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Short communication

Palladium redispersion at high temperature within the Pd@SiO$_2$ core@shell structure

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ABSTRACT

Maintaining high dispersion of palladium is critical for Pd-based catalysts, which suffer from deactivation due to sintering at high temperatures (≥800 °C). Here, we report direct evidence that Pd nanoparticles (~4 nm) of a palladium silica core@shell (Pd@SiO$_2$) catalyst can redisperse into nanoclusters (≤2 nm) after aging at 800 °C, where severe Pd sintering would be expected on supported Pd catalysts. The Pd redispersion was confirmed by *in situ*, as well as *ex situ*, high resolution transmission electron microscopy, and is manifested by a remarkably decreased light-off temperature for CO oxidation after aging.

1. Introduction

Sintering of platinum group metals (PGM) at high temperatures is a well-known issue, and is often responsible for the loss of catalytic performance in emission control catalysts. Recently, researchers have suggested tackling this sintering problem by designing unique catalyst formulations [1–3] and structures such as embedded [4] and core@shell [5,6] geometries, where a PGM core is surrounded by an oxide shell. Different synthesis methods have been developed to prepare catalysts with a Pd core and SiO$_2$ shell (Pd@SiO$_2$) [7–9] with improved thermal stability. However, to the best of our knowledge, few articles report the stability of Pd-based core@shell catalysts at temperatures above 800 °C [10], where thermal PdO-to-Pd decomposition occurs and severe sintering is expected [11–13]. Instead, most Pd@SiO$_2$ catalysts reported in the literature were aged only up to about 700 °C, at which no severe sintering is expected. In fact, previous studies carried out with CO oxidation over supported Pd catalysts [12–15] showed that aging at 700 °C may induce Pd redispersion *via* the formation of PdO under an oxidizing atmosphere. Therefore, testing the thermal stability of Pd@SiO$_2$ at temperatures above the temperature of PdO decomposition (800 °C) [11] is important to demonstrate the thermal stability benefit resulting from the core@shell geometry.

An example of Pd sintering and redispersion in core@shell geometry is illustrated in a study by Zhang et al. [16]. By studying a Pd@CeO$_2$ supported on Si-functionalized Al$_2$O$_3$, they observed that the Pd core underwent structural reconfiguration, *i.e.* simultaneous sintering and redispersion of the Pd nanoparticles into both larger particles as well as smaller entities at temperatures between 500 °C and 800 °C. This observation may hint at a possible redispersion of encapsulated Pd particles. However, Pd@CeO$_2$ catalysts by themselves were not thermally stable and the core@shell morphology was lost after high temperature exposure [17]. Therefore, it is difficult to isolate the behavior of the Pd apart from the recrystallization of the CeO$_2$ shell and such reconstruction would result in an outcome similar to PGM trapping onto reducible oxides such as CeO$_2$ [18–20]. Here, we report direct evidence of high-temperature Pd redispersion within a Pd@SiO$_2$ model catalyst. By maintaining the core@shell geometry throughout the high temperature aging at 800 °C, we could isolate the behavior of Pd from the effect of the shell morphology change. Our findings of high-temperature redispersion of PGM over a non-reducible oxide [21] in a core@shell structure may give new perspectives for the preparation of thermally stable PGM catalysts.

2. Experimental

2.1. Synthesis, aging, and characterizations of Pd@SiO$_2$ core@shell catalyst

The Pd@SiO$_2$ catalyst with a 4.0 nm Pd core diameter and a 22 nm SiO$_2$ shell thickness was synthesized by following a general procedure for a modified, one-pot, two-step method [8,22]. Tetradecyltrimethylammonium bromide protected Pd nanoparticles (Pd-np)

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were prepared by using $Pd(NO_3)_2$. Pd-np were then encapsulated by SiO_2 by direct addition of ethanol-diluted tetraethoxysilane in the aqueous suspension of Pd-np. After 24 h stirring, the catalyst was collected by centrifugation, followed by washing with water (3 times) and ethanol (6 times). For comparison, a conventional supported Pd on SiO_2 catalyst with similar Pd loading was also prepared by the incipient wetness impregnation of $Pd(NO_3)_2$ solution.

Aging of the same batch (dried at 80 °C in air) $Pd@SiO_2$ catalysts was carried out in a muffle furnace under ambient air or in a CO oxidation reactor in air flow at different temperatures (500 °C for 2 h, or 500 °C for 2 h followed by 800 °C for 4 h). Nitrogen physisorption at 77 K was carried out on a Micromeritics ASAP 2020. Energy dispersive spectroscopy (EDS) was used to analyze the bulk composition on a Phillips XL30FEG SEM. XRD (Rigaku Rotating Anode) was carried out with CuKα radiation (20 mA, 40 kV). Although the collection of as-synthesized catalyst was washed by DI water (3 times) followed by ethanol (6 times), the removal extent and temperature of the residual surfactant was evaluated by thermogravimetric analysis (TA™Q500 TGA analyzer) coupled with gas-phase FTIR (Thermo Nicolet 380) under a flow of 100 ml/min (10% O_2 with balance N_2).

2.2. Catalytic activity measurement and TEM characterization

Since CO oxidation is a structure insensitive reaction on a Pd surface, CO oxidation was used as a catalytic probe reaction to evaluate the effect of aging. The catalytic performance was performed in a continuous flow system using a quartz reactor (ID 4.00 mm) under 1% CO and 1.5% O_2 (bal. N_2) in a total 200 ml/min flow. Typically, 60 mg of 500 °C calcined catalyst was used to obtain a CO oxidation light-off curve using a heating rate of 2 °C/min from 50 to 500 °C. Subsequently, the catalyst was *in situ* heated to 800 °C for aging for 4 h in air flow, and the CO light-off curve was again obtained on this 800 °C aged catalyst.

Different TEM characterizations of the catalyst were carried out in three instruments. Standard bright-field transmission electron micrographs (BF-TEM) images were recorded using a JEOL 2010 TEM (LRTEM). High-resolution dark-field scanning transmission electron microscopy (HAADF-STEM) images were recorded by JEOL 3100 TEM (HRTEM). For the *in situ* reaction experiments, a 200 kV JEOL 2200FS (*in situ* TEM) (S)TEM with aberration correction for the illumination lenses (CEOS) was used. The *in situ* experiments were carried out by holding the sample at each temperature for 30 min then cooling down to 200 °C for imaging. Detailed experimental procedures are further described in the Supporting Information.

3. Results and discussion

The geometry of the $Pd@SiO_2$ catalyst particles was characterized and confirmed by LRTEM. The catalysts calcined at 500 °C and 800 °C did not show much morphological change (*i.e.* core@shell structure), except for some Pd core particle size change (Fig. S1a, b) and the expected loss of mesoporosity of the SiO_2 shell after aging at 800 °C (Fig. S1). The Pd core particle size after aging at 800 °C appeared smaller than that after calcination at 500 °C. EDS analysis showed very similar Pd loadings between 500 °C (2.85 wt%) calcined and 800 °C aged (2.83 wt%) catalysts, indicating no measurable mass loss of Pd during aging. In addition, carbon and bromine signals were not detected by EDS for these samples indicating the complete removal of surfactant by washing and a 500 °C calcination. The complete removal of the residual surfactant after 500 °C calcination was also confirmed by TGA-FTIR, where all dTG and corresponding CO_2 peaks appeared below 500 °C.

As a structure insensitive reaction, the CO oxidation conversion is closely correlated with the number of available Pd surface atoms and the dispersion of Pd, *i.e.*, the smaller the Pd particles, the lower the light-off temperature of CO conversion. An interesting and remarkably improved CO oxidation conversion (*i.e.*, lower light-off temperature) was observed (Fig. 1) on the catalyst aged at 800 °C over its counterpart calcined only at a lower temperature of 500 °C. The light-off temperatures (50% CO conversion) after aging at 500 °C and at 800 °C were 250 °C and 229 °C, respectively, a *decrease* of 21 °C for the 800 °C sample. These CO oxidation light-off curves were repeatable across two different batches of samples and for multiple cycles on one sample, giving confidence that the observations of CO catalytic oxidation are statistically valid. To verify the distinct aging impact, a conventional Pd/SiO_2 supported catalyst with a similar Pd loading (2.90% Pd, EDS) was aged in the same way for comparison. The CO light-off temperature after aging at 800 °C was 270 °C, a 21 °C *increase* from the value after calcination at 500 °C, an expected trend for the conventional Pd supported catalysts where Pd undergoes sintering with aging at 800 °C (Fig. S2), where PdO can decompose to metallic Pd under oxidizing environment [13]. The opposite behavior observed for the $Pd@SiO_2$ catalysts is extraordinary and may be an indicator of the Pd redispersion originating from the core@shell geometry.

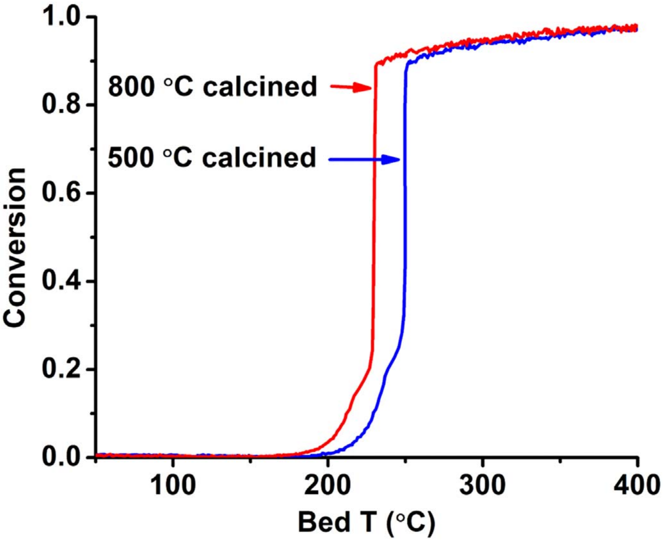

Fig. 1. CO-light-off curves of $Pd@SiO_2$ after aging 500 °C (blue) and 800 °C (red) in air. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

High angle annular dark field (HAADF) images were taken to investigate the origin of the improvement of $Pd@SiO_2$ performance after aging at 800 °C. Fig. 2 shows typical HAADF images (in which Pd appears bright) of $Pd@SiO_2$ catalysts as-prepared, after *ex situ* calcination at 500 °C for 2 h in air, and after *ex situ* calcination at 500 °C followed by aging at 800 °C for 4 h in air. The as-prepared (Fig. 2a) and the 500 °C calcined (Fig. 2b) catalysts did not show any obvious changes in the Pd core morphology, except oxidation of metallic Pd cores to PdO, confirmed by XRD (Fig. S3). In comparison, after further aging at 800 °C, multiple new Pd atom clusters with diameters of < 2 nm were clearly visible, as shown in Fig. 2c. Since this catalyst was aged at 800 °C for 4 h after calcination at 500 °C, one can conclude that the redispersion of Pd nanoparticles only resulted from the aging at 800 °C. This surprising and unexpected result could confirm and explain the enhanced CO oxidation performance, as shown in Fig. 1. Previously, high thermal stability around 700 °C has been reported in the literature for Pd-based core@shell catalysts [7–9], because Pd redispersion can occur when thermally treated at 700 °C in air [14]. However, to the best of our knowledge, Pd redispersion on a SiO_2 surface [23], especially by aging near 800 °C, is not very common, because of rapid sintering caused by the PdO-to-Pd decomposition [13].

As the CO oxidation comparison between the $Pd@SiO_2$ and the supported Pd/SiO_2 showed different trends in aging response, the high-temperature Pd redispersion can be related to the core@shell architecture. To clearly demonstrate these different aging behaviors, an atmospheric *in situ* TEM experiment was carried out in 150 Torr O_2,