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# Synthesis and adsorption properties of colloid-imprinted mesoporous carbons using poly(vinylidene chloride-co-vinyl chloride) as a carbon precursor

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**Abstract** A facile synthesis of micro- and mesoporous carbons has been proposed using colloidal silica nanoparticles with diameter of ∼24 nm and poly(vinylidene chloride-co-vinyl chloride) (Saran) as a carbon precursor. The resulting carbons possessed large specific surface area, ∼800 $m^2/g$, and approximately the same volume of micro- and mesopores, each about 50% of the total pore volume. While the size of micropores was around 1 nm, the large and uniform spherical mesopores (about 24 nm) resemble the diameters of silica colloids used. Nitrogen adsorption measurements proved that these mesopores were interconnected and accessible. The well-developed microporosity was created mainly by decomposition of Saran copolymer during carbonization.

**Keywords** Colloidal imprinting method · Micro- and mesoporous carbons · Adsorption properties

## 1 Introduction

Nanoporous materials such as active carbons, zeolites, silica gels and metal oxides play an important role in science and technology, especially in adsorption, catalysis, separations and purification. Recently, many attempts have been made to prepare nanomaterials possessing precisely designed surface and structural properties (Kresge et al. 1992; Wu and Bein 1994; Mann and Ozin 1996; Holland et al. 1998; Kyotani 2000; Ryoo et al. 2001; Choma et al. 2004). In particular, nanoporous carbons have attracted considerable attention because of their unique adsorption and catalytic properties (Inagaki 2000; Deryło-Marczewska and Goworek 2002; Nguyen-Thanh and Bandosz 2006; Seredych and Bandosz 2007; Choma et al. 2008b). In general, ordered mesoporous carbons (OMCs) have been prepared by the hard-templating method using porous siliceous templates, especially ordered mesoporous silicas (OMSs) such as MCM-48 and SBA-15. According to this method, OMCs have been prepared by filling the pores of the desired OMS template with a suitable carbon precursor resulting in a carbon precursor-OMS composite, which after carbonization and template dissolution gave a stable inverse carbon replica of the template. Carbons obtained by this method exhibit well ordered mesopores up to about 7 nm (Ryoo et al. 1999; Jun et al. 2000; Lee et al. 2001). Some limitations of using OMSs as templates include the difficulty in the synthesis of exact inverse carbon replicas with mesopores larger than 6 nm, since OMSs typically possess pore walls of about 1–6 nm. Thus, generation of larger pores and thicker carbon pore walls requires different hard-templates such as colloidal silica with tunable diameters (Zakhidov et al. 1998; Li and Jaroniec 2001, 2003).

By mixing the colloidal dispersions of silica nanoparticles with carbon precursors, followed by drying, carbonization and silica dissolution, carbons with uniform spherical mesopores can be obtained. Despite of the disordered nature of such carbons, their pores and pore wall thickness are considerably larger than those in the OMS-templated OMCs. Another important feature of the colloid-templated carbons is a good accessibility of mesopores due to the existing interconnections as well as the easiness of tailoring their shape and size by selecting appropriate silica colloids as templates.

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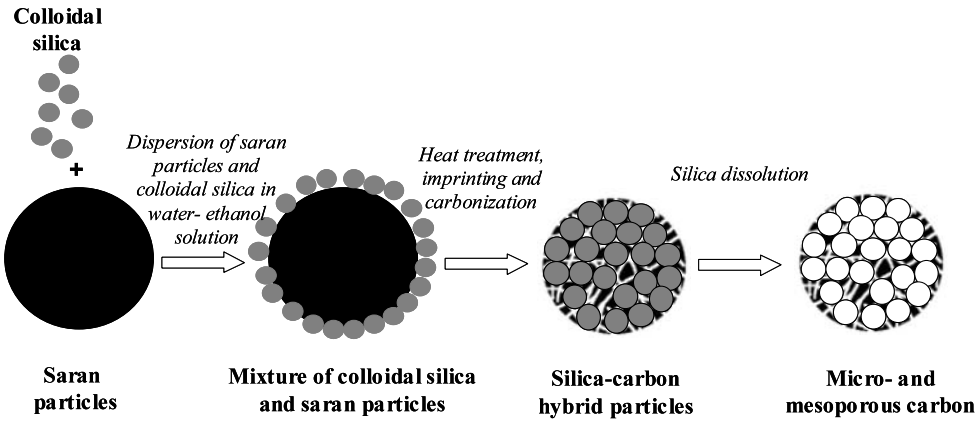


**Fig. 1** Illustration of colloidal imprinting synthesis of micro- and mesoporous carbons

In the case of pitch used as a carbon precursor the synthesis of mesoporous carbons can be simplified by elimination of solvents (Li and Jaroniec 2001, 2004a, 2004b; Li et al. 2002; Gierszal and Jaroniec 2004). Heating a mixture of silica colloids and pitch particles above pitch softening point facilitates inclusion of silica colloids into viscous pitch particles. Since this process involves an interpenetration of colloidal silica particles and pitch particles (solid carbon precursor), it was called as colloidal imprinting in contrast to the colloidal templating, in which carbon precursors (liquid or vapor) are introduced to the pores of silica template. By adjusting the synthesis conditions it is possible to control the amount of incorporated silica colloids into pitch particles, and consequently, to create mesopores on the surface of pitch particles or in the entire volume of these particles. After pyrolysis and etching of the silica template, mesoporous carbons with tailored pore volume and low microporosity are obtained (Li and Jaroniec 2001).

The extension of the colloidal imprinting for the synthesis of mesoporous carbons from other sources, which assure higher microporosity, is demonstrated here for the first time. By using the poly(vinylidene chloride-co-vinyl chloride) (Saran) and colloidal silica, carbons with approximately the same volume of micro- and mesopores have been obtained according to the scheme shown in Fig. 1. Thus, not only the mesopore shape, diameter and pore wall thickness can be tailored by selecting appropriate silica colloids, but also the microporosity can be tuned by using suitable carbon precursors. This study shows that the use of appropriate silica colloids and carbon precursors permits not only to tailor mesoporosity but also microporosity of the resulting carbons.

## 2 Experimental

### 2.1 Synthesis of mesoporous carbons

The colloidal imprinting synthesis of mesoporous carbons was performed by using the poly(vinylidene chloride-co-vinyl chloride) particles (also known as Saran) and silica colloids of ∼24 nm. In the typical procedure 2 g of poly(vinylidene chloride-co-vinyl chloride) (Sigma-Aldrich, Chemie, Germany; 240–320 μm particle size) was dispersed in 40 $cm^3$ of ethanol under vigorous stirring for ∼30 min. Then, 40 $cm^3$ of colloidal silica Ludox AS-40 (Sigma-Aldrich, Chemie, Germany; 40% wt of silica colloids having diameter of ∼24 nm ) was slowly added to the mixture ($SiO_2$/Saran = 10:1). Subsequently, all reagents were stirred at 55 °C allowing for the slow evaporation of the solvent. The resulting thick gel was then transferred to a horizontal quartz tube furnace and treated at 250 °C for 3 hours in flowing nitrogen. This material was then thermally treated at 190 °C for 14 h in air flow in order to prevent further penetration of the silica colloids into Saran matrix. After stabilization, the saran-silica nanocomposite was carbonized in flowing nitrogen at 850 °C for 2 h with a heating rate of 5 °C/min. The silica colloids were etched from the carbon nanocomposites with an aqueous solution of HF (15% w/w) for 72 h at room temperature. This carbon was thoroughly washed with butanol and hexane (Chempur, Poland), and dried at 80 °C for 12 h. The weight of the final product was of ∼0.5 g, which was finally labeled as CIC-S1.

Analogous synthesis recipe was used to prepare other three carbons by varying the silica to saran weight ratios and temperature for the colloidal imprinting and stabilization steps. Mesoporous carbon labeled as CIC-S2 was synthesized with $SiO_2$/Saran = 4:1 by introducing 15.5 $cm^3$ of colloidal silica to the reaction mixture. The carbons denoted as CIC-S3 and CIC-S4 were prepare analogously to CIC-S1 sample. In both cases the temperature of colloidal imprinting was lowered to 180 °C. Then, the stabilization process for CIC-S3 was done at 150 °C, while this step was not performed for the CIC-S4 carbon.

### 2.2 Adsorption measurements and calculations

Nitrogen adsorption-desorption isotherms were measured at −196 °C by using a volumetric analyzer from Micrometrics

(Norcross, GA, USA). Prior to adsorption measurements the carbon samples were outgassed in vacuum at 200 °C for at least 2 h. The specific surface area was calculated according to the standard Brunauer-Emmett-Teller (BET) method (Gregg and Sing 1982) in the relative pressure range of 0.05–0.20 using the cross-sectional area of 0.162 $nm^2$ per nitrogen molecule. The total pore volume (Gregg and Sing 1982) was evaluated from the amount adsorbed at a relative pressure of 0.99.

The carbon samples studied were analyzed using the $\alpha_s$-plot (Gregg and Sing 1982; Jaroniec and Kaneko 1997), where $\alpha_s$ is the standard relative adsorption defined as the amount adsorbed at a given pressure to the amount adsorbed at a relative pressure of 0.4 for a reference adsorbent. The $\alpha_s$-plots for the carbonaceous materials studied were obtained by using the nitrogen adsorption data for nongraphitized Cabot BP280 carbon black (Cabot Co., Special Blacks Division, Billerica, MA, USA) measured by Kruk et al. (1997). The $\alpha_s$-plot was constructed by plotting the amount adsorbed for the investigated sample as a function of the relative adsorption $\alpha_s$ for the aforementioned reference material (Cabot BP280).

The pore size distributions (PSDs) were calculated from the adsorption branch using the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951). The BJH method is based on the Kelvin equation, which correlates the capillary condensation pressure and pore diameter. In this method we used the statistical film thickness for the Cabot BP280 carbon black (Kruk et al. 1997), which was obtained by fitting the reference isotherm on this carbon to the multilayer range of the t-curve established on the basis of MCM-41 materials (Choma et al. 2002).

## 3 Results and discussion

Nitrogen adsorption-desorption isotherms measured at −196 °C are shown on Fig. 2. According to the IUPAC classification (Sing et al. 1985), the nitrogen adsorption isotherms for all samples studied are type IV with steep capillary condensation steps, reflecting the uniformity of mesopores.

The structural parameters calculated from nitrogen adsorption isotherms are listed in Table 1. All carbons studied exhibit high BET surface area in the range from 712 $m^2/g$ for CIC-S1 to 848 $m^2/g$ for CIC-S4. A relatively high adsorption at low pressures suggests the existence of large amount of micropores; the volume adsorbed in those pores was found to be ∼200 $cm^3$ STP/g. Also, the volume adsorbed in uniform mesopores was found to be approximately the same, 200 $cm^3$ STP/g. In addition, a nearly flat midsection of the isotherms (0.1–0.9 $p/p_o$) reflects negligible textural porosity, indicating only the presence of two well-resolved types of pores: small micropores and relatively large mesopores. It is noteworthy that all CIC-samples possessed very small external surface area (3–7 $m^2/g$) due to

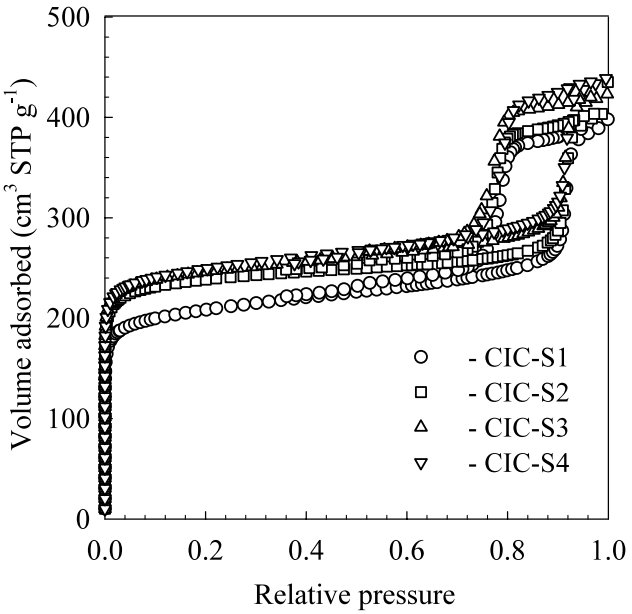


**Fig. 2** Nitrogen adsorption-desorption isotherms at −196 °C for the micro- and mesoporous carbons obtained by colloidal imprinting method

**Table 1** Adsorption parameters for the micro- and mesoporous carbons obtained by colloidal imprinting

| Adsorbent | $S_{BET}$ $m^2/g$ | $V_t$ $cm^3/g$ | $V_{mi}^{\alpha_s}$ $cm^3/g$ | $V_{mi}^{BJH}$ $cm^3/g$ | $V_{me}^{\alpha_s}$ $cm^3/g$ | $V_{me}^{BJH}$ $cm^3/g$ | $w_{BJH}^{mi}$ nm | $w_{BJH}^{me}$ nm |
|---|---|---|---|---|---|---|---|---|
| CIC-S1 | 712 | 0.60 | 0.27 | 0.26 | 0.32 | 0.31 | 1.17 | 25.1 |
| CIC-S2 | 813 | 0.62 | 0.34 | 0.33 | 0.26 | 0.28 | 1.13 | 24.2 |
| CIC-S3 | 836 | 0.65 | 0.33 | 0.37 | 0.31 | 0.30 | 1.17 | 24.4 |
| CIC-S4 | 848 | 0.67 | 0.33 | 0.32 | 0.33 | 0.32 | 1.15 | 25.3 |

$S_{BET}$ BET specific surface area, $V_t$ single-point total pore volume calculated for $p/p_o = 0{,}99$, $V_{mi}^{\alpha_s}$ volume of micropores obtained by $\alpha_s$-method, $V_{mi}^{BJH}$ volume of micropores obtained by integration of PSD, $V_{me}^{\alpha_s}$ volume of mesopores obtained by $\alpha_s$-method, $V_{me}^{BJH}$ volume of mesopores obtained by integration of PSD, $w_{BJH}^{mi}$ and $w_{BJH}^{me}$ micropore and mesopore diameters at the maxima of the PSD curve

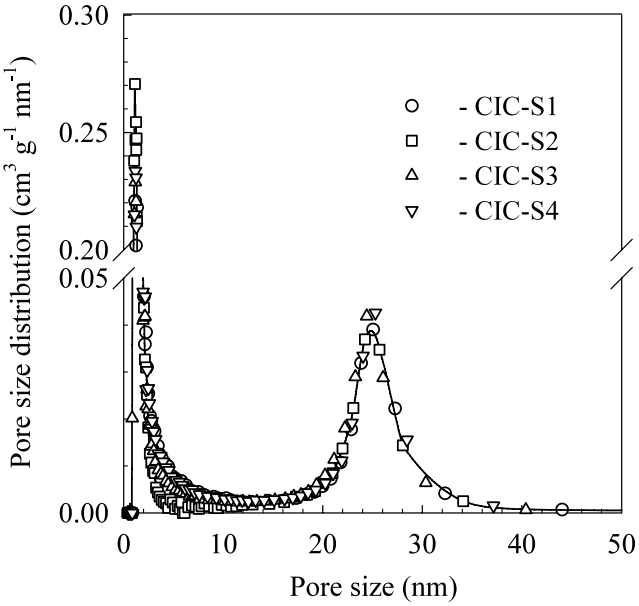


**Fig. 3** Pore size distributions calculated by the BJH method for the micro- and mesoporous carbons obtained by colloidal imprinting method

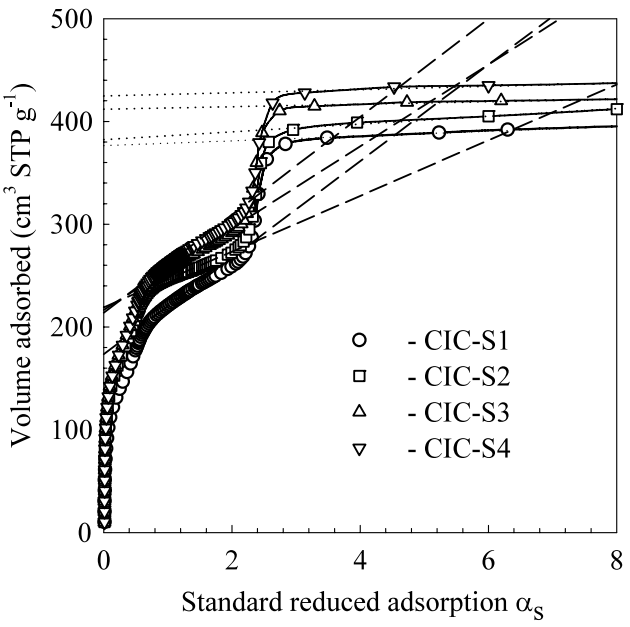


**Fig. 4** The $\alpha_s$-plots for the micro- and mesoporous carbons obtained by colloidal imprinting method

the negligible textural porosity. The single-point total pore volume, $V_t$, estimated from the amount adsorbed at a relative pressure $p/p_o$ of 0.99 was found to gradually increase within the series from 0.60 cm$^3$/g for CIC-S1 to 0.67 cm$^3$/g CIC-S4.

The pore size distribution (PSD) curves presented in Fig. 3 were calculated from adsorption branches by the improved BJH method (Choma et al. 2002, 2008a) using the statistical film thickness ($t$-curve) for the carbon surface, BP280 carbon black (Kruk et al. 1997). Each of the plots consists of a very sharp and narrow peak corresponding to the micropores and a broader peak attributed to mesopores. The first system of pores possesses maxima at 1.1–1.2 nm. The origin of micropores is probably due to the thermal decomposition of Saran; the gaseous products released afford the tiny channels formation in the polymer gel. The peaks with maxima at about 24 nm clearly resemble the size of silica nanoparticles used and prove that the colloidal imprinting process is responsible for formation of mesostructure. The volume of micropores ($V_{mi}^{BJH}$) and mesopores ($V_{me}^{BJH}$) obtained by integration the PSD curves are reported in Table 1. As it was mentioned before, the micropores and mesopores contribute equally, ~0.3 cm$^3$/g each, to the total pore volume.

These observations were confirmed by $\alpha_s$-plots shown in Fig. 4. Each plot expresses the amount adsorbed on the surface of the carbon studied as a function of the standard reduced adsorption $\alpha_s$. The $\alpha_s$ was determined on the basis of the nitrogen adsorption data obtained for nongraphitized BP280 carbon black (Kruk et al. 1997). As can be seen from these plots, all carbon materials exhibit not only quite big content of micropores but also the significant amount of mesopores. The micropore volume $V_{mi}^{\alpha_s}$ calculated in the range of 0.8–1.2 (dashed line) was found to vary from 0.27 cm$^3$/g for CIC-S1 to 0.34 cm$^3$/g for CIC-S2. The $\alpha_s$ section from 3.0 to 8.0 was used to estimate the volume of micropores $V_{mi}^{\alpha_s}$ and mesopores $V_{me}^{\alpha_s}$, which gradually increases within whole series from 0.59 cm$^3$/g (CIC-S1) to 0.66 cm$^3$/g (CIC-S4). Those findings demonstrate a very good agreement between two different ways of the pore volume determination.

## 4 Conclusions

In summary, the imprinting of colloidal silica nanoparticles in poly(vinylidene chloride-co-vinyl chloride) (Saran) large particles represents a facile way of preparation of micro- and mesoporous carbon materials. The microporosity of these materials is largely generated during thermal decomposition of the polymeric carbon precursor at 850 °C, while the mesopores were created by the dissolution of silica colloids. The calculated diameters of the mesopores agreed well with the size of silica nanoparticles used, in this case, 24 nm. The results obtained for four carbon samples proved the effectiveness and reproducibility of the colloidal imprinting synthesis. The use of Saran particles as a carbon precursor allows the synthesis of carbons with desired mesopore diameters and well-developed microporosity. Moreover, this method is suitable for the preparation of carbons with quite high specific surface area and similar micro- and mesopore volumes. Further increase in the volume of mesopores may

be achieved by reducing the size of Saran particles. Other post-synthesis treatments of these carbons such as graphitization or surface oxidation can further extend the range of their potential applications in catalysis, separations and energy-related processes. Also, the low cost and availability of the carbon precursor and colloidal silica makes large scale production of these carbons a feasible process.

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