



Synthesis and application of highly dispersed ordered mesoporous silicon-doped Pd-alumina catalyst with high thermal stability



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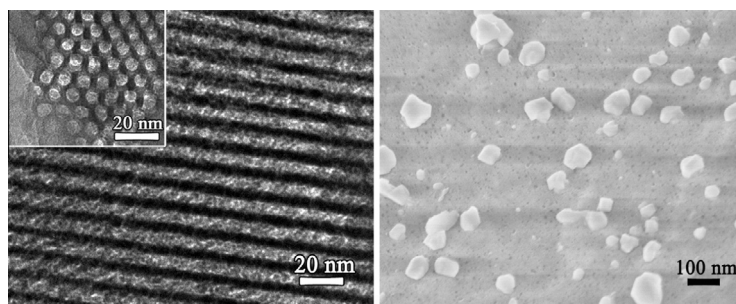
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HIGHLIGHTS

- Ordered mesoporous alumina with high surface area was obtained by a simple process.
- Silicon-doped ordered mesoporous γ -alumina exhibits superior thermal stability.
- Highly dispersed ordered mesoporous Pd- Al_2O_3 catalyst has well catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Employing P123 as a structure directing agent and acetic acid as an interfacial protector, ordered mesoporous silicon-doped γ -alumina with high thermal stability was synthesized through a modified sol-gel process by adding aluminum isopropoxide in batches to control the hydrolytic and condensation rate of Al^{3+} . When the silicon content was 10–25 wt%, the specific surface area of the as-obtained samples were higher than others. Especially when the silicon content up to 20 wt%, the sample still maintained ordered mesoporous γ - Al_2O_3 phase with a large specific surface area of $139.8 \text{ m}^2 \text{ g}^{-1}$ and narrow pore size distribution even the calcination temperature up to $1100 \text{ }^\circ\text{C}$. Taking as-synthesized ordered mesoporous alumina (OMA) as carrier, the catalysts with high thermal stability supported by Pd were obtained by a facile process of thermal incipient wetness impregnation, which shows highly dispersed nano-particles and ordered mesostructure. When applied the catalysts in the catalytic converters of simulated exhaust automobile gases, it was found that the ordered mesostructure and high surface area showed significant effects in promoting catalytic activity. The as-synthesized ordered mesoporous Pd-alumina catalyst exhibited an excellent catalytic activity for gas mixture including CO, NO and hydrocarbon (HC).

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1. Introduction

With pollution of automobile exhaust intensified and the improvement of exhaust emission standard, the catalysts of automobile exhaust purification were required to have a longer service

life and higher catalytic activity. Currently, the main carrier of catalyst was γ - Al_2O_3 and people had paid a lot of effort to improve the thermal stability of γ - Al_2O_3 due to its high-temperature phase transition and sintering causing catalyst activity reduced [1]. OMA possesses many desirable textural properties, including high surface area, highly uniform channels and narrow pore size distribution [2], which make it widely applied as catalyst supports [3–5]. The as-prepared OMA is expected to effectively restrain the behavior of phase transition and sintering. Morris et al. [6] synthesized a

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series of OMA-supported metal oxides with large surface area and high thermal stability via one-pot method, the as-obtained sample still sustained ordered mesoporous structure after calcined at 900 °C. Wu et al. [7] yielded OMA materials with variable pore architectures and high mesoporosity as well as crystalline framework through nanocasting pathway with mesoporous carbon as hard template. But the pore structure of as-synthesized sample was difficult to maintain ordering at high temperature due to its particles overgrowth in the synthesis process. Niesz [8] was the first to report the successful synthesis of OMA with a hexagonal arrangement by using Pluronic P123 as template via a sol-gel route. However, the framework structure of the as-prepared alumina was amorphous. Yuan [2] employing a modified sol-gel route synthesized the OMA with citric acid as pH adjustor, the as-prepared sample showed large surface area and narrow pore size distribution, and it still preserved ordered mesostructure after calcined at 1000 °C. Moreover, OMA with high thermal stability has been widely used as a catalyst support. Li [9] using OMA as carrier synthesized catalyst with Pd and Pt highly dispersed, which sustains ordered mesoporous structure after calcined at 700 °C. Employed the OMA in CO oxidation reaction, which exhibits a high catalytic activity. Bordoloi [10] applied the evaporation-induced self-assembly (EISA) process to achieved Co-Al₂O₃ with highly ordered mesoporous structure. When the Co loading was 15%, the ordered mesoporous 15Co-Al₂O₃ with excellent catalytic activity was obtained. Yuan [11] reported the metal supported meso-8CeAl nanocatalyst with CeO₂ highly dispersed. This novel material exhibited an excellent catalytic activity for CO oxidation reaction. The results above indicated that alumina-supported catalysts with ordered mesostructure show superior catalytic performances compared to ordinary alumina supports.

Our group extended the sol-gel route to synthesize thermally stable OMA by introducing the zirconium and cerium as dopants [12]. The as-obtained samples still maintained ordered γ -Al₂O₃ mesoporous structure after calcined at 1000 °C. But its surface area was only 115 m² g⁻¹. Besides, we introduced silicon to further stabilize the pore structure of OMA, which remains ordered mesostructure with large surface area of 235–250 m² g⁻¹ after calcined at 1000 °C [13]. But the surface area of which begin to significantly decrease when the content of silicon was more than 11 wt%. Further research showed that when the calcination temperature up to 1100 °C, the specific surface area of which was only 92.5 m² g⁻¹. So we need to improve the synthesis method to synthesize the OMA with high thermal stability as catalyst carriers, which is conducive to the improvement of catalytic activity.

In the synthesis system of sol-gel method with hydrochloric acid as pH adjustor, the coordination of Cl⁻ with Al³⁺ might destroy the charge balance in the interface between organic aluminum source and template, resulting in the self-assembly process between them disturbed. Organic acids were usually used as interface protection agents [11]. Besides, the research of De [5,14] showed that a very crucial factor to govern the stability of ordered pore structure is to control the hydrolysis and condensation rate of the alumina precursor. The effective control of hydrolysis rate is necessary to obtain the ordered framework due to the fast hydrolysis rate of aluminium isopropoxide does not allow the ordered structure easily formed. We assume that the introduction of acetic acid is beneficial to the thermal stability and large BET surface area of OMA because it can be easily removed at lower temperature due to its volatility, leading to the ordered pore structure less changed. Therefore, considering the influence of these two points, we developed early synthetic method by adding acetic acid as interfacial protector, leading to the improvement of the ordered mesoporous structure. Then adding aluminum isopropoxide in batches in the synthesis process was to effectively control the hydrolysis and condensation rate of Al³⁺, which enhance the thermal stability and

ordering degree of the samples. On the other hand, Horiuchi [15] reported that the silicon can more effectively restrain the behavior of phase transition and sintering compared to the rare earth metals and alkaline earth metal and the suitable silicon doping quantity is 13 wt%. In our previous work, when the silicon content was more than 11 wt%, the specific surface area begin to significantly decrease under the calcination temperature of 1000 °C. Therefore, the effect of silicon content on the structure and thermal stability of the alumina were also investigated.

Herein, by introducing acetic acid and adding aluminum isopropoxide in batches, we report this modified sol-gel route for not only synthesizing silicon-doped OMA with crystalline pore walls but also improving the thermal stability under high temperature. The as-synthesized Si-doped γ -alumina still maintained ordered mesoporous structure with a large specific surface area of 139.8 m² g⁻¹ after the calcination temperature up to 1100 °C, the BET surface area of which was obviously improved compared to our previous work (92.5 m² g⁻¹). The more important is that we took the as-synthesized OMA as carrier and employed a facile process of thermal incipient wetness impregnation to obtain the catalysts with highly dispersed nano-particles and ordered structure, which shows excellent activity for gas mixture including CO, HC and NO when applied in the system of simulated automobile exhaust. The as-synthesized OMA is a potential application prospect in automobile exhaust purification.

2. Experimental

2.1. Synthesis of catalyst support

In a typical synthesis, 1.00 g P123 (EO₂₀PO₇₀EO₂₀, EO = ethylene oxide, PO = propylene oxide) was dissolved in 15 mL anhydrous ethanol and 1.0 mL of hydrochloric acid (37 wt%) was added to form solution A with the final pH of ca. 0.56. Meanwhile, different amounts of tetraethyl orthosilicate (TEOS) were added into 5 mL isopropanol to form solution B. The two solutions were mixed together to form a new solution C, which was constantly stirred for 30 min. Then 0.01 mol aluminum isopropoxide was slowly added to solution C in batches (4 times) under vigorous stirring for 2 h and 1.5 mmol acetic acid was added to adjust the pH value of ca. 0.72. The resulting solution was aged at room temperature for 12 h to get a gel. Then it was put into a drying oven (60 °C) to undergo the solvent evaporation process to get a dried gel. The resulting samples were calcined in the air at 400 °C with a ramping rate of 1 °C min⁻¹ and held for 4 h, then calcined at 800 °C, 1000 °C and 1100 °C for 1 h with a ramping rate of 10 °C min⁻¹. All the as-obtained samples were labeled as Si-OMA-x, where x represents the theoretical content of Si (wt%) (x = 0, 5, 10, 15, 20, 25 and 30).

2.2. Catalysts preparation

Taking the as-synthesized silicon-doped OMA as carrier, the supported Pd/Si-OMA-x catalysts were prepared by a thermal incipient wetness impregnation. The Pd loading of which was 0.5 wt% (theoretic value). Specific steps were as follows: carriers were immersed in an aqueous Pd(NO₃)₂ solution under room temperature and 60 °C for 6 h, respectively. The impregnated samples were dried in a drying oven at 110 °C for 5 h. Then the calcination was carried out in the air at 1000 °C and 1100 °C for 1 h with a temperature ramp of 10 °C min⁻¹, respectively. The as-prepared samples were marked as Pd/Si-OMA-x, in which x represents the Si content (wt%). In order to make comparison, commercial alumina supported Pd catalysts were also prepared (denoted as Pd/CA).

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