Formation of an ink-bottle-like pore structure in SBA-15 by MOCVD†

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Metallorganic chemical vapor deposition is used as a simple pore-modifying method to fine tune the pore-opening size of SBA-15 materials without significant loss in pore volume and surface area.

SBA-15 is a mesoporous silica material composed of two-dimensional hexagonal arrays of channels that typically range from 5 to 9 nm in diameter.[1] Due to its appealing textural properties, high surface area, and appreciable thermal and hydrothermal stability, SBA-15 has recently attracted much research attention for potential applications in catalysis,[2,3] gas adsorption,[4–6] membrane separation,[7–9] advanced optics device[10] and media for immobilization of biomolecules[11–13] with different shapes, sizes and functionalities. Significant efforts have been dedicated to increasing the number of available mesostructures by varying the templating agent and synthesis conditions in order to improve the adsorbent's shape- or size-selectivity and/or adsorption capacity.[14–16] Narrowing the pore mouth of mesoporous adsorbents can improve the adsorption capacity in low concentration regions.[17] Hence, an ink-bottle-like pore structure has a great potential for hydrogen storage, due to its advantage of high adsorption affinity (narrowed pore mouth), large capacity (large pore body) and fast mass transfer (large pore body). Hydrogen can be released quickly when it is required, which is a significant advantage over the small pore-size adsorbents such as carbon nanotubes. The ink-bottle-like pore structure is also preferred for the adsorption of volatile organic compounds (VOCs).[17] Therefore, narrowing the pore-opening size of mesoporous materials has been a very interesting field in recent years. The deposition of thin silica layers on zeolites,[18,19] tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) on MCM-41 to reduce the pore-opening size has been studied by a chemical vapor deposition (CVD) method.[20] In our recent work,[21] the synthesis of copper nanorods using SBA-15 as template and Cu(acac)$_2$ as precursor by MOCVD method reveals that copper can be uniformly deposited in the pore channels when the SBA-15 is pretreated by a carbon-coating process.

In this study, a pore modification method as schematically shown in Fig. 1 was developed. Through carbon coating and metallorganic chemical vapor deposition (MOCVD) steps, the pore-opening size of SBA-15 materials can be modified by depositing carbon and copper layers to form an ink-bottle-like pore structure. In this way, the surface area and pore volume can be largely retained while the pore-opening sizes can be fine-tuned by the MOCVD process.

The preparation procedure of SBA-15 has been described in our previous work.[21] A total of 0.2 g SBA-15 was dried at 383 K for 12 h and then the carbon coating was conducted *in situ* at 1073 K using a gas mixture of nitrogen (0.8 ml s^{-1}) and acetylene (0.2 ml s^{-1}) (*i.e.* $C_2H_2 : N_2$ ratio of 1/4) for 2 min and SBA-15 as the substrate in the home-made carbon CVD system as schematically shown in Fig. 1a. The SBA-15 coated with a thin layer of carbon is denoted as SBA-C. For the MOCVD process, a rotated MOCVD reactor system schematically shown in Fig. 1b was used. Hydrogen, which acted as a reducing reactant and carrier gas, was supplied to the CVD reactor at a flow rate of 0.5 ml s^{-1}. The solid mixture of SBA-C and the precursor, copper(II) acetylacetonate (Aldrich

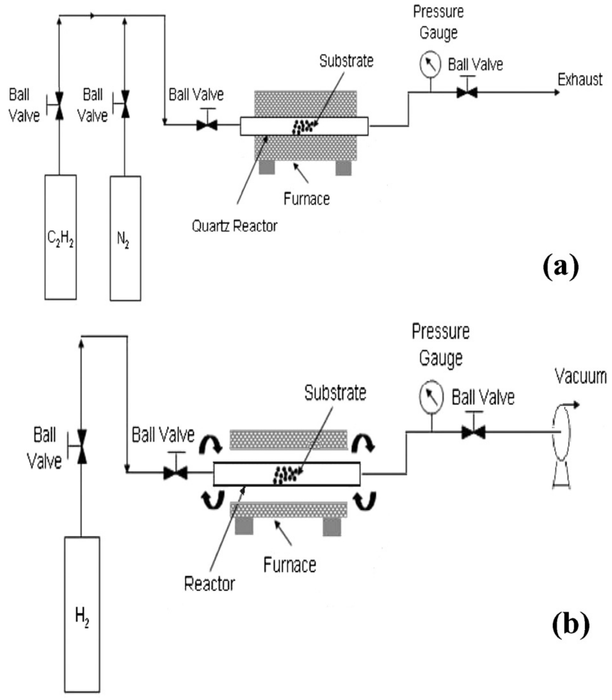

Fig. 1 Schematic diagram of (a) carbon-coating setup and (b) MOCVD reactor system for metal deposition.

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Chemical Co. 97%) with a mass ratio of 1 : 1 was housed inside the reactor vessel. The whole system was evacuated (2 kPa) using a vacuum pump and heated to 463 K for 30 min to sublime the solid organometallic precursor. Deposition was assumed to start when the system temperature reached 623 K. After a deposition process of 30 min, it was stopped by rapidly cooling the reactor to room temperature using compressed air flow.

The resulting product was denoted as SBA-C-Cu, which possesses an ink-bottle-like pore geometry Samples before and after modification were characterized by physical adsorption of nitrogen, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The nitrogen adsorption–desorption isotherms of the SBA-15 samples before and after modification, along with their BJH pore-size distribution curves are shown in Fig. 2. The nearly identical position of the hysteresis loops for the adsorption branch indicates that the pore body retains its original size (5.7 nm), while the shift of the hysteresis loops for the desorption branch to a lower p/p_0 position suggests that the pore-opening size has been narrowed after the carbon coating and MOCVD treatment. The pore size distribution of SBA-C is broader and features a double maximum which indicates the non-uniformity of the pore-mouth diameter. Since the purpose of carbon deposition is to provide a surface with a high adsorption affinity for the organometallic precursor, the structural uniformity is not important at this step. The MOCVD process can further polish the pore mouth but will not over-reduce the pore-opening size due to the steric hindrance of the organometallic precursor according to our previous work.[21] This is confirmed by the enlargement and parallel shape of the hysteresis loop of the SBA-C-Cu sample, indicating a perfect ink-bottle-like pore structure shown as the sharp pore-size distribution in Fig. 2b, which was calculated by the Barrett–Joiner–Halenda (BJH) method based on the desorption branch. This is explained below. After the MOCVD process, the desorption of N_2 molecules from SBA-C-Cu occurs at a much lower relative pressure than that of unmodified SBA-15, indicating that desorption of N_2 molecules from the larger cavity is retarded by the smaller necks. However, the adsorption branch is almost the same as that of unmodified SBA-15, indicating that there is little change in the pore body after modification. For ink-bottle-like pores, desorption of N_2 occurs from the narrow neck and this is replenished from the larger parts of the pore.[22] The pore-size distribution of the modified SBA-15 samples shown in Fig. 2b confirms that the pore mouth of SBA-15 has been reduced from 5.78 nm to a range of 3.7 to 5 nm after the carbon-coating process, indicating a partial modification of the pore mouth of SBA-15. An enhanced narrower steep peak of SBA-C-Cu at 3.7 nm after the MOCVD process suggests that the pore-opening size of SBA-15 has been uniformly reduced to 3.7 nm. As listed in Table 1, the effective pore-opening size (d_{mouth}), BET surface area (S_{BET}) and pore volume (V_t) have been reduced from 5.78 to 3.7 nm, 656 to 402 $m^2\ g^{-1}$ and 0.88 to 0.65 $cm^3\ g^{-1}$ respectively, after the MOCVD modification process. The fairly small reduction in porosity after modification indicates that the MOCVD process allows symmetrical copper deposition at the pore mouth to form an ink-bottle-like pore-structured SBA-15 material.

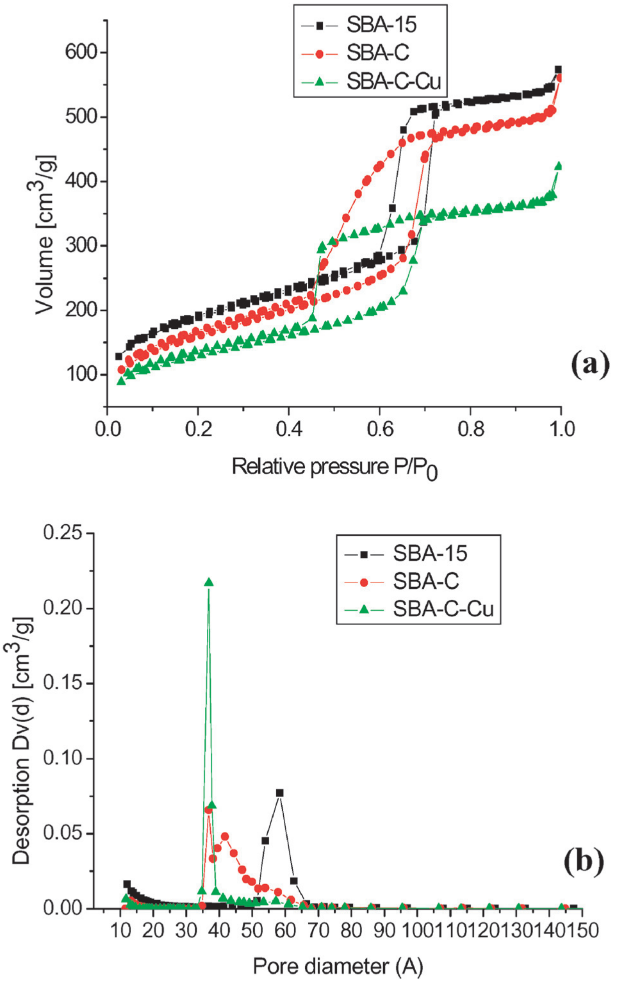

Fig. 2 (a) N_2 adsorption isotherms and (b) pore-size distribution of SBA-15 before and after pore modification with carbon CVD and MOCVD.

The mechanism of this method was presented as schematically shown in Fig. 3. The decomposition of C_2H_2 results in the carbon deposition in the pore mouth to form a thin carbon layer under appropriate conditions (C_2H_2 flow rate of 0.2 ml s^{-1}, N_2 flow rate of 0.8 ml s^{-1}, C_2H_2 feeding time of 2 min). The carbon-coating treatment of SBA-15 provides a better adsorption affinity for the organometallic precursor. Hydrogen was used as the reducing agent to help the dissociation of organometallic precursor to form smaller sized cupriferous organic intermediates to more easily diffuse onto the inner surface of the pore mouth and deposit there.[21,23]

The effect of C_2H_2 feeding time and $C_2H_2 : N_2$ ratio on the carbon deposition process has been investigated and the

Table 1 Pore properties of SBA-15 before and after modification with carbon coating and MOCVD

Sample	$S_{\mathrm{BET}}/m^2\ g^{-1}$	$V_t/cm^3\ g^{-1}$	d_{mouth}/nm
SBA-15	656	0.88	5.78
SBA-C	507	0.86	3.68
SBA-C-Cu	402	0.65	3.67

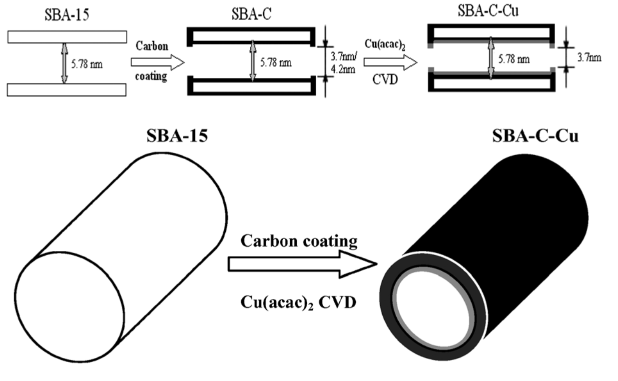

Fig. 3 Schematic model for modifying the pore-opening size of SBA-15.

results are available in the ESI.† Furthermore, the influence of the $Cu(acac)_2$: SBA-C ratio and the number of cycles of MOCVD on the pore modification was also studied. The results indicated that increasing the $Cu(acac)_2$: SBA-C ratio and the number of cycles of MOCVD cannot further reduce the pore-opening size but only deposit more copper on the exterior surface of SBA-C due to the steric hindrance of organometallic precursor according to our previous work.[21]

To investigate the particle morphology and periodic pore arrangement, the ink-bottle-structured SBA-C-Cu composite was further characterized with XRD and TEM techniques. Three resolved diffraction peaks [(100), (110) and (200)] are observed in the XRD pattern of SBA-15 samples before and after modification, as shown in Fig. 4, indicating that the ink-bottle-like SBA-C-Cu composite still maintains a highly ordered hexagonal pore structure. The preservation of the hexagonal, ordered pore structure is further confirmed by the TEM images of SBA-15 and SBA-C-Cu shown in Fig. 5. Moreover, some black dots are observed at the hexagonal cross section of SBA-C-Cu, which can be visualized as the copper layer deposited on the pore mouth of SBA-C.

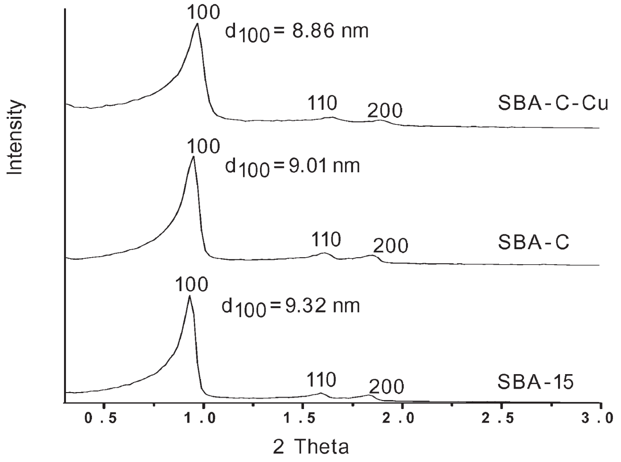

Fig. 4 XRD patterns of SBA-15 samples before and after modification.

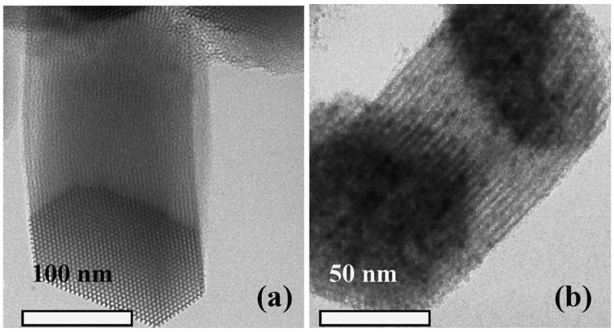

Fig. 5 TEM images of (a) SBA-15 and (b) ink-bottle-like SBA-C-Cu composite.

In conclusion, a simple route of MOCVD technique has been developed as an effective pore-modification method. This technique allows for the modification of the pore-opening size of SBA-15 to form an ink-bottle-like pore structure without significant loss in pore volume and surface area.

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