A novel route for synthesizing carbon mesoporous materials (CMMs) with well-dispersed, highly stable platinum nanoparticles (2-3 nm) favorable for applications as carriers for hydrogen storage and as supported electrodecatalysts for fuel cell (FC) has been developed.

1. INTRODUCTION

The R&D of safe and effective hydrogen storage systems is one of the key issues in future realization of hydrogen energy applications, particularly in commercialization of fuel cell vehicles [1]. Among various adsorbents, nano-structured carbon materials are promising candidates for hydrogen storage due to their high surface area and light-weight characteristics, however, no available storage materials are capable of meeting the US-DOE target (6.5 wt%) for commercial exploitation at present [2]; a further 40-50% increase in storage capacity is needed for currently available carbon-based materials, such as carbon nanotubes, activated carbon and carbon nanofibers [3]. Recent development in carbon mesoporous materials (CMMs) have drawn some attention in R&D [4] owing to their potential applications as catalytic supports [5], hydrogen fuel storage [3b,6], and fuel cells [7]. In particular, fabrications of metal-incorporated CMMs, which normally invoke methods such as adsorption [5], impregnation [7], and ion-exchange [8], also received much attention. However, these conventional synthesis routes normally lead to uncontrollable growth of metal-particles particularly in terms of their sizes and shapes. We report herein a novel synthesis route to fabricate tubular CMMs with well-dispersed Pt nano-particles studded on the pore walls. Their performances on hydrogen adsorption, carbon monoxide tolerance, and cyclic voltammetry test were also investigated.

2. EXPERIMENTAL

The SBA-15 template used in this work was synthesized following the procedures reported earlier [9]. Platinum-incorporated CMMs (Pt-CMMs) were prepared by mixing ca. 0.5 g of calcined SBA-15 template with desirable amounts of platinum acetylacetonate (98%, Acros), furfuryl alcohol (FA) (98%, Acros), trimethylbenzene (TMB) (98%, Acros), and oxalic acid (98%, Acros). The latter was used as the acid catalyst for polymerization of carbon sources, which was carried out first at 333 K then 353 K for 12 h under air. The resultant composite was treated at 423 K for 3 h under vacuum, followed by raising the temperature to 573 K at a rate of 1 K/min, then with a rate of 5 K/min to 1073 K and kept for 3 h. The resultant black powders were leached with HF (1%) aqueous solution for at
least 24 h to remove the silica template, washed, then dried at 373 K to yield the Pt-CMMs [10] whose Pt contents were analyzed by atomic absorption spectroscopy. All Pt-CMMs samples were further characterized by powdered XRD, N₂ adsorption/desorption measurements, and TEM. Hydrogen (99.9999% purity) adsorptions were done at 77 K over a pressure range of 0-4,000 torr on a home-built volumetric apparatus. CO tolerance tests by competing adsorption with H₂ were performed on an automated chemisorption apparatus. First, ca. 500 ppm of CO was pre-adsorbed onto the sample at 328 K for 0.5 h, then H₂ (10%) was pulse-injected with Ar carrier gas till a saturated coverage of H₂ was achieved. Electrocatalytic activity measurements were performed on a µ Autolab potentiostat at a scan rate of 10 mV/s. The glossy carbon thin-film electrode was prepared by the following steps, first, ca. 5 mg of Pt-CMMs was added into 2.5 mL deionized water followed by ultrasonic treatment for 0.5 h. Then, ca. 20 µL of the resultant suspension mixture was withdraw and injected onto the glassy carbon electrode followed by drying in air at 333 K for 1 h. Finally, 20 µL 5% Nafion solution was added as a binder under N₂ environment. Electrooxidation of MeOH was carried out with an electrolyte of 0.5 M H₂SO₄ and 1 M MeOH between −0.2 and 1.0 V at room temperature.

3. RESULTS AND DISCUSSION

As illustrated by the TEM images in Fig. 1a, Pt-CMMs exhibit uniform array of mesopores with long-range order and bimodal mesopore distribution with average diameters of ca. 2.5 and 4.5 nm, similar to that of CMM. This is in excellent agreement with the BJH pore sizes and physical properties derived from N₂ adsorption/desorption isotherms (Type IV with pronounced hysteresis loop; not shown) summarized in Table 1. Similar to CMK-3 [11], the CMM sample was replicated from SBA-15 but in the absence of Pt source (platinum acetylacetonate). The smaller pore with constant pore size of 2.3 nm may be ascribed due to the voids generated after the removal of silica template, whereas the larger pore, which appears to decrease with increasing Pt loading, is attributed to the formation of hollow, tubular mesoporous carbon similar to that of CMK-5 [7a]. Interestingly, most of the Pt particles were studded and dispersed uniformly on the inner carbon walls with a narrow particle-size distribution of ca. 2-3 nm. Notable decreases in both BET surface area (S) and total pore volume (V) upon increasing Pt loading (Table 1). Moreover, compared to the Pt-CMM-0.6 sample, Pt-CMM-11.5 reveals the existence of only the pore with size of 2.3 nm indicating that the formation of hollow tubular carbon is greatly hindered. This is in accordance with the findings obtained from XRD measurements (not shown), which revealed that the concentration of
Table 1: Physical and adsorptive properties of CMM and Pt-CMMs with varied Pt loading.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt (wt%)</th>
<th>S (m² g⁻¹)¹</th>
<th>D (nm)ᵇ</th>
<th>V (cm³ g⁻¹)ᶜ</th>
<th>C (wt %)ᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMM</td>
<td>---</td>
<td>2,195</td>
<td>2.3; 4.4</td>
<td>1.67</td>
<td>1.89</td>
</tr>
<tr>
<td>Pt-CMM-0.6</td>
<td>0.6</td>
<td>1,818</td>
<td>2.3; 4.0</td>
<td>1.30</td>
<td>2.04</td>
</tr>
<tr>
<td>Pt-CMM-0.6I</td>
<td>0.6</td>
<td>1,508</td>
<td>2.5; 4.3</td>
<td>1.16</td>
<td>1.54</td>
</tr>
<tr>
<td>Pt-CMM-11.5</td>
<td>11.5</td>
<td>997</td>
<td>2.3</td>
<td>0.65</td>
<td>--</td>
</tr>
</tbody>
</table>

¹BET surface areas. ᵇPore diameters derived by the BJH method using adsorption branches. ᶜTotal pore volumes. ᵈHydrogen adsorption capacities obtained at 850 mmHg and 77 K. ⁵Sample prepared by conventional wet impregnation method.

the Pt precursor and hence the density of the Pt particles greatly affect the structure of the carbon support formed, as suggested earlier by Xiao and co-workers [7b]. In addition, by comparing the results obtained from Pt-CMM-0.6 to the Pt-CMM-0.6I sample prepared by conventional impregnation method [7], it is obvious that much larger and non-uniformly distributed Pt particles (typically ca. 10-20 nm in size; see Fig. 1b) were formed. Hydrogen adsorption isotherms observed for CMM and Pt-CMMs at 77 K all show typical Langmuir-type curves (not shown). A hydrogen capacity of 2.04 wt% was obtained (at 77 K and 850 mmHg) for the Pt-CMM-0.6 sample (S = 1,818 m² g⁻¹ and V = 1.30 cm³ g⁻¹). By comparison, the H₂ adsorption capacities for the CMM and Pt-CMM-0.6I samples were lower by ca. 8% and 25%, respectively. This implies that H₂ may be adsorbed on Pt-CMMs by not only physisorption but also chemisorption.

To investigate CO tolerance of Pt-CMMs, a competitive adsorption of CO and H₂ on PtCMM-0.6 and PtCMM-0.6I were carried out at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. As shown in Fig. 2, all curves reach their respective plateaus after ca. 0.5 h of H₂ adsorption. It is estimated that the metallic surface area of Pt-CMM-0.6 is ca. 190 m²/g Pt among which ca. 78% remained stable after exposing 500 ppm of CO. On the contrary, for the Pt-CMM-0.6I sample, nearly all of Pt surfaces became inactive after poisoned by CO. This result indicates that the Pt-CMM-0.6 sample has a far superior CO tolerance than that prepared by conventional impregnation method.

![Fig. 2. H₂ chemisorption on Pt-CMM-0.6 (a) without and (b) with pre-adsorption of CO; ibid, but for Pt-CMM-0.6I (c) without and (d) with CO preadsorption.](image1)

![Fig. 3. Cyclic voltammograms of methanol oxidation on (a) commercial Johnson Matthey Pt/C and (b) Pt-CMM-11.5 catalysts in 0.5 M H₂SO₄ and 1 M MeOH at 10 mV/s.](image2)
Figure 3 displays the cyclic voltammograms for methanol oxidation activities of a commercial Johnson Matthey PtC catalyst (20 wt% Pt on Vulcan XC-72) and the Pt-CMM-11.5 sample. It is indicative that the our sample, which possesses well-dispersed, highly stable Pt nano-sized particles on porous carbon supports, exhibits catalytic activities surpassing that of the commercial Johnson Matthey catalyst. In particular, a lower oxidation peak potential was observed. In terms of the ratio of the forward anodic peak current density ($I_f$) to the reverse anodic peak current density ($I_b$), the $I_f/I_b$ ratio obtained for the Pt-CMM-11.5 and the commercial Johnson Matthey PtC were found to be 4.23 and 1.03, respectively, indicating that the latter is more vulnerable to coking by carbonaceous deposits [12] and less tolerance towards CO poisoning.

4. CONCLUSIONS

By incorporating carbon-rich metal presursor, such as Pt(CH(COCH$_3$)$_2$), as co-feeding carbon source during replicated synthesis using mesoporous silicas with well-defined pore sizes as templates, tubular CMMs with well-dispersed metal nanoparticles and tailored sizes can be obtained. These metal-CMMs, which can be easily fabricated with controllable loading even with multifunctional metal characteristics, were found to possess high surface areas, highly accessible and stable active sites, improved hydrogen adsorption capacities, and superior electrocatalytic properties. Moreover, in view of the high metal dispersion that favor reduction of metal required to reach the same catalytic activity per unit mass, these novel metal-CMMs should render future practical and cost-effective commercial applications in hydrogen-energy related areas, for examples, as adsorbents for hydrogen fuel storage and as supported electrocatalysts for proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).

REFERENCES