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**PRELIMINARY RESULTS ON SYNTHESIS
OF ACTIVATED CARBON SUPPORTED WITH SILVER NANOPARTICLES
IN SUPERCRITICAL WATER MEDIUM**

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Activated carbon supported with silver nanoparticles was synthesized in supercritical water condition at 673 K and 30.0 MPa in a batch reactor. The reaction time was 30 min with concentration of silver acetate solution at 0.02 M. Synthesized activated carbon-Ag particles were characterized by X-ray diffraction, Fourier transformation confirmed infrared spectroscopy and scanning electron microscopy. X-ray diffraction measurement indicated the presence of metallic silver. Fourier transformation infrared spectroscopy traces of primary activated carbon, activated carbon treated in supercritical water condition and synthesized activated carbon-Ag showed slight shift near 1629 cm^{-1} due to silver bonding to activated carbon via carbonyl and carboxyl groups. There was also observed chain-like structure of activated carbon-Ag with size of around 100 nm when scanned by electron microscopy.

Keywords: activated carbon; silver nanoparticles; supercritical water condition; scanning electron microscopy; X-ray diffraction; infrared spectroscopy; Fourier transformation.

Introduction

Supercritical water technology has become useful platform for synthesizing nanomaterials in the last two decades. There are many different methods of supercritical water technology such as the method of rapid expansion of supercritical

solution, gas antisolvent processes, processes of particle preparation from gas saturated solutions [1], the hydrothermal synthesis method [1, 2], and the method of reverse micelles. Among them supercritical hydrothermal synthesis is generally acknowledged as a method for preparing metal and metal oxide crystals from metal salts via hydrolysis and dehydration [3, 4].

The activated carbon (AC) has high adsorption capacity due to their internal structure which consists of a large number of interconnecting fine pores [5]. It is well known that silver among the various metals has been considered as an effective antimicrobial agent, food preservative agent and water purifying agent. Hence, the combination of activated carbon and silver nanoparticle may suggest an efficient material for water purification because of their exceptional high surface area and antibacterial properties. Other researchers have conducted investigation on preparation of silver nanoparticle loaded materials by different methods such as vacuum impregnation [6], liquid phase reduction method [7] and hydrothermal synthesis [7, 8]. The silver nanoparticles deposited via supercritical water technique on porous activated carbon prepared from Mongolian natural anthracite could be an attractive material for water purification in rural areas in Mongolia where pure water source is scarce. The aim of present study is to prepare an activated carbon particle with well deposited silver nanoparticles in supercritical water condition.

2. Experimental

2.1. Materials

Silver acetate reagent (CH_3COOAg) with 99.5% purity was used in experimental studies. Reagent was purchased from Shanghai Macklin Biochemical Co.Ltd. Activated carbons were obtained by chemical activation with KOH from anthracite.

2.2. Preparation of activated carbons

Activated carbon were prepared from anthracite by chemical activation with KOH following the same method as described in previous publication [4]. Raw anthracite was supplied from "Ikh Gobi Energy" Co.Ltd mine located in the Mandakh soum, East-Gobi province, Mongolia. The raw samples were first grounded into small particles and sieved. In the experiments raw anthracites with fractions size of $< 53 \mu\text{m}$ were activated by impregnation of carbon precursor with concentrated potassium hydroxide at a ratio of 1:3 for 2 h at 750°C under N_2 atmosphere in a tubular furnace. Prior to chemical activation the impregnated samples with KOH were preheated at 450°C for 2 h and then continuously heated to activation temperature to remove inner moisture and other volatile contaminants under N_2 atmosphere. After activation, the activated carbons were washed with deionized water and 0.5 M HCl until the pH reached to 7.0. The obtained samples were dried at 105°C for 24 h in a vacuum oven.

2.3. Hydrothermal synthesis of AC supported silver nanoparticles

Hydrothermal synthesis of AC supported silver nanoparticles were carried out under supercritical water conditions at 673 K and 30.0 MPa in pressure-resistant tube reactor (INC 315) with inner volume of 5.0 mL. The reactor was loaded with 3.0 mL, 0.02 M of metal salt (CH_3COOAg) aqueous solution and 0.06 g of activated carbon powder. The reactors were then capped tightly and put in temperature controlled an electric furnace (Nabertherm). The temperature was maintained at 673 K while the reaction pressure was assumed to be 30 MPa based on literature data. The reaction was

performed for 30.0 min and terminated by quenching in a cold water bath. After quenched, the sample was washed by distilled water. Finally, the products were dried at 110°C in a vacuum oven.

2.4. Characterization of prepared samples

The prepared activated carbon samples were characterized by nitrogen adsorption and desorption equilibrium data obtained at 77 K (Micrometrics ASAP 2020, USA). The specific surface area of the activated carbon was calculated according to the Brunauer-Emmett-Teller (BET) method using the nitrogen adsorption isotherm. The pore size distribution, pore volume and pore size were determined using the Horvath and Kawazoe (HK) and the Barrett-Joyner-Halenda (BJH) methods, respectively. The obtained samples, which are silver particles deposited on the activated carbon surface were identified crystallographic by X-ray diffraction (XRD) measurement which were taken on a Maxima-X XRD-7000. The morphologies of the nanoparticles were studied by using the scanning electron microscopy (SEM) (Topcon SM-300 electron microscope operated at 20 kV). The chemical bonds on the surface of products were evaluated by Fourier transform infrared spectroscopy (FTIR, IR Prestige-21).

3. Results and Discussions

3.1. Characterization of AC

The nitrogen adsorption and desorption isotherm and the pore size distributions curves of AC are shown in Fig. 1(a) and (b), respectively. In this study, prepared AC presents the type I isotherm according to the IUPAC classification. The first step is a steeply increasing region at low relative pressures less than 0.02, which stands for the adsorption or condensation in small micropores. Then the adsorption amount slowly increases with relative pressures without any notable hysteresis which represents the progressive filling of large micropores and mesopores. Finally, the adsorption amount increases abruptly at near the saturation pressure of nitrogen because of active capillary condensation cf. Fig. 1 (a). The pore size distributions of the AC show a wide range of well-developed pores from 0.6 to 3 nm with a narrow peak at a pore width around of 0.7-1.1 nm as shown in Fig. 1(b). It is shown that the AC has a properly developed small mesopores and more clearly micropores in the range of 0.7-1.1 nm. All physical characterization data of AC based on the adsorption and desorption isotherms of nitrogen are listed in Table 1. BET surface area of AC is 1227 m²/g, the micropore volume is 0.61 cm³/g, the micropore size is 0.53 nm, and the mesopore size is 2.7 nm, respectively.

3.2. Characterization of AC supported silver nanoparticles

AC supported silver nanoparticles were prepared via simple hydrothermal synthesis due to the ease of the controllability of thermodynamics and transport properties by pressure and temperature. There is no clear peak for activated carbon because of its amorphous nature. A slight rise of diffraction background at lower angle was caused amorphous nature of the AC. Around 34-42, 2 θ was observed low intensity broad peak which cannot be assigned to any crystalline compound. However, one can see clear peak of the metal silver as shown in Fig. 2.

Table 1

The physical properties of AC

Activated carbon	S_{BET} (m ² /g)	Pore volume (cm ³ /g)			Pore diameter (nm)		V_{micro}/V_{total}	Yield wt%
		V_{micro}	V_{meso}	V_{total}	D_{micro}	D_{meso}		
AC	1227	0.61	0.09	0.70	0.53	2.7	0.87	58.4

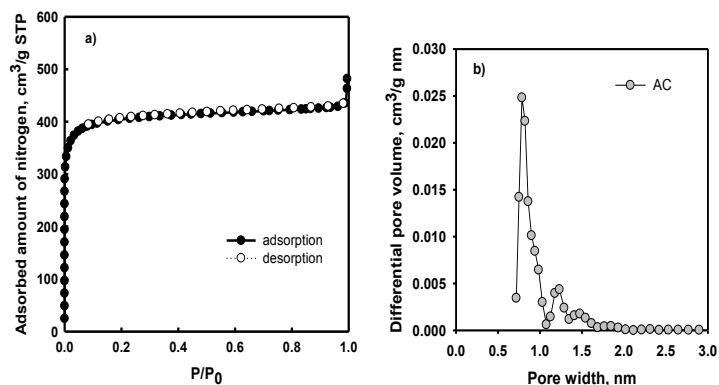


Fig. 1. The nitrogen adsorption/desorption isotherm (a) and the pore size distributions of AC (b)

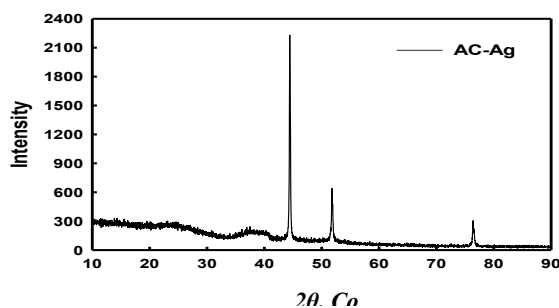


Fig. 2. X-ray diffraction patterns of the AC-Ag sample

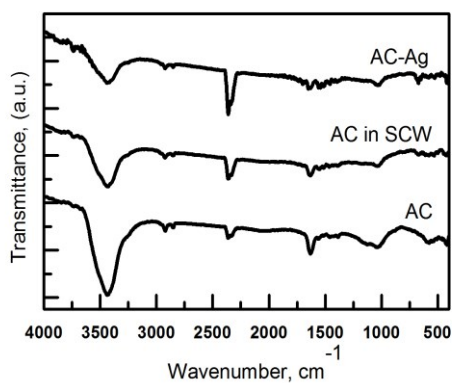


Fig. 3. FTIR spectrum of primary AC, AC in SCW and AC-Ag

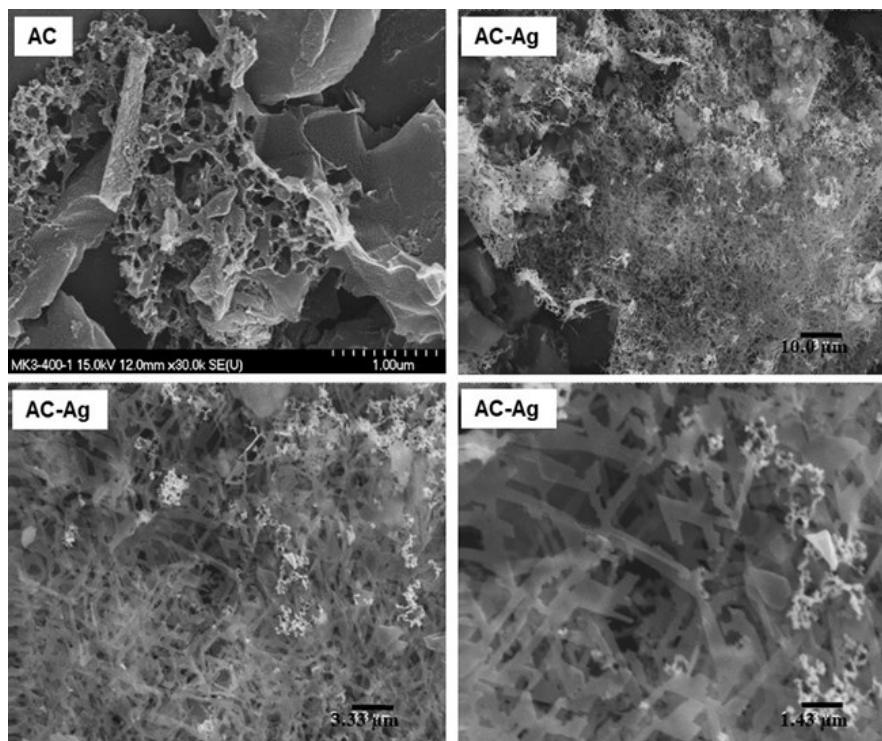


Fig. 4. SEM images of primary activated carbon and synthesized AC-Ag at different magnifications.

The bonding state of samples were evaluated and compared. IR spectrum of all three samples, primary AC, AC and AC-Ag in supercritical water supercritical water (SCW) were shown in Fig. 3. It shows slight shift near 1629 cm^{-1} of carbonyl and carboxyl group (-C=O), possibly the silver was bonded via carbonyl and carboxyl group of activated carbon. However, there was not observed bonding of metal silver which should be caused by its appearance at wavenumber below 400 cm^{-1} .

The morphologies of the primary AC and synthesized AC-Ag was observed by SEM and the images were showed in Fig. 4.

As it shown in Fig. 4, we compared the SEM image of primary activated carbon and synthesized AC-Ag imaged at different magnification. Silver nanoparticles were deposited on the layered crystallites. Possibly there occurred crystallization of some compounds under supercritical condition, though, XRD revealed presence of well crystallized silver crystals. Presence of the low intensity, broad peak at $34\text{-}42, 2\theta$ degrees in the XRD pattern (Fig. 2) may also be caused by formation of the layered crystals which discussed above. Silver particles with size of around 100 nm were connected each other creating a chain-like structure as it can be seen from the SEM images, cf. Fig. 4. There are also agglomerations of silver particles on the AC surface were observed because of reaction time and/or the metal salt concentrations are not at their optimum condition. Possibly the concentration of the silver acetate and reaction time was higher than to form uniformly distributed silver nanoparticles on AC. By

studying further in detail we could prepare well distributed silver nanoparticles on porous structure of activated carbon. The simple method demonstrated here could be useful for synthesizing new materials for various applications. Further optimization of the AC-Ag preparation is underway and will be reported in our next publication.

Conclusions

We have demonstrated a simple method to fabricate activated carbon supported silver nanoparticles by the hydrothermal synthesis at 673 K and 30.0 MPa in a batch reactor. At the reaction time of 30 min, the 0.02 M concentration of salt solution and 2 wt, % AC was observed crystallization of chain-like bonded silver particles of 100 nm in size on the surface of AC. Crystallized silver is likely to be attached via carbonyl and carboxyl group to activated carbon surface. Agglomeration of silver particles indicates that further optimization of the reaction condition required in order to prepare uniformly distributed silver nanoparticles on the surface of AC.

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РЕЗУЛЬТАТЫ ПРЕДВАРИТЕЛЬНЫХ ИССЛЕДОВАНИЙ
ПО ПОЛУЧЕНИЮ АКТИВИРОВАННОГО УГЛЯ С НАНЕСЕННЫМИ
НАНОЧАСТИЦАМИ СЕРЕБРА В СВЕРХКРИТИЧЕСКОЙ ВОДЕ

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Активированный уголь с нанесенными наночастицами серебра, получен при 673К и 30.0 МПа в сверхкритической воде с использованием реактора периодического действия. Реакцию проводили в течение 30 мин при концентрации ацетата серебра 0.02 М. Полученный АС-Ag охарактеризован методами рентгенодифракционного анализа, ИК спектроскопии с использованием преобразования Фурье и сканирующей электронной микроскопии. Результаты рентгенодифракционного анализа подтвердили присутствие металлического серебра. При сравнительном ИК анализе активированного угля как исходного, так и обработанного в сверхкритической воде, а также синтезированного активированный уголь-Ag наблюдались соответственно небольшие сдвиги при 1629 см⁻¹ за счет присоединения атомов серебра к углю через карбонильные и карбоксильные группы. На изображениях сканирующей электронной микроскопии активированный уголь-Ag прослеживались цепочки размером около 100 нм, образованные наночастицами серебра.

Ключевые слова: активированный уголь, наночастицы серебра, сверхкритическая вода, сканирующая электронная микроскопия, рентгенодифракционный анализ, инфракрасная спектроскопия, Фурье преобразование