Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides under low temperature

Teh-Long Lai [a,b], Jyong-Yue Liu [a], Kim-Fui Yong [b], Youn-Yuen Shu [b,*], Chen-Bin Wang [a,*]

[a] Department of Applied Chemistry and Materials Science, Chung Cheng Institute of Technology, National Defense University,
Tahsi, Taoyuan 33509, Taiwan, ROC
[b] Environmental Analysis Laboratory, Department of Chemistry, National Kaohsiung Normal University, Kaohsiung 802, Taiwan, ROC

Abstract

Microwave-enhance catalytic degradation (MECD) of 4-chlorophenol (4-CP) using nickel oxide was studied. A mix-valenced nickel oxide was obtained from nickel nitrate aqueous solution through a precipitation with sodium hydroxide and an oxidation by sodium hypochlorite (assigned as PO). Then, the as-prepared PO was irradiated under microwave irradiation to fabricate a high active mix-valenced nickel oxide (assigned as POM). Further, pure nanosized nickel oxide was obtained from the POM by calcination at 300, 400 and 500 °C (labeled as C300, C400 and C500, respectively). They were characterized by X-ray (XRD), infrared spectroscopy (IR) and temperature-programmed reduction (TPR). Their catalytic activities towards the degradation of 4-CP on the efficiency of the degradation were further investigated under continuous bubbling of air through the liquid-phase and quantitative evaluation by high pressure liquid chromatography (HPLC). Also, the effects of temperature, pH and kinds of catalysts on the efficiency of the degradation have been investigated. The results showed that the 4-CP was degraded completely by MECD method within 20 min under pH 7, $T = 40\,^{\circ}C$ and $C = 200\,g\,dm^{-3}$ over POM catalyst. The relative activity was affected significantly with the oxidation state of nickel.
© 2008 Elsevier B.V. All rights reserved.

Keywords: Nickel oxide; Microwave-enhance catalytic degradation (MECD); 4-Chlorophenol

1. Introduction

Wastewaters containing phenolic compounds present a serious environmental problem. Aromatic pollutants, in particular phenol, chlorophenol compounds and phenolic derivatives, have been listed on the EPAs priority pollutants since 1976 [1]. These compounds are considered hazardous pollutants because of their potential to harm human health. Indeed, it is necessary to eliminate them from industrial wastewater before it is discharged. The degradation of hazardous pollutants has attracted considerable attention due to worldwide concern about the toxicity. Different methods of treatment have been reported, such as ultrasonic degradation [2–4], photocatalytic degradation [5–7], photo-Fenton degradation [8], photoelectrocatalytic degradation [9], advanced oxidation process with UV/H$_2$O$_2$ (AOP) [10],

catalytic oxidation [11] and the microwave-enhanced advanced oxidation processes [12–16]. One of the most promising technologies is the utilization of microwave-enhanced catalytic for the degradation of 4-chlorophenol [17]. Microwave radiation technology has already been applied to industrial, family, medical science and environmental organic pollution for polycyclic aromatic hydrocarbons (PAHs) [18–20] and polychlorinated biphenyls (PCBs) [21] etc. The use of microwaves as a source of energy is rapidly becoming economized and gaining convenient advantages.

4-Chlorophenol (4-CP) is a toxic organic compound that is low in biodegradability and a persistent pollutant, posing serious risks to the environment [22]. It is commonly detected in soil, sediments, surface water and wastewater and causes severe environmental problems. Many efforts have been dedicated to minimizing the deleterious effect. Liquid-phase oxidation using a solid catalyst provides a potential method for the removal of dissolved toxic organic pollutants from wastewaters by transforming them into harmless species [23]. Transition metal oxides have proved to be active in the catalytic reactions of

the degradation of chlorophenols and its derivatives [24–27]. Low-temperature aqueous-phase catalytic oxidation is a promising alternative for the detoxification of wastewaters containing toxic substances. Catalytic oxidation reactions could provide complete mineralization of organic substances while being environmentally friendly.

In a previous work, we have succeeded in performing the degradation of phenol and 4-chlorophenol with microwave-enhanced catalytic degradation (MECD) method [28,17]. For this reason, the present work focuses on the low-temperature MECD method on the degradation of 4-CP. Variable factors can influence the activity, such as temperature, pH and types of catalysts. Based on the above considerations, the major objective of this study adopts nickel oxide as active components and combines the microwave irradiation technology to promote the degradation of 4-CP.

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 coupled with microwave method in an aqueous solution. The process was carried out under $70\,^\circ C$ with drop-wisely added 50 ml of 0.6 M $Ni(NO_3)_2 \cdot 6H_2O$ solution into the 100 ml of 3.2 M NaOH solution to obtain the as-prepared $Ni(OH)_2$. Further, a 100 ml of NaOCl (wt. 12%) oxidizing agent was introduced drop by drop under constant stirring to oxidize the $Ni(OH)_2$ (assigned as PO). Then, the as-prepared PO was irradiated for 10 min in a microwave apparatus (100 W, 2450 MHz, CEM, USA). The precipitate was then filtered, washed with deionized distillated water and dried in an oven at $110\,^\circ C$ for 20 h. The dried product was ground and put in a desiccator as fresh sample (marked as POM). Further, pure nanosized nickel oxide was obtained from the POM by calcination at 300, 400 and $500\,^\circ C$ (labeled as C300, C400 and C500, respectively) for 3 h.

2.2. Characterization of nickel oxide

Thermal gravimetric analysis (TG/DTG) was carried out using a Seiko SSC5000 TG system. The rate of heating was maintained at $10\,^\circ C\,min^{-1}$ and the mass of the sample was ∼10 mg. The measurement was carried from RT to $700\,^\circ C$ under nitrogen flowing with a rate of $100\,ml\,min^{-1}$.

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å) at 40 kV and 30 mA with a scanning speed in 2θ of $4^\circ\,min^{-1}$. 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 tonnes.

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% H_2/N_2 gas mixture at a flow rate of $10\,ml\,min^{-1}$. During TPR, the temperature was increased by $7\,^\circ C\,min^{-1}$ increment from room temperature to $600\,^\circ C$.

Transmission electron micrographs (TEMs) were 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 catalysts in ethanol, which was then deposited and dried on a holey carbon film on a copper grid.

Nitrogen adsorption isotherms at $-196\,^\circ C$ were performed volumetrically with Micrometritics ASAP 2010. The nickel oxides were pre-outgassed to 5×10^{-5} Torr for 3 h at $110\,^\circ C$. The surface area was determined according to the adsorption isotherm.

2.3. Degradation of 4-chlorophenol

The MECD experiments for degradation of 4-CP 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 (temperature, pH and catalysts). A 60 ml of aqueous 4-CP 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, $0.2\,\mu m$, Japan) for each experimental data for quantitative analysis with HPLC. The absorbance of 270 nm was used to measure the concentration of 4-CP.

The chromatographic experiment 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 $20\,\mu l$, flow rate was 1.0 ml/min, UV detector wavelength was 270 nm and column oven temperature was maintained at $25\,^\circ C$. 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-CP in the range 0.1–200 mg/l ($R^2 = 0.9997$, S.D. = 2.15).

3. Results and discussion

3.1. Characterization of as-prepared materials (PO and POM)

Fig. 1 shows the XRD patterns of the as-prepared materials, PO and POM. All the diffraction peaks can be perfectly indexed to the nickel oxyhydroxide [JCPDS card, no. 06-0141]. The as-prepared materials have the peaks at ca. 19.0° and 38.4° and these locations are the β-NiOOH with the peaks at (0 0 1) and (0 0 2) planes.

The infrared spectra of the as-prepared 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 that the as-prepared materials possess the in-
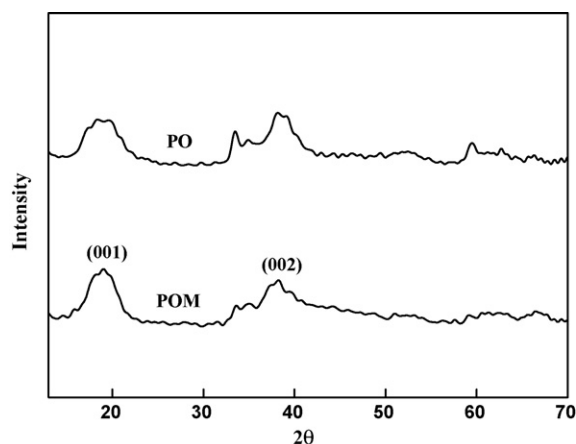
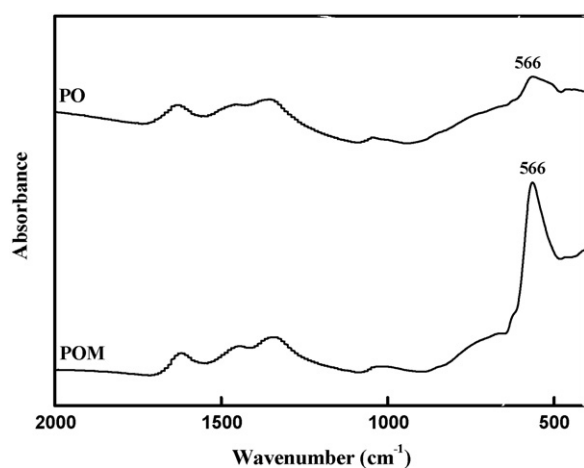Fig. 1. XRD patterns of the as-prepared materials.

Fig. 2. IR spectra of the as-prepared materials.

plane vibration of hydrogen-bonded hydroxyl group. From the strength of absorption, we know that the as-prepared POM has more hydrogen-bonded hydroxyl groups than the as-prepared PO.

Fig. 3 shows the TG/DTG curves of the as-prepared PO and POM under a dynamic nitrogen (100 ml min^{-1}) environment.
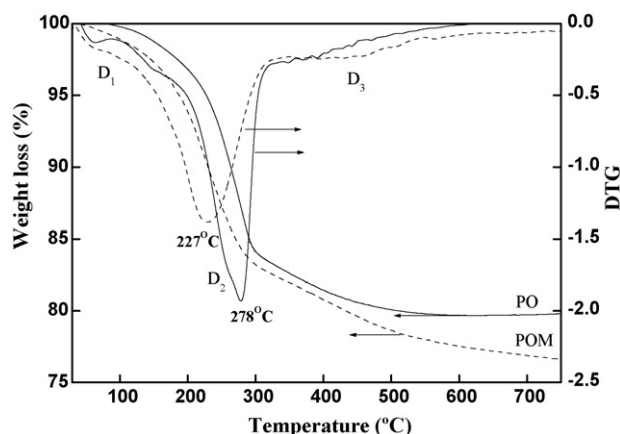

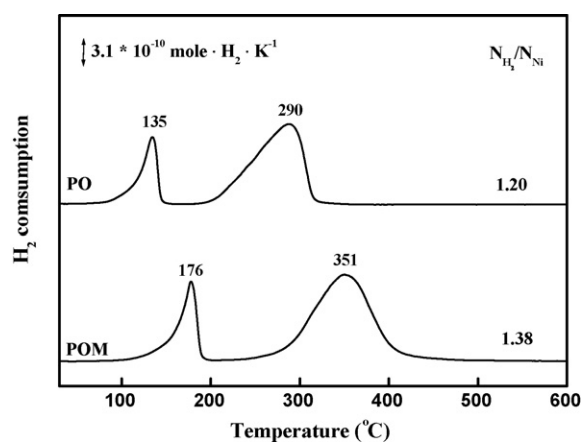Fig. 3. TG/DTG profiles of the fabricated PO and POM in a dynamic nitrogen environment.

Fig. 4. TPR profiles of the as-prepared materials.

The TG curve shows three weight loss steps (assigned as D_1, D_2 and D_3) and the DTG curve shows the maximum loss rate of a D_2 step at 227 °C for POM and at 278 °C for PO, while the D_3 step is not obvious. Prior to 100 °C, the rapid weight loss (D_1 step) should come from the desorbing of water on PO and POM surface in heating process. The weight loss of 18% in D_2 and D_3 steps is accompanied by the dehydration and desorbing of oxygen from β-NiOOH that transfers into NiO according to Eq. (1).

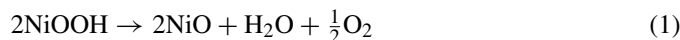$$2NiOOH \rightarrow 2NiO + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

Fig. 4 shows the TPR profiles of the as-prepared materials, PO and POM. The reductive signal of the as-prepared PO and POM in TPR proceeds by two consecutive steps according to Eqs. (2) and (3). Reduction profiles of the as-prepared materials are similar to those observed in supported nickel catalysts [29,30]. These profiles point to a two-step reduction process: the first step is low intensity at 135 °C for PO and 176 °C for POM; the more intense second step whose maximum occurs at 290 °C for PO and 351 °C for POM.
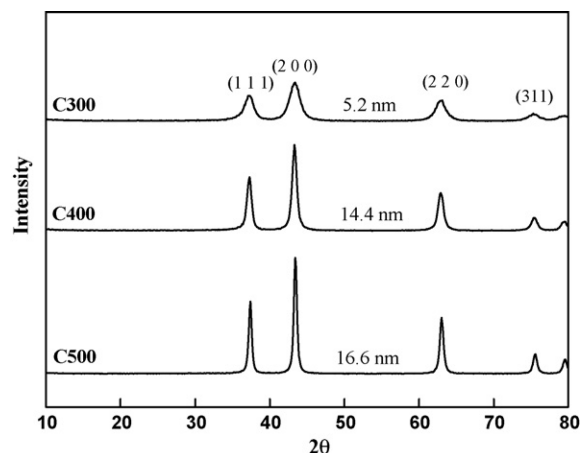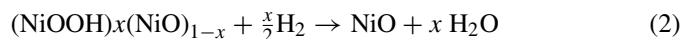
$$(NiOOH)x(NiO)_{1-x} + \tfrac{x}{2}H_2 \rightarrow NiO + x\,H_2O \qquad (2)$$

$$NiO + H_2 \rightarrow Ni + H_2O \qquad (3)$$

Fig. 5. XRD patterns of nickel oxides.

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

Catalyst	XRD		S_{BET}	TPR		Degradation of 4-CP	
	Structure	d (nm)	m^2/g	T_{red} (°C)	NH$_2$/NNi	α_{20}[a] (%)	k (min^{-1})
POM	Hexagonal	2.2	211	176, 351	1.38	100	0.637
C300	Cubic	5.2	139	306, 356	1.10	15	0.006
C400	Cubic	14.4	89	334, 370	1.13	12	0.004
C500	Cubic	16.6	33	334, 378	1.13	10	0.004

[a] Degree of phenol conversion is determined at 20 min.

The NH$_2$/NNi ratio is determined to be 1.20 for PO and 1.38 for POM. This shows that the as-prepared PO and POM is confirmed to be a high valence nickel oxide with a non-stoichiometric chemical formula of $(NiO)_{0.8}(NiOOH)_{0.2}$ for PO and $(NiO)_{0.6}(NiOOH)_{0.4}$ for POM. The content of Ni^{3+} may be the factor to affect the activity for the degradation of 4-CP.

3.2. Characterization of nanosized nickel oxides

In order to obtain pure nanosized nickel oxide (NiO) particles and understand the thermal characterizations, the as-prepared POM is further calcined at 300, 400 and 500 °C (the calcined temperature assigned as T_C), respectively.

Fig. 5 presents XRD patterns of nanosized nickel oxides. The effect of the calcined temperature on the crystallite size of NiO particles can be demonstrated. Traces of NiO crystallite phases (1 1 1), (2 0 0), (2 2 0) and (3 1 1) are detected in the XRD pattern for all samples. Apparently, the sharpness of the XRD peak (i.e., high crystallinity) increases with the T_C. According to the (2 0 0) diffraction pattern of NiO crystalline, the particle size of NiO can be calculated from the full width at half-maximum using the Scherrer equation. The particle size (d) of nickel oxide grows from 5.2 nm to 16.6 nm (given in the 3rd column of Table 1) with the T_C.

Fig. 6 presents IR spectra of nanosized nickel oxides. The absorption band at 1530–1320 cm^{-1} indicates the existence of carbonates. Compared with the as-prepared POM (Fig. 2), the absorption band around 566 cm^{-1} disappears for the refined nickel oxides and a new absorption band appears around

400 cm^{-1}. The main IR absorption maximum of NiO lies between 390 and 403 cm^{-1} [31]. According to the results of IR and combined with the analysis of XRD, we further confirm the purity of nickel oxide.

Fig. 7 displays the TPR profiles of nanosized nickel oxides. All the samples show a similar TPR profile. A qualitative analysis of the TPR profile shows that the reduction peak (T_{red}) shifted to higher temperatures as the T_C increased (as can be seen in the 5th column of Table 1) i.e., the T_{red} of sample C300 is 306 °C and 356 °C, while, the T_{red} of sample C500 is 334 and 378 °C. According to the calculated particle sizes of nickel oxide from XRD, we know that the shift in the T_{red} toward higher temperature is marked with the increasing of particle size. The more reducible nickel oxide is located mainly in the mean diameter of ∼5 nm and the less reducible oxide is located in the mean diameter larger than 15 nm. So, we can assign the overlapped TPR profiles to the mixtures of various sizes of nickel oxides: smaller size (<5 nm) species reduces around 300 °C, middle size (5–15 nm) species reduces around 330–360 °C and larger size (>15 nm) species reduces around 380 °C, respectively. Also, the ratio of reduced nickel oxide can be quantitatively determined from the consumption of hydrogen in TPR traces (given in the 6th column of Table 1). This shows that the dominant species upon calcination at 300–500 °C is NiO, where the x approaches 1.0.

The TEM images of C300, C400 and C500 powers are shown in Fig. 8. From this image it can be clearly seen that the C300 particle has nearly uniform size and well dispersion in the bulk state with diameter around 3–8 nm. As the thermal treatment
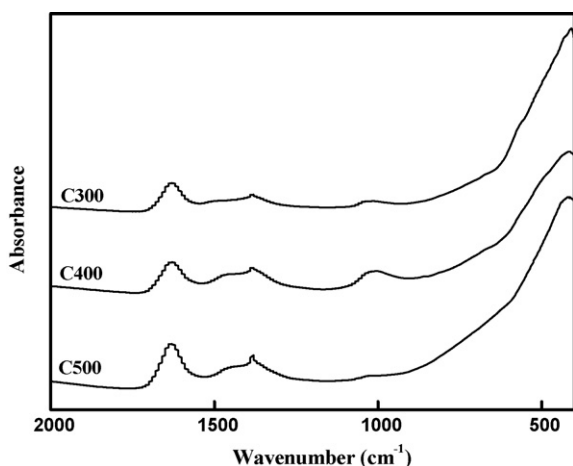

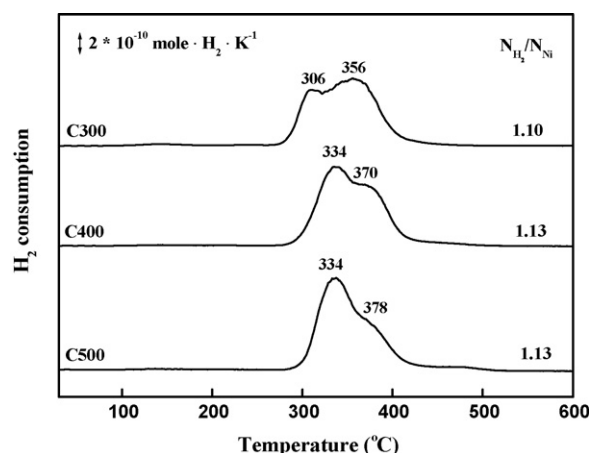Fig. 6. IR spectra of nickel oxides.
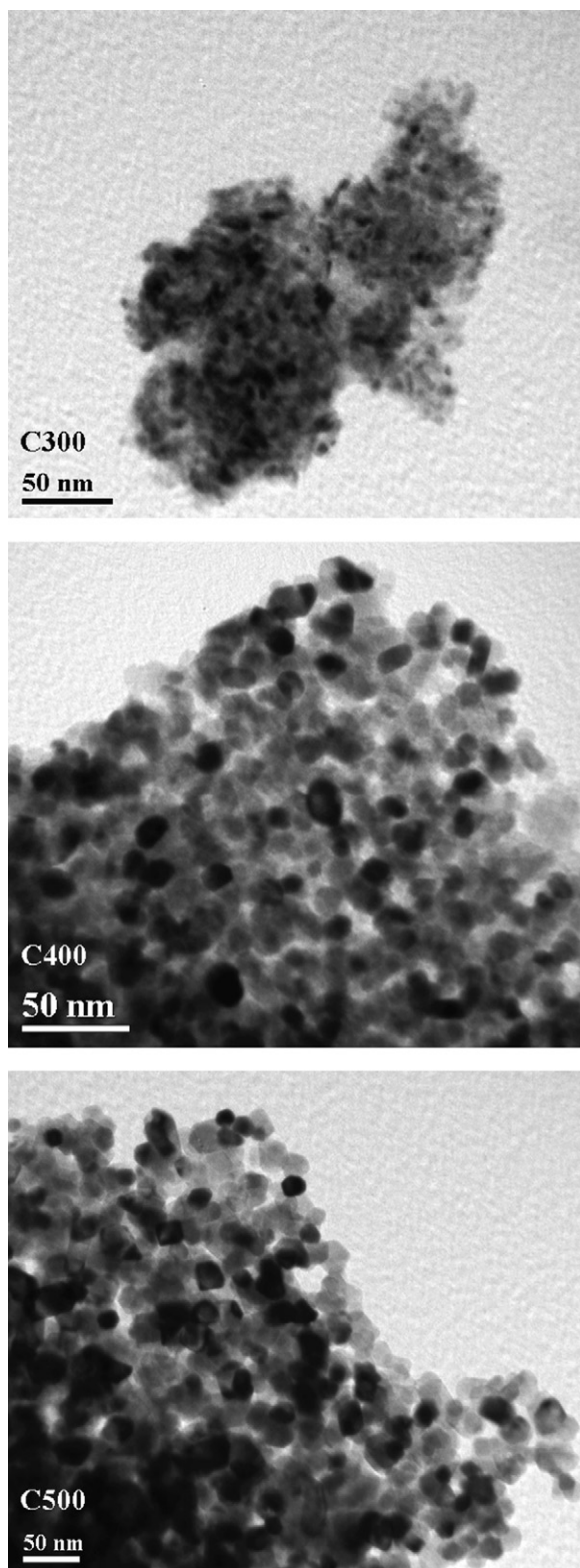

Fig. 7. TPR profiles of nickel oxides.

Fig. 8. TEM images of nickel oxides.
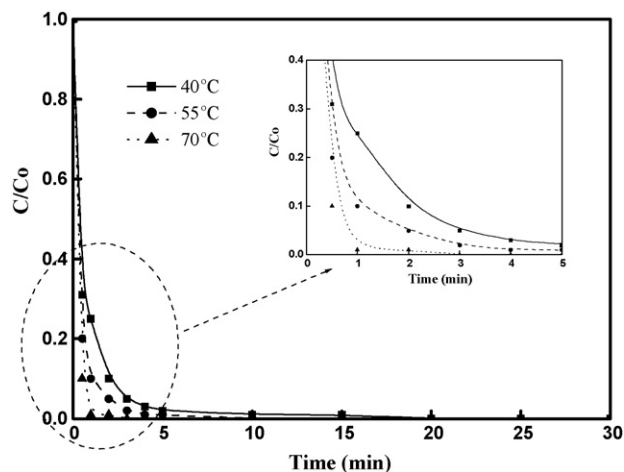

Fig. 9. The effect of the temperature on the degradation of 4-CP by MECD method over as-prepared POM (0.12 g) catalyst at pH 7 and C = 200 g dm^{-3}.

3.3. Degradation of 4-chlorophenol

Since the degradation of 4-CP is controlled under constant bubbling of air into 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.

The effect of temperatures on the activity by MECD method over as-prepared POM catalyst is investigated in the temperature ranges from 40 to 70 °C under pH 7 and C = 200 g dm^{-3}. It can be seen from Fig. 9 that the fastest rate of 4-CP degraded occurs within 1 min under the temperature ranges of 40–70 °C. Whereas, the decrease of residual 4-CP concentration after 1 min inverses slightly with temperature. A complete degradation is achieved after 3 min under 70 °C, 10 min for 55 °C and within 20 min under 40 °C. Since the larger of the dielectric loss tangent (tan δ) can promote rapid heating of the system [32,33], we urgently want to understand the effect of microwave of reaction media under various temperature. The measured tan δ in the 2450 MHz frequency of Agilent 8714 ET Vector Network is 0.099, 0.087 and 0.072 for 4-CP aqueous solution under 40, 55 and 70 °C, respectively. Also, the tan δ for the suspension of POM and 4-CP aqueous solution is 0.2502, 0.2036 and 0.1467 under 40, 55 and 70 °C, respectively. Obviously, it is suitable for microwave absorbance under lower temperature, so we are trying to understand the mechanism on the degradation of 4-CP at 40 °C.

In order to understand whether the content of Ni^{3+} over the fabricated POM can participate in and promote the activity for the degradation of 4-chlorophenol, the analysis of TPR for used catalyst (after 30 min on the degradation of 4-CP at 40 °C) is proceeding. Comparison of the TPR of fresh (Fig. 4) with used (Fig. 10) POM catalyst, the shift of T_{red} for R$_1$ and R$_2$ accompanied with the decreasing of R$_1$ area further suggests that the surface active oxygen initiates catalytic oxidation of 4-CP at about 40 °C. Based on the degradation of 4-chlorophenol under microwave condition, Zhang et al. [34] and Bond et al. [35] suggested that the hot spot in the catalytic bed could be presented.
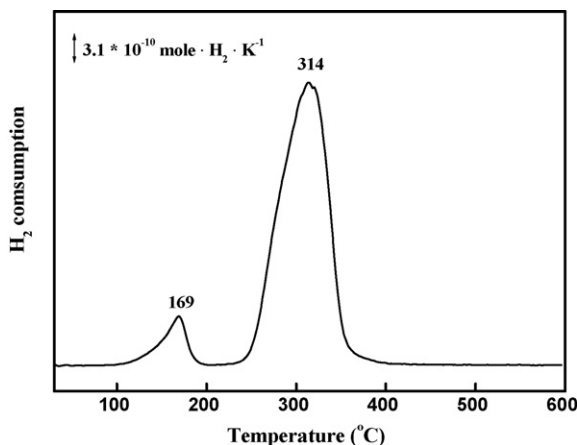
temperature increases, the agglomeration of particles is present. The irregular morphology of C400 and C500 particle shows larger diameter around 10–20 nm and 15–35 nm. Generally, it can be considered that the agglomeration of nanoparticles comes from the interfacial reaction.

Fig. 10. TPR profile of the fabricated POM after degradation of 4-CP at $T = 40\,^\circ C$.

Fig. 12. HPLC spectra of 4-CP degraded during MECD method over fabricated POM under pH 4 and $T = 40\,^\circ C$: (a) initial; (b) 30 s; (c) 5 min; (d) 20 min.

The temperature of the spatial hot spot within the catalyst bed is different from the average temperature of the catalyst bed. To understand the change of the phase structure for used catalyst, the XRD has been advanced. Fig. 11 shows the XRD pattern of POM after degradation of 4-CP at 40 °C. Comparison the XRD of fresh POM catalyst (Fig. 1) with used catalyst, triple phases of β-NiOOH, β-Ni(OH)$_2$ and NiO was obtained. In the study of oxidation of cyclohexanol, Yi et al. [36] found that the used NiOOH catalyst transferred to Ni(OH)$_2$. We confirm that part of POM catalyst on the degradation of 4-CP can reduce to β-Ni(OH)$_2$.

In order to trap the intermediates, the HPLC has been advanced. Fig. 12 shows the HPLC spectra of 4-CP degraded during MECD over the POM under pH 4 and $T = 40\,^\circ C$. The peak appears at 2.6 min which is the species of 4-CP. This peak gradually diminishes with the proceeding of the MECD. In the same time, other small peaks appear at 0.9, 1.6 and 3.1 min that are found to be the intermediates after 5 min degradation [Fig. 12(c)] and disappear after complete degradation [Fig. 12(d)]. We suggest that the 4-CP is degraded completely into harmless products (CO$_2$, H$_2$O and mineral acids).
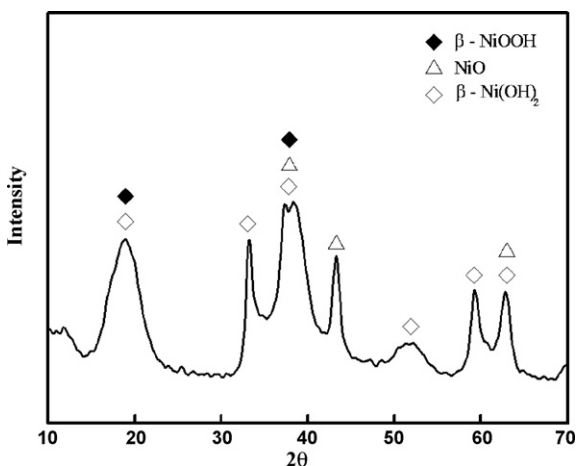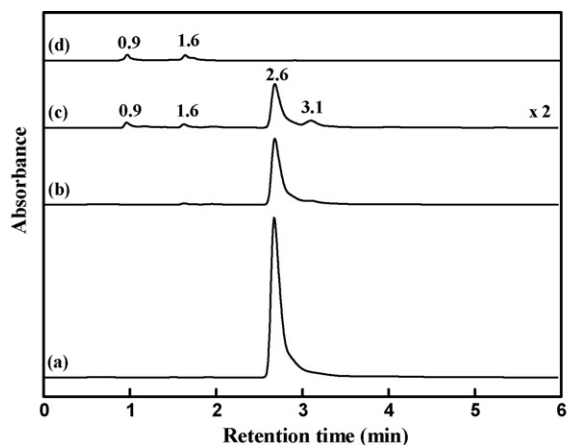
Fig. 13 shows the effect of pH on the degradation of 4-CP over as-prepared POM catalyst at $T = 40\,^\circ C$ and $C = 200\,g\,dm^{-3}$. It demonstrates that the degradation of 4-CP is affected significantly by the pH value. The fastest rate of 4-CP degraded occurs within 1 min under different pH conditions (degree of conversion attains 80% for pH ≤ 7 but 50% for pH 10). Under neutral and acidic solutions (pH ≤ 7), 4-CP can be degraded completely within 20 min, while only 70% 4-CP can be degraded within 30 min under basic solution (pH > 7).

Fig. 14 compares the degradation of 4-CP over POM with the refined pure nickel oxides (C300, C400 and C500) under 40 °C, pH 7 and $C = 200\,g\,dm^{-3}$. The degradation of 4-CP over each catalyst generally increased with the reaction time. Clearly, the activity of the as-prepared POM (including high valence nickel oxide) is better than other nickel oxides. Within 20 min, the 4-CP can be degraded completely over as-prepared POM. However, even within 30 min, the 4-CP only approaches 15% degradation over NiO (C300, C400 and C500). To compare the relative activity of the catalysts, kinetic parameters of the degree of conversion (α_{20}, determined at the 20 min) and rate constant (k) are listed in the 7th and last columns of Table 1. The rate constant on POM catalyst is two orders of magni-
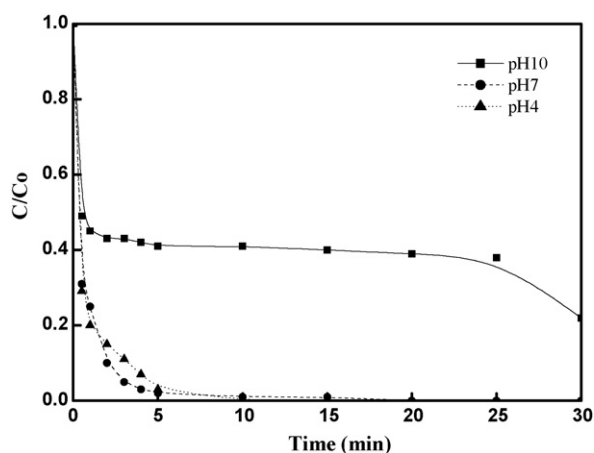

Fig. 11. XRD pattern of the fabricated POM after degradation of 4-CP at $T = 40\,^\circ C$.

Fig. 13. The effect of the pH on the degradation of 4-CP by MECD method over as-prepared POM (0.12 g) catalyst at $T = 40\,^\circ C$ and $C = 200\,g\,dm^{-3}$.
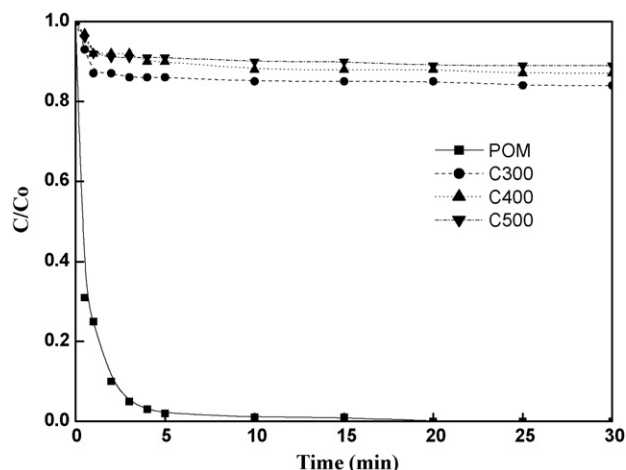
Fig. 14. Comparison of the degradation of 4-CP by MECD method over nickel oxides (0.12 g) under pH 7, $C = 200\,\text{g}\,\text{dm}^{-3}$ and $T = 40\,°C$.

tude higher than C300, C400 and C500 catalysts. The driving force for POM is probably the existence of Ni^{3+} that provides active surface oxides rapidly to promote the conversion. According to the TPR result, the lower temperature reduction (R_1) reveals that the bond strength of Ni–O on NiO_x is weak and provides easily oxygen to oxidize the 4-CP. In addition to the character of high valence state of nickel, compared to the S_{BET} (the 4th column of Table 1) of nickel oxides, the activity also increases somewhere by increasing the S_{BET}, i.e., fabricated POM ($S_{BET} = 211\,\text{m}^2\,\text{g}^{-1}$) > C300 ($S_{BET} = 139\,\text{m}^2\,\text{g}^{-1}$) > C400 ($S_{BET} = 89\,\text{m}^2\,\text{g}^{-1}$) > C500 ($S_{BET} = 33\,\text{m}^2\,\text{g}^{-1}$).

4. Conclusion

An effective and environmentally friendly process for the degradation of 4-CP has been succeeded development over fabricated POM catalyst with microwave-enhance catalytic degradation method under low temperature. The following conclusions have been made as follows:

(1) The as-prepared POM is confirmed to be a high valence nickel oxide with a non-stoichiometric chemical formula of $(NiO)_{0.6}(NiOOH)_{0.4}$.
(2) Degradation of 4-CP is affected significantly by the pH value. The fastest rate of 4-CP degraded occurs within 1 min under different pH conditions (degree of conversion attains 80% for pH $\leq$ 7 but 50% for pH 10).
(3) 4-CP is degraded completely by MECD method within 20 min under pH 7, $T = 40\,°C$ and C = 200 g dm^{-3} over POM catalyst.
(4) Activity of 4-CP degraded is strongly dependent on the oxidation state of nickel, decreases slightly with the particle size and increases surface area of nickel oxide.

References

[1] L.H. Keith, W.A. Telliard, Environ. Sci. Technol. 13 (1979) 416.
[2] N.N. Mahamuni, A.B. Pandit, Ultrason. Sonochem. 13 (2006) 165.
[3] C. Berberidou, I. Poulios, N.P. Xekoukoulotakis, D. Mantzavinos, Appl. Catal. B74 (2007) 63.
[4] J.K. Kim, F. Martinez, I.S. Metcalfe, Catal. Today 124 (2007) 224.
[5] M.S. Vohra, K. Tanaka, Water Res. 37 (2003) 3992.
[6] C. Adan, A. Bahamonde, M.F. Garcia, A.M. Arias, Appl. Catal. B72 (2007) 11.
[7] J. Lukac, M. Klementova, P. Bezdicka, S. Bakardjieva, L. Subrt, L. Szatmary, Z. Bastl, J. Jirkovsky, Appl. Catal. B74 (2007) 83.
[8] M.P. Moya, M. Graells, L.J. Valle, E. Centelles, H.D. Mansilla, Catal. Today 124 (2007) 163.
[9] X. Zhao, T. Xu, W. Yao, C. Zhang, Y. Zhu, Appl. Catal. B72 (2007) 92.
[10] J. Matos, J. Laine, J.M. Herrmann, Appl. Catal. B18 (1998) 281.
[11] A. Kunz, P.P. Zamora, N. Duran, Adv. Environ. Res. 7 (2003) 197.
[12] J.F. Akyurtlu, A. Akyurtlu, S. Kovenklioglu, Catal. Today 40 (1998) 343.
[13] D.H. Han, S.Y. Cha, H.Y. Yang, Water Res. 30 (2004) 2782.
[14] J.G. Mei, S.M. Yu, J. Cheng, Catal. Commun. 5 (2004) 437.
[15] Z. Ai, P. Yang, X.H. Lu, Chemosphere 60 (2005) 824.
[16] Z. Ai, P. Yang, X.H. Lu, J. Hazard. Mater. 124 (2005) 147.
[17] T.L. Lai, W.F. Wang, Y.Y. Shu, Y.T. Liu, C.B. Wang, Mol. Catal, J. Mol. Catal. A273 (2007) 303.
[18] Y.Y. Shu, T.L. Lai, J. Chromatogr. A927 (2001) 131.
[19] Y.Y. Shu, T.L. Lai, H.S. Lin, T.C. Yang, C.P. Chang, Chemosphere 52 (2003) 1667.
[20] Y.Y. Shu, R.C. Lao, C.H. Chiu, R. Turle, Chemosphere 41 (2000) 1709.
[21] Y.Y. Shu, S.S. Wang, M. Tardif, Y.P. Huang, J. Chromatogr. A1008 (2003) 1.
[22] F.J. Benitez, J. Beltran-Heredia, J.L. Acero, F. Javier Rubio, Chemosphere 41 (2000) 1271.
[23] M. Stoyanova, St.G. Christoskova, M. Georgieva, Appl. Catal. A249 (2003) 295.
[24] M. Stoyanova, St.G. Christoskova, M. Georgieva, Appl. Catal. A248 (2003) 249.
[25] St.G. Christoskova, M. Stoyanova, Water Res. 35 (2001) 2073.
[26] M. Stoyanova, St.G. Christoskova, M. Georgieva, Appl. Catal. A208 (2001) 243.
[27] St.G. Christoskova, M. Stoyanova, Water Res. 36 (2002) 2297.
[28] T.L. Lai, C.C. Lee, K.S. Wu, Y.Y. Shu, C.B. Wang, Appl. Catal. B68 (2006) 147.
[29] B. Mile, D. Stirling, M.A. Zammitt, A. Lovell, M. Webb, J. Catal. 114 (1988) 217.
[30] K. Nakagawa, R. Konaka, T. Nakata, J. Org. Chem. 27 (1962) 1597.
[31] L. Wu, Y. Wu, H. Wei, Y. Shi, C. Hu, Mater. Lett. 58 (2004) 2700.
[32] H.M. Kingston, L.B. Jassie, Introduction to Microwave Sample Preparation, American Chemical Society, Washington, 1988, p.7.
[33] H.M. Kingston, S.J. Haswell, Microwave-Enhanced Chemistry, American chemical society, Washington, 1997, p.3.
[34] X. Zhang, D.O. Hayward, D.M.P. Mingos, Catal. Lett. 88 (2003) 33.
[35] G. Bond, R.B. Moyes, D.A. Whan, Catal. Today 17 (1993) 427.
[36] Q. Yi, J. Zhang, W. Huang, X. Liu, Catal. Commun. 8 (2007) 1017.