NaOCl (wt. 12%) oxidizing reagent was introduced drop by drop under a constant stirring. The obtained precipitate was marked as PO. Similar preparation condition was carried out as PO, but the suspension was irradiated in a microwave apparatus (100 W, 2450 MHz, CEM, USA) for 10 min. The obtained precipitate was assigned as PMO.

2.2. Characterization of nickel oxide

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu K_{α1} radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA with a scanning speed in 2θ of 4° min^{-1} . The crystallite size of nickel oxides was estimated using the Scherrer equation.

The infrared spectra were obtained by a Nicolet 5700 FT-IR spectrometer in the range of 500–4000 cm⁻¹. One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr and subjected to a pressure of 8 tons.

Reduction behavior of nickel oxide was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was heated in a flow of 10% H₂/N₂ gas at a flow rate of 10 mL min⁻¹. During TPR, the temperature was increased by 7 °C min⁻¹ increment from room temperature to 600 °C.

Transmission electron micrograph (TEM) was taken on a PHILIPS (CM-200) microscope at an accelerating voltage of 200 kV. The samples for TEM were prepared by ultrasonic dispersing the powder products in ethanol, which was then deposited and dried on a holey carbon film on a copper grid.

2.3. Degradation of 4-nitrophenol

The MECD experiments for degradation of 4-NP were carried out in a thermostated static microwave apparatus (CEM. Discover, USA, 2450 MHz, 300 W, temperature was controlled with IR sensor) upon continuous stirring, likewise providing an equal level of all parameters describing the state of the system (catalyst, temperature, pH, initial concentration and dosage of catalyst). A 60 mL of aqueous 4-NP solution was used for each experimental run. Air was bubbled in the solution for 30 min before adding the catalyst. Then, a fit amount of catalyst was suspended in the solution. The air was continuously bubbled during the runs. To draw 3–5 mL the upper layers of suspension after static 10 min and filtrated with syringe filters (Cellulose Acetate, 0.2 μm, Japan) for each experimental data for quantitative analysis with HPLC. The absorbance of 326 nm was used to measure the concentration of 4-NP.

The degradation of 4-NP and the production was performed using high pressure liquid chromatograph Agilent 1100 Series equipped with diode array detector and a column oven. A 125 mm × 4 mm reverse-phase C-18 column (chrompack) was used for separation. The injection volume was 20 μL, flow rate was 1.0 mL/min, UV detector wavelength was 326 nm and column oven temperature maintained 25 °C. The compounds were eluted with acetonitrile–water (v/v, 50/50). Calibration graphs at five concentration levels were prepared from working solutions containing the 4-NP in the range 0.1–200 g dm⁻³ ($R^2 = 0.9997$, SD = 2.15). Identification of intermediates was performed using gas chromatography and coupled to a mass spectrometer (GC–MS). Typically a 5 mL sample (before 15 min degradation) containing 4-NP and intermediate was extracted three times with dichloromethane (15 mL for each time). The extract was dried over anhydrous sodium sulfate and concentrated to 2 mL. Then, about 1 μL volume of extract was injected into GC–MS.

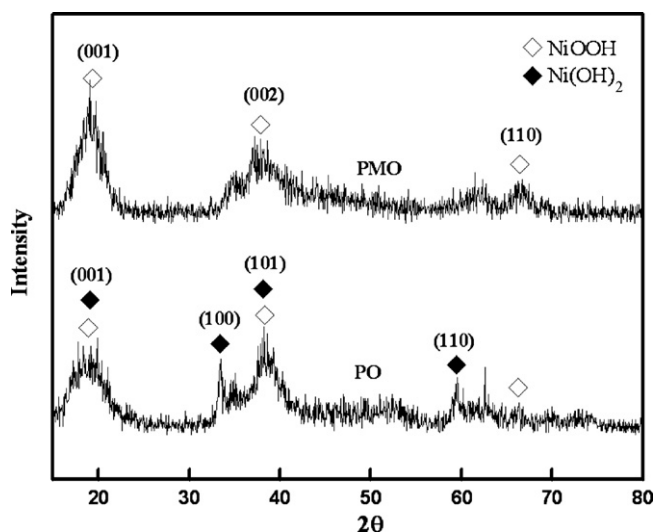


Fig. 1. XRD patterns of the nanosized materials: PO and PMO.

3. Results and discussion

3.1. Characterization of nanosized nickel oxides

Fig. 1 shows the XRD patterns of the nanosized materials, PO and PMO. The diffraction peaks can be perfectly indexed to the nickel oxyhydroxide [JCPDS 06-0141 file]. The as-prepared PO and PMO materials display the peaks at ca. 19.0° and 38.4° and these locations are the planes of (001) and (100) for β -NiOOH. Besides, the XRD pattern of PO sample presents additional peaks: (001) [overlaps with the (001) plane of NiOOH], (100), (101) [overlaps with the (111) plane of NiOOH] and (110) that matches the JCPDS 14-0117 file of β -Ni(OH)₂ [41]. The results show that the PO sample presents a mixed phase [NiOOH and Ni(OH)₂] and PMO sample presents β -NiOOH phase.

In order to understand the vibration of the Ni–O bond, the IR absorption spectra are measured. The infrared spectra of the nanosized materials are shown in Fig. 2. The absorption band at 1530 – 1320 cm^{-1} indicates the existence of carbonates. The absorption band at 566 cm^{-1} indicates the in-plane vibration of

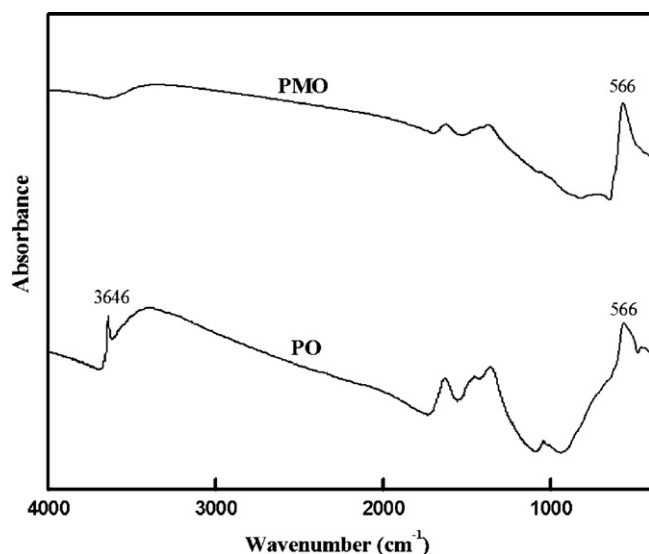


Fig. 2. IR spectra of the nanosized materials: PO and PMO.

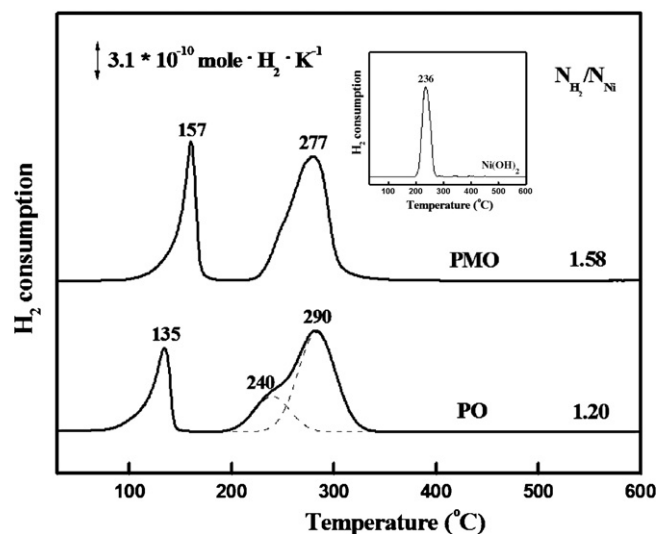
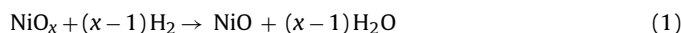


Fig. 3. TPR profiles of the nanosized materials: PO and PMO. The inset displays the TPR of Ni(OH)₂.

hydrogen-bonded hydroxyl group. Comparison the strength of absorption at 566 cm^{-1} , we know that the PMO sample possesses stronger absorption ability than the PO. The PO spectrum displays a sharp ν_{OH} (–OH group stretching vibration) peak around 3646 cm^{-1} and this confirms that the PO sample contains Ni(OH)₂ phase [42].

In order to understand the reduction behavior and the oxidation state of nickel oxide, the TPR analysis has been derived. Fig. 3 shows the TPR profiles of the nanosized materials, PO and PMO. Reduction profiles are similar to those observed in supported nickel catalysts [43,44]. The TPR signal of the PO and PMO samples go forward by two consecutive steps according to Eqs. (1) and (2). These profiles point to a two-step reduction process: the first step (R_1) is low intensity at 135°C (157°C) and the more intense second step (R_2) whose maximum occurs at 290°C (277°C) for PO (PMO) sample according to the following equations:



Little variation of R_2 for the PO sample is probably due to the merged together of two phases [XRD measurement reveals the existence of Ni(OH)₂ and NiOOH] that affects the shape of the reduction profile. Compared to the TPR of Ni(OH)₂ (see inset Fig. 3) and de-convolution of R_2 peak, the lower temperature signal (240°C) belong to the reduction of Ni(OH)₂ and the higher temperature signal (290°C) attributes to the reduction of NiO.



Comparison the reductive temperature of high valence state of nickel, the PMO is higher than PO sample. Also, the content of high valence state of nickel is more for PMO sample. The $N_{\text{H}_2}/N_{\text{Ni}}$ ratio is determined quantitatively to be 1.20 and 1.58 for PO and PMO samples. This shows that the nanosized PO and POM samples are confirmed to be a high valence nickel oxide. The content of Ni³⁺ may be the factor to affect the activity for the degradation of 4-NP.

The TEM images of PO and PMO nickel oxide powders show in Fig. 4. From this image it is clearly seen that the PO and PMO particles show nearly needle-shaped and well dispersion in the bulk state with length around 5–10 nm for PO and 20–25 nm for PMO. This shows that the needle-shaped of the sample in the TEM images are probable to be a NiOOH. Comparison the distribution and amounts of the needle-shaped species, the content of the high

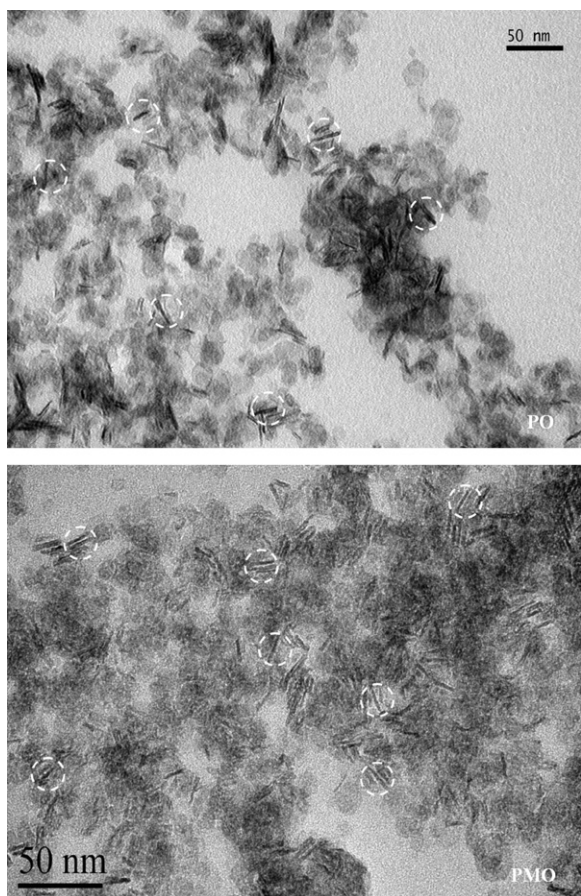


Fig. 4. TEM images of nanosized materials: PO and PMO.

valence state of nickel species in PMO is more than PO sample. The analysis results may be consistent with the quantitative analysis of TPR.

3.2. Degradation of 4-nitrophenol

Since the degradation of 4-NP is controlled under constant bubbling of air in the solution, in each experiment it provides stationary concentration of oxygen on the surface of the catalyst. This means that the reaction rate is independent of the concentration of dissolved oxygen.

Figs. 5, 6, 8–10 show catalytic activities of MECD for 4-NP over nickel oxides. Fig. 5 compares the degradation of 4-NP over the PO with the PMO sample under 40 °C, pH 0 and C = 200 ppm. The degradation of 4-NP over each fresh catalyst generally increased with the reaction time. Clearly, the activity of the PMO is better than that of the PO sample. Within 15 min, the 4-NP can be degraded completely over the PMO sample while there is only 83% degradation for the PO sample. The relative concentration of 4-NP (C/C_0) in aqueous solution in natural logarithm scale is plotted in Fig. 4 against microwave irradiation time on PO and PMO. The relationship between $\ln(C/C_0)$ and time in Fig. 4 is approximately linear, and so the rate constant k for the degradation of 4-NP by MECD method could be calculated for each catalyst from the slope, according to the equation:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (4)$$

where C_0 and C is the initial concentration of 4-NP and the concentration at each irradiation time (min), respectively. To compare the relative activity of both catalysts, kinetic parameters of the degree

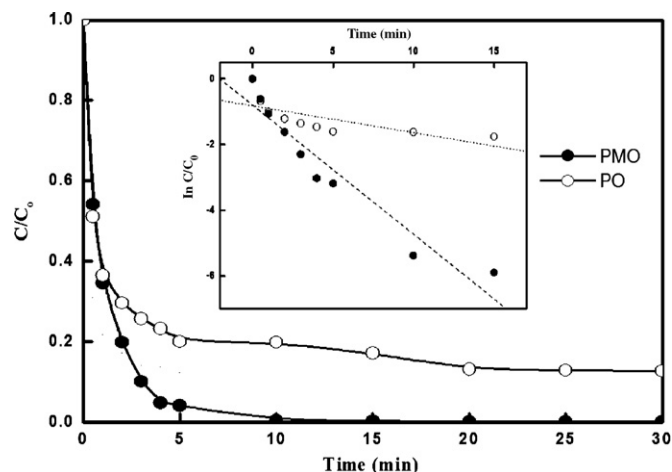


Fig. 5. Comparison of the degradation of 4-NP by MECD method over PO and PMO (0.12 g) under pH 0, C = 200 ppm and T = 40 °C.

of conversion (α_{15} , determined after 15 min reaction) and rate constant (k) are listed in the last two columns of Table 1. The rate constant on the PMO is twice the magnitude of the PO sample. According to the TPR analysis (Fig. 3), the lower temperature of the 1st step (R_1) reveals that the bond strength of Ni–O on the high valence nickel oxide is weak and easily provides oxygen to oxidize the 4-NP under a microwave-irradiated environment. Obviously, the driving force for the PMO sample is probably the larger content of Ni^{3+} [NH_2/N_{Ni} ratio from TPR analysis: 1.58 (PMO) > 1.20 (PO)] that rapidly encourages the degradation of 4-NP. The relative activity significantly affects the oxidation state of nickel.

The effect of temperature on the activity by MECD method over PMO sample for degradation of 4-NP is evaluated under pH 0 and C = 200 ppm. It can be seen from Fig. 6 that the fastest rate of 4-NP degradation occurred within 1 min in the temperature ranges from 40 to 70 °C. Whereas, the degradation of residual 4-NP concentration inverses with temperature after 2 min. The residual 4-NP rapidly decreases under 40 °C and less changed at 70 °C. A complete degradation is achieved after 15 min under 40 °C. The result is similar with the previous research [36–38]. It found that the degradation of phenol and 4-chlorophenol with microwave irra-

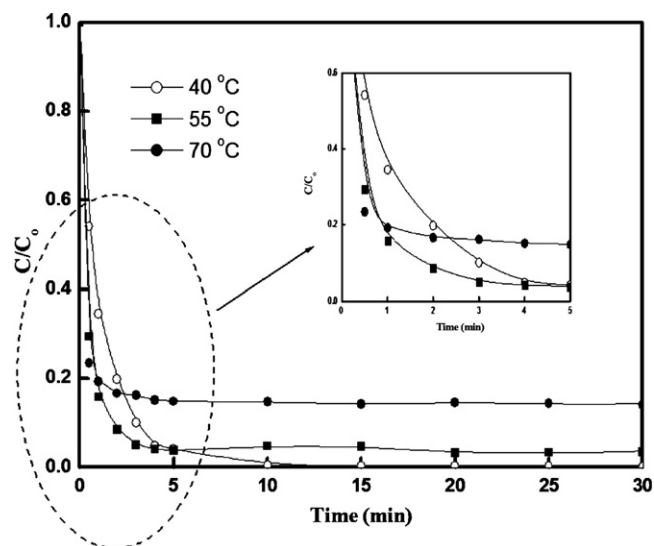


Fig. 6. The effect of the temperature on the degradation of 4-NP by MECD method over PMO (0.12 g) catalyst at pH 0 and C = 200 ppm.

Table 1
Characterization and rate constant of the 4-NP degradation over nickel oxides.

Catalyst	XRD		IR	TPR	N_{H_2}/N_{Ni}	Degradation of 4-NP		
	Phase	d (nm)	ν_{OH} (cm^{-1})	T_{red} ($^{\circ}C$)		α_{15}^a (%)	First order equation	k
PO	Ni(OH) ₂ , NiOOH	1.8	566, 3646	135, 290	1.20	83	$\ln C/C_0 = -0.082t - 0.821$	0.082
PMO	NiOOH	2.1	566	157, 277	1.58	100	$\ln C/C_0 = -0.394t - 0.793$	0.394

^a Degree of 4-NP conversion is determined at 15 min.

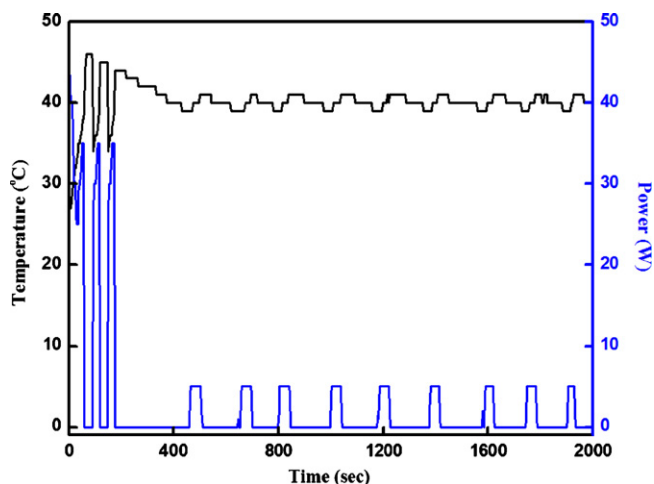


Fig. 7. The plot of time–temperature–power under MECD (the temperature is set 40 °C).

diate is favorite the low temperature. Obviously, it is suitable for microwave absorbance under low temperature to enhance catalysis degradation of 4-NP. From Fig. 7 we can explain the fastest rate of 4-NP degradation occurred within 1 min. When the temperature does not reach the set value (40 °C), the microwave can be irradiated continuously. So, the microwave effect more enhanced catalysis degradation occurs. If the temperature reaches the set value, it is appeared only the thermal effect in degradation system.

Fig. 8 demonstrates the degradation of 4-NP in the pH range of 0–10 in 30 min using the MECD method with the PMO catalyst under 40 °C and $C=200$ ppm. Obviously, the fastest rate of 4-NP degradation occurred within 1 min (degree of conversion attains 70% under pH 0 but only 1% for pH 10) under acidic conditions. Complete degradation is achieved after 10 min under pH 0. The

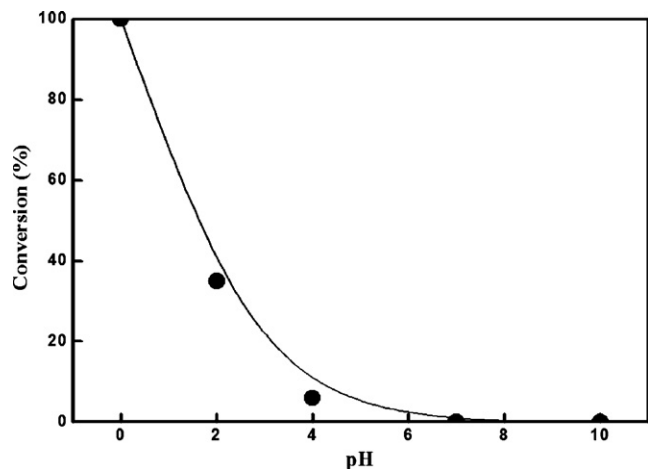


Fig. 8. The effect of the pH on the degradation of 4-NP by MECD method over PMO (0.12 g) catalyst at $T=40^{\circ}C$ and $C=200$ ppm.

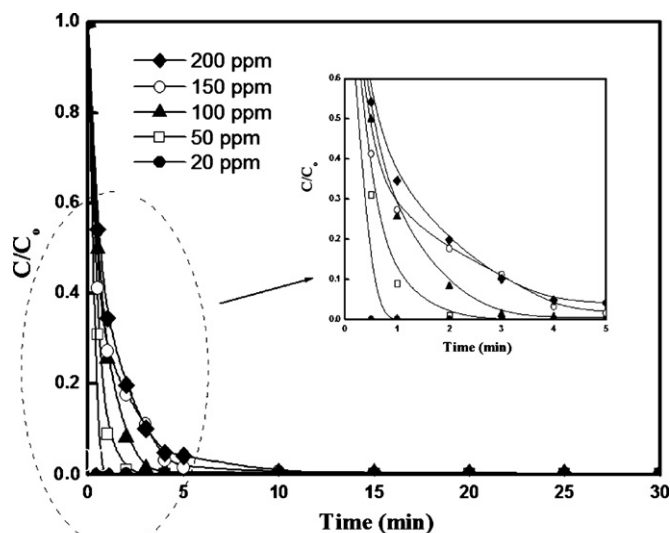


Fig. 9. The effect of the initial concentration on the degradation of 4-NP by MECD method over PMO (0.12 g) catalyst at pH 0 and $C=200$ ppm.

activity decreases with the pH and becomes virtually ineffective in its ability to degrade the 4-NP under neutral and basic solutions. The MECD method demonstrates the major effect of pH on the removal of 4-NP. In the present study, the ionic species of 4-NP is predominant when the pH exceeds 7 (pK_a value of 4-NP at 25 °C is 7.15), but the molecular species is predominant when the pH is less than the pK_a . The fraction in the molecular state of 4-NP was larger when the pH was lower [45]. A similar effect on the pH has been observed with liquid phase oxidation of phenol using a similar catalytic system [46]. Therefore, a strong acidic solution can facilitate the adsorption of the 4-NP molecule and promote a better MECD

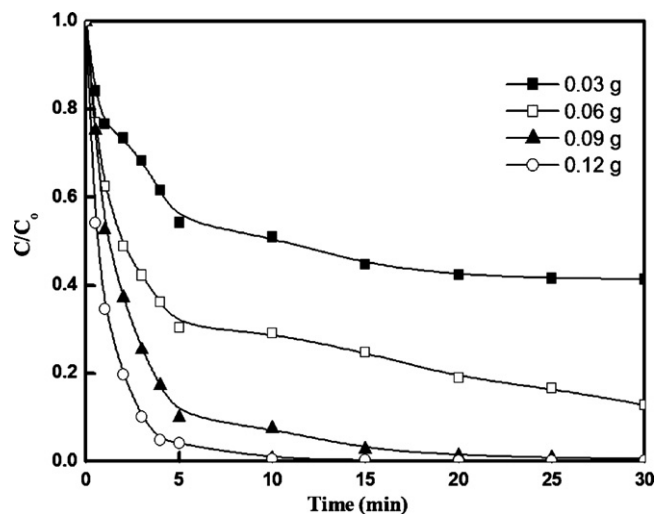


Fig. 10. The effect of the loading of catalyst on the degradation of 4-NP by MECD method over PMO catalyst at pH 0, $T=40^{\circ}C$ and $C=200$ ppm.

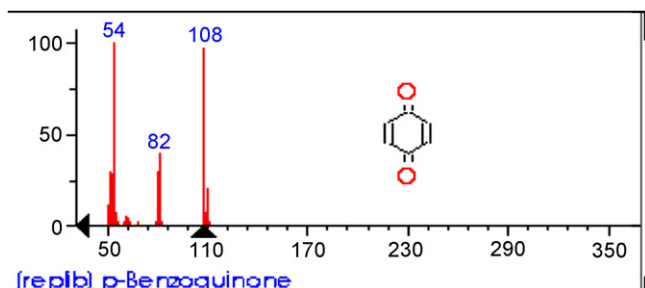


Fig. 11. GC-MS spectrum of the MECD of 4-NP.

reaction. The other reason of promoting factor is that the solubility of nickel oxide increases in acid medium [47]. The available oxygen has released to aqueous solution during the degradation process. The free active oxygen in aqueous solution will increase the activity of the MECD.

The effect of initial concentration on the activity by MECD method over PMO catalyst is investigated in the concentration ranges from 20 to 200 ppm under pH 0 and 40 °C. It can be seen from Fig. 9 that the 4-NP is completely degraded within 15 min even at high concentration. As the concentration below 100 ppm, 4-NP can be removed within 10 min. The initial concentration increase, more organic substances are adsorbed on the surface of catalyst, but the microwave irradiation time and high valence nickel oxide are constant. From these results, the rate constant of the MECD decreases with increasing the initial concentration of the 4-NP. Fig. 10 compares the loading of PMO catalyst for degradation of 4-NP under 40 °C, pH 0 and C=200 ppm. It shows that the removal of 4-NP increases linearly with the catalyst loading. According to these results, we can conclude that the MECD is a promising technique for high organic pollutant concentrations.

The degradation of 4-NP and the production separation was performed using a HPLC instrument. The intermediate appears at 3.3 min which in the treatment of 4-NP by MECD was identified by GC-MS. The GC-MS analysis and the Nist library search (see Fig. 11) shows that the intermediate, p-benzoquinone, is detected. The p-benzoquinone intermediate can be further oxidized into a ring opening compound of CO₂ and H₂O products.

Fig. 12 demonstrates the effect of catalyst and microwave irradiation on the degradation of 4-NP. The results clearly showed that, with catalyst, the removal of 4-NP was much higher than the only microwave irradiation that do not use catalyst. Figs. 5 and 13

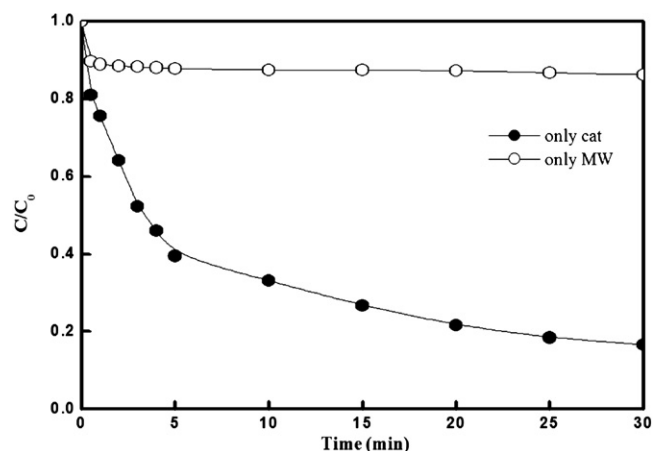


Fig. 12. Comparison of 4-NP degradation efficiency of different methods at pH 0 and C=200 ppm.

indicate that microwave can improve the efficiency of traditional process. However, if the system can be coupled microwave with catalyst, the removal efficiency for the phenolic compounds increased obviously, and the removal percentage was more than that of summation of the respective increase.

Fig. 13 shows the formation of electrophilic oxygen at the nickel oxide surface. It is believed that even in the absence of oxygen in the gas phase electrophilic oxygen species may appear at the surface as intermediates in the transfer of oxygen from the lattice in to the gas phase in the process of dissociation of the solid. Nickel oxide is an excellent material to absorb microwave energy. The microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. Electrophilic oxygen have charge transfer (transfer polarization) can be unstable by electromagnetic energy. Both of unstable electrophilic oxygen species and microwave effect can to promote degradation of organic pollutants.

We investigated microwave-enhanced catalytic activity of nickel oxide on the degradation of 4-NP in water. Table 1 summarizes the properties and microwave-enhanced catalytic activity of nickel oxide. PMO shows better catalytic activity than PO. We attributed the reason for the high catalytic activity of PMO is probably due to the synergistic effect of high valence nickel oxide and microwave effect.

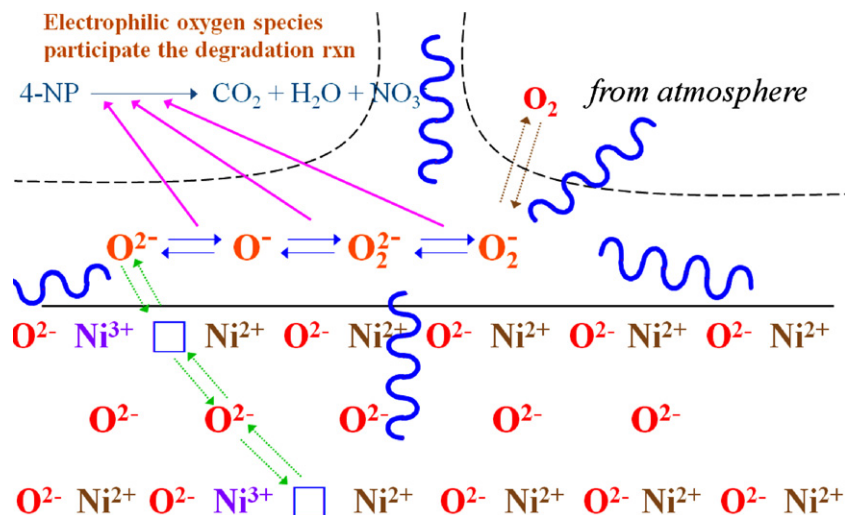


Fig. 13. Microwave-enhanced formation of electrophilic oxygen on the surface of nickel oxide.

4. Conclusion

In this work, a novel and environmentally friendly process for the degradation of 4-NP has been successfully developed. The following conclusions have been made:

- (1) Nanosized PO and POM samples are confirmed to be a high valence nickel oxide.
- (2) 4-NP can be degraded completely using the high efficiency MECD method within 15 min under pH 0, $T=40^{\circ}\text{C}$ and $C=200$ ppm with a PMO sample.
- (3) Activity of 4-NP degradation depends strongly on the oxidation state of nickel.

Acknowledgements

We are pleased to acknowledge the financial support for this study by the National Science Council of the Republic of China under contract numbers NSC 97-2811-M-017-001 and NSC 99-2113-M-606-001-MY3.

References

- [1] L.H. Keith, W.A. Telliard, Priority pollutants I—a perspective view, *Environ. Sci. Technol.* 13 (1979) 416–423.
- [2] N.N. Mahamuni, A.B. Pandit, Effect of additives on ultrasonic degradation of phenol, *Ultrason. Sonochem.* 13 (2006) 165–174.
- [3] C. Berberidou, I. Poullos, N.P. Xekoukoulotakis, D. Mantzavinos, Sonochemical and sonophotocatalytic degradation of malachite green in aqueous solutions, *Appl. Catal. B74* (2007) 63–72.
- [4] J.K. Kim, F. Martinez, I.S. Metcalfe, The beneficial role of use of ultrasound in heterogeneous Fenton-like system over supported copper catalysts for degradation of p-chlorophenol, *Catal. Today* 124 (2007) 224–231.
- [5] M.S. Vohra, K. Tanaka, Photocatalytic degradation of aqueous pollutants using silica-modified TiO_2 , *Water Res.* 37 (2003) 3992–3996.
- [6] C. Adan, A. Bahamonde, M.F. Garcia, A.M. Arias, Structure and activity of nano-sized iron-doped anatase TiO_2 catalysts for phenol photocatalytic degradation, *Appl. Catal. B72* (2007) 11–17.
- [7] J. Lukac, M. Klementova, P. Bezdička, S. Bakardjieva, J. Subrt, L. Szatmary, Z. Bastil, J. Jirkovsky, Influence of Zr as TiO_2 doping ion on photocatalytic degradation of 4-chlorophenol, *Appl. Catal. B74* (2007) 83–91.
- [8] M.P. Moya, M. Graells, L.J. Valle, E. Centelles, H.D. Mansilla, Fenton and photo-Fenton degradation of 2-chlorophenol: multivariate analysis and toxicity monitoring, *Catal. Today* 124 (2007) 163–171.
- [9] X. Zhao, T. Xu, W. Yao, C. Zhang, Y. Zhu, Photoelectrocatalytic degradation of 4-chlorophenol at Bi_2WO_6 nanoflake film electrode under visible light irradiation, *Appl. Catal. B72* (2007) 92–97.
- [10] J. Matos, J. Laine, J.M. Herrmann, Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon, *Appl. Catal. B18* (1998) 281–291.
- [11] A. Kunz, P.P. Zamora, N. Duran, Hydrogen peroxide assisted photochemical degradation of ethylenediaminetetraacetic acid, *Adv. Environ. Res.* 7 (2002) 197–202.
- [12] J.F. Akyurtlu, A. Akyurtlu, S. Kovenklioglu, Catalytic oxidation of phenol in aqueous solutions, *Catal. Today* 40 (1998) 343–352.
- [13] D.H. Han, S.Y. Cha, H.Y. Yang, Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/ H_2O_2 process and kinetic study, *Water Res.* 38 (2004) 2782–2790.
- [14] J.G. Mei, S.M. Yu, J. Cheng, Heterogeneous catalytic wet peroxide oxidation of phenol over delaminated Fe–Ti–PILC employing microwave irradiation, *Catal. Commun.* 5 (2004) 437–440.
- [15] Z. Ai, P. Yang, X.H. Lu, Degradation of 4-chlorophenol by microwave irradiation enhanced advanced oxidation processes, *Chemosphere* 60 (2005) 824–827.
- [16] Z. Ai, P. Yang, X. Lu, Degradation of 4-chlorophenol by a microwave assisted photocatalysis method, *J. Hazard. Mater.* 124 (2005) 147–152.
- [17] T.L. Lai, W.F. Wang, Y.Y. Shu, Y.T. Liu, C.B. Wang, Evaluation of microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides, *J. Mol. Catal. A273* (2007) 303–309.
- [18] Y.Y. Shu, T.L. Lai, Effect of moisture on the extraction efficiency of polycyclic aromatic hydrocarbons from soils under atmospheric pressure by focused microwave-assisted extraction, *J. Chromatogr. A* 927 (2001) 131–141.
- [19] Y.Y. Shu, T.L. Lai, H.S. Lin, T.C. Yang, C.P. Chang, Study of factors affecting on the extraction efficiency of polycyclic aromatic hydrocarbons from soils using open-vessel focused microwave-assisted extraction, *Chemosphere* 52 (2003) 1667–1676.
- [20] Y.Y. Shu, R.C. Lao, C.H. Chiu, R. Turle, Analysis of polycyclic aromatic hydrocarbons in sediment reference materials by microwave-assisted extraction, *Chemosphere* 41 (2000) 1709–1716.
- [21] Y.Y. Shu, S.S. Wang, M. Tardif, Y.P. Huang, Analysis of polychlorinated biphenyls in aqueous samples by microwave-assisted headspace solid-phase microextraction, *J. Chromatogr. A* 1008 (2003) 1–12.
- [22] M.S. Dieckmann, K.A. Gray, A comparison of the degradation of 4-nitrophenol via direct and sensitized photocatalysis in TiO_2 slurries, *Water Res.* 30 (1996) 1169–1183.
- [23] V. Augugliaro, L. Palmisano, M. Schiavello, A. Sclafani, Photocatalytic degradation of nitrophenols in aqueous titanium dioxide dispersion, *Appl. Catal.* 69 (1991) 323–340.
- [24] R.W. Matthews, M. Abdullah, G.K. Low, Photocatalytic oxidation for total organic carbon analysis, *Anal. Chim. Acta* 233 (1990) 171–179.
- [25] S. Guittonneau, J. Laat, M. Dore, J.P. Duguet, C. Honnel, Comparative study of the photodegradation of aromatic compounds in water by UV and hydrogen peroxide-UV, *Environ. Technol. Lett.* 9 (1988) 1115–1128.
- [26] A. Di Paola, V. Augugliaro, L. Palmisano, G. Pantaleo, E. Savinov, Heterogeneous photocatalytic degradation of nitrophenols, *J. Photochem. Photobiol. A155* (2003) 207–214.
- [27] S.S. Hong, M.S. Lee, C.S. Ju, G.D. Lee, S.S. Park, K.T. Lim, Photocatalytic decomposition of p-nitrophenol over titanium dioxides prepared in water-in-carbon dioxide microemulsion, *Catal. Today* 93 (2004) 871–876.
- [28] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C.Y. Chang, Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution, *Appl. Catal. B21* (1999) 1–8.
- [29] N. San, A. Hatipoğlu, G. Koçtürk, Z. Çınar, Photocatalytic degradation of 4-nitrophenol in aqueous TiO_2 suspensions. Theoretical prediction of the intermediates, *J. Photochem. Photobiol. A146* (2002) 189–197.
- [30] V. Loddo, G. Marcò, C. Martò, L. Palmisano, V. Rives, A. Sclafani, Preparation and characterisation of TiO_2 (anatase) supported on TiO_2 (rutile) catalysts employed for 4-nitrophenol photodegradation in aqueous medium and comparison with TiO_2 (anatase) supported on Al_2O_3 , *Appl. Catal. B20* (1999) 29–45.
- [31] V. Maurino, C. Minero, E. Pelizzetti, P. Piccinini, N. Serpone, H. Hidaka, The fate of organic nitrogen under photocatalytic conditions degradation of nitrophenols and aminophenols on irradiated TiO_2 , *J. Photochem. Photobiol. A109* (1997) 171–176.
- [32] V. Kavitha, K. Palanivelu, Degradation of nitrophenols by Fenton and photo-Fenton processes, *J. Photochem. Photobiol. A170* (2005) 83–95.
- [33] L. Bo, X. Quan, S. Chen, H. Zhao, Y. Zhao, Degradation of p-nitrophenol in aqueous solution by microwave assisted oxidation process through a granular activated carbon fixed bed, *Water Res.* 40 (2006) 3061–3068.
- [34] A. Tauber, H.P. Schuchmann, C. Sonntag, Sonolysis of aqueous 4-nitrophenol at low and high pH, *Ultrason. Sonochem.* 7 (2000) 45–52.
- [35] W. Lu, W. Chen, N. Li, M. Xu, Y. Yao, Oxidative removal of 4-nitrophenol using activated carbon fiber and hydrogen peroxide to enhance reactivity of metal-lopthalocyanine, *Appl. Catal. B87* (2009) 146–151.
- [36] T.L. Lai, C.C. Lee, K.S. Wu, Y.Y. Shu, C.B. Wang, Microwave-enhanced catalytic degradation of phenol over nickel oxide, *Appl. Catal. B68* (2006) 147–153.
- [37] H. Will, P. Scholz, B. Ondruschka, Microwave-assisted heterogeneous gas-phase catalysis, *Chem. Eng. Technol.* (2004) 113–122.
- [38] S. Horikoshi, A. Matsubara, S. Takayama, M. Sato, F. Sakai, M. Kajitani, M. Abe, N. Serpone, Characterization of microwave effects on metal-oxide materials: zinc oxide and titanium dioxide, *Appl. Catal. B91* (2009) 362–367.
- [39] T.L. Lai, C.C. Lee, G.L. Huang, Y.Y. Shu, C.B. Wang, Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides, *Appl. Catal. B78* (2008) 151–157.
- [40] T.L. Lai, J.Y. Liu, K.F. Yong, Y.Y. Shu, C.B. Wang, Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides under low temperature, *J. Hazard. Mater.* 157 (2008) 496–502.
- [41] T.L. Lai, Y.Y. Shu, G.L. Huang, C.C. Lee, C.B. Wang, Microwave-assisted and liquid oxidation combination techniques for the preparation of nickel oxide nanoparticles, *J. Alloys Compd.* 450 (2008) 318–322.
- [42] W.R. Bushing, H.A. Levy, Neutron diffraction study of calcium hydroxide, *J. Chem. Phys.* 26 (1957) 563–568.
- [43] B. Mile, D. Stirling, M.A. Zammit, A. Lovell, M. Webb, The location of nickel oxide and nickel in silica-supported catalysts: two forms of “NiO” and the assignment of temperature-programmed reduction profiles, *J. Catal.* 114 (1988) 217–229.
- [44] K. Nakagawa, R. Konaka, T. Nakata, Oxidation with nickel peroxide: I. Oxidation of alcohols, *J. Org. Chem.* 27 (1962) 1597–1601.
- [45] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, Photosonochemical degradation of phenol in water, *Water Res.* 35 (2001) 3927–3933.
- [46] M. Stoyanova, St.G. Christoskova, M. Georgieva, Low-temperature catalytic oxidation of water containing 4-chlorophenol over Ni-oxide catalyst, *Appl. Catal. A248* (2003) 249–259.
- [47] St.G. Christoskova, N. Danova, M. Georgieva, O.K. Argirov, D. Mehandzhiev, Investigation of a nickel oxide system for heterogeneous oxidation of organic compounds, *Appl. Catal. A128* (1995) 219–229.