Kinetics and Catalytic Activity of Carbon-Nickel Nanocomposites in the Reduction of 4-Nitrophenol

Jiulong Li[*], Jeong Won Ko[*], and Weon Bae Ko[*,**,†]

[*]Department of Convergence Science, Graduate School, Sahmyook University, Seoul 139-742, Korea
[**]Department of Chemistry, Sahmyook University, Seoul 139-742, Korea

Abstract: Carbon-nickel nanocomposites were prepared by the reaction of fullerene (C_{60}) and nickel hydroxide in an electric furnace at 700°C for 2 h. The hybrid carbon-nickel nanocomposites were characterized by X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. The kinetics and catalytic activity of the carbon-nickel nanocomposites in the reduction of 4-nitrophenol were confirmed by UV-vis spectroscopy.

Keywords: carbon-nickel nanocomposites, catalytic activity, kinetics, 4-nitrophenol

Introduction

Metallic nanoparticles have been extensively studied for use as catalysts because of their special properties and high surface-to-volume ratios.[1-3] Inorganic metal nanoparticles can be important components of nanomaterials, imparting unique catalytic, optical, electronic, or magnetic properties to the nanomaterials.[4] In recent years, novel metal nanomaterials, such as Fe, Cu, Ni, Co, Zn, etc. have been prepared. Also, metal-carbon materials with different morphologies such as graphite–Cd, nickel–carbon, and Ni_3C have been prepared.[5-7] Among the nanomaterials, nanocomposites encapsulated with magnetic nanoparticles have shown unique catalytic and magnetic properties.[7-10] Nitrophenols and their derivatives are important water pollutants that have raised considerable global concern.[3,11] Aminophenol is an important intermediate used in the preparation of analgesics and antipyretics and as a corrosion inhibiting agent and photographic developer.[3,11-13] Therefore, identifying new catalysts for the reduction of nitrophenol to aminophenol is an important topic of research. Pal *et al.* proposed a model reaction for the conversion of 4-nitrophenol into 4-aminophenol by using sodium borohydride ($NaBH_4$).[14,15] Significant effort has been devoted to enable the use of metallic nanoparticles as catalysts for the reduction of nitrophenols in the presence of $NaBH_4$.[16,17]

Among various d-block metals, nanosized nickel shows excellent catalytic properties in the catalytic hydrogenation of nitrophenol.[12,18,19] In the present work, nickel nanoparticles and fullerene (C_{60}) have been used to prepare a novel nanocomposites that incorporates the magnetic properties of the nickel nanoparticles and the efficient catalytic activity of nanosized carbon materials.[6,10] The Langmuir-Hinshelwood mechanism has been used to model the surface-controlled reaction and to analyze the kinetics of the reaction.[14,15,20] The nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. Furthermore, the catalytic hydrogenation of 4-nitrophenol was analyzed by using ultraviolet-visible (UV-vis) spectroscopy.

Experimental

1. Reagents and instruments

Nickel(II)acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$), sodium hydroxide (NaOH), ethanol, and tetrahydrofuran (THF) were purchased from Samchun Chemical, Co., Korea. Sodium borohydride ($NaBH_4$) was purchased from Kanto Chemical Co., Inc., Japan. Fullerene (C_{60}) was supplied by Tokyo Chemical Industry Co., Japan.

A Bruker D8 Advance X-ray diffractometer was used to examine the structure of the nanocomposites. The surface of

the sample was observed by SEM (JEOL Co., JSM-6510) at an accelerating voltage of 0.5 to 30 kV. A UV-vis spectro-photometer (Shimazu UV-1691PC) was used to characterize the catalytic activity of the carbon-nickel nanocomposites.

2. Preparation of the carbon- nickel nanocomposites

Nickel hydroxide ($Ni(OH)_2$) powder was obtained by the reaction of nickel(II)acetate tetrahydrate and NaOH in 1:2 molar ratio. The mixture was stirred in ethanol for 4 h at room temperature and subsequently transferred to a conical flask, which was placed in a water bath and subjected to microwave irradiation for 5 min (15 s × 20 times). Then, the sample was washed 5 times with a mixture of ethanol and water (1:1 v/v). $Ni(OH)_2$ powder was obtained after drying the sample in an electric oven at 80°C for 24 h. A mixture
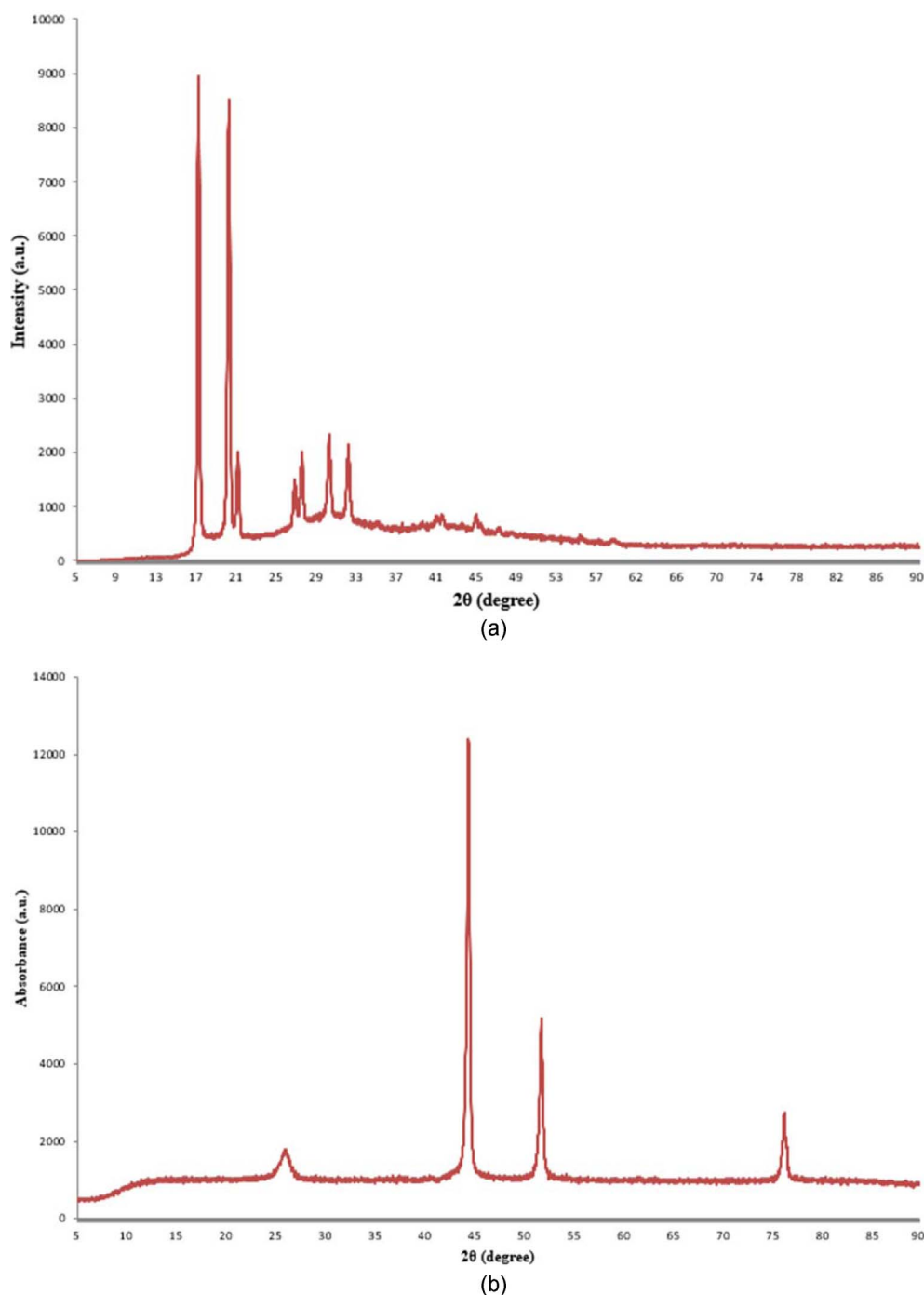
Figure 1. (a) XRD pattern of pure fullerene (C_{60}) powder, (b) XRD pattern of carbon-nickel nanocomposites.

of $Ni(OH)_2$ and fullerene (C_{60}) (2:1 w/w) was calcined at 700 °C in Ar for 2 h to obtain the carbon-nickel nanocomposites.

3. Catalytic reduction of 4-nitrophenol

The peaks of UV-vis absorbance spectrum of 4-nitrophenol at 400 nm were formed in the presence of 10 mg of $NaBH_4$ dissolved in 10 mL of distilled water. The carbon-nickel nanocomposites (10 mg) were added as a catalyst for the catalytic hydrogenation of 4-nitrophenol. The UV-vis spectrophotometer was used at 5 min intervals to characterize the reductive product of 4-nitrophenol.

4. Characterization of the carbon-nickel nanocomposites

Microstructural observation of the nanocomposites was carried out by using SEM. XRD patterns of the carbon-nickel nanocomposite were obtained by using a Bruker D8 Advance system with Cu Kα radiation. Raman spectroscopy was used to characterize the properties of the carbon-nickel nanocomposites and thus analyze the D-band, G-band, and 2D-band peaks.

Results and Discussion

1. Characterization of the carbon-nickel nanocomposites

The structural changes of carbon-nickel nanocomposites were examined by XRD. Figures 1(a) and 1(b) show the XRD patterns of pure fullerene (C_{60}) powder and the carbon-nickel nanocomposites, respectively. After heating fullerene (C_{60}) with $Ni(OH)_2$, the fullerene (C_{60}) 2θ peaks at 10.79°, 17.70°, 20.77°, 27.41°, 28.12°, 30.88°, and 32.79° disappeared; instead, a 2θ peak at 26.13° was observed as a diagnostic peak of graphitic carbon. In addition, peaks due to the nickel nanoparticles were seen at 2θ = 44.45°, 51.81°, and 76.31°.[10,12] The results showed that the $Ni(OH)_2$ powder was transformed into nickel nanoparticles upon heating at 700°C for 2 h. Comparison of the XRD patterns of the carbon-nickel nanocomposites with those of fullerene (C_{60}) clearly showed that the fullerene (C_{60}) structure changed and was eventually transformed into the graphitic carbon nanocomposites.

Raman spectroscopy was also used in our research to characterize the carbon nanomaterials.[21] Diamond crystals, having sp^3 hybridization bonds, appear at around 1332 cm^{-1}, and should be changed while large graphite crystals, having sp^2 hybridization bonds, appear at around 1580 cm^{-1} as Raman shift.[6,21] Amorphous graphitic carbon exhibited a broad asymmetric Raman peak at 1000-1600 cm^{-1} as a Raman shift.[6] Figure 2 shows the D-band, which appears as a broad peak at around 1341 cm^{-1}, and the G-band, which appears as a broad asymmetric peak at around 1575 cm^{-1}. In addition, the 2D-band was observed at around 2683 cm^{-1}. From the Raman shift data, the carbon-nickel nanocomposites may be seen as graphitic carbon crystals resulting from the transformation of fullerene (C_{60}) into carbon nanocomposites.[8,21]

Figure 3 shows the results for the electron microscopic studies of the carbon-nickel nanocomposites. The SEM images
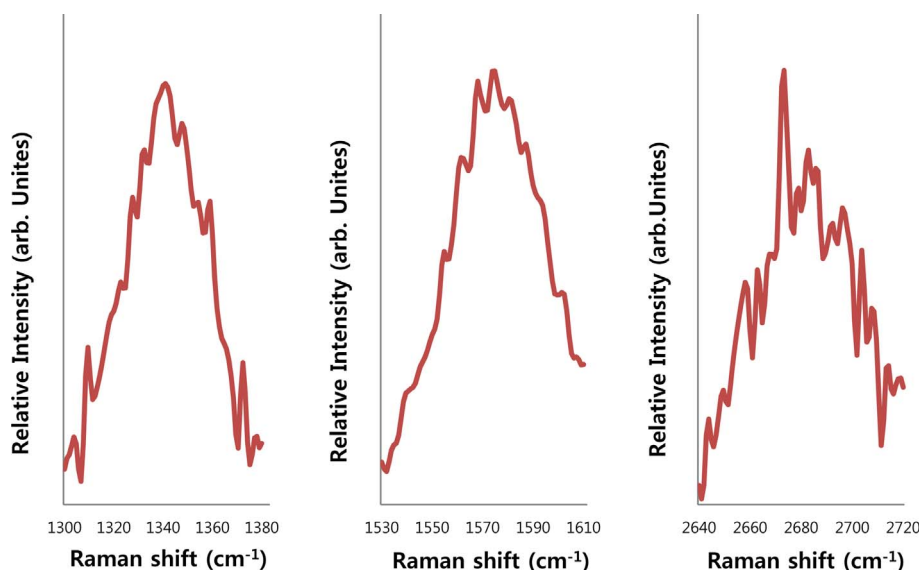
Figure 2. Raman spectrum of carbon-nickel nanocomposites.
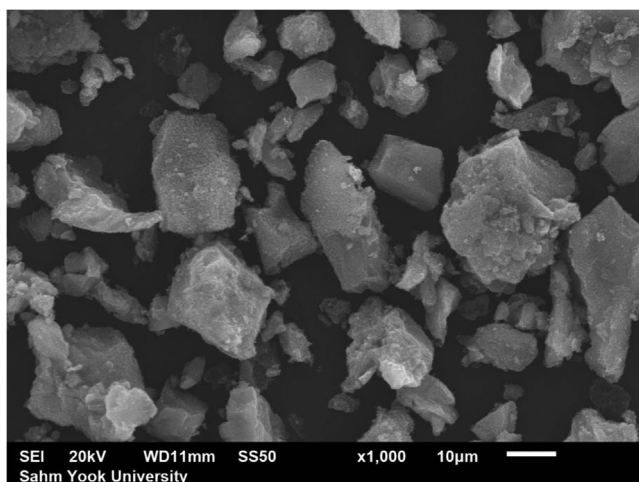
Figure 3. SEM images of carbon-nickel nanocomposites.

reveal a stone-like morphology of the carbon-nickel nanocomposites; further, the nickel nanoparticles were located on the carbon nanocomposites.

2. Catalytic activity of the carbon-nickel nanocomposites

A series of experiments were performed to study the reduction of 4-nitrophenol by using $NaBH_4$. Previously, it was shown that in the absence of a suitable catalyst, $NaBH_4$ hardly induced the reduction of 4-nitrophenol even after a prolonged reaction.[14,15,22] In the present study, the reduction of 4-nitrophenol was carried out to explore the effect of carbon-nickel nanocomposites as a catalyst. Figure 4 shows the results obtained from UV-vis spectroscopy for the reduction of 4-nitrophenol in the presence of $NaBH_4$ and a nanocatalyst. As the reaction progressed, the peak at 400 nm diminished and a new peak simultaneously appeared at 300 nm (Figure 4). The peak at 400 nm was the result of the formation of 4-nitrophenolate ions under alkaline conditions after the addition of $NaBH_4$.[15] Moreover, a color change from light yellow to colorless was observed during the reduction of 4-nitrophenol.

3. Kinetics of the reduction of 4-nitrophenol

Reaction rate is one of the key criteria for evaluating the efficiency of a nanocatalyst. In this experiment, the concentration of $NaBH_4$ was controlled at 1000 mg/L. It was assumed that the $NaBH_4$ concentration remained constant throughout the reaction. Based on this assumption, pseudo-first-order kinetics could be applied to evaluate the experimental kinetics data. The Langmuir-Hinshelwood model has been applied in many cases to study the kinetics of 4-nitrophenol reduction.[3,11,15,23] The kinetic equation for the reduction of 4-nitrophenol can be written as follows:
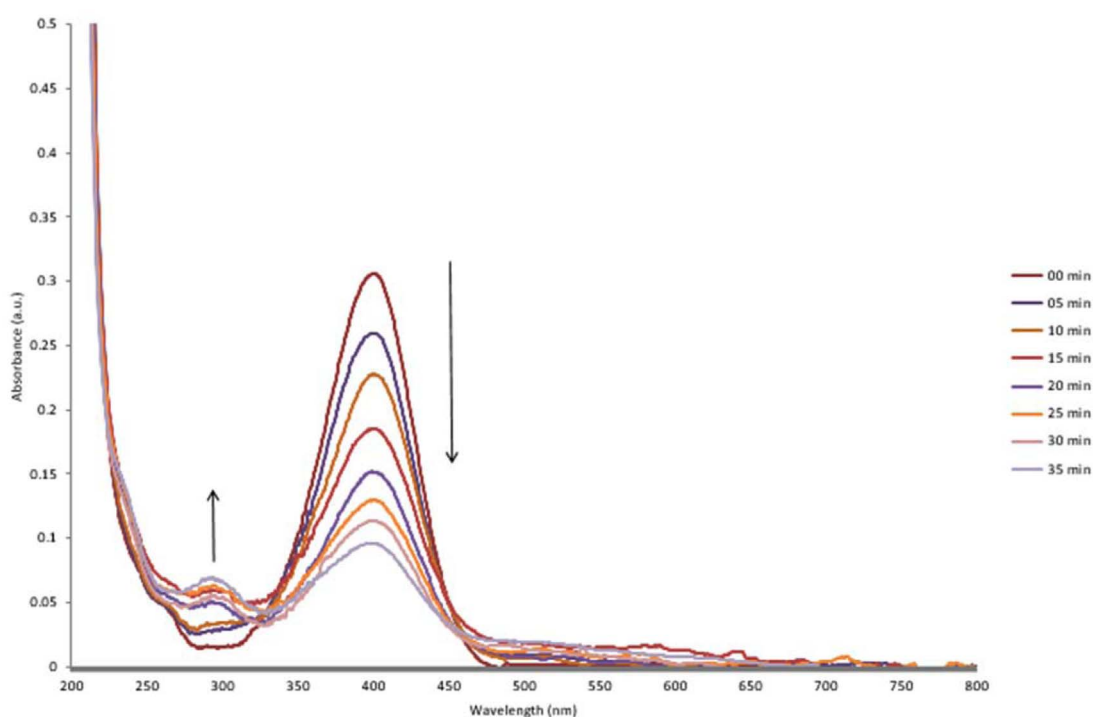
Figure 4. UV-vis spectra for the reduction of 4-nitrophenol with carbon-nickel nanocomposites as a catalyst in the presence of $NaBH_4$.
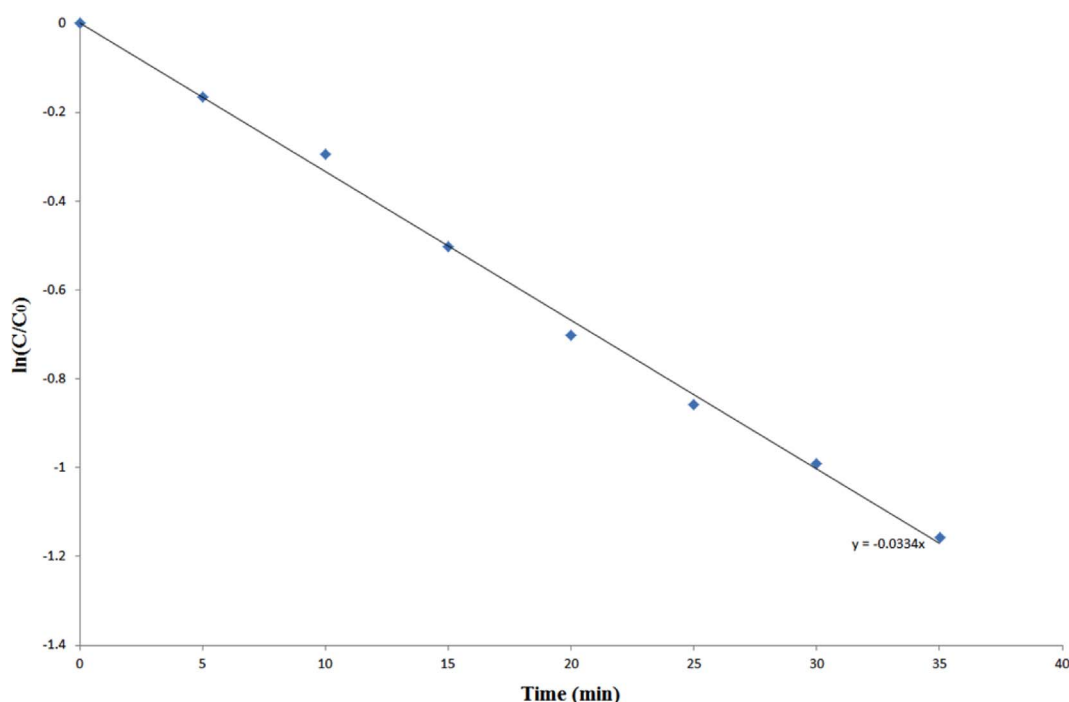
Figure 5. Kinetics for the reduction of 4-nitrophenol using carbon-nickel nanocomposites as a catalyst.

Table 1. Concentration Ratio $\ln(C/C_0)$ for the Reduction of 4-Nitrophenol with Carbon-Nickel Nanocomposites Catalyst as a Function of Time

Time (min)	0	5	10	15	20	25	30	35
4-Nitrophenol	0	-0.165	-0.295	-0.502	-0.703	-0.857	-0.991	-1.157

$$\ln (C/C_0) = -\,kt$$

where C_0 is the initial concentration of 4-nitrophenol, C is the concentration at time t, and k is the rate constant. Figure 5 shows that the reduction of 4-nitrophenol obeys a pseudo-first-order rate law. Table 1 lists the kinetics data for the catalytic reduction of 4-nitrophenol with carbon-nickel nanocomposites as a catalyst.

Conclusion

Carbon-nickel nanocomposites were synthesized through the reaction of $Ni(OH)_2$ and fullerene (C_{60}) at 700°C for 2 h. XRD patterns showed that the fullerene (C_{60}) structure changed and eventually transformed into a graphitic carbon nanocomposites. In the Raman spectrum, the D-band appeared at around at 1341 cm^{-1}, the G-band at around 1575 cm^{-1}, and the 2D-band at around 2683 cm^{-1}. SEM images showed that the product had a stone-like morphology and that the nickel nanoparticles were located on the carbon

nanocomposites. The results of UV-vis spectroscopy showed that the synthesized nanocatalyst exhibited excellent activity for the reduction of 4-nitrophenol in the presence of $NaBH_4$ at room temperature. Moreover, the kinetics of the catalytic activity of 4-nitrophenol followed the Langmuir-Hinshelwood model as a pseudo-first order reaction.

Acknowledgements

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