

Short communication

# Fabrication of a mesoporous Pt-carbon catalyst by the direct templating of mesoporous Pt-alumina for the methanol electro-oxidation

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## Abstract

Mesoporous Pt-carbon catalysts were directly fabricated using mesoporous Pt-alumina as a template with a metal source and using poly(divinylbenzene) as a carbon precursor. Two types of mesoporous Pt-alumina templates were prepared by employing different calcination conditions (PtAl-A and PtAl-N were produced by the calcination in a stream of air and nitrogen, respectively). Both the mesoporous Pt-aluminas served as efficient templates for the fabrication of replicated Pt-carbon catalysts (PtC-A and PtC-N). The PtC catalysts showed high surface area with a narrow pore size distribution centered at ca. 4.0 nm. Together with pore-confined metal growth, the characteristic feature of the template, such as a strong interaction of metal species with the support was beneficial for the formation of highly dispersed Pt particles on the replicated mesoporous carbon catalysts. The mesoporous Pt-carbon (PtC) catalysts exhibited a higher metal dispersion than Pt catalyst impregnated on CMK-3 (Pt/CMK-3). Furthermore, the PtC-N catalyst exhibited a higher metal dispersion than the PtC-A catalyst. Methanol electro-oxidation experiments revealed the catalytic performance was closely related to the metal dispersion in the supported catalysts. The PtC-N catalyst with the highest metal dispersion exhibited the best catalytic performance in methanol electro-oxidation.

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*Keywords:* Mesoporous Pt-alumina template; Mesoporous Pt-carbon catalyst; Methanol electro-oxidation

## 1. Introduction

Carbon materials have been widely employed in many fields of science and engineering. In particular, the porous nature of carbon materials such as high surface area and large pore volume makes them well suited as supporting materials for active metals in catalysis [1,2]. Although activated carbon, a typical carbon material, can serve as an efficient support for highly dispersed metal catalysts, such supported catalysts often exhibit a lower catalytic performance than would be expected due to the irregular and microporous characteristics of the activated carbon. A new family of carbon materials has been recently prepared, in which ordered mesoporous silicas are used as templates [3,4]. These carbon materials, so called ordered mesoporous carbons (OMCs), were found to have an

ordered pore structure with a uniform pore size. Due to their remarkable textural properties, OMCs have been extensively used as catalyst supports, adsorbents and electrode materials [5,6]. In particular, the regular pore structure of OMCs with a high surface area makes them more adequate for use as catalyst supports in polymer electrolyte fuel cells, where carbon supported Pt catalysts with a high metal loading (typically, in excess of 20 wt.%) are required to achieve a desirable power density. In previous studies, for example, it was demonstrated that the uniform pore size and high surface area of OMCs could induce spontaneous sintering-resistive properties, and a fine metal dispersion in the supported catalyst [7]. However, pore blocking and metal aggregation were inevitable even though silica-based OMCs were used as supports. In addition, it is rather tedious to prepare the Pt/OMC catalysts by a conventional method, i.e., impregnation and subsequent reduction, because a very long time is required for the synthesis of OMC and post-fabrication steps such as surface

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modification of OMC and metal supporting are required. On the other hand, mesoporous alumina that would be prepared by using an alkyl carboxylate as a structure-directing agent can be used as a template for the preparation of a mesoporous carbon (MC). Although mesoporous alumina template does not produce a mesoporous carbon having a pore structure with long-range orderness, there would be several advantages over the preparation method using mesoporous silica as a template. It is possible to prepare mesoporous alumina with metal component by one-step sol–gel method. Furthermore, when such alumina system is used as a template for the preparation of mesoporous carbon, a strong interaction with metal and alumina can prevent from aggregation of metal during carbonization step.

In this report, we propose a new fabrication method for producing uniform sized mesoporous Pt-carbon catalysts using mesoporous Pt-alumina as a template with a metal source. Compared to the conventional impregnation method, this method does not require an additional Pt deposition step on the support because the template itself serves as a metal source. Furthermore, a Pt-alumina template can be readily synthesized by a one-step sol–gel method under ambient conditions (room temperature) and can be prepared within a short time compared to conventional mesoporous silica templates. Therefore, the fabrication method herein provides a time saving route for the preparation of a Pt catalyst supported on a mesoporous carbon.

## 2. Experimental

### 2.1. Sample preparation

In order to prepare the mesoporous Pt-alumina template (PtAl), known amounts of an aluminum precursor ( $\text{Al}(\text{sec-OBu})_3$ , Aldrich) and a surfactant ( $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ , Fluka) mixed with a platinum source ( $\text{H}_2\text{PtCl}_6$ , Aldrich) were separately dissolved in *sec*-butyl alcohol, and the two solutions were then mixed with constant stirring. Small amounts of de-ionized water were added, dropwise to the mixture ( $0.2 \text{ ml min}^{-1}$ ), until a yellow precipitate began to form. The resulting slurry was stirred for a further 20 h, and the precipitate was isolated and dried in air. The crude product was calcined at 723 K in a stream of either air or nitrogen (denoted as PtAl-A and PtAl-N, respectively). In the preparation of PtAl-N, a swelling agent (trimethylbenzene, TMB, Aldrich) was added to the surfactant solution (weight ratio of surfactant: TMB = 2.0:1.0). For the preparation of the mesoporous Pt-carbon (PtC-A and PtC-N) catalyst, each corresponding template (PtAl-A and PtAl-N) was impregnated with appropriate amounts of divinylbenzene (DVB) solution containing a free radical initiator (azobisisobutyronitrile, AIBN), followed by polymerization at 343 K for 12 h. The resulting PtAl-polymer composites were carbonized at 1073 K, and the alumina template was then removed using a concentrated NaOH solution. The product was finally washed with copious

amounts of de-ionized water. SEM-EDX analyses revealed that metal loadings in the PtC-A and PtC-N catalysts were 22 and 23 wt.%, respectively. The Pt loadings in the PtC catalysts could be easily controlled by adjusting the amounts of Pt source used during the template preparation step. For purposes of comparison, a Pt catalyst supported on an ordered mesoporous carbon (CMK-3 [8]) was prepared by an incipient impregnation method using  $\text{H}_2\text{PtCl}_6$  as a Pt precursor. The metal loading of Pt/CMK-3 was determined to be 22 wt.% by SEM-EDX analysis.

### 2.2. Characterization and methanol electro-oxidation

Nitrogen adsorption isotherms were obtained with an ASAP-2010 (Micromeritics) apparatus. The pore size distribution was determined by the BJH method applied to the desorption branch of the  $\text{N}_2$  isotherm. The size and location of Pt particles on the catalyst surface were confirmed by transmission electron microscopy (TEM (Joel, JXA-8900R) and HR-TEM (JEM-3000F)) using an ultrasonically dispersed catalyst sample (in ethanol) deposited on a carbon grid.

Methanol electro-oxidation was carried out in a conventional three-electrode system with saturated calomel and a platinum gauge as a reference and a counter electrode, respectively. The working electrode was prepared by coating small amounts of catalyst ink on disk-type graphite. Prior to the coating, the graphite surface was polished with alumina paste, followed by washing with de-ionized water. Cyclic voltammograms were obtained at room temperature at a scan rate of  $20 \text{ mV s}^{-1}$  in 0.5 M  $\text{H}_2\text{SO}_4$  solution containing 1 M  $\text{CH}_3\text{OH}$  using an EG & G 263A potentiostat.

## 3. Results and discussion

$\text{N}_2$  adsorption–desorption behaviors and textural properties of the templates and the corresponding Pt catalysts are shown in Fig. 1 and Table 1, respectively. All the samples exhibited IV-type isotherm with H2 hysteresis loop. The pore size of PtAl-N was slightly larger than that of PtAl-A due to the swelling effect of TMB. However, both the PtC-A and PtC-N catalysts showed similar pore size distributions, centered at around 4.0 nm because the pores of PtC catalysts were generated from the wall of the PtAl templates via geometrical replication. The BET surface areas and pore volumes of the PtC catalysts were higher than those of the PtAl templates because of the density difference between alumina and the carbon framework. The surface areas and pore volumes were  $626 \text{ m}^2 \text{ g}^{-1}$ ,  $0.46 \text{ cm}^3 \text{ g}^{-1}$  and  $592 \text{ m}^2 \text{ g}^{-1}$ ,  $0.45 \text{ cm}^3 \text{ g}^{-1}$  for PtC-A and PtC-N, respectively. Compared to the CMK-3 support, on the other hand, the Pt/CMK-3 catalyst showed a slightly deformed isotherm and pore size distribution. In addition, the surface area and pore volume of CMK-3 was drastically decreased after Pt impregnation, indicating pore blocking or plugging of CMK-3 by Pt aggregates in the Pt/CMK-3 catalyst. This was also confirmed from the TEM

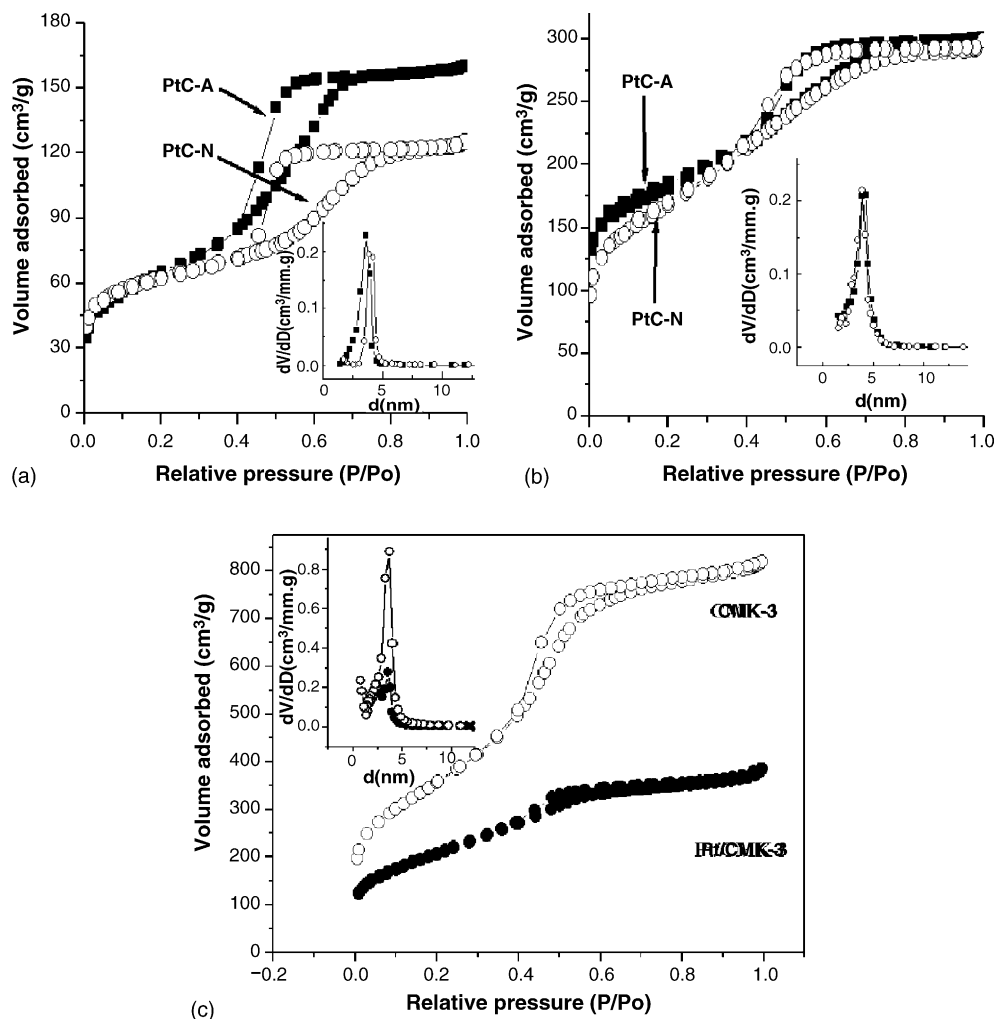


Fig. 1.  $N_2$  adsorption-desorption isotherms and pore size distributions (insets) for (a) PtAl templates, (b) replicated PtC catalysts and (c) CMK-3 and Pt/CMK-3.

image (Fig. 2e), where cylindrical pores and Pt aggregates with broad size distribution ranging 3–7 nm were observed.

TEM images of PtAl templates and the corresponding PtC catalysts are shown in Fig. 2. Pt particles in both PtAl-A and

Table 1  
Physical properties of PtAls, CMK-3, and the corresponding Pt-carbon catalysts

Sample	Surface area ( $m^2 g^{-1}$ ) <sup>a</sup>	Pore volume ( $cm^3 g^{-1}$ )	Pore size (nm) <sup>b</sup>	Average Pt particle size (nm) <sup>c</sup>
PtAl-A	232	0.25	3.6	2.3
PtAl-N	218	0.19	4.1	2.0
PtC-A	626	0.46	4.0	3.3
PtC-N	592	0.45	3.9	2.8
CMK-3	1280	1.23	3.8	–
Pt/CMK-3	550	0.53	3.8	4.5

Particle size distributions were obtained by selecting 100 particles in the HR-TEM image for each sample.

<sup>a</sup> Surface areas were calculated using BET equation.

<sup>b</sup> Pore size distributions were determined by BJH model.

<sup>c</sup> Average particle sizes were determined from the equation,  $d = (\sum n_i d_i) / n_i$ .

PtAl-N could barely be resolved in the TEM images, indicating a high dispersion of Pt particles on the mesoporous alumina. The PtAl-A retained slightly larger Pt particles than the PtAl-N, which might result from the facile metal aggregation in a reactive gas stream (oxygen) at the calcination step. Although the size of the metal particles of the PtC catalysts was slightly increased after carbonization, it could still be observed from TEM images and particle size data that the highly dispersed Pt particles with mesoporosity were formed (especially, in the PtC-N catalyst). The fact that metal growth was retarded through heat treatment at high temperatures is quite unusual. However, it is well known that alumina is very reactive toward metal species, and thus, a strong interaction between alumina and metal can be induced [9–11]. Therefore, we conclude that this interaction and pore-confined metal growth contributed to the generation of fine metal particles in the PtC catalysts. For purposes of comparison, we attempted to prepare a Pt incorporated mesoporous silica (PtS) template and the corresponding mesoporous Pt-carbon catalyst. However, these attempts to prepare a finely dispersed mesoporous Pt-carbon catalyst with high metal loading were unsuccessful.

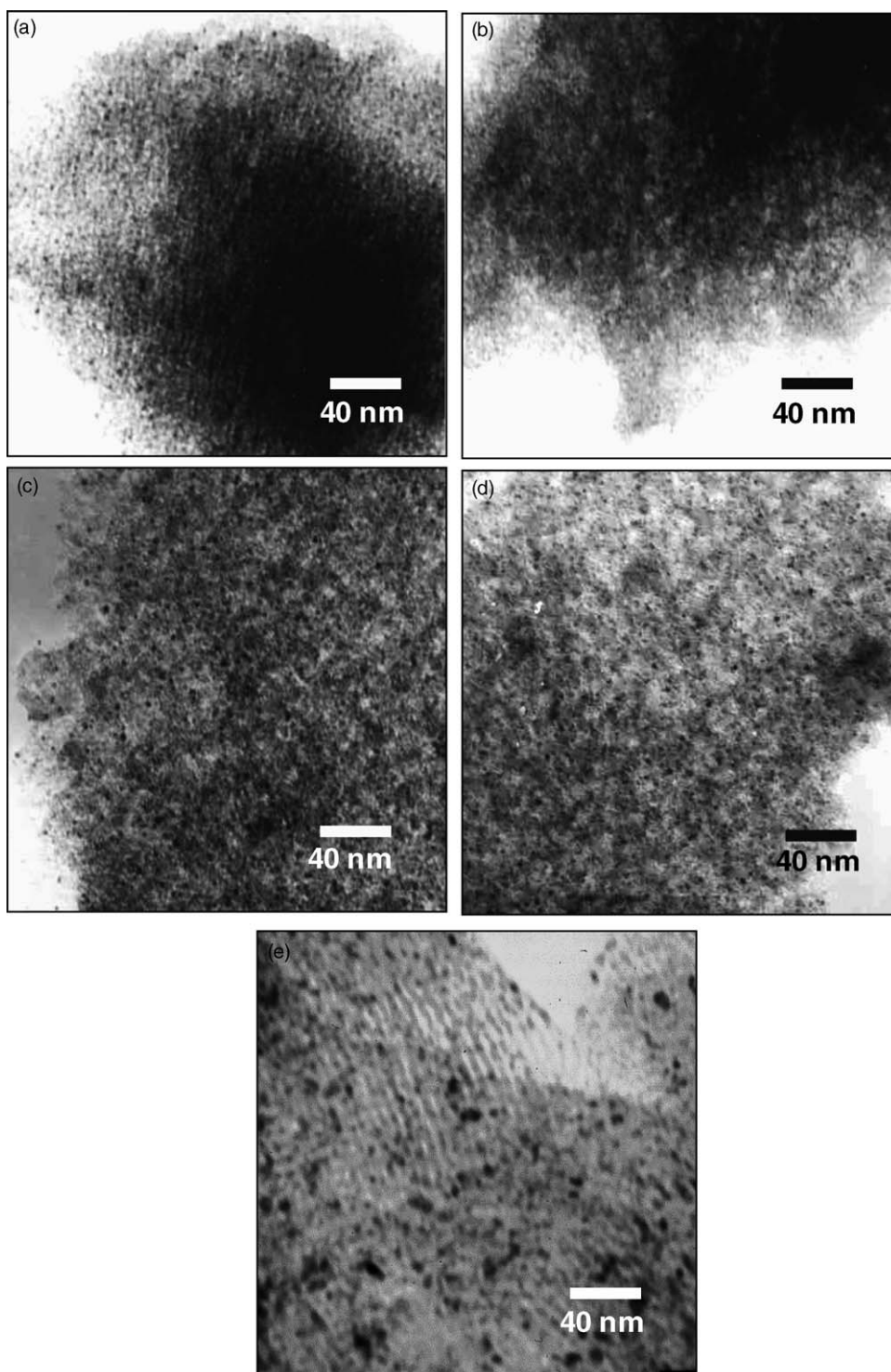


Fig. 2. TEM images of templates ((a) PtAl-A, (b) PtAl-N), replicated PtCs ((c) PtC-A, (d) PtC-N) and (e) Pt/CMK-3.

ful. Furthermore, even though PtS with desirable properties was synthesized, the resulting mesoporous Pt-carbon catalyst retained irregular and relatively large metal particles. This suggests that the PtAl templating method reported in this work was much more efficient for the preparation of a highly dispersed Pt catalyst on a mesoporous carbon than

other templating methods. In addition, PtC catalysts prepared by this method would be expected to show thermal sintering-resistant characteristics because the catalysts were treated at high temperatures in the carbonization step.

To test the catalytic performance of the prepared Pt catalysts, methanol electro-oxidation was carried out in a half-cell

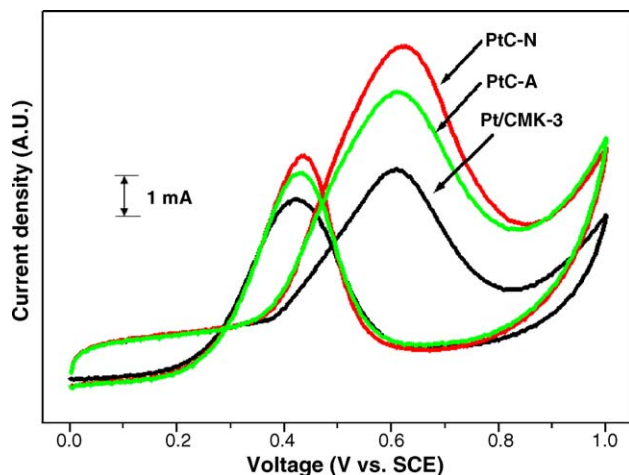


Fig. 3. Cyclic voltammograms of PtCs and Pt/CMK-3 catalysts on a glass carbon disk electrode (working electrode) in  $\text{H}_2\text{SO}_4$  (0.5 M) containing  $\text{CH}_3\text{OH}$  (1 M). All samples were pre-reduced at 393 K with a diluted hydrogen stream. The Pt loadings on working electrode were identical in all the cases (scan rate =  $20 \text{ mV s}^{-1}$ ).

reactor using a conventional three-electrode cell (Fig. 3). Methanol electro-oxidation occurred at ca. 0.4 V in all Pt-carbon catalysts, a typical feature for non-alloyed Pt-carbon catalysts [12–16]. However, the maximum current density observed at 0.6 V for the PtC catalysts (especially, PtC-N) was higher than that for the impregnated Pt-carbon (Pt/CMK-3) catalyst. Although a few factors can affect the catalytic performance in methanol electro-oxidation, it can be inferred that the high metal dispersion of PtCs was responsible for their enhanced catalytic performance.

#### 4. Conclusions

Pt-carbon catalysts were directly prepared using mesoporous Pt-alumina templates. The Pt-carbon catalysts retained a well-developed mesoporosity with a high surface area and a large pore volume. Furthermore, the mesoporous Pt-carbon (PtC) catalysts showed a higher metal dispersion

and better electro-catalytic performance than the impregnated Pt-carbon (Pt/CMK-3) catalyst. The fabrication method described in this work constitutes a very efficient and time saving route for the preparation of highly dispersed and thermally stable Pt-carbon catalyst with mesoporosity.

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