



A trimodal porous carbon as an effective catalyst for hydrogen production by methane decomposition



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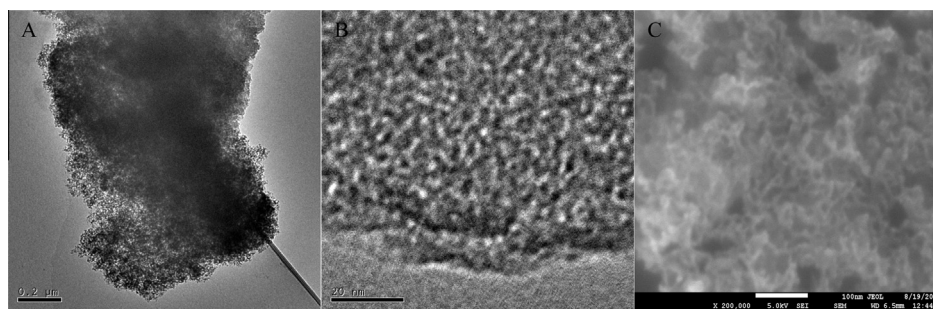
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HIGHLIGHTS

- Interconnected trimodal porous carbon synthesized by nanocasting method.
- High surface area and large pore volume carbon as catalyst.
- As-synthesized carbon provide abundant active sites and space for chemical reactions.
- Carbon catalyst used for hydrogen production by thermal decomposition of methane.
- Carbon catalyst produced high methane conversion and hydrogen yield.

GRAPHICAL ABSTRACT

TEM (A and B) and FESEM (C) micrographs of the as-synthesized carbon.



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ABSTRACT

A new type of porous carbon with an interconnected trimodal pore system is synthesized by a nanocasting method using nanoparticulated bimodal micro-mesoporous silica particles as the template. The synthesized template and carbon material are characterized using transmission electron microscopy (TEM), field emission electron scanning microscopy (FESEM) and nitrogen adsorption–desorption test. The synthesized carbon material has an extremely high surface area, a large pore volume and an interconnected pore structure, which could provide abundant active sites and space for chemical reactions and minimize the diffusion resistance of the reactants. The resulting carbon is used as the catalyst for hydrogen production by the thermal decomposition of methane. The catalytic results show that the as-synthesized carbon in this study produces much higher methane conversion and hydrogen yield than the commercial carbon materials.

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1. Introduction

To reduce the emission of greenhouse gases and mitigate global warming, hydrogen has been accepted as a promising energy carrier to achieve sustainable energy production in the near future.

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The production of hydrogen has attracted great interest in the academia and industry [1–3]. For decades, steam reforming of natural gas using nickel as a catalyst has been the most widely used process for the production of hydrogen [4,5]. However, the production of hydrogen by this multistep process results in high emissions of carbon dioxide and carbon monoxide and the end-products always contain some quantities of carbon monoxide, which prevent the resulting hydrogen from being directly used in fuel cells. Thermocatalytic decomposition (TCD) of methane is an alternative

method to produce hydrogen without the emission of greenhouse gases and air pollutants [6,7]. An important by-product of this process is clean carbon.

Thermocatalytic decomposition of methane is an endothermic process and the direct thermal decomposition of methane requires temperatures above 1200 °C for complete decomposition of methane into hydrogen and carbon [8]. Thus, for large-scale hydrogen production by TCD of methane, it is necessary to use catalysts to reduce the reaction temperature and to accelerate the kinetics of the process [9]. For decades, transition metals, such as Fe, Co and Ni, and their alloys have been widely studied as catalysts for the TCD of methane due to the good conversion of methane to hydrogen. In industrial production, the regeneration of the deactivated metallic catalysts by burning off or gasifying the deposited carbon would waste the valuable by-product of carbon and produce large amounts of CO₂, which nullifies the benefits of TCD [10]. In recent years, carbonaceous catalysts have been used for the TCD of methane because of their availability, durability and low cost [11–21]. The significant advantage in the use of carbonaceous catalysts is to produce hydrogen with high purity which can be directly utilized in fuel cells and other applications. Furthermore, the produced carbon materials can be directly used without any further separation and purification processes. Muradov and co-workers had initiated and made significant contributions in the field of TCD of methane using various carbonaceous catalysts including activated carbons (ACs), carbon blacks (CBs), carbon nanotubes and fullerenes, graphite, glassy carbon, etc. [11,22,23]. Subsequent to Muradov's seminal work [22], many other articles were published in which ACs [12–15], CBs [24–26], or both [27,28] were widely studied as catalysts for the TCD of methane. For instance, Abbas and Daud [29–31] studied the catalytic performance of palm-shell-based activated carbon for the TCD of methane. It was found that the catalytic activity was closely related to the ordering degree of the carbons. Disordered amorphous carbons were observed to be more active as compared with ordered turbostratic and graphitic carbons. Pinilla et al. [9] and Suelves et al. [32] also conducted extensive studies on the catalytic activities of carbonaceous catalysts for the TCD process. It was reported that the commercial carbon black (BP2000) exhibited the highest carbon yield of 6.13 g carbon per gram of catalyst. Moliner et al. [15] investigated the catalytic activities of ACs with different textural properties and surface chemistry. It was found that the surface chemistry and the pore size distribution played a decisive role in the initial conversion rate of methane and the long-term sustainability of the catalyst. Serrano et al. [33,34] and Botas et al. [35,36] investigated the TCD of methane using synthesized ordered mesoporous carbons CMK-5 and CMK-3. The CMK-5 showed outstanding catalytic performance in terms of hydrogen production rate and carbon yield because of its high surface area and bimodal pore structure. A remarkably high carbon yield, 31 g carbon per gram of catalyst, was obtained [36]. Shilapuram et al. [37,38] also studied the catalytic performance of CMK-3 and DUT-19. It was confirmed that CMK-3 and DUT-19 carbons showed better catalytic performance for methane decomposition than the commercial carbons.

In spite of great efforts made by researchers from the academia and industry, the catalytic performance of carbonaceous catalysts is still very limited since the methane conversions reported were quite low. Furthermore, these catalysts suffer from rapid deactivation due to the decreasing number of active sites and increasing methane diffusion resistance accompanying carbon deposition. Recently, hierarchical porous carbons have been of great interest for applications in fuel cells, batteries and capacitors because of their large surface areas and unique pore structures [39]. Such structural characteristics render hierarchical porous carbons to be good potential candidates for TCD of methane because of the

large number of active sites and low diffusion resistance to the reactants. However, very limited work has been reported on the use of hierarchical carbons as catalysts for methane decomposition [40]. In this work, a new type of hierarchical porous carbon material was synthesized using nanoparticulated bimodal micro-mesoporous silica particles as the template. The resulting carbon exhibited an extremely high surface area, a large pore volume and an interconnected trimodal pore structure. The hierarchical porous carbon was used as a catalyst for the TCD of methane and its catalytic performance was compared with those of two types of commercial carbons.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) and Tween 20 were used as the precursor and surfactant for the synthesis of silica template, respectively. Furfuryl alcohol and oxalic acid were used as the carbon source and subsequently further processed as the catalyst for the synthesis of the carbon material. Hydrofluoric acid was used to etch the silica template.

2.2. Synthesis of silica template

The SiO₂ template was synthesized using a well-established sol-gel technique [41]. A nontoxic and biodegradable ethoxylated sorbitan ester, namely, Tween 20, was used as the structure-directing agent. The detailed procedures are as follows: 1 ml of Tween 20 surfactant was dissolved into 40 ml of distilled water. 5 ml of tetraethyl orthosilicate (TEOS) was then added into the solution. After stirring for 30 min, 2.5 ml of HCl solution with a concentration of 0.1 M was slowly introduced into the mixture in droplets. The mixture was stirred for 2 h and then transferred into an oven and aged at 100 °C for 24 h. The resulting solid was collected by filtration and washed with distilled water. The dried powder was calcined at 550 °C for 4 h to remove the surfactant.

2.3. Synthesis of carbon material

The calcined silica powder was dried overnight at 120 °C under vacuum and then used as template to prepare the carbon material. The carbon material was synthesized using the nanocasting method [42]. The detailed procedures are as follows: 6.5 ml of furfuryl alcohol and 0.13 g of oxalic acid were dissolved into 15 ml of ethanol. 12 ml of the solution was impregnated into 3.5 g of template at room temperature. After the polymerization of the initial loading of furfuryl alcohol at 80 and 350 °C for 12 and 6 h under N₂ atmosphere, respectively, the remaining furfuryl alcohol solution was impregnated into the mixture and polymerized under the same conditions. The mixture of template and poly furfuryl alcohol was transferred into a furnace and the temperature was raised to 900 °C with a heating rate of 5 °C/min, dwelled for 4 h and then the furnace temperature was reduced. A nitrogen gas stream with a flow rate of 50 ml/min was introduced into the furnace during the carbonization process. After the temperature had cooled down to room temperature, the resulting silica-carbon composite was etched using hydrofluoric acid to remove the silica template.

2.4. Characterization tests

A transmission electron microscope (TEM, JSM2010, JEOL) and a field emission scanning electron microscope (FESEM, JSM-5600LV, JEOL) were used to observe the morphology of the samples. To

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