FULL PAPER

Effects of the addition of nano-MnO₂ on in situ catalytic formation of carbon nanotubes during the coking of phenolic resin

Jin-Yu LI^{1,2}, Bing-Jie TANG¹, Jun-Bo TU^{1,†}, Jun-Cong WEI^{1,2} and Yi-Long WANG³

¹North China University of Science and Technology, Hebei province key laboratory of inorganic nonmetallic materials, 063009 Tangshan, PR China

²The State Key Laboratory of Refractories and Metallurgy (Wuhan University of Science and Technology), 430081 Wuhan, PR China

³Tangshan Guoliang Special Refractory Company, 063000 Tangshan, PR China

Hollow multi-walled carbon nanotubes (MWCNTs) were formed in situ by catalytic cracking of phenolic resin with addition of nano-manganese dioxide (nano-MnO₂) as a catalyst. The effects of catalyst content, coking temperature and heating rate on in situ growth of carbon nanotubes (CNTs) were investigated. The composition and microstructure were characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy and laser-Raman spectrum. The results showed that nano-MnO₂ could catalyze phenolic resin to partly form MWCNTs inside of the materials, which transformed pyrolytic carbon structure and improved graphitization degree of the material after carbonization. With the increase of catalyst content, the length of CNTs decreased and the optimum addition amount was at 1.0 wt %. The higher the carbonization temperature, the bigger the activity of catalyst particles. The optimum growth temperature of CNTs was at 1200°C. At a higher heating rate, hydrocarbon molecules were hard to deposit on the surface of the catalyst particles to form CNTs. CNTs obtained at a heating rate of 2°C/min possessed the highest degree of graphitization. The growth of carbon nanotubes was accordance with the mechanism of top growth.

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1. Introduction

MgO-C refractories have been widely used in the linings of converters, electric arc furnaces, refining ladles due to their excellent thermal, chemical and mechanical properties.^{1),2)} These excellent performances depend on the content of the residual carbon in MgO-C refractories.³⁾ However, conventional MgO-C refractories comprise a high amount of carbon up to 10–18 wt %, which would cause some problems in service, such as high heat loss during the process of smelting and carbon pick-up in clean steel and high purity steel making. Meanwhile, there will be a large number of CO and CO₂ emissions, which enhance greenhouse effect. To overcome these, low-carbon MgO-C refractories have been widely developed and employed.⁴⁾ However, the decrease in carbon content of magnesia carbon refractories lead to a series of problems. For example, the thermal conductivity decreases and elastic modulus of MgO-C composites increase and hence the thermal shock resistance of the materials becomes worse. Meanwhile, the wettability of molten steel and slag to refractories is enhanced and the corrosion increase.

In view of this problem, the concept of nanoscale refractories was put forward in the early 21 century.⁴⁾ That is to

say, nano particles are the core and consist of refractory powder, binder and so on. The design of nanostructured matrix was initially achieved by introducing nano scale carbon black or composite graphitic carbon black into the binder or matrix. Japan's Kyushu firewood Co., Ltd.^{5)–8)} took the lead in reporting the use of a binder doped with B₄C composite graphitic carbon black, and developed a low carbon magnesia carbon brick with a carbon content of 1.0 wt %. It was found that its performance was similar to that of magnesia carbon bricks with carbon content of 18 wt %. With the development of nanostructured substrates, researchers have tried to introduce carbon nanotubes (CNTs)/carbon nanofibers and other one-dimensional nanostructured carbon into matrix.^{9)–15)} Compared with nano carbon black, CNTs are curled up by single or multilayer graphite sheets with high strength and modulus of elasticity, which can produce enhanced toughening effect in composite materials, such as pulling out, bridging and micro crack deflection. The introduction of CNTs/carbon nanofibers into carbon composite refractories will improve the strength and fracture toughness of materials. In the past studies, CNTs/carbon nanofibers were often introduced into refractory materials by adulteration in binder or directly added to the matrix. For example, Aneziris et al. partially or completely substituted CNTs for flake graphite or other carbon materials, in Al₂O₃-C

[†] Corresponding author: J.-B. Tu; E-mail: tujunbo@126.com

refractories. It was founded compared with blank sample, the modulus of rupture of the materials with 0.3 wt % CNTs increased by about 94%.¹⁶⁾ The relative plasticity deformation of the material increased by 36% under the 40% critical load, and the crack propagation rate of the material reduced about one order of magnitude. The fracture toughness of the materials was greatly improved. Thus the thermal shock resistance of the low carbon composite refractories was significantly improved. Luo ming et al. substituted commercial CNTs as carbon source for a part of graphite to prepare Al₂O₃-C refractories and also found that the addition of CNTs not only improved the cold bending strength of the refractories but also the elastic modulus significantly.¹⁷⁾

Though the direct addition of CNTs in carbon containing composites could significantly improve the performance of low carbon composite refractory materials in some way, it is prone to encounter the difficulties of heterogeneity and expensive costs. In recent years, the modification of phenolic resin or coal-tar pitch by transition metal elements has become one of the hotspots in improving the secondary carbon structure of carbon composite refractories. Its principle was that the hydrocarbon gas released by the phenolic resin or coal-tar pitch during the pyrolysis process were cracked into carbon microspheres, CNTs and carbon nanofibers under the action of the catalyst, thus forming an anisotropic secondary carbon structure, improving the carbon residue rate and oxidation resistance of secondary carbon.^{18)–21)} Zhu Tianbin et al. added nickel catalyst in low carbon MgO-C bricks finding that pyrolysis carbon structure was changed after carbonization and the thermal performance was improved as well.²²⁾ Wei Guoping et al. prepared CNTs by adding iron catalysts and found the oxidation resistance of the products was improved significantly compared with the samples without catalysts.²³⁾

At present, many researches on in situ growth of CNTs focus on the use of transition metal as catalysts, such as iron, cobalt, nickel and their alloy.^{24)–28)} Luo Ming et al.²⁴⁾ reported the fabrication of CNTs using a thermosetting phenolic resin as a carbon source and a catalyst made of nickel nitrate dissolved ethanol solution and heating at a certain temperature. H. M. Cheng et al.²⁹⁾ achieved single-walled carbon nanotubes using benzene as a carbon source and ferrocene as a catalyst heating at a temperature range about 1100–1200°C. Stamatina et al.³⁰⁾ fabricated a large number of multi-walled carbon nanotubes (MWCNTs) by doping phenolic resin with ferrocene as a catalyst and heating at 900°C in Ar atmosphere. The aim of this experiment is to explore a new kind of effective catalyst. Manganese is also a transition metal element and relatively cheap and easy to obtain. In the present work, a kind of nano-manganese dioxide (nano-MnO₂) catalyzed phenolic resin was synthesized and its pyrolysis carbon structure was investigated compared with as-received phenolic resin. This method is simple, free from environmental temperature, and also feasible in industrial production. The results of the study are expected to provide theoretical

guidance for the performance optimization of carbon containing refractory materials such as low carbon magnesia carbon bricks.

2. Experimental

2.1 Materials

Raw materials used were thermosetting phenolic resin powder, nano manganese dioxide (MnO₂, purity ≥ 99.9 wt %, d ≥ 50 nm).

2.2 Preparation of modified phenolic resin

A suitable amount of nano-MnO₂ was added to the phenolic resin powder, and then the modified phenolic resin was obtained after mixing evenly. Then a certain amount of doped phenolic resins were weighed and filled into a mould and then pressed at a pressure of 150 MPa by hydraulic pressure to cylindrical samples of $\varnothing 30$ mm × 10 mm. The pressed samples were dried at 110°C for 12 h, and then further tempered at 200°C for another 24 h. Finally the as-cured samples were treated in an electric furnace to coking temperatures for 3 h in a sagger with graphite powder. The flowchart is shown in **Fig. 1**.

2.3 Characterization

The phase compositions of specimens was characterized by X-ray-diffraction (XRD, D/MAX2500PC, Rigaku Corporation, Japan). Data was collected over Bragg's angles (2θ) range of 10–90° at a speed of 10°/min. The morphology was observed using scanning electron microscope (SEM, S-4800, Japan) and transmission electron microscope (TEM, JEM-2010, Japan), respectively. The graphitization degree of pyrolysis carbon was characterized by Laser Raman spectrometer ($\lambda = 523$ nm, power = 3.0 mW, 10 times objective). The calculation formula was as follows: $R = I_D/I_G$ [I_D -1350 cm⁻¹ amorphous carbon peak (D peak) area, I_G -1580 cm⁻¹ crystalline graphite peak (G peak) area]. The smaller the R value, the higher the degree of graphitization. The thermal decomposition

Fig. 1. The experimental flow chart.

temperature of CNTs was measured through differential thermal/thermo-gravimetric analyzer (DSC, NETZSCH STA449C, Germany), by heating from room temperature to 1000°C at the rate of 10 °C/min in air atmosphere.

The outer part of the samples after carbonization was cut off and the inter part of materials was grinded into 200 mesh powders for XRD, DSC and Raman spectra. The samples also were broken into 3 mm × 3 mm × 3 mm particles for microstructure detection.

3. Results and discussion

3.1 Catalyst concentration

In order to investigate the effects of nano-MnO₂ and its additions on the catalytic cracking of phenolic resin, 0%, 1.0, 1.5 and 2.0 wt % nano-MnO₂ powder were incorporated into phenolic resin to obtain four different doped phenolic resin samples, respectively.

Figure 2 shows the microstructure of the samples after coking at 1200°C. Compared with the reference sample without addition of nano-MnO₂, the samples with 1.0, 1.5 and 2.0 wt % nano-MnO₂ catalyst in situ formed a large amount of fibrous substances. The fibrous substances in the specimen with 1.0 wt % nano-MnO₂ developed well, with the length of 1.93–2.45 μm and uniform distribution. As the catalyst content increased to 1.5 wt %, the length of the fibrous substances decreased significantly, which was 1.45–1.83 μm. But the quantity of fiber produced increased. Further increasing the content of the catalyst to 2.0 wt %, the quantity of the fibrous substances increased while the length decreased to 1.02–1.43 μm.

Higher magnification (**Fig. 3**) revealed that the formed fiber had a hollow structure. Combined with the XRD analysis in **Fig. 4**, the fiber was deduced to be CNTs produced by nano-MnO₂ catalytic cracking inside of the modified phenolic resin. Moreover, with the increase of the catalyst addition amount, the length of the CNTs decreased obviously. The reason is that the higher the catalyst content in phenolic resin, the more active sites inside the materials, so the number of in situ formed CNTs increased. However, the amount of hydrocarbon gas produced by cracking of

phenolic resin was limited. Therefore, with the increase of catalyst content, the number of in situ formed CNTs increased and the length decreased inside of the materials. CNTs in the samples with 1.0 wt % nano-MnO₂ catalyst had the greatest length, quantity and uniform distribution. Based on the content of catalyst and the growth of CNTs modified in situ synthesis of phenolic resin, a conclusion could be drawn that 1.0 wt % is the optimum amount for catalytic cracking of phenolic resin by nano-MnO₂.

XRD analysis (**Fig. 4**) was performed for all the samples with different amount of nano-MnO₂ catalyst to examine the phase evolution after coking. For all the nano-MnO₂ doped samples, diffraction peak was detected at $2\theta = 26.55^\circ$ corresponding to the graphite (002) crystal plane, which indicated that there was crystalline graphite formed due to the catalysis of nano-MnO₂. However, with increase in catalyst content, the intensity of the diffraction peak of graphite was gradually weakened. Combined with the microstructure observation (**Fig. 2**), it could be deduced that as the amount of the catalyst increased, the quantity of CNTs formed increased while the crystallization degree of the resulting CNTs decreased. The optimum effect on improving pyrolysis carbon structure of phenolic resin was achieved when 1.0 wt % nano-MnO₂ as catalyst was added.

Fig. 3. The higher magnification SEM images of the sample shown of **Fig. 2(b)**.

Fig. 2. The SEM micrographs of the modified phenolic resin samples with different amount of nano-MnO₂ after coking at 1200°C for 3 h: (a) 0%, (b) 1.0 wt %, (c) 1.5 wt %, (d) 2.0 wt %.

Fig. 4. The XRD patterns of the samples with 0%, 1.0, 1.5, 2.0 wt % nano-MnO₂ coked at 1200°C.

The added nano-MnO₂ catalyst could adsorb the hydrocarbon gas generated during the pyrolysis of phenolic resin and deposit it to form CNTs inside of the material. As increasing the catalyst amount, the catalyst particles in pyrolytic carbon gradually increased and the active sites capable of adsorbing and depositing hydrocarbon molecules increased. Therefore, the quantity of the formed CNTs increased and the length decreased notably. Moreover, as the distribution density of the catalyst particles increased, the CNTs reunited with each other winding seriously and consequently the graphitization degree reduced. In comparison, the CNTs of the specimens with 1.0 wt % nano-MnO₂ had a well developed morphology, higher length and uniform distribution, which could strengthen and toughen up the materials.

3.2 Coking temperature

In order to investigate the effects of coking temperature on the growth of CNTs by nano-MnO₂ catalytic pyrolysis of phenolic resin in situ, the coking temperature of the modified phenolic resin with 1.0 wt % nano-MnO₂ catalyst was set at 800, 1000 and 1200°C, respectively.

Figure 5 shows the microstructure of the modified phenolic resin coked at different temperatures. After coking at 800 and 1000°C [Figs. 5(a) and 5(b)], no new substances were observed except some small particles scattering inside of the material. As further increasing the coking temperature to 1200°C, some CNTs of 1.56–4.36 nm in diameter and 85.17–234.37 nm in length appeared. The reason may be that the activity of nano-MnO₂ catalyst was not high enough at a lower temperature to adsorb the hydrocarbon gas produced by catalytic cracking. With increase in temperature, the activity of nano-MnO₂ catalyst was improved and could adsorb hydrocarbons in time to form CNTs.

Snoeck and his teammates studied the growing mechanism of carbon fiber prepared by chemical vapor deposition and pointed out that the chemical potential between the active carbon atom and the carbon fiber structure generated by hydrocarbon cracking was the driving force of carbon

fiber growth.³¹⁾ Based on this theory, the reaction equilibrium constant (K) of the nucleation of the CNTs can be expressed as follows:

$$K = \exp\left(-\frac{\mu_C^0 + 2\mu_{H_2}^0 - \mu_{C_{xH_y}}^0}{RT}\right) \quad (1)$$

Where $T(K)$ is the carbonization temperature. According to the expression of equilibrium constant K , the nucleation power of CNTs increases with the increasing heat treatment temperature. According to the kinetics, the higher heat treatment temperature, the higher the activity of the catalyst, which was helpful to the nucleation of CNTs. The theoretical analysis is consistent with the experimental results obtained in Fig. 5.

Figure 6 shows the XRD patterns of the modified phenolic resin with 1.0 wt % nano-MnO₂ catalyst fired at different temperature. No new phase was detected and pyrolytic carbon existed still as an amorphous state at 800 and 1000°C, indicating that nano-MnO₂ had no catalytic effect on the phenolic resin at lower temperatures. At 1200°C, the diffraction peaks of graphite appeared at $2\theta = 26.73^\circ$, indicating that the catalytic activity of nano-MnO₂ was improved and could adsorb and deposit the activated carbon atoms to form CNTs.

Figure 7 displays the laser Raman spectra of samples with 1.0 wt % nano-MnO₂ catalyst coked at different temperature. The calculations indicated that the R value at temperature of 800, 1000 and 1200°C were 1.76, 1.50 and 1.16, respectively. The graphitization degree of the modified phenolic resin carbonized at 1200°C was the highest, which was in accordance with the above microstructure observation. Consequently, it could be concluded that nano-MnO₂ catalysis pyrolysis of phenolic resin in situ to produce the CNTs requires a higher processing temperature, and the temperature of 1200°C is suitable temperature for the CNTs growth.

In summary, nano-MnO₂ show no catalytic effect on phenolic resin at a lower carbonization temperature of 800, 1000°C and could not adsorb carbon-containing gas to deposit on the surface of the catalyst particles. As the temperature increased to 1200°C, the activity of nano-MnO₂ increased, adsorbed carbon-containing gas mole-

Fig. 5. The SEM micrographs of the specimen with 1.0 wt % nano-MnO₂ catalyst after coking at different temperatures: (a) 800°C, (b) 1000°C, (c) 1200°C.

Fig. 6. The XRD patterns of the specimen with 1.0 wt % nano-MnO₂ catalyst fired at 800, 1000 and 1200°C.

Fig. 7. The Raman spectra of the specimen with 1.0 wt % nano-MnO₂ catalyst fired at 800, 1000 and 1200°C.

Fig. 8. The SEM micrographs of the specimen with 1.0 wt % nano-MnO₂ catalyst fired at 1200°C at different heating rates: (a) 2°C/min, (b) 5°C/min, (c) 10°C/min.

cules, deposited them on the catalyst surface, catalyzed them into active carbon atoms, and finally formed a proper amount of CNTs.

3.3 Heating rate

In order to investigate the effects of heating rates on the in situ formation of CNTs by nano-MnO₂ catalytic pyrolysis of phenolic resin, the samples with 1.0 wt % of nano-MnO₂ were coked at 1200°C for 3 h at the heating rates of 2, 5 and 10°C/min, respectively.

After coking at 1200°C for 3 h, CNTs could be all observed at the heating rates of 2, 5 and 10°C/min in Figs. 8(a)–8(c). The CNTs [Fig. 8(a)] exhibited smooth surface and uniform distribution. And the length of CNTs was 85.17–234.37 nm. As the heating rate increased to 5°C/min, the length of the CNTs increases to 38.62–45.63 μm, but the surface was rough [Fig. 8(b)]. The microstructure of CNTs formed at 10°C/min showed in Fig. 8(c). The CNTs obtained had not only a small number, but also a smaller length, convolving each other heavily.

The reason may be as follows: during the growth process of CNTs, hydrocarbon molecules generated by nano-MnO₂ catalytic cracking could be adsorbed and deposited to form CNTs. At a lower heating rate, there were less hydrocarbon gas formed so that the quantity and length of

Fig. 9. XRD patterns of the specimen with 1.0 wt % nano-MnO₂ catalyst fired at 1200°C at different heating rates.

CNTs were also limited. The catalyst had enough time to adsorb and deposit carbon and hydrogen atoms to form CNTs with smooth surface and uniform structure. As the heating rate increased to 5°C/min, there were a large number of hydrocarbon molecules produced depositing on the catalyst surface to generate longer CNTs. At this heating rate, the catalytic activity of the catalyst was unstable, and the activity of the activated carbon atoms was not high, resulting in the heterogeneous structure of the CNTs. At higher heating rates of 10°C/min, the volatilization rate of the hydrocarbon gas from the pyrolytic carbon was too high to hard to be timely adsorbed and deposit to form CNTs with bigger length.

Figure 9 shows XRD patterns of the samples with 1.0 wt % nano-MnO₂ catalyst after coking at 1200°C at different heating rates. For all samples, graphite phase was detected. Nevertheless, the intensity of the diffraction peak was different. The specimen at the heating rate of 5°C/min presented the weakest intensity peak, indicating low graphitization degree. In contrast, the peak intensity of the graphite crystal of the sample at 2°C/min was the highest, suggesting the highest crystallinity.

Figure 10 is the Raman spectra of the specimens with 1.0 wt % nano-MnO₂ catalyst coked at 1200°C at heating rates of 2, 5, 10°C/min, respectively. The calculations indicate that the R values were 1.16, 1.38 and 1.31, respectively. By comparison, the graphitic degree was the lowest at 5°C/min, and highest at 2°C/min. The results are consistent with the XRD analyses.

Accompanying with the analyses of Fig. 8, the curling degree and surface roughness of CNTs increases with an increase in heating rate and in-situ formed CNTs with the highest graphitization degree were achieved with relatively straight shape and evenly distribution at the heating rate of 2°C per minute. Comprehensive analyses shows that the uniformity of CNTs is related to heating rate and graphitization degree.

In order to clarify the antioxidation effect of the in-situ formed CNTs in modified phenolic resin at different heating rates. The thermal decomposition temperature of CNTs was measured by heating from room temperature to 1000°C at the rate of 10°C/min in air atmosphere. It can be clearly seen from Fig. 11 that the decomposition tem-

Fig. 10. The Raman spectra of the specimens with 1.0 wt % nano-MnO₂ catalyst fired at 1200°C at different heating rates.

Fig. 11. The DSC curves of the specimens after coking at different heating rates.

perature of pyrolytic carbon decreased with the increase of heating rate. The samples fabricated at 2°C/min exhibited the biggest thermal decomposition temperature to the highest degree of graphitization of pyrolytic carbon. The sample at the heating rate of 10°C/min formed a small amount of in situ CNTs intertwining with each other and had the lowest thermal decomposition temperature. The samples treated at 5°C/min showed intermediate thermal decomposition temperature.

The above experimental results showed that the amount of CNTs generated at different heating rates was different, and the degree of graphitization was also different. When the heating rate was at 2°C/min, the CNTs catalyzed by nano-MnO₂ had well developed morphologies, uniform structure, and evenly dispersion in pyrolytic carbon and the highest crystallinity. As increasing heating rate to 5°C/min, the amount of hydrocarbon molecules deposited on the catalyst surface increased and hence the amount of CNTs generated significantly increased. However, the catalytic effect of nano-MnO₂ weakened due to a few number of real activated carbon atoms. As a result, although the great amount of CNTs generated at high heating rate, the degree of graphitization was low. As increasing the heating rate to 10°C/min, the hydrocarbon gas generated during the cracking escaped from system failing to be deposited on the surface of the catalyst particles. Consequently, the catalyst adsorbed less carbon-containing gas, forming CNTs of intertwined, curl shape.

Fig. 12. The SEM micrographs of 1.0 wt % nano-MnO₂ modified phenolic resin fired at 1200°C.

3.4 The growth mechanism of CNTs by catalysis of nano-MnO₂

Figure 12 shows the microstructure of 1.0 wt % nano-MnO₂ catalyzed phenolic resin specimens coked at 1200°C. On the top of each CNT there was one particle, identified as MnO₂ by EDS analysis [Fig. 12(b)], suggesting nano-MnO₂ catalytic pyrolysis of phenolic resin to form in situ CNTs according with the top growth mechanism.

In order to further investigate CNTs growth mechanism of the manganese dioxide catalytic cracking of phenolic resin in situ, high resolution transmission electron microscope was employed to determine the specimen. It could be seen clearly that the fiber had a hollow structure [Figs. 13(c) and 13(d)] and the tube wall was curled by multi-layer graphite sheet [Figs. 13(e) and 13(f)]. The interlayer spacing was 0.3460 nm in conformity with the spacing of graphite (002) crystal plane detected by XRD, implying that the fibrous structure belongs to the MWCNTs. The inner diameter range of the CNTs was 30.40–58.72 nm, while the outer diameter was 60.30–89.90 nm. The diffraction patterns of the CNTs [Fig. 13(g)] were composed of three concentric circles, corresponding to the crystal plane (002), (100) and (110) of graphite according to calculation, respectively.

A particle was clearly observed at the top of the CNT in Figs. 13(a) and 13(b). The EDS spectrum of point A [Fig. 13(b)] proved to be the catalyst of MnO₂ [Fig. 13(h)]. A conclusion could be drawn that in situ formation of CNTs by catalytic cracking of phenolic resin by nano-MnO₂ was accordance with top growth mechanism.

The top growth model views: hydrocarbon gas produced by heat treatment catalytic cracking is adsorbed on the surface of catalyst particles, then transform active carbon atoms under the affect of one catalyst. The active carbon atoms will diffuse or across the catalyst reaching at the interface between CNTs and catalyst. The accumulation of a large number of active carbon atoms could achieve sustained growth of CNTs. During the growth of CNTs, the catalyst particles are always located at the top of CNTs and migrate with the growth of CNTs.

4. Conclusions

MnO₂ modified phenolic resin was synthesized at 1200°C and the phase composition and microstructure of pyrolysis carbon of as-received thermosetting phenolic resin were investigated. The effects of catalyst content, coking temperature and heating rate on the morphology

Fig. 13. The TEM photographs of pyrolytic carbon doped with 1.0 wt % nano-MnO₂ after coking at 1200°C.

and microstructure of catalytic formation of CNTs were investigated and the growth mechanism of CNTs was also discussed. Based on the above results, the follow conclusions can be drawn:

(1) MnO₂ nano-particles could act as a catalyst in in situ growth of CNTs by catalytic cracking of phenolic resin. With increase in catalyst content, the quantity of in situ formed CNTs inside of the materials increased and more catalysts were left while the length was significantly reduced. 1.0 wt % nano-MnO₂ is the optimum content of in situ growth of CNTs in phenolic resin.

(2) Nano-MnO₂ particles as catalyst had low activity at low temperature, and was hard to adsorb hydrocarbon molecules produced by pyrolytic cracking of phenolic resin. Increasing the coking temperature could improve the activity of the catalyst. In this experiment, 1200°C was the optimum coking temperature for in situ CNTs growth of nano-MnO₂ catalyzed phenolic resin.

(3) At a lower heating rate, the number of hydrocarbon molecules produced by catalytic cracking was limited and hence a small amount of CNTs with low length were pro-

duced. At a higher heating rate, hydrocarbon molecules was not easy to be deposited on the surface of the catalyst and the intertwined CNTs with lower length are formed. Research suggested that CNTs heated at 2 °C/min had good morphology, uniform structure and the highest degree of graphitization. The CNTs formed at 5 °C/min had the biggest length.

(4) The nano-MnO₂ particles as catalyst were always located at the top of CNTs and migrated with the growth of CNTs, which belonged to the top growth mechanism.

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References

- 1) E. M. M. Ewais, *J. Ceram. Soc. Jpn.*, **112**, 517–532 (2004).
- 2) E. P. Heikkinen, T. Kokkonen, R. Mattila and T. Fabritius, *Steel Res. Int.*, **81**, 1070–1077 (2010).
- 3) M. Bag, S. Adak and R. Sarkar, *Ceram. Int.*, **38**, 4909–4914 (2012).
- 4) T. Ochiai, *Refract.*, **56**, 152–159 (2004).
- 5) S. Behera and R. Sarkar, *Ironmak. Steelmak.*, **43**, 130–136 (2016).
- 6) S. Takanage, T. Ochiai and S. Tamura, UNITECR'03, Osaka, Japan (2003) pp. 521–524.
- 7) S. Tamura, T. Ochiai and T. Matsui, *Nippon Steel Tech. Rep.*, **98**, 18–28 (2008).
- 8) T. Ochiai, *J. Tech. Assoc. Refract. Jpn.*, **25**, 4–11 (2005).
- 9) D. Yoshitsugu, K. Morikawa and J. Yoshitomi, UNITECR'07, Dresden, Germany (2007) pp. 349–352.
- 10) T. B. Zhu, Y. W. Li, S. B. Sang, S. L. Jin, Y. B. Li, L. Zhao and X. Liang, *Ceram. Int.*, **40**, 4333–4340 (2014).
- 11) C. G. Aneziris, S. Dudczig, J. Hubalkova, M. Emmel and G. Schmidt, *Ceram. Int.*, **39**, 2835–2843 (2013).
- 12) V. Rongos and C. G. Aneziris, *Ceram. Int.*, **38**, 919–927 (2012).
- 13) Y. Lwahori, S. Ishiwata and T. Ishikawa, *J. Jpn. Soc. Compos. Mater.*, **30**, 219–226 (2004).
- 14) Y. Matsuo, M. Tanaka, J. Yoshitomi, S. Yoom, J. Miyawaki and I. Mochida, UNITECR'11, Kyoto, Japan (2011) pp. 959–962.
- 15) V. Pilli and R. Sarkar, *J. Alloy. Compd.*, **735**, 1730–1736 (2017).
- 16) M. Bag, S. Adak and R. Sarkar, *Ceram. Int.*, **38**, 2339–2346 (2012).
- 17) M. Luo, Y. W. Li, S. L. Jin, S. B. Sang, L. Zhao and Y. B. Li, *Mater. Sci. Eng.*, **548**, 134–141 (2012).
- 18) I. Stamatina, A. Morozan, A. Dumitru, V. Ciupina, G. Pradan, J. Niewolski and H. Figiel, *Physica E*, **37**, 44–48 (2007).
- 19) Y. Nabae, S. Moriya, K. Matsubayashi, S. M. Lyth, M. Malion, L. B. Wu, N. M. Lslam, Y. Koshigoe, S. Kuroki, M. Kakimoto, S. Miyata and J. Ozaki, *Carbon*, **48**, 2613–2624 (2010).
- 20) S. H. Xu, F. Y. Zhang, Q. Kang, S. H. Liu and Q. Y. Cai, *Carbon*, **47**, 3233–3237 (2009).
- 21) K. Z. Li, J. Wei, H. J. Li, Y. L. Zhang, C. Wang and

- D. S. Hou, *Appl. Surf. Sci.*, **253**, 7365–7368 (2007).
- 22) T. B. Zhu, Y. W. Li, S. L. Jin, S. B. Sang and N. Liang, *Ceram. Int.*, **41**, 3541–3548 (2015).
- 23) G. P. Wei, B. Q. Zhu, X. C. Li and Z. Ma, *Ceram. Int.*, **41**, 1553–1566 (2015).
- 24) C. Quan, A. M. Li and N. B. Gao, *J. Hazard. Mater.*, **179**, 911–917 (2010).
- 25) A. Morozan, L. Stanatin, F. Nastase, A. Dumitru, S. Vulpe, C. Nastase, I. Stamatina and K. Scott, *Phys. Status Solidi*, **204**, 1797–1803 (2010).
- 26) M. Luo, Y. W. Li, S. B. Sang, L. Zhao and Y. B. Li, *Mat. Sci. Eng. A-Struct.*, **558**, 533–542 (2012).
- 27) O. Aaboubi, A. Y. Ali Omar, A. Franczak and K. Msellak, *J. Electroanal. Chem.*, **737**, 226–234 (2015).
- 28) J. Q. Hu, Z. L. Guo, W. Chu, L. Li and T. Lin, *J. Energy Chem.*, **24**, 620–625 (2015).
- 29) H. M. Cheng, F. Li, G. Su, H. Y. Pan, L. L. He, X. Sun and M. S. Dresselhaus, *Appl. Phys. Lett.*, **72**, 3282–3284 (1998).
- 30) I. Stamatina, A. Morozan, A. Dumitru, V. Ciupina, G. Prodan, J. Niewolski and H. Figiel, *Physica E*, **37**, 44–48 (2007).
- 31) J. W. Snoeck, G. F. Froment and M. Fowles, *J. Catal.*, **169**, 240–249 (1997).