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ARAŞTIRMA MAKALESİ **RESEARCH PAPER**

Synthesis of Environmentally Friendly Carbon Nano Fibers with Methanol by Using CVD Technique

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Abstract: This study aims to investigate the suitability of methanol as a carbon source for the synthesis of carbon nanofibres (CNFs), currently used in wastewater, water, and air purification systems, by chemical vapor deposition (CVD) in the presence of NiO catalyst. Experimental studies were carried out in a tube furnace under isothermal conditions. Catalyst particles were loaded onto silicon wafers with <100> orientation by dip coating to grow CNFs. The reduction behavior of NiO powder at 1000 K under non-isothermal and isothermal conditions was investigated before CNF synthesis studies. The percentage reduction of NiO powder under non-isothermal conditions was 82.03%. The percentage reduction under isothermal conditions for 30 min was 78.03%. The experimental result obtained is very close to the theoretical value (78.57%). During CNF synthesis experiments, it was observed that CNF formation was not achieved at temperatures of 1000 - 1100 K due to the poor thermal decomposition of methanol. Pyrolysis of methanol increased with increasing synthesis temperature (1200-1300 K) and the resulting reducing gases reduced NiO to nickel and promoted CNF synthesis. SEM analysis revealed morphologically dense CNF formation under isothermal conditions for 20 min at 1300K synthesis temperature.

Keywords: Carbon nano fiber, chemical vapor deposition, environmentally friendly, methanol, NiO catalyst.

Çevre Dostu Karbon Nano Fiberlerin KBB Tekniği Kullanılarak Metanol ile Sentezlenmesi

***Sorumlu yazar:**
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Öz: Bu çalışma, NiO katalizör varlığında kimyasal buhar biriktirme (KBB) yöntemiyle günümüzde atık su arıtma, su ve hava arıtma sistemlerinde kullanılmaya başlanan karbon nano fiberin (KNF) sentezlenmesi üzerinde karbon kaynağı olarak metanolün uygunluğunun araştırılması amaçlamaktadır. Deneysel çalışmalar tüp fırında izotermal şartlar altında yapılmıştır. Karbon nanofiberlerin büyütülmesi için <100> yönelimli bir silikon levhalar daldırma kaplama yöntemi ile yüklenmiştir. NiO tozunun 1000 K'de izotermal olmayan ve izotermal koşullar altında indirgenme davranışı KNF sentezi çalışmalarından önce incelenmiştir. NiO tozunun izotermal olmayan koşullar altında indirgenme yüzdesi %82,03'tür. İzotermal koşullar altında 30 dakika boyunca indirgenme yüzdesi %78,03'tür. Elde edilen deneysel sonuç teorik değere (%78,57) çok yakındır. KNF sentez deneylerinde 1000-1100 K sıcaklıklarında metanolün zayıf termal parçalanma derecesi nedeniyle KNF oluşumu sağlanmadığı gözlemlenmiştir. Metanolün pirolizi artan sentez sıcaklığı (1200-1300 K) ile artmış ve ortaya çıkan indirgeyici gazlar NiO' in nikele indirgeyerek KNF sentezini teşvik etmiştir. Sentez sıcaklığı 1300 K olduğunda ise morfolojide 20 dakika izotermal şartlar altında yoğun KNF mikroyapısı oluştuğunu yapılan SEM analiz sonuçları ortaya koymuştur.

Anahtar kelimeler: Çevre dostu, karbon nano fiber, kimyasal buhar biriktirme, metanol, NiO katalizör .

INTRODUCTION

The potential for using lightweight, durable, and economical materials is constantly under investigation in materials science. In recent years, much attention has focused on researching environmentally friendly materials. One of these materials is carbon fiber (CF). CFs have applications in building materials and construction (Grace & Singh, 2005; Hegde et al., 2019), water and air purification systems (Chen et al., 2020; Roegiers & Denys, 2021), wastewater treatment (Matsumoto et al., 2012; Nawaz et al., 2022), wind energy and transport vehicles (Falzon, 2022; Puttaraju et al., 2020).

CF is composed primarily of carbon atoms and offers numerous benefits including exceptional rigidity, high tensile strength, low weight, remarkable chemical resistance, excellent heat tolerance, and minimal thermal expansion (Bhatt & Goe, 2017). CFs are produced using viscous liquid or softenable solid organic raw materials such as polyacrylonitrile, polyethylene, and phenolic resins (Özsin & Pütün, 2018). It is also manufactured by CVD using a hydrocarbon or carbon monoxide vapor phase, which allows the synthesis of nanoscale carbon fibers (CNFs) such as carbon nanotubes (CNTs). Chemical vapor deposition (CVD) is a technology for the deposition of a solid-state thin film on substrates from vapor species by chemical reaction (Lee & Hyun, 2016). The CVD synthesis of CNFs uses hydrocarbons such as propane, benzene, ethylene, acetylene, and natural gas as carbon sources (Manawi et al., 2018). The catalytic reaction is carried out by a transition metal/transition metal oxide catalyst such as Ni, Fe, Co or Fe_2O_3, Fe_3O_4 (Altay & Eroglu, 2013a, 2013b) or a metal alloy such as Fe-Ni or Ni-Cu (Altay & Eroglu, 2012).

CNFs were synthesized via the CVD method utilizing methanol, differing from the carbon sources documented in the literature (Manawi et al., 2018). NiO powder was used as a catalyst to synthesize carbon fiber. Scanning electron microscope (SEM) analysis characterized the obtained products' microstructures.

MATERIAL AND METHOD

The experimental apparatus is schematically shown in Figure 1. The experimental setup consists of a carrier gas cylinder (Ar), a horizontal tube furnace (MTI GS1100x) with a single heating zone programmable to a maximum temperature of 1373 K, and a ball gas flow meter (Dwyer). NiO powder was purchased from Sigma-Aldrich (Cat. No 637130, 99.8% purity based on trace metals analysis). Liquid methanol (99.5 % CH_3OH) was used as the source for reducing NiO to Ni. Methanol was transported to the reaction zone with high-purity argon gas (99.999%). Since carbon fiber synthesis occurs at high temperatures (1000 K-1300 K), the synthesis was carried out in a horizontal tube furnace. Argon gas was used to create an inert atmosphere in the thermal cycle stages at a 42.5 cm^3/min flow rate. Argon gas also played an important role in sweeping the air in the furnace before the experimental work. NiO particle size was stated to be 10-20 nm by the manufacturer. In the preparation phase of silicon wafer samples with <100> orientation substrates, alcohol was used to disperse nickel oxide particles by ultrasound, and then silicon wafers were dipped into the suspension. The silicon wafers were then submerged in the solution, enabling the loading of nickel oxide particles onto the substrate. The average methanol partial pressure in the experimental studies was 0.1716 atm. The flow rate of methanol (CH_3OH) ($F_{methanol}$) was estimated to be 8.8 cm^3/min according to Equation 1:

$$F_{methanol} = F_{Ar}\, P_m / (P_t - P_m) \quad (1)$$

Where F_{Ar} represents the flow rate of Ar gas (42.5 cm^3/min), P_m represents the vapor pressure of methanol vapor at 293.68±0.72 K and P_t represents the total pressure (1 atm) (Altay & Eroglu, 2019).

To investigate the reduction reaction between NiO powder and methanol derivatives under non-isothermal and isothermal conditions at 1000 K, oxide powder mass was measured before and after the experiment at room temperature by using an electronic balance (Radwag brand AS 220.R2 model) with a sensitivity ± 10^{-4} g. The rate of reduction percentage was calculated by Equation 2.

$$\text{Rate of reduction (\%)} = (m_p/m_i)x100 \quad (2)$$

where m_p is the mass of the product after the reaction and m_i is the mass of NiO mass before the reaction.

The experiments were carried out at a heating rate of 10 K/min. In the experimental study, parameters such as heating rate and holding time were programmed with the help of a temperature control unit. The experimental studies used a Quartz tube with 2.1 (O.D.) x 50 (L) cm. Before the experiment, NiO powders were positioned in the hot zone in alumina boats with dimensions of 13.90 mm x 8.53 mm x 80.68 mm. In the experimental setup, the outlet gas was given to the external environment in a controlled manner through a gas-washing bottle. Before each experiment, the ambient temperature of methanol was measured and methanol partial pressure was calculated (Altay & Eroglu, 2019). All CNF synthesis experiments were carried out under isothermal experimental conditions. Morphological characterization of the products obtained from the experimental studies was also carried out SEM device (Quanta FEG 250, FEI Company).

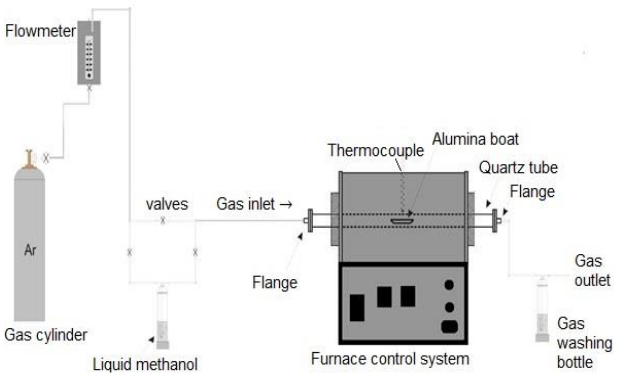

Figure 1. The schematic of the experimental apparatus.

RESULTS

The reduction behavior of NiO powder at 1000 K under non-isothermal and isothermal conditions was investigated before the CNF synthesis studies. The percentage reduction rate of NiO powder under non-isothermal conditions is 82.03%. At 1000 K for 30 minutes, the percentage reduction rate is 78.03%. The percentage reduction rate of theoretical NiO to nickel is 78.57%. The experimental result obtained is very close to the theoretical reduction value of NiO to Ni.

At 1000 K (within 30 and 45 minutes) and 1100 K (within 30 minutes) experimental conditions, it was determined from the SEM analysis results that carbon fiber was not synthesized. Fourier transform infrared spectroscopy (FTIR) and Differential Scanning Calorimeters (DSC) analysis results of NiO powder are given in previous studies (Altay & Eroglu, 2016). The FTIR results indicated that the minor $Ni(OH)_2$ phase was in the oxide powder. NiO's slight reduction to Ni was observed in the Ar atmosphere from the endothermic peak observed at 1150K in the DSC analysis (Altay & Eroglu, 2016). Figure 2 (a-d) shows SEM morphology images of the products obtained at 1200 K (at a higher temperature) for 30 and 60 minutes. In Figure 2 (a-b), it can be seen that CNFs are formed in small numbers in the microstructure after 30 minutes. In Figure 2 (c-d), CNFs are relatively more numerous after 60 minutes. The diameter of the CNFs synthesized after 30 minutes is approximately 64.44 nm, while those synthesized after 60 minutes are about 218.91 nm. As a result of the time for diffusion of the carbon atoms or the sintering of the catalyst particles, the diameter of the CNFs may be increased (Altay & Eroglu, 2013b).

SEM morphology images of the products were obtained at 1300 K for 20 and 45 minutes are given in Figure 3 (a-b). As shown in Figure 3 (a-b), the morphology of the CNFs was more homogenous and intense compared to Figure 2 (a-d). From the morphology, the CNF's diameter was approximately 78.99 nm and 92.32 nm after 20 min and 45 min, respectively. An increase in the tube diameter of the CNFs has been observed as the synthesis time increases.

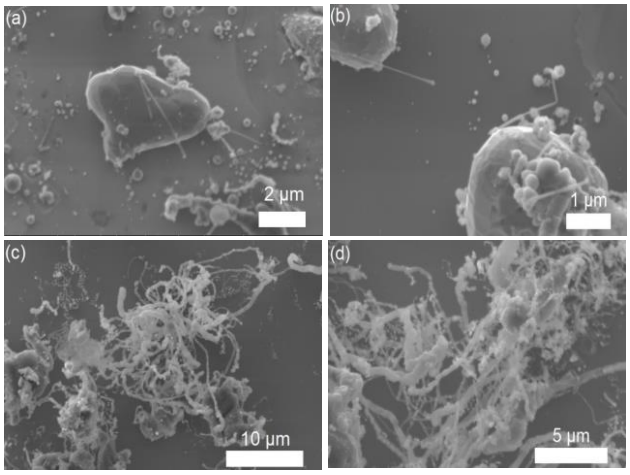

Figure 2. SEM morphology images of the products; (a-b) obtained at 1200 K for 30 min, (c-d) obtained at 1200 K for 60 min.

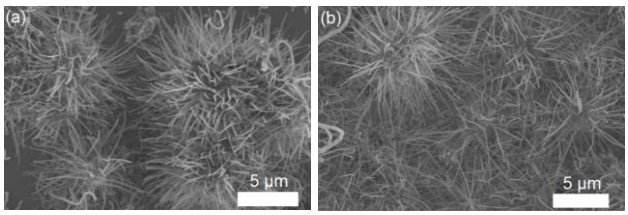

Figure 3. SEM morphology images of the products; (a) obtained at 1300 K for 20 min, (b) obtained at 1300 K for 45 min.

DISCUSSION

Methanol decomposition is a common practice. It produces hydrogen and carbon monoxide and the reaction equation can be expressed as Equation 3 (Bai et al., 2018).

$$CH_3OH \rightarrow CO + 2H_2 \quad (3)$$

As seen in Equation 3, hydrogen and carbon monoxide, which are important reducing gases, are released by the decomposition of methanol. In the growth of nanostructured carbon, it is important that the catalyst is in the form of a metal rather than a metal oxide. (Altay & Eroglu, 2013b). Reducing gases formed by the decomposition of methanol helps the growth of CNFs by reducing the oxide catalyst powder (Altay & Eroglu, 2012) It is thought that the lack of growth of CNFs is due to the inability of NiO to catalytically convert to metallic nickel at low synthesis temperatures.

The reduction of NiO to Ni was due to H_2 and CO produced by the CH_3OH pyrolysis reaction. In the reducing condition at 1200-1300 K, the methanol–derived species (e.g., H_2, CO) can reduce NiO to Ni via the following overall reactions as given in Equations 4 and 5.

$$NiO_{(s)} + H_{2(g)} \rightarrow Ni_{(s)} + H_2O_{(g)} (\Delta G^\circ_r = -49267J \text{ at } 1200 K;\ \Delta G^\circ_r = -52112J \text{ at } 1300 K) \quad (4)$$

$$NiO_{(s)} + CO_{(g)} \rightarrow Ni_{(s)} + CO_{2(g)} (\Delta G^\circ_r = -46101J \text{ at } 1200 K; \Delta G^\circ_r = -46007J \text{ at } 1300 K) \quad (5)$$

The general chemical reactions for the reduction of NiO with CH_3OH can occur, based on the Gibbs free energy values at 1200 and 1300 K of the equilibrium solid and gas phase compositions, as shown in Equation 4 and Equation 5.

CONCLUSION

This study investigated the synthesis of environmentally friendly CNFs with methanol at the temperature range of 1000 K to 1300 K using the CVD technique. The experimental results indicate that the decomposition of CH_3OH is not sufficient for the formation of C at temperatures of less than 1200 K. It was demonstrated that CNFs were grown at substrate temperatures in the range of 1200–1300 K. It is proposed that at high temperatures of 1200 and 1300 K, NiO is essentially reduced to Ni by a CH_3OH decomposition product, H_2, and CO. As the diameter size of CNFs is related to the particle size of the catalyst, it is revealed that as the catalyst particles are sintered at higher temperatures and for a longer synthesizing duration, the diameter growth of CNFs also increases. This study revealed that CNFs used in wastewater treatment and water/air purification systems can be synthesized by CVD technique using a readily available methanol source.

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