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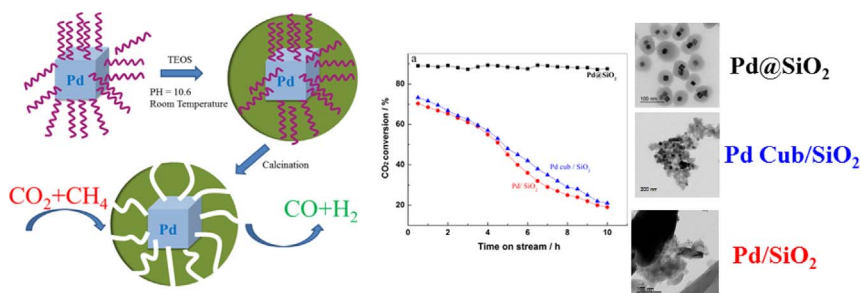
# Thermal-stable Pd@mesoporous silica core-shell nanocatalysts for dry reforming of methane with good coke-resistant performance

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Dry reforming of methane (DRM) reaction is an environment-friendly process to convert greenhouse gases, methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) into synthesis gases for industrial application. However, the catalysts used for DRM reaction always deactivate at high temperatures due to the sintering of metal nanoparticles and coking on the active surface. Core-shell structures composed of metal cores surrounded by oxide shells (core-shell structures) have been confirmed to be thermal-stable by solving the two problems. Pd@SiO<sub>2</sub> core-shell nanocatalyst has been prepared by using a sol-gel process, along with two supported catalysts prepared by using impregnation method in this work. The catalysts were characterized by using transmission electron microscopy (TEM), X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption isotherms, CO chemisorption, inductively coupled plasma optical emission spectrometry (ICP-OES). The Pd@SiO<sub>2</sub> after thermal treatment at 700 °C for 6 h exhibits no obvious sintering. For DRM reaction catalyzed by Pd@SiO<sub>2</sub> core-shell nanocatalyst, the conversions of CO<sub>2</sub> and CH<sub>4</sub> are 89% and 83% respectively, which show no significant decrease for > 10 h. However, two supported Pd catalysts (Pd cub/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>) deactivate to a very low activity (conversion lower than 20%). The results suggest that the Pd@SiO<sub>2</sub> nanocatalyst is excellent for DRM reaction, which also can be used for other heterogeneous catalysis reaction at high temperatures.

## 1. Introduction

Dry reforming of methane (DRM) has been extensively studied to produce valuable synthesis gas by consumption of two major

greenhouse gases, CH<sub>4</sub> and CO<sub>2</sub>. Transition metals, including Ni, Ru, Pt, Pd, are usually used as active catalysts for DRM reaction [1–5]. Many studies on these catalysts indicate that non-noble metals are highly coke sensitive due to methane decomposition and Boudouard

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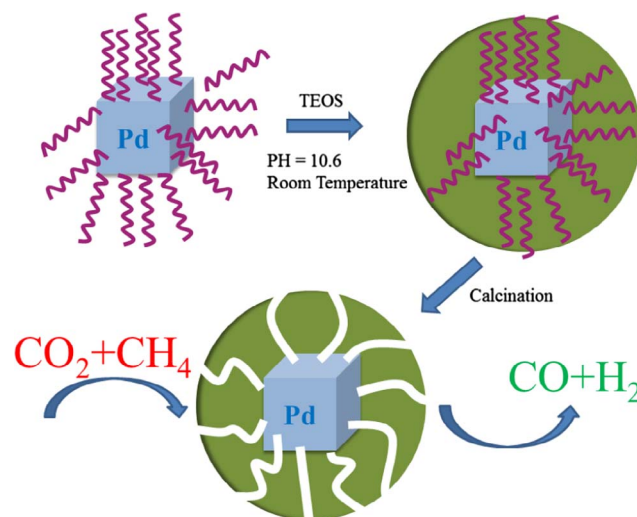
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reaction [6–10]. In noble metals, Pd is a better choice because it's less expensive than Pt and Au, along with its fine nature for C–H activation which is in favor of promoting the DRM reaction. Singha et al. [11] found the addition of Pd to Ni/MgO catalysts could decrease by 90 °C for the DRM initiation temperature and enhanced the low temperature activity. The stability of catalysts was also improved to a very high level. The group also investigated Pd-CeO<sub>2</sub> catalysts for DRM reaction up to 800 °C. A certain decrease in activity was observed due to sintering of Pd particles [12]. Costilla et al. [13] prepared Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts with low loaded amount (< 0.5 wt%). The catalysts exhibited a high initial activity (CO<sub>2</sub> conversion > 50%) for DRM reacted at 650 °C, but deactivated significantly (CO<sub>2</sub> conversion decreased to 15% after 5 h) due to carbon nanofibers and sintering. Active Pd supported on ordered mesoporous aluminum is prepared for DRM reaction using co-impregnation method by Tsubaki's Group [14]. The initial conversion of CH<sub>4</sub> at 750 °C was about 75%, but the conversion dropped to less than 10% within 8 h.

DRM reaction is a highly endothermic reaction, which means a higher conversion of CH<sub>4</sub> and CO<sub>2</sub> (> 80%) requires a very high temperature (> 750 °C) [15]. However, catalysts always deactivate at such high temperatures due to two main routes: coking (the blocking of the metal surface by accumulation of carbon on the metal) and sintering (the formation of larger metal particles, which lowers overall surface area and activity) [16]. Catalysts deactivation is not economical, because the operation processes must be shut down to regenerate or replace the catalysts. To solve this problem, unique structures consisting of metal cores surrounded by oxide, carbon or other metal shells (core-shell structures) have been proposed. The outer shells can isolate the catalytically active nanoparticle cores and prevent the possibility of sintering of core particles during reactions at high temperatures. The mesopores within the shells formed during the removal of organic capping agents or templates through calcination ensures the direct access of reacting molecules to internal cores and the exit of product molecules to outside [17].

Pt@mesoporous silica core-shell catalysts have been successfully used for CO oxidation at 330 °C without aggregation, while severe aggregation occurred for TTAB-capped Pt on silicon wafer and Pt/MCF catalysts. Even on heating the catalysts as high as 750 °C, the morphology of most Pt@mSiO<sub>2</sub> was maintained [18]. Pd@CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> core-shell catalyst (Pd core @CeO<sub>2</sub> shell supported on Al<sub>2</sub>O<sub>3</sub>) was adapted to catalyze methane combustion by Cargnello's group [19]. In comparison with conventional Pd/CeO<sub>2</sub> or Pd-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, the complete conversion temperature decreased by 300 °C because of the strong interaction of core-shell Pd@CeO<sub>2</sub> units. Pd@CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> showed a stable activity for CH<sub>4</sub> oxidation over the range of temperatures from 250 to 850 °C, with no decrease in activity during heating and cooling curves. Lu et al. [20] coated Pd NPs with Al<sub>2</sub>O<sub>3</sub> layer by layer accurately by using atomic layer deposition. The ensembles of Pd atoms are too small to support coke formation and the channels in the shell can inhibit carbon filament formation due its size is smaller than carbon filament. In a word, the core-shell structure catalysts can overcome the sintering problem as well as coking effectively. However, few literatures about Pd@M<sub>x</sub>O<sub>y</sub> core-shell catalysts using for DRM reaction have been reported.

Because of a better resistivity to water poisoning (produced by water-gas shift reaction) of Pd core with irreducible oxide (e.g. SiO<sub>2</sub>) shell than that of Pd core with reducible shell (e.g. CeO<sub>2</sub>, ZrO<sub>2</sub>) [21], SiO<sub>2</sub> was chosen as the shell material. In this work, Pd core@SiO<sub>2</sub> shell nanocatalysts were synthesized by the Stöber method [22]. The (1 0 0) plane of Pd is favor of methane dissociation which is essential for methane dry reforming [13], so Pd nanocube exposed (1 0 0) plane is chosen as the active core (Scheme 1). In comparison, two supported catalysts Pd/SiO<sub>2</sub> prepared by wet-impregnation method were also prepared. The catalytic experiments of the three Pd-based catalysts for DRM reaction have been carried out in a fixed-bed reactor. The results show that Pd@SiO<sub>2</sub> catalyst possesses high activity and excellent



Scheme 1. Schematic illustration of the formation process of Pd@SiO<sub>2</sub> nanocatalysts.

stability up to 750 °C for DRM reaction due to its core-shell structures, which means core-shell catalysts can be used for hydrocarbon reforming, cracking or oxidation reaction at high temperatures.

## 2. Experimental

### 2.1. Materials

Potassium tetrachloropalladate (II) (K<sub>2</sub>PdCl<sub>4</sub>, mass fraction 99.95%), palladium nitrate (Pd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), ascorbic acid (AA, mass fraction 99.99%), potassium bromide (KBr, mass fraction 99.95%), polyvinylpyrrolidone (PVP, MW = 58,000), silicon dioxide (SiO<sub>2</sub>, mass fraction 99.9%, size = 10 μm) were purchased from Aladdin Industrial Co., Shanghai, China. Acetone (CH<sub>3</sub>COCH<sub>3</sub>, mass fraction 99.5%), methanol (CH<sub>3</sub>OH, mass fraction 99.5%), ethanol (CH<sub>3</sub>OH, mass fraction 99.5%), ammonium hydroxide (NH<sub>4</sub>OH, mass fraction 28%), tetraethylorthosilicate (TEOS, mass fraction 99.5%), cetyltrimethylammonium bromide (CTAB, mass fraction 99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were employed without further purification. Ultrapure water with a resistivity above 1.82 × 10<sup>5</sup> Ω·m at 25 °C was produced from a Millipore Q3 system.

### 2.2. Synthesis

#### 2.2.1. Synthesis of PVP stabled Pd nanocubes

In a typical preparation process [23], 163 mg of K<sub>2</sub>PdCl<sub>4</sub> and 278 mg of PVP together with 1.5 g of KBr were dissolved in 15 mL of H<sub>2</sub>O. Then the mixture was heated to 85 °C for 5 min followed by adding 5 mL of aqueous solution containing 150 mg of AA to it. Afterwards, the reaction solution was kept stirred for 5 h, and then collected by diluting the resultant solution with acetone and centrifuging (6000 rpm, 10 min). The black precipitation was washed 3 times with water and acetone to remove excess raw material. The collected Pd colloids were stored in 5 mL water for further use.

#### 2.2.2. Synthesis of Pd@SiO<sub>2</sub> core-shell nanoparticles

The synthesis of Pd@SiO<sub>2</sub> nanoparticles was carried out as follows: 250 μL of Pd colloids (2.5 × 10<sup>-5</sup> mol) dispersed in 25 mL of H<sub>2</sub>O was added to 21 mL of methanol. Then, 70 mg of CTAB was added to the mixture, and stirred for 1 h. Afterwards, a certain amount of NH<sub>4</sub>OH was added to the solution to adjust the pH to 10.6. A controlled amount of 10 vol% TEOS diluted with methanol was added to the basic solution dropwise to initiate the silica polymerization (TEOS/Pd = 5/1). The as-synthesized Pd@SiO<sub>2</sub> was calcined at 500 °C for 3 h in air to remove

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