Pseudo Continuous Reactor with Microwave-plasma for Preparation of High Surface Area Activated Carbon

Purichaya KUPTAJIT, Kyuya NAKAGAWA, Tetsuo SUZUKI, and Noriaki SANO†
(Received January 5, 2021)

A new activation method using a pseudo continuous reactor with microwave-induced plasma is examined to prepare activated carbon. Carbonized carbon gel is mixed with potassium hydroxide before being activated by microwave irradiation. The specific surface area of the product is investigated by varying microwave-retention time. The results show that the activated carbon with specific surface area of 3,054 m² g⁻¹ and total pore volume of 1.35 cm³ g⁻¹ can be obtained within 510 s, although hour-level time is necessary to obtain similar activated carbon if conventional methods are used. Temperature change of the carbon precursor caused by microwave irradiation was measured in batch mode to estimate the temperature at pseudo continuous system based on the retention time. It was found that the retention time to reach 700°C of the carbon precursor can be essential factor to achieve high surface area and large pore volume. In addition, the activated carbon synthesized by the proposed method can show an average mass yield percentage of 24.2%, which is much higher than that from conventional methods, 4.5-5.0%. Based on the influence of the microwave retention time, reaction mechanism is discussed. The fast rate and high yield shown here should contribute to energy-saving process.

Key Words
Microwave plasma, High surface area, Porous material, Fast activation, Microstructure

1. Introduction
High surface area activated carbon is a carbon material with specific surface area in the range of 500-3,000 m² g⁻¹. Structure of activated carbon consists of micropores (pore diameter < 2 nm), mesopores (2 nm < pore diameter < 50 nm), and macropores (pore diameter > 50 nm). Because of its pore properties, activated carbon can be used in various chemical processes including water purification, carbon dioxide capture and conversion, and catalyst supports for acetylene hydrochlorination, phosgene formation, syngas production, and so forth.

Conventionally, activated carbon with high specific surface area can be made by mixing carbon precursor with activating agents and heated at high temperature for several hours. There are various activating agents that have been using in industry such as potassium hydroxide, sodium hydroxide, potassium carbonate, zinc chloride, and steam. Since the mixture of carbon precursors and activating agents must be heated for a long period, such activated carbon preparation process is limited to be operated in batch system, leading to the difficulty to produce activated carbon in fast way. If the activation time can be shortened, this process can be improved to be continuous operation, and fast and energy-saving production of activated carbon can become possible.

Previous study reported that some types of electrical plasma can be used to modify surface structure of carbon materials. For example, Su et al. reported that atmospheric dielectric barrier discharge plasma can be used to modify LiMn_{0.8}Fe_{0.2}PO_4/nitrogen-doped carbon, which is a part of lithium-ion battery. Moreover, work of Das et al. shows that microwave-induced plasma can successfully use to synthesize of multiwall carbon nanotubes.

A microwave-induced plasma can be generated by irradiating microwave onto electrically conductive materials with suitable shape such as a metal needle with sharp-edge or porous carbon materials. For the porous carbon materials, the microwave-induced plasma can be generated because electron is discharged in micropores of the porous carbon materials.
Zheng et al.\textsuperscript{17} reported that activated carbon with specific surface area of 1,036 m\textsuperscript{2} g\textsuperscript{-1} can be prepared using microwave irradiation in CO\textsubscript{2} environment within 90 min. From our previous study\textsuperscript{18}, the activation method using microwave-induced plasma with potassium hydroxide activation had been successfully developed to prepare activated carbon with surface area of 2,000 m\textsuperscript{2} g\textsuperscript{-1} or higher within 80-330 s. Due to the significantly short activation time, the results can contribute to the development of continuous reactor system for the preparation of high surface area activated carbon.

As a first step toward the development of the continuous reactor, this research has developed a new activation method using pseudo continuous reactor system with feeding carbon precursor (carbonized carbon gel) mixed with potassium hydroxide under microwave-induced plasma to prepare high surface-area activated carbon.

2. Experimental

2.1 Preparation of carbon precursor (carbonized carbon gel)

In this research, carbonized carbon gel has been used as a carbon precursor for the preparation of activated carbon. Carbon gel was prepared from phenol and formaldehyde with sodium carbonate, which is served as the catalyst\textsuperscript{19}. Here, molar ratio between phenol and formaldehyde was fixed to 0.5 and molar ratio between phenol and sodium carbonate was fixed to 1.5. The mixture was stirred and kept at 95\textdegree C for 72 h before being left at room temperature for another 72 h to complete the reaction and obtain a synthetic carbon gel. The synthetic carbon gel was dried at 110\textdegree C with a temperature-elevation rate of 10 \textdegree C min\textsuperscript{-1} for 1 h before being carbonized at 700 \textdegree C with a temperature-elevation rate of 10 \textdegree C min\textsuperscript{-1} for 1 h under nitrogen atmosphere to obtain carbonized carbon gel. The carbonized carbon gel was mixed with potassium hydroxide at 86\%wt and ground thoroughly. Then, the mixture was activated using a pseudo continuous microwave reactor system as described later.

2.2 Preparation of activated carbon using pseudo continuous microwave reactor

Here, a pseudo continuous microwave reactor system was developed as presented in Fig. 1. An L-shape quartz tube was placed in a microwave oven, and motor was driven to move a ceramic boat containing the carbon precursor with potassium hydroxide. The moving speed was controlled to 0.03-0.12 mm s\textsuperscript{-1}. The path of this moving boat was adjusted so that the carbon precursor was carried through the microwave-concentrated zone. The length of the microwave reaction zone in the moving direction was estimated to be 14.3 mm. Microwave was generated at 2.45 GHz and 500 W there. The retention time of the carbon precursor in the microwave reaction zone is defined by the reaction zone length divided by the boat moving-speed. This microwave retention time was varied for 120-510 s. Nitrogen gas was introduced to the quartz tube at 300 ml min\textsuperscript{-1} so that the activation reaction can occur in inert gas environment. After the precursor-contained ceramic boat passed the microwave reaction zone, the boat was dropped down at the L-shape part in the quartz tube. After the activation, the resulted activated carbon was washed with distilled water until the filtrate became neutral before being dried at 50\textdegree C for 12 h.

A radiation thermometer (Japan Sensor, FTHX-0200S V-1563) was used to observe the temperature-change of the carbon precursor mixed with potassium hydroxide in this reactor. This measurement was conducted in batch mode when the moving speed of the precursor-contained boat was stopped, so that the time-dependency of the precursor temperature could be obtained. When the pseudo continuous operation is conducted in this reactor, the temperature of the precursor at the microwave reaction zone can be estimated by the microwave retention time related with this time-dependency of the precursor temperature.

2.3 Investigation on pore structure of activated carbon

An automatic physisorption-based surface area analyzer (MicrotracBEL, BELSORP-mini II-S) was used to observe nitrogen adsorption-desorption isotherms of the activated carbon. The adsorption-desorption isotherms have been used to investigate pore properties. Specific surface area, micropore volume, and total pore volume of the activated carbon can be calculated from the nitrogen adsorption-desorption isotherms.
sorption isotherms. Micropore volume was calculated from t-plot method. Mesopore volume was calculated from the difference between total pore volume and micropore volume. Mass yield percentage of activated carbon is defined by Eq. (1).

\[
\text{mass yield percentage (\%)} = \frac{\text{mass of activated carbon (g)}}{\text{mass of carbonized carbon gel (g)}} \times 100
\] (1)

3. Results and Discussion

3.1 Heating feed mixture by microwave

The temperature change of the carbon precursor in batch mode was measured as presented in Fig. 2. The result suggests that the maximum of activation temperature is 787 °C and the temperature-elevation rate is 90 °C min⁻¹, as calculated from the period of time used to rise temperature from 500 to 787 °C.

It should be noted that the temperature of the carbonized carbon gel cannot reach the activation temperature unless potassium hydroxide is mixed. When microwave was irradiated to 0.1-0.7 g of ground carbonized carbon gel without mixing potassium hydroxide for 10 min, its temperature could not reach above 200 °C, which is the minimum limit of the radiation thermometer used here. Then, further temperature-increase was not observed even when the microwave-retention time was prolonged. From this result, potassium hydroxide seems to play a role not only for reaction to open pores on carbon but also for increasing the temperature of the feed for activation of carbon. When microwave is irradiated to pure potassium hydroxide, the temperature became 450 °C at maximum.

The electrically-conductive high-crystallinity carbon can absorb microwave by its free electrons, and electric current induced in such carbon causes Joule heating. However, if the carbon material does not have high electrical conductivity due to its inclusion of amorphous structures, the microwave heating may not be so efficient. The analyses using X-ray diffractometer and Raman spectroscopy were conducted on the carbonized carbon gel, suggesting that there is no signals to prove the existence of graphitic structures. Thus, the main structure of the carbonized carbon gel should be amorphous, and such structure should lead to the difficulty of the temperature elevation of the carbonized carbon gel without potassium hydroxide.

In the present pseudo continuous microwave reactor system, the temperature-change may be caused not only by the absorption of microwave by carbon-KOH mixture, but also by conduction from the hot plasma generated above it. During the microwave irradiation to the carbon precursor, bright plasma occurs in the gas zone above the carbon precursor as reported previously. According to the reported measurement by the analysis on the emission spectra, the temperature of the plasma there is thought to be 5,500 °C or higher. Since the carbon mixture is contacted with this plasma, the temperature of the carbon precursor can be raised up to the activation temperature with the high temperature-elevation rate. The high temperature-elevation rate might be a key factor in this microwave-activation, and it could govern pore formation step and determine pore structure of the activated carbon.

3.2 Nitrogen adsorption-desorption isotherms

The nitrogen adsorption-desorption isotherms of the activated carbon prepared from the pseudo continuous microwave-reactor is shown in Fig. 3. The results indicate that the products obviously have micropores when the microwave-retention time is higher than 210 s, suggested by the sharp slope at the low-pressure range seen in the products with the retention time from 210 to 510 s. In this range, the microporous structure of the activated carbon seems to increase as microwave-retention time increases. Considering with the result of the temperature-change shown in Fig. 2, it should be necessary to experience the temperature higher than about 730 °C to generate micropores.

The result shown in Fig. 3 also indicates that the micropore volume increases as microwave-retention time prolongs. This trend seems significant. Moreover, each isotherm shows a hysteresis loop, relating to capillary condensation taking place in mesoporous structure. This hysteresis loop also tends to increase when the microwave-retention time prolongs. However, the trend of the
hysteresis loop depending on the microwave-retention time does not seem so significant compared with the trend of the micropore volume. The quantitative comparison between these trends is explained later.

3.3 Specific surface area, micropore and mesopore volumes

Fig. 4 presents the specific surface area of the activated carbon prepared by the pseudo continuous microwave reactor system. The results indicate that the specific surface area of the activated carbon increases as the microwave-retention time is prolonged. It should be noted that the specific surface area can continue growing even after 300 s, when the temperature becomes maximum at 787 °C. At the microwave-retention time of 510 s, when the specific surface area becomes the largest, the temperature of the carbon precursor may become down to about 500 °C, as suggested in Fig. 2. This result indicates that under the irradiation of the microwave, the growth of the pores can continue in the temperature range, 500-788 °C. This temperature range is considered to be lower compared with typical temperature for activation in conventional ways by ordinary heat conduction. From this fact, one may consider that there would be unique effect of microwave irradiation to enhance pore formation reactions.

From the nitrogen adsorption-desorption isotherms, micropore and mesopore volume of the activated carbon prepared from the pseudo continuous microwave reactor system can be calculated as shown in Fig. 5. The results indicate that both of micropore and mesopore structure increase as microwave-retention time prolongs. In the conditions when the microwave retention time is long enough to clearly exhibit pore volumes, namely when microwave retention time is longer than 210 s, the ratio of the micropore volume to mesopore volume does not seem to depend on the microwave retention time. Overall, the micropore volume is about three times larger than mesopore volume.

3.4 Mass yield percentage of activated carbon

Fig. 6 shows the mass yield percentage of the activated carbon prepared using the pseudo continuous microwave reactor system. In this work, activated carbon using the microwave-retention time of 120-510 s shows the mass yield percentage of 21.7-71.2%. The yield of the activated carbon significantly decreases as microwave-retention time increase from 120 to 210 s. However, the yield of the activated carbon shows the slightly decrease as the microwave-retention time increases from 210 to 510 s,
although the temperature of the feed mixture may become about 787 °C at 300 s within this time range as stated earlier.

This tendency can be explained by considering that the carbonized carbon gel consists of stable structures and relatively weak structures. Within 210 s of the microwave-retention time, the weak structure could be reacted with potassium hydroxide, leading to the drastic decrease in the mass yield percentage. This consumption does not generate pores so much without the significant increase of specific surface area of the activated carbon. After this time range, the temperature of the carbon precursor becomes higher than about 700 °C as mentioned above, which can be high enough to generate micro and meso pores at the remaining stable parts in the structure of carbonized carbon gel. Therefore, the yield-decreasing rate while the pores are generated at high temperature after 210 s can be obviously lower than that while the weak parts are consumed within 210 s.

The average mass yield percentage of the activated carbon was calculated for the condition when the specific surface area becomes higher than 1,000 m² g⁻¹. The calculation results show that the average yield of the activated carbon is 24.2%. It should be noted that the average yield of activated carbon obtained from the conventional method using ordinary heat conduction is only 4.5-5.0% when this level of specific surface area is required. Improvement of the production yield by use of the microwave irradiation can contribute to lowering the production cost.

3.5 Mechanism of pore formation

According to the results mentioned earlier, model of pore formation of activated carbon prepared by pseudo continuous microwave reactor system can be summarized as illustrated in Fig. 7. The consumption of carbonized carbon gel can start at its weak parts in the short retention time range within 210 s without generating significant amount of pores. After the microwave retention time reaches 210 s, the micro and mesoporous structures start to be generated on the stable parts of the carbonized carbon gel. One should be reminded that micropore volume is dominant over mesopore volume during the pores are generated. Finally, the activated carbon with high specific surface area of 3,000 m² g⁻¹ with micropore-dominant structure can be achieved within 8-9 min.

4. Conclusion

Toward the development of a continuous reactor system to produce large surface area activated carbon, the pseudo continuous microwave reactor system is firstly investigated. Here, carbonized carbon gel mixed with potassium hydroxide is used for feed material to produce activated carbon. The results regarding the surface area, the pore volume, and the production yield have been discussed based on the microwave retention time defined by the reaction zone length divided by the feed moving-
speed through the microwave reaction zone. The nitrogen adsorption-desorption isotherms of the activated carbon produced by the proposed system reveal that pore volume and specific surface area can increase significantly when the microwave retention time is long enough to achieve about 700 °C of the temperature at the carbon precursor. Overall, micropore volume become more dominant over mesopore volume. The production yield decreases drastically in the short microwave retention time range when the temperature of the carbon precursor is lower than about 700 °C, and this decrease becomes slight when the microwave retention time is long enough to reach above about 700 °C. This tendency can be explained by considering that the fed carbonized carbon gel consists of weak parts and stable parts, and the weak parts are consumed when the microwave retention time is short. When the microwave retention time was set to 510 s, the specific surface area of the activated carbon reached 3054 m² g⁻¹ by use of the proposed system. The fast rate and high yield shown here should contribute to energy-saving process.

Acknowledgment

The authors gratefully acknowledge the Asahi Glass Foundation (AF) and the Japan ASEAN Science, Technology and Innovation Platform (JASTIP) under the Japan Science and Technology Agency (JST).

References

1) Tomul, F.; Arslan, Y.; Başıoğlu, F. T.; Babuçcuoğlu, Y.; Tran, H. N., J. Environ. Manage, 238, 296-306 (2019)
2) Wang, H.; Li, X.; Cui, Z.; Fu, Z.; Yang, L.; Liu, G.; Li, M., J. Colloid Interface Sci., 578, 491-499 (2020)
3) Liu, Y.; Zhang, H.; Li, X.; Wang, L.; Dong, Y.; Li, W.; Zhang, J., Appl. Catal. A-Gen, 117902, (2020)
4) Rossi, G. E.; Winfield, J. M.; Mitchell, C. J.; Meyer, N.; Jones, D. H.; Carr, R. H.; Lennon, D., Appl. Catal. A-Gen, 117688, (2020)
5) Shi, K.; Yan, J.; Luo, X.; Lester, E.; Wu, T., Energy Procedia, 142, 1640-1646 (2017)
6) Wang, H.; Xu, J.; Liu, X.; Sheng, L., J. Clean. Prod., 124671, (2020)
7) Dai, C.; Wan, J.; Shao, J.; Ma, F., Mater. Lett., 193, 279-282 (2017)
8) Sangon, S.; Hunt, A. J.; Attard, T. M.; Mengchang, P.; Ngernyen, Y.; Supanchaiyamat, N., J. Clean. Prod., 172, 1128-1139 (2018)
9) Pezoti, O.; Cazetta, A. L.; Bedin, K. C.; Souza, L. S.; Martins, A. C.; Silva, T. L.; Santos, O. O.; Visentainer, J. V.; Almeida, V. C., Chem. Eng. J., 288, 778-788 (2016)
10) Vu, M. T.; Chao, H. P.; Trinh, T. V.; Le, T. T.; Lin, C. C.; Tran, H. N., J. Clean. Prod., 180, 560-570 (2018)
11) Mármuez-Montesino, F.; Torres-Figueroedo, N.; Leumas-Santana, A.; Trejo, F., Chem. Eng. Technol., 43, 1716-1725 (2020)
12) Gao, Y.; Yue, Q.; Gao, B.; Li, A., Sci. Total Environ., 141094, (2020)
13) Fu, J.; Zhang, J.; Jin, C.; Wang, Z.; Wang, T.; Cheng, X.; Ma, C., Bioresour. Technol., 123413, (2020)
14) Su, C. Y.; Wu, C. Y.; Hsu, S. Y.; Wu, C. Y.; Duh, J. G., Mater. Lett., 127880, (2020)
15) Das, D.; Roy, A., Appl. Surf. Sci., 146043, (2020)
16) Itaya, Y.; Matsubara, K.; Tanaoka, R.; Kobayashi, N., Fuel, 242, 382-388 (2019)
17) Zheng, Z. Q.; Xia, H. Y.; Srinivasakannan, C.; Peng, J. H.; Zhang, L. B., Chem. Eng. Process, 82, 1-8 (2014)
18) Kuptajit, P.; Sano, N., Appl. Phys. Express, 12, 086001 (2019)
19) Mukai, S. R.; Tamitsuji, C.; Nishihara, H.; Tamon, H., Carbon, 12, 2628-2630 (2005)
20) Zhao, Y.; He, J., Carbon, https://doi.org/10.1016/j.carbon.2021.03.048, in press, journal pre-proof, (2021)
21) Sulaiman, N. S.; Hashim, R.; Amini, M. H. M.; Danish, M.; Sulaiman, O., J. Clean. Prod., 198, 1422-1430 (2018)