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Preparation of Ag-Doped Composite Carbon Molecular Sieves†

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The copolymer of acrylonitrile and γ-methacryloxypropyltrimethoxysilane (KH-570) was synthesized with Ag^+ by inverse suspension copolymerization as carbon precursor, through carbonization and co-reduction, to obtained Ag-doped composite carbon molecular sieves . The thermal stability and microstructure of samples were studied by TGA, FTIR, XRD and nitrogen adsorption at 77 K, respectively. Result showed that during the high-heat treatment, precursor displayed similar pyrolysis behaviour, carbon residue increasing from 12 to 31 % with KH-570 content decreased; after carbonization, the inorganic phase (Si) was incorporated into carbon molecular sieves successfully and Ag^+ was reduced to silver form. With the KH-570 content increasing, carbonization products possess a higher specific surface area (reached 1056 m^2/g) and larger micropore volume (reached 0.45 cm^3/g, account for *ca.* 70 %).

Key Words: Carbon-silica, Catalyst, Ag-doped, Composite, Carbon molecular sieves.

INTRODUCTION

Carbon molecular sieves (CMS), as an emerging high efficiency energy saving absorbent material with developed pore structure, uniform pore size distribution and high stability, has been widespread concerned, especially in the flied of catalyst supports[1-3], membranes[4,5], air adsorption/separation[6,7] and energy storage[8,9]. In recent years, design and preparation of composite carbon molecular sieves and membranes is gaining great interest. Compare with conventional molecular sieves, composite carbons have several advantages, such as excellent permeability with lower loss in selectivity, thermal and chemical stability[10]. Some other advanced application can be find in the areas of gas separation, heterogeneous catalysts and fuel cells[11,12]. In present research activitites, the studies on synchronous prepared metal-doped hybrid CMS by carbonization and co-reduction of silicon-containing copolymer and transition metal salt have been very limited so far. Therefore, if inorganic phase (Ag, Si) could be loaded in highly dispersed CMS, it will expand the application field of catalyst.

EXPERIMENTAL

In this communication, it is reported that a novel approach to the synthesis of Ag-doped composite CMS particles from inverse suspension copolymerization. The γ-methacryloxypropyltrimethoxysilane (KH-570) is introduced into polyacrylonitrile (PAN) main chain, the copolymer as carbon precursor after hydrolysis under acidic condition. The molar ratio of KH-570 to acrylonitrile (AN) are 1:3, 1:5, 1:7 and 1:10, denoted as AN-Si-1, AN-Si-2, AN-Si-3 and AN-Si-4, respectively. After high-heat treatment at a heating rate of 5 °C/min under a flow of nitrogen gas and holding at 750 °C for 2 h the carbon-silica composite CMS is obtained. The silica template is dissolved in 40 % aqueous HF, products are denoted as C-Si-1, C-Si-2, C-Si-3, C-Si-4, respectively. In the process of precursor synthesis, -CN hydrolyze to -COOH groups, comp-lexation with Ag^+, make for metal catalyst disperse evenly; KH-570 plays two important roles, one can provides inorganic phase as a silicon source, the other can controls the pore structure of CMS as template by partial hydrolysis.

RESULTS AND DISCUSSION

The thermogravimetric analysis of all samples was done under nitrogen atmosphere at 10 °C/min and displayed similar pyrolysis behaviour. Fig. 1 shows the samples decomposition mainly through two processes, the weight loss peaks at about 250 and 400 °C, respectively (Inset). It is seen that the initial weight loss is due to the cleavage of the numerous C-H bonds in unhydrolyzed part of KH-570, which increased from 12 to 48 % with increasing KH-570 content at a temperature lower

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than 320 °C (1st stage); When the temperature is above 320 °C, the covalent bonds between Ag and carboxyl oxygen are damaged, the -COOH groups start to decompose and with cyclization[13] in the range of 320-450 °C (2nd stage). Finally, there is *ca.* 18, 22, 31 % carbon residue for AN-Si-2, AN-Si-3 and AN-Si-4, respectively.

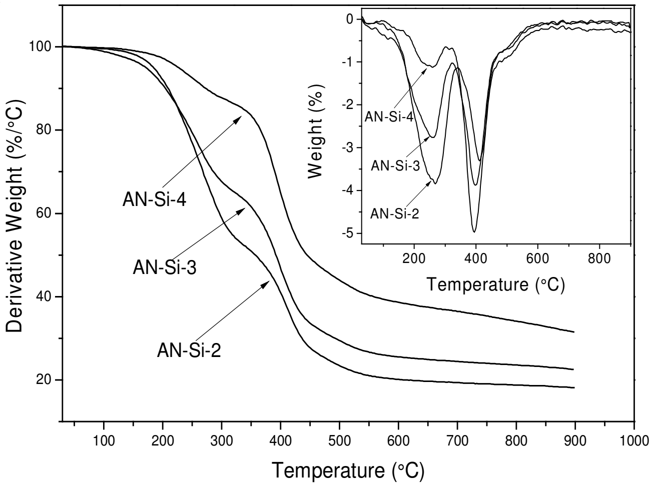


Fig. 1. TG and DTG (inset) curves of AN-KH-750 copolymer with different molar ratio

Fig. 2 is the FTIR spectra of the AN-KH-570 copolymer with different molar ratio before and after carbonization. -CN- groups have been completely hydrolyzed, the stretching vibration (2260-2220 cm^{-1}) disappear, meanwhile the characteristic of -C=O is observed at 1720 cm^{-1} in copolymer. Through high-heat treatment, the methylene ($-CH_2-$ stretching, 2920 and 2850 cm^{-1}) and methyl ($-CH_3$ stretching, 1460 cm^{-1}) decompose, the absorptions disappear, illustrating that the dehydrogenation reaction have been finished. The characteristic absorption bands at 1215 and 1115 cm^{-1} belong to the stretching vibrations of $Si-CH_3$ and Si-O, respectively. After carbonization and treatment by HF, a weaker absorption band is still observed at 1215 cm^{-1}. Results indicate that C-Si-O groups were incorporated in CMS and template SiO_2 has been washed completely by HF. The signal at 1570 cm^{-1} is attributed to stretching vibration of the C=C in six-membered unsaturated ring[13,14], which indicate that the precursor cyclization was accompanied by thermal decomposition. As the carbonization temperature increasing to 850 °C, the flat network structure has no further dehydrogenation to generate the amorphous graphite in high temperature. This may be due to the Si involves in cyclization, Si and C cross-linked hinder the network structure fragmentation[15]. The diffraction peak locate at 45° in X-ray pattern can also demonstrate that the formation of hexagonal planar network structure[13] (Fig. 3). In addition, the Ag exhibit two typical diffractions appear at 40° and 66°, indicating that the Ag^+ could be reduced to silver form by carbonization.

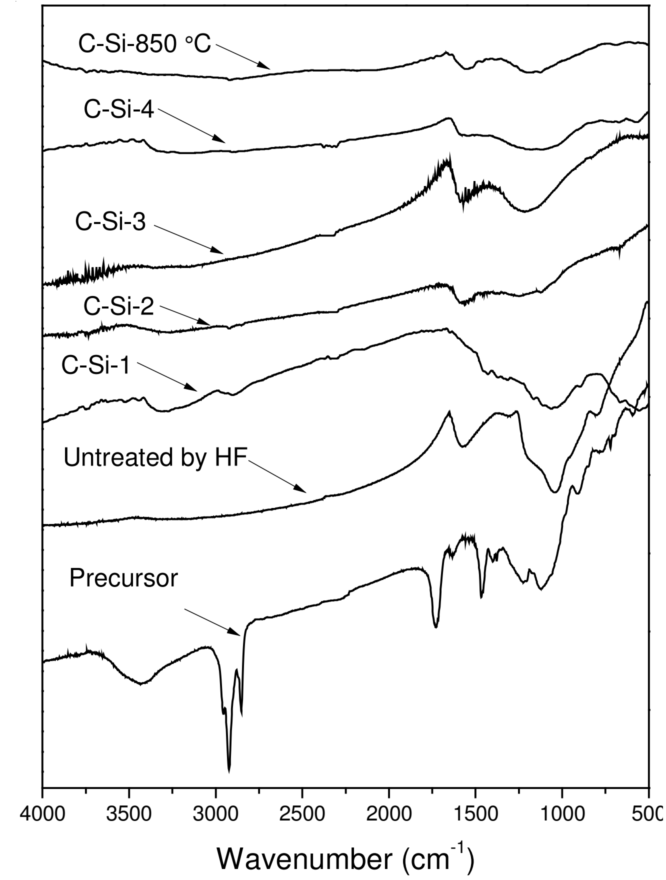


Fig. 2. FTIR spectra of the carbon precursor before and after high-heat treatment. C-Si-850 °C, AN-Si-4 high-heat treatment at 850 °C under nitrogen atmosphere

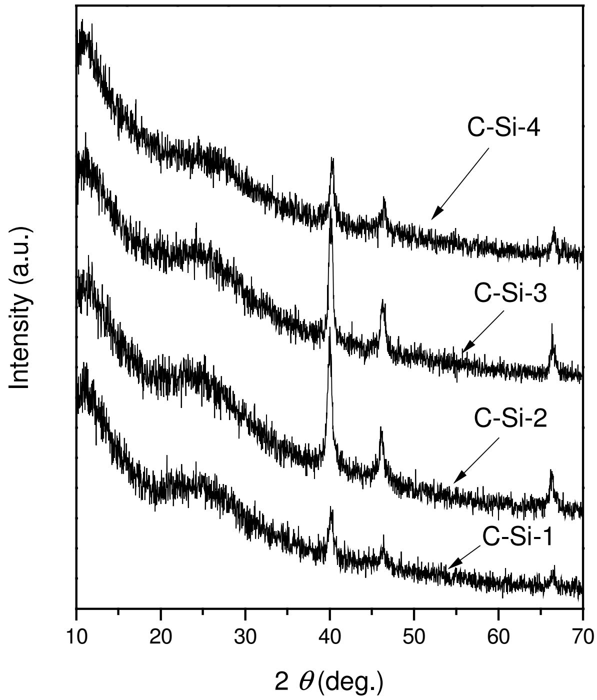
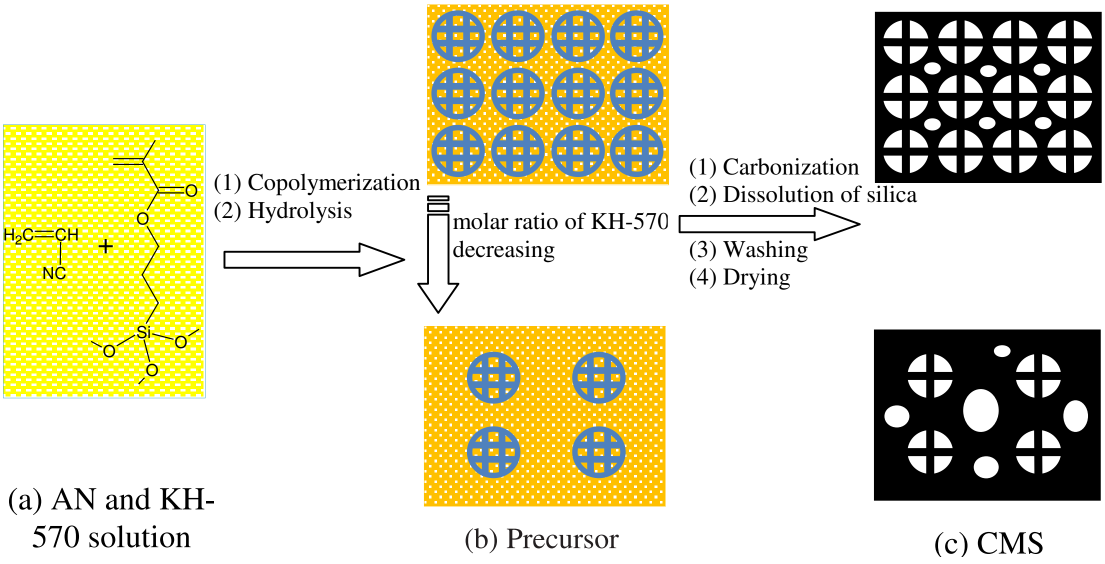


Fig. 3. XRD of CMS at different carbonization temperatures

The N_2 adsorption-desorption data are summarized in Table-1. The N_2 adsorption isotherms of carbonization products is showed at Fig. 5, all the isotherms belong to type IV (BDDT classification) of the IUPAC classification with H4 hysteresis loops[16]. The low-pressure absorption steps are the result of the micropore filling with N_2. The samples exhibit a higher N_2 uptake in this region ($P_0/P < 0.2$), indicating a higher micropore volume. Due to the different situation of copolymer and SiO_2 cover each other in carbon precursor, the different evolution of pore size is observed (Fig. 4).



(a) AN and KH-570 solution

(b) Precursor

(c) CMS

Fig. 4. Synthetic process for Ag-doped composite CMS

TABLE-1
NITROGEN SORPTION DATA OF THE COMPOSITE CMS AT 750 ºC

Sample	S_{BET} (m^2/g)	S_{me} (m^2/g)	D_{av} (Å)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	V_{total} (cm^3/g)
C-Si-1	1056	134	21.8	0.45	0.16	0.57
C-Si-2	667	161	43.2	0.29	0.48	0.72
C-Si-3	666	98	23.2	0.27	0.14	0.38
C-Si-4	699	94	25.4	0.28	0.18	0.44

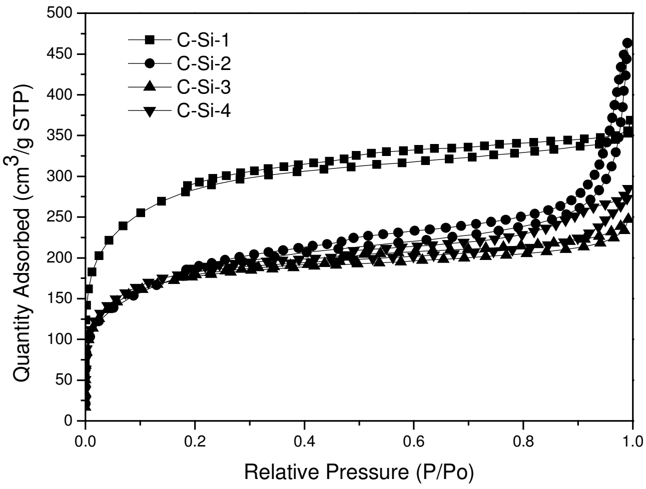


Fig. 5. N_2 adsorption-desorption isotherms of AN-KH-570 copolymer treated at 750 °C.

The formation of pores form two parts, a part of precursor fill into the skeleton pores of silica, the narrow pore distribution of micropore could be obtained after carbonization; the other fill up the space between templates, the products should exhibit a wider pore distribution. Therefore, the more uniform pore distribution and the larger micropore volume fraction can be obtained with a higher content of KH-570 and proved by the data in Table-1. C-Si-1 exhibits a very high micropore volume, to 0.45 cm^3/g, achieving *ca.* 79 % by total volume, BET surface area (1056 cm^3/g) is much higher than other samples; C-Si-2 contain large amount of mesopore structure, the volume to 0.48 cm^3/g, total pore volume is higher than the others; as the amount of KH-570 incorporated decreasing, the pore volume of samples show a slight change, with a higher micropore contain about 70 %. The hysteresis loops in the isotherms without significant adsorption platform, implying that the samples belong to the micro- and mesopore mixed adsorbents, with narrow fissures hole[16]. As shown by BJH pore size distribution (Fig. 6) and the carbons show a narrow pore size distribution in mesopore range. The mesopore size distribution of C-Si-1 mainly center at 2 nm. C-Si-2 is predominated by mesopores and the wider mesopore size distribution can be observed. As the molar ratio of KH-570 decreasing, by comparison, the mesopore size of sample is increased and the mesopore size distribution center to 4 nm gradually.

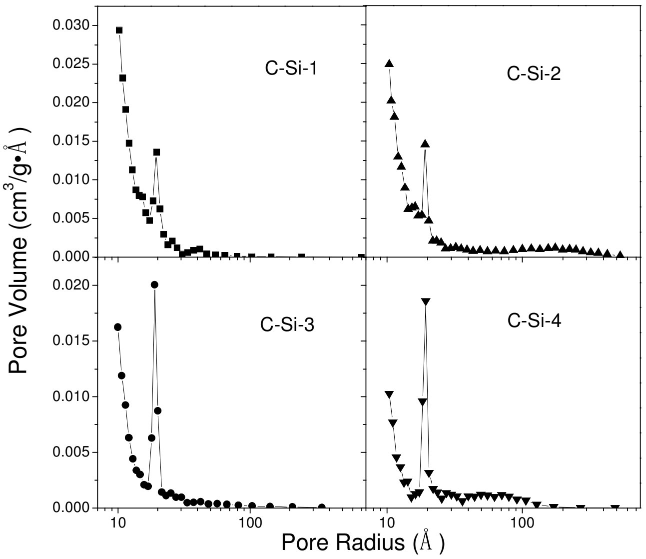


Fig. 6. dV/dR pore volume of AN-KH-570 copolymer treated at 750 °C by nitrogen adsorption/desorption isotherms.

Conclusion

The inorganic species is successfully incorporated into Ag-doped ordered porous CMS by copolymerization with acrylonitrile and KH-570. N_2 adsorption/ desorption measurement is used to prove that the pore size distribution of composite carbons shrank gradually from meso- to micropore through increasing the molar ratio of KH-570. The synthetic method reported here could be very effective for preparation micro- or mesoporous CMS with adjustable pore structure.

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