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INFLUENCE OF TIME AND CONCENTRATION ON TEXTURAL PROPERTIES OF MESOPOROUS CARBONS OF GELATIN PREPARED BY HARD-TEMPLATING PROCESS

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ABSTRAK

Karbon mesopori dengan sifat tekstural yang berbeda dibuat dari gelatin melalui proses cetakan padat. Pengaruh kondisi pelepasan silika (waktu dan konsentrasi asam) pada sifat nanokomposit telah dipelajari selama proses sintesis. Waktu pelepasan silika yang dipilih adalah 1, 6 dan 24 jam menggunakan konsentrasi HF 10%, 20%, 30% dan 40%. Sifat tekstural dan mikrostruktur nanokomposit telah dikarakterisasi menggunakan difraksi sinar X dan mikroskop transmisi electron, spektroskopi energy dispersive sinar-X dan adsorpsi desorpsi N_2. Hasil menunjukkan bahwa waktu saat proses pelepasan silika menyebabkan nukleasi dan pertumbuhan karbon mesopori pada permukaan. Semakin menurun waktu pelepasan silika dna konsetrasi HF maka menyebabkan semakin meningkatnya luas permukaan dan volume total karbon dari 410 hingga 760 m^2/g dan 0,14–0,99 cm^3/g dengan rata-rata diameter pori yang hampir sama yaitu 4,1 nm. Selanjuntya, telah teramati adanya lebih banyak distribusi pori homogen dengan semakin menurunnya waktu pelepasan silika dan konsentrasi HF. Kesimpulannya adalah waktu pelepasan silika dan konsentrasi asam memegang peranan penting pada sifat tentural karbon mesopori dimana hal ini memberi pengaruh besar dalam performa adsorpsi senyawa sulfur dalam minyak bumi.

***Kata kunci:** karbon mesopori, pelepasan silika, waktu, konsentrasi asam*

ABSTRACT

Mesoporous carbons with different textural properties were prepared with gelatin by hard templating process. The effect silica removal condition (time and acid concentration) on the nanocomposite properties was studied during synthesis process. 1, 6, and 24 h silica removal times and 10%, 20%, 30% and 40% HF concentraton were chosen. Textural properties and microstructure of the nanocomposites were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDAX), and N_2 adsorption– desorption. Results showed that removal silica time process led to mesoporous nucleation and growth on the surface of mesoporous carbon. At decreasing of removal silica time and HF concentration the surface area and total pore volume increased from 410 to 760 m^2/g and 0.14–0.99 cm^3/g with almost same of the average pore diameter considerably at 4.1 nm. Furthermore, it was observed more homogeneous pore distribution with decreasing the silica removal time dan HF consentration. In conclusion, the silica removal time and acid concentration play an important role on textural properties of mesoporous carbon which could have a major effect on adsorption properties of sulfuric compound in the fuel.

***Key Word:** mesoporus carbon, silica removal, time, acid concentration*

INTRODUCTION

Sulfuric compounds in the fuel have many problems on the environment [1]. The removal of sulfur is carried out through desulfurization. Adsorption is a favourable process for fuel desulfurization [2]. Mesoporous carbons have high adsorption capacity due to large specific surface area, high order structure and mesoporosity. The use of microporous adsorbents such as activated carbons, clays, metal oxides and supported metals (often in combined formulations) for the removal of diverse sulphur compounds from various streams is documented in several report [4–6]. It was reported that microporous adsorbed an small amount of sulfuric compund [13]. A good adsorption performance was linked to the development of mesoporosity. The mesoporous material speed up the adsorption rate of sulfuric compound due to the large pore and high total volume.

Some researchers have carried out the synthesis of mesoporous carbon by the hard templatel method [7-9]. The synthetic routes of hard templating process based on the infiltration of carbon precursor the use pore of inorganic solids. A number of carbon precursor as sucrose, gliserol, aromatic polyamides and poly(vinylidene chloride-co-vinyl chloride)[10-13]. New precursors from low cost materials are needed in order to produce mesoporous carbons. Our research has been working on gelatin as precursor carbon due to high carbon and posses the amino functional groups which can strongly interact with silica species by hydrogen bonds [14-15].

The synthesis of mesoporous carbon was performed by infiltration of carbon precursor onto solid matrix, carbonization and removal solid template by dissolving in HF. The obtained carbons are either the replica of the template or exhibit a new structure [16]. The unfilled template pores produce new pore system of the mesoporous carbon. Previous research report that removal solid template with HF caused starting formation of new pore systems (Kerstin). The physical and chemical processes during on pore formation of mesoporous carbon with HF is importance to understand. However, information of the effect of HF treatment condition to textural properties of mesoporous carbonis very rare in the literature. In this study, mesoporous carbons (MC) were prepared from gelatin. The development of the textural and stucturel properties of mesoporous carbon during silica removal with HF have been investigated in detail of time and concentration. Characterization of meso-porous carbon using nitrogen gas adsorption, SAXRD and TEM.

II. EXPERIMENTAL SECTION

2.1. Preparation of mesoporous carbons

Mesoporous carbon material was synthesized by using SBA-15 mesoporous material as a silica template (particle size 0,1 μm, pore diameter 7-8 nm, surface area 550 m^2/g, pore volume 1,0 cm^3/g) and gelatin as the carbon source which extracted from Javanese cow bone as previous report [14-15]. The step of synthesis of mesoporous carbon were: 1 g of template (mesoporous silica material) was added to a solution obtained by dissolving 1 g of gelatin and 0.13 g of H_2SO_4 in 6 g of water, and keeping the mixture in an oven for 7 h at 110 °C. Subsequently, the oven temperature was raised to 150 °C for 7 h. In order to obtain fully polymerized and carbonized gelatin inside the pores of the silica template, 0,5 g of gelatin, 0.11 g of H_2SO_4 and 5 g of water were again added to the pre-treated sample and the mixture was subjected to the thermal treatment described above. The template–polymer composites were then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 3 h to carbonize the polymer.

a. Variation of HF treatment time

The silica-carbon composites from sample were stirred 200 rpm with 5% HF to remove the silica template by variation of the treatment time at 1, 6 and 24 h. Finally, the obtained carbon material was washed with distilled water and dried in air at 110 °C for 24 h. The The resulted sample has been denoted as OMCG-nh, with *n* represent of HF treatment time.

b. Variation of HF concentration

The concentration of HF in the dissolving solution was varied from 10% up to 40% for 1 h. The resulted carbon material was washed with distilled water and dried in air at 110 °C for 24 h. The obtained sample has been denoted as OMCG-HF*m*%, with m represent of HF concentration.

2.2. Characterization

Nitrogen adsorption and desorption isotherms were measured on a Quantachrome Autosorb 1 sorption analyzer. All samples were outgassed at 300 °C for 3 h prior to the nitrogen adsorption measurements. The specific surface area was calculated using the Brunauer–Emmett– Teller (BET) method. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms by Barrett–Joyner–Halenda method. The ordering of mesoporous carbon mesostructure analyze using small-angle powder X-ray diffraction (SAXRD) pattern. Sample was recorded with a Bruker D4 powder X-ray diffractometer (Germany) using Cu Ka radiation (40 kV, 40 mA) with 0.02° step and 4 s/$^\circ$ scanning rate within $0.02^\circ < 2\theta < 5^\circ$ range. The measurements were conducted under a nitrogen atmosphere. An empty pan was used as a reference. The morphologies of all the synthesized samples were characterized by a transmission electron microscopy (TEM) instrument (Philips CM30) operating at 120 kV. Each sample was dispersed in absolute ethanol and a drop was placed on a Cu grid covered with perforated carbon film.

RESULT AND DISCUSSION

a. Effect of HF treatment time

Fig.1 was the nitrogen sorption results which showed typical type IV isotherm with type H2 hysteresis loop, concluding that this material has cylindrical pore channels type. The nitrogen sorption isotherm in low P/Po range of 0.0–0.1 indicates that large amounts of micropores were formed on the carbon porewall. All isotherms sample at relative pressure (P/Po) more than 0.35 exhibit a sharp step characteristic of capillary condensation of nitrogen within uniform mesopores. The diameter of the mesopore represented by the inflection point of the p/po position [18].

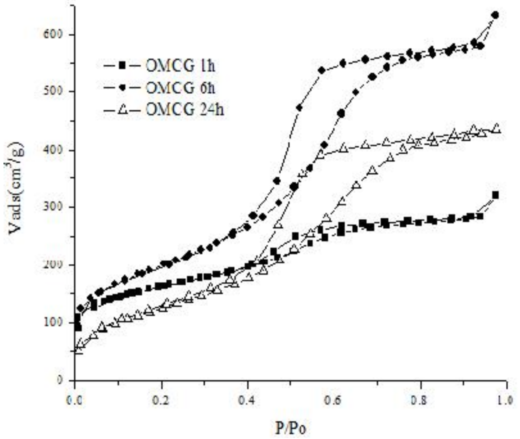

Fig.1. Nitrogen adsorption–desorption isotherms of mesoporous carbon materials treated at different time of removal silica

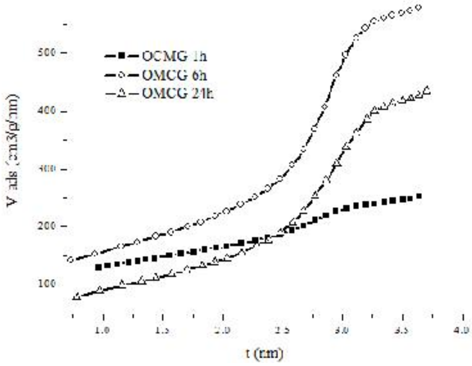

Fig. 2. Curve of *t*-plot mesoporous carbon materials treated at different time of removal silica

Fig. 2 exhibits the t-plot of all sample by Harkins and Jura equation which is the intercept and the slope of the linear fit represent micropores and surface area. OMCG-6h shows higher micropore than other sample. Precursor carbon during carbonization loss hydrogen, oxygen and nitrogen atoms, if present, that can create a microporosity [19]. Removal silica for longer time can cause slower diffusion generating microporosity of carbon. This fact is due not only to molecular size, but also to the affinity of fluorin ion with the silica matrix. The result implies that a longer time during removing silica could enhance micropores due to small pore originate from diffusion effect.

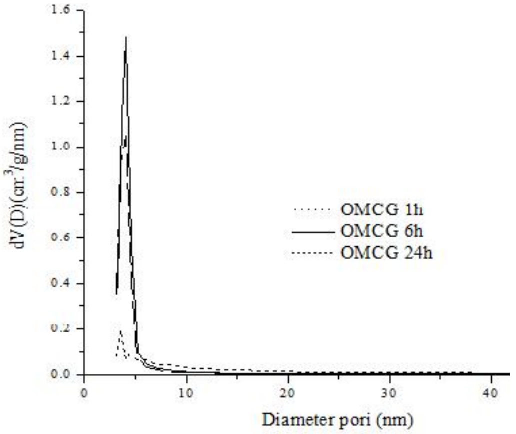

Fig. 3. BJH adsorption pore size distribution of mesoporous carbon treated at different time of removal silica

Fig. 3 shows the adsorption pore size distribution of all sample treated by HF at different time. All sample show uniform pore size distribution which possesses narrow pore size distribution. The calculated pore diameters of the all the samples are in the range of 4.0 up to 5.2 nm. In addition, no clear trend in the pore diameter versus the degree of pore filling is observed.The adsorption pore size distribution curve combined with particle size distribution extracted from TEM image (Fig. 4) indicates that all sample has uniform pore size.

Fig 5. shows the TEM image of all sample which is clearly exhibited an ordered mesoporous structure with linear array of

Table 1. Textural parameters of mesoporous carbon materials after removal silica at different condition

Sample	S_{BET} (m^2/g)	S_{me} (m^2/g)	% me	V_t (cm^3/g)	D_a (nm)	D_b nm)	a_o (nm)	*t* *(nm)*
OMCG-1h	536	443	83	0,52	3,5	3,5	TD	TD
OMCG-6h	756	636	85	0,99	5,2	4,3	10,53	5,43
OMCG-24h	480	373	78	0,97	4,5	4,1	10,06	5,36

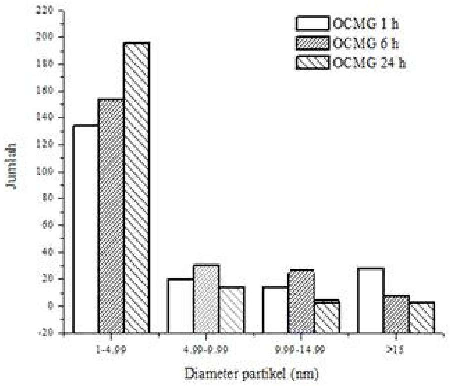

Fig. 4. Hystogram of TEM particle size distribution of mesoporous carbon treated at different time of removal silica

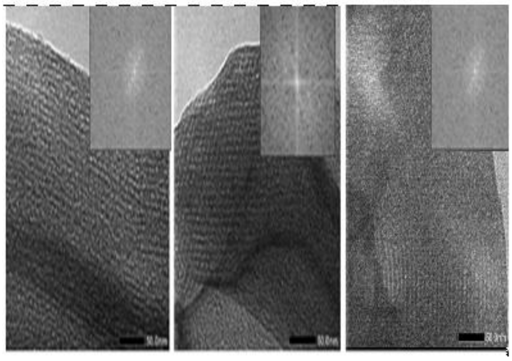

Fig 5. TEM images of mesoporous carbons after removal silica for a. 1h; b.6h and c. 24 h.

mesopores separated by carbon walls and some carbon deposits on the external surface. The structural order of the materials treated with HF at different time show significant differences. It is also interesting to follow changes in the structure of carbon materials treated with HF at different time. OMCG-1h shows mesoporous channels with a small disordered mesoporous structure because of the incomplete silica removal. OMCG-6h exhibited a highly ordered mesoporous structure with linear array of mesopores from the mesoporous silica framework after the HF treatment for 6 hour. The longer time probably enough to ensure complete removal of all silica speciel from composite. In contrast, OMCG-24 show decreasing mesopores strucuture that mainly due to the shrinkage effect during longer dissolving time.

Fig. 6 shows the small angle X-ray scattering patterns of mesoporous carbon materials prepared at different template removal time. All the samples except exhibit a sharp diffraction peak at low angle and two higher order peaks which can be indexed to the (100), (110) and (200) reflections of the hexagonal space group p6mm with *q* value at 0.72; 0.79; dan 1.09. This indicates that all the materials possess hexagonally ordered uniform mesoporous structure with long range order [20] The hexagonal unit cell a_0 parameter is calculated using the for The intensity of the (100) diffraction peaks of the samples, namely, OMCH-6h is much higher as compared to the samples treated with HF for longer time. The reduction in the peak intensity could be mainly due to the possibility of higher degree of removing silica.

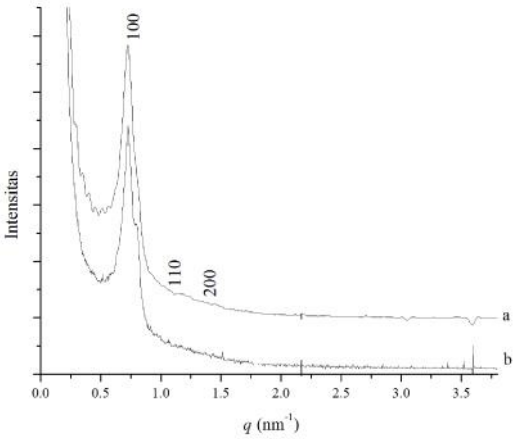

Fig 6. SAXS patterns of mesoporous carbons after removal silica process for a. 6h; and b. 24 h

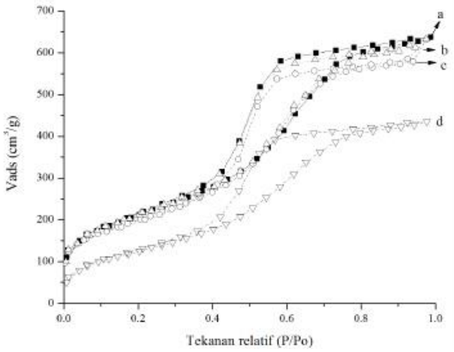

Fig 7. Nitrogen adsorption–desorption isotherms of mesoporous carbon materials after removal silica using: a. HF 10%; b.HF 20%; c. HF 30% and d. HF 40%.

The suprising note that the specific surface area of the mesoporous carbon materials increase with increasing the HF time treatment for 1 and 6 h but decrease at 24 h (Table 1). The specific surface area amounts to 536 m^2/g for OMCG-1h and increases to 756 m^2/g for OMCG-6h. The higher surface area of OMCG-6h could be attributed to increase in heterogeneity of surface and micropores in the materials because of the complete removing of silica template in carbon pore. The pore thickness of OMCG-6h higher than OMCG-24h due to the shrinkage phenomenon during silica removal. The longer time of dissolving silica probably would enhance the interaction of fluorin ion with species silica that caused shrinkage of carbon channels. In addition can be concluded that an optimized control of time during silica removal is needed to preserve the high ordering structure of mesoporous of carbons with good textural parameters.

b. Effect of HF concentration

Information about the optimal concentration of HF is necessary in order to form stable and defined pore structures after template removal. The nitrogen adsorption–desorption isotherm for all sample is shown in Fig. 7. The isotherms are essentially of type IV with a hysteresis loops that indicate the sample have mesoporous type [21-22]. The corresponding textural parameters, including specific surface area (S_{BET}), total pore volume (V_t) and average diameter pore (D) values are presented in Table 1. The sharp inflection of the mesoporous carbon isotherm in P/P_0 range from 0.5 to 0.7 is characteristic of capillary condensation within uniform pores. This mesoporous silica has a steep nitrogen uptake at relatively high P/Po due to its large uniform mesopores and narrow pore size distribution (PSD) centered at 3.5 up to 4.8 nm (Fig. 8).

The hysteresis loop of OMCG-10% shifts to lower pressure from OMCG-20% indicating decrease of the pore size of the sample at low HF concentration compared to the sample treated at higher concentration. This is to be expected, because the relatively wide pores of OMCG-10% have been replaced with carbon nanopipes. This mesoporous carbon shows a relatively uniform pore size with maxima around 4.8 nm (Table 1). The nitrogen adsorption isotherm for OMCG-10% sample exhibits relatively high adsorption at low pressures, indicating the presence of micropores. The increasing HF concentration systematically decrease the surface area of all sample. The OMCG-HF10% exhibits considerably higher surface area (756 m^2/g, Table 1) compared to OMCG-HF 20% (740 m^2/g) due to more void spaces generated after treated at high HF concentration.

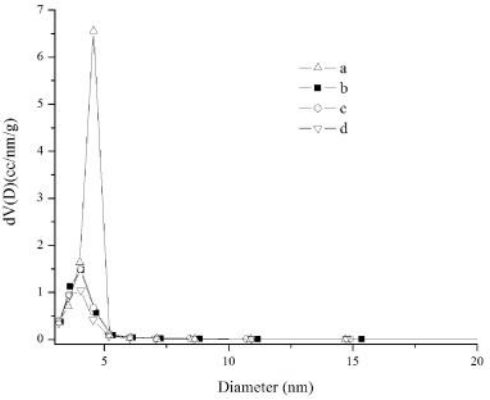

Fig 8. Pore size distribution of mesoporous carbon materials after removal silica using: a. HF 10%; b.HF 20%; c. HF 30% and d. HF 40%.

In Fig. 8 the pore size distribution of the carbon materials on the HF concentration in the synthesis solution is shown. If the concentration of HF used for silica removal is too high, huge parts of the silica molecule remain removed and no stable carbon walls will be formed. After template removal, one can obtain either a non-porous carbon or a carbon material which exhibits a narrow pore size distribution. The carbon composite treated by 10% HF concentration shows a pore size distribution with one maximum at about 4.5 nm.

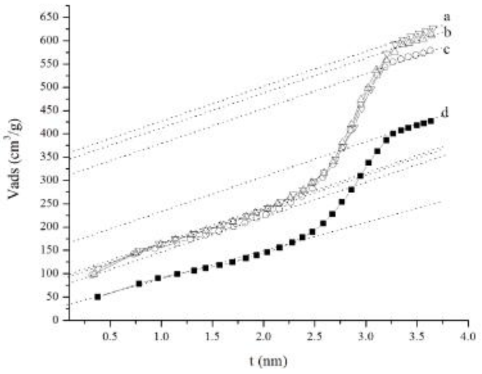

Fig 9. *t*-plot curve of mesoporous carbon materials after removal silica using: a. HF 10%; b.HF 20%; c. HF 30% and d. HF 40%

Fig. 9 shows *t*-plot of sample treated with different HF concentration. T-plot determine that surface area of OMCG-HF10% is higher than the other sample due to a lot of micropore generate on the surface. In contrast, surface area of OMCG-HF 40% lower than OMCG 10% that mainly caused by increasing speed of silica dissolution. The high speed of silica removal probably produce disorder carbon that increasing macroporous site whereas decreasing surface area. It is can conclude that HF concentration influence the textural parameter of mesoporous carbon.

Fig. 10 shows SAXS pattern of mesoporous carbon after treated in different HF concentration. The resulting SAXS pattern for OMCG-HF10%, obtained in the 2h range of 0.05–4°, together with those of other sample different HF concentration for

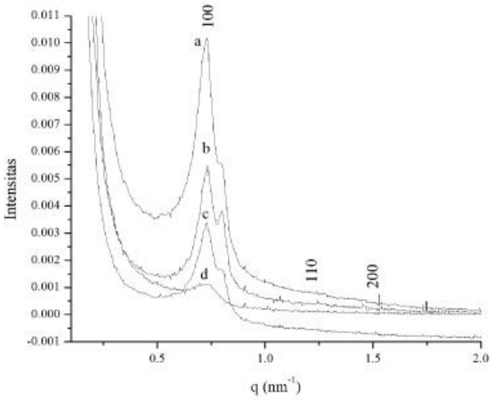

Fig 10. SAXS scattering of mesoporous carbon materials after removal silica using: a. HF 10%; b.HF 20%; c. HF 30% and d. HF 40%

comparison. All sample of mesoporous carbon displays three well resolved peaks indexed as (100), (110) and (200), characteristic of the two-dimensional hexagonal space group p6mm [40]. The SAXS patterns of the resulting mesoporous carbon also show ordered mesostructures with p6mm symmetry, as evident from the presence of (100), (110) and (200) reflections, indicating that they have retained the ordered structure of their parent silica template [23-25]. As shown in Fig. 10, the diffraction peaks of the mesoporous carbons are slightly shifted to higher 2h values, which can be related to smaller d-spacings as well as smaller cell parameters.

The unit cell parameters for OMCG treated with HF 10% up to 40% were 10.20; 10,14; 10,05 and 10.00 nm, respectively (Table 1). The unit cell parameter of OMCG-10 is higher than the silica other sample which probably results from low structural shrinkage of the carbon/silica composite material during pyrolysis at high temperature. Weaker (100) peaks of OMCG-30% and OMCG-HF40% compared to OMCG-10% are also the result of structural shrinkage, which cause some decrease in the structural ordering of the carbon replicas. Structural shrinkage also results in poor resolution of the (110) and (200) diffraction peaks of the mesoporous carbons

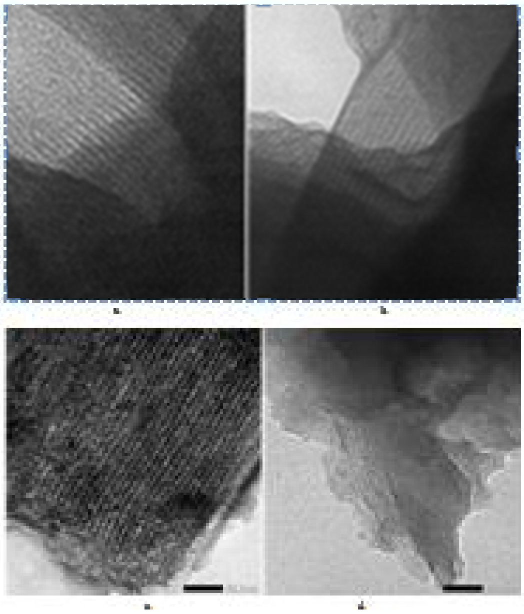

Fig. 11 TEM image of mesoporous carbon materials after removal silica using: a. HF 10%; b.HF 20%; c. HF 30% and d. HF 40%.

Fig. 11 shows the TEM image that represent morphologies of the synthesized mesoporous carbon samples. The images confirm the results obtained from SAXS and N_2 adsorption. The mesoporous carbon OMCG-HF10% shows a well ordered hexagonal structure in which ordered arrays of the carbon nanopipes are separated by ordered arrays of mesoporous tubes, demonstrating the existence of the bimodal pore system. As shown in Fig. 11, the single types of pores systems can be clearly identified in the structure of OMCG-HF10%, corresponding to the tube pores left by removing the silica template. From the TEM image of OMCG-HF1-%, the average pore diameter was estimated to be 4.3 nm which is higher than other sample in different HF concentration. TEM show that larger of stacking faults of OMCG-HF40% as effect of increasing removal template. It is implies that disordered structure can occur if removal template process on high speed. All mesoporous carbon sample show that relusting carbon not significant differ with previous research.

CONCLUSION

In order to get the information about structure stability of nanosized mesoporous carbon particles, HF in different time and concentration of was used to remove the silica particles from composite mesoporous carbon. Results showed that HF 10% at 1 hour was effective to improve the removal of nanosized silica particles when the proper amount added. Pore volume and BET surface area of mesoporous carbon increased up to 0.999 cm^3/g and 756 m^2/g, respectively after the removal process with HF 10%. The HF used in the present study not only participated in the removal of silica particles, but also took part in the formation of small mesopores as well as blocking the micropores.

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