

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Confined Ultrathin Pd-Ce Nanowires with Outstanding Moistureand SO2- Tolerance in Methane Combustion

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201803393 Angew. Chem. 10.1002/ange.201803393

Link to VoR: http://dx.doi.org/10.1002/anie.201803393 http://dx.doi.org/10.1002/ange.201803393

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Confined Ultrathin Pd-Ce Nanowires with Outstanding Moistureand SO₂- Tolerance in Methane Combustion

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Abstract: Pd-CeO_x solid solutions have demonstrated promising performance in industrial and environmental catalysis. However, challenges such as severe growth and aggregation of Pd and thermal-, vapor- or SO2-induced poisoning still obstruct their path toward real-world applications. Herein we develop an efficient strategy (enhanced metal-oxide interaction and core-shell confinement to inhibit the sintering of noble metal) for design and synthesis of confined ultrathin Pd-CeO_x nanowire (2.4 nm) catalysts for methane combustion, which enable CH4 total oxidation at a low temperature of 350°C, much lower than that (425 °C) of a commercial Pd/Al₂O₃ catalyst. Importantly, unexpected stability was observed even under harsh conditions (e.g., 800 °C, water vapor, and SO₂), owing to the confinement and shielding effect of the porous silica shell together with the promotion of CeO2. Pd-CeOx solid solution nanowires (Pd-Ce NW) as cores and porous silica as shells (Pd-CeNW@SiO2) were rationally prepared by a facile and direct self-assembly strategy for the first time. This strategy is expected to inspire more active and stable catalysts for use under severe conditions (e.g., vehicle emissions control, reforming, and water gas shift reaction).

Natural gas is widely used in power generation and other heating applications on account of its abundance worldwide and its high hydrogen/carbon ratio. Methane, the main component of natural gas, is known to be a serious greenhouse gas with an effect about 20 times that of CO_2 .^[1] Catalytic total combustion of methane at low temperature is an effective method of preventing it from polluting the atmosphere. It is widely acknowledged that palladium (Pd)-based catalysts are the most active ones for methane combustion.^[2] However, the catalytic activity of Pd alone

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is somewhat limited, and the high surface energy of Pd nanospecies often leads to the sintering and growth of Pd during high-temperature process.^[1b, 3]

Cerium oxide has been used in catalytic methane combustion as a robust support material.^[4] It exhibits excellent redox properties as well as outstanding oxygen storage capacity.^[4b, 5] The Pd-CeO₂ catalytic system is especially attractive for its high activity and stability in CH₄ combustion, which is contributed by not only the active component (PdO_x) but also the strong Pd-CeO₂ interaction.^[6] Considering the similar radius of the Pd²⁺ ion (0.86 Å) and the Ce4+ ion (0.87 Å), the formation of the solid solution or highly dispersed Pd-Ce-O mixed oxide is considerably enhanced, which can generate more surface oxygen vacancies and undercoordinated oxygen atoms.^[7] Accordingly, the catalytic activity and the thermal stability of ceria supported noble metal catalysts for methane combustion can be greatly improved.^[8] Encapsulation of metal nanoparticles (NPs) into a nanoporous shell to assemble a core@shell structure is an effective strategy to resist particle aggregation and to protect active centers from poisoning species.^[9] It could restrain the contact between metal NPs to keep active sites stable even under harsh conditions, meanwhile allowing the free diffusion of reactant molecules into and out of the shells.^[9c] Cargnello et al. reported a catalyst with PdO encapsulated in small cerium oxide NPs, which showed high thermal stability for inhibiting the sintering of Pd nanoparticles in methane combustion.^[2c] However, the pure CeO₂ shell was not stable at high reaction temperatures and was subjected to sintering.^[1c]



Scheme 1 Formation process and catalytic application of Pd-CeNW@SiO2.

To combine the unique characteristics of the $Pd-CeO_2$ solid solution or highly dispersed Pd-Ce mixed oxide with the enhanced metal-oxide interaction and the confinement effect of

core-shell structured materials, in this communication, we developed an all-in-one versatile strategy to design high-performance catalysts for CH₄ total combustion (Scheme 1). Briefly, the aqueous solution of Pd(NH₃)₄(NO₃)₂ and Ce(NO₃)₃ was added into cyclohexane mixed with the surfactant NP-5 (polyethylene glycol mono-4-nonylphenyl ether) solvent to form the micro-emulsion system and then ammonia added to form the ultrathin Pd-Ce-O(H)_x nanowires. Lastly, the silica source tetraethoxysilane (TEOS) was introduced to grow around the initially formed Pd-Ce nanowires to form the elongated morphology (Scheme S1). The as-prepared product was calcined at 600 °C in air to obtain the final Pd-CeNW@SiO₂ catalyst. The detailed synthesis protocol was presented in the supporting information (Experimental section). The Pd-CeNW@SiO2 catalyst with untrathin Pd-Ce-O solid solution nanowire (2.4 nm in width) as the core and microporous silica as the shell showed excellent performance in methane combustion due to the microporous shell protected the active sites from sintering, and the strong Pd-CeO₂ interaction played a significant role in the remarkable performance for methane catalytic combustion.

The morphologies of Pd-CeNW@SiO2 were initially identified by transmission electron microscopy (TEM); the results are shown in Figure 1a. It can be seen that worm-like Pd-Ce nanowires are encapsulated inside the microporous silica shell to form the special elongated morphology and the average width of a nanowire is approximately 2.40 nm (Figure 1a inset), which is one of the smallest Ce based nanowires. For comparison, Pd-Ce supported on silica spheres as a reference catalyst was also prepared via the conventional wet impregnation method (Pd-Ce/SiO₂). The Pd-Ce-O composite oxides spread out on the silica surface and were much larger, with a mean particle size of 5.35 nm (Figure S1). From the high resolution TEM (HRTEM) image of Pd-CeNW@SiO₂ (Figure 1b and S2), the lattice spacings derived from Fast Fourier Transform (FFT) of 0.31 nm and 0.26 nm can be clearly observed. For the lattice spacing of 0.31 nm, it is difficult to distinguish whether it belongs to CeO_2 (111) or PdO (100); and for the other lattice spacing of 0.26 nm is also difficult to distinguish whether it belongs to PdO (101) or CeO₂ (200) due to the highly dispersed Pd-Ce mixed oxide or solid solution structure. High-angle annular dark field scanning TEM (HAADF-STEM) image and line scanning profiles of Pd-CeNW@SiO₂ are displayed in Figure 1 (c, d). The Pd and cerium (Ce) signals have the same intensity in the same position, demonstrating that Pd and Ce atoms are evenly dispersed in the center of the particle. It is evidently verified that the highly dispersed Pd-Ce mixed oxides were formed. Moreover, silicon and oxygen have a stronger intensity than the Pd and Ce signals, evidencing the formation of the Pd-Ce nanowire core and SiO₂ shell structures.





Figure 1 (a) TEM (inset is the width distribution of Pd-Ce-O nanowires); (b) HRTEM images; (c) HAADF-STEM image; (d) line scan and (e, f) XPS profiles of Pd-CeNW@SiO2 and related catalysts.

The X-ray photoelectron spectroscopy (XPS) spectra of Pd-CeNW@SiO₂ and Pd-Ce/SiO₂ samples were collected, as the results shown in Figure 1 (e, f), to study their surface composition. The compositions of both samples were subjected to quantification analysis (XPS and inductively coupled plasma spectroscopy [ICP]); the results are summarized in Table S1. ICP results showed that Pd and Ce bulk contents were similar in Pd-CeNW@SiO₂ and Pd-Ce/SiO₂ samples. However, the XPS results showed a great difference. The surface content measured by XPS is lower than that measured by ICP, indicating that Pd and Ce are mainly distributed in the center of Pd-CeNW@SiO₂ core-shell sample, which matches well with the results of TEM and line scanning analysis. Compared with the Pd-Ce/SiO₂ sample, the Pd-CeNW@SiO₂ sample showed weaker Pd 3d and Ce 3d signals. Peaks with binding energy at 342.58 eV (Pd 3d_{3/2}) and 337.28 eV (Pd 3d_{5/2}) were assigned to the oxidized Pd species (Pd(II)).[9b, 10]

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Figure 2. (a) HAADF-STEM image; (b, c and d) EDX mapping and (e, f) N_2 adsorption/desorption isotherm and pore size distribution of Pd-CeNW@SiO_2.

Further information about the spatial distribution of Pd and Ce in Pd-CeNW@SiO₂ catalyst was provided by HAADF-STEM and EDX-mapping images. **Figure 2b-d** show the Pd and Ce mappings and their overlap, respectively. These mappings give direct evidence of the homogeneous distribution of Pd and Ce atoms in every particle in the same position. All of the Pd-Ce nanowires are totally encapsulated in silica nanoshells, as can be clearly witnessed in the HAADF-STEM image (**Figure 2a**). The mapping pictures (**Figure 2b, c and d**) show clearly that Pd is mixed and coexists closely with Ce, which is further verified that the sample with highly dispersed Pd-Ce-O oxides or solid solution nanowire as a core and microporous silica as a shell was successfully prepared.

To obtain the phase composition and crystal structure of the Pd-CeNW@SiO₂ sample, X-ray diffraction (XRD) technique was chosen. As shown in **Figure S3**, Pd-CeNW@SiO₂ displays a broad peak in the 2θ range of 15 - 35°, which was assigned to the amorphous silica. No diffraction peaks related to Pd species were detected, which was similar to that of Pd@SiO₂. The result is consistent with the TEM images showing the particle size of PdOx or Pd-Ce-O is ultra-small. The Pd-Ce/SiO₂ sample has the

same broad peaks as the amorphous silica, and a strong diffraction peak at 33.8° is attributed to the PdO (JCPDS NO.41-1445), meaning that the sample has larger PdO crystalline sizes than Pd-CeNW@SiO₂ and Pd@SiO₂, which is well in line with TEM results.

The N₂ adsorption-desorption isotherm curves are shown in **Figure 2e** and the quantification results are listed in **Table S2**. Pd-CeNW@SiO₂ displays typical type IV isotherms with H₁ hysteresis loops, which are evidenced by the presence of the capillary condensation step at P/P₀ = 0.8 -1.0. The pore size distribution (**Figure 2f**) showed the sample possessing both mesopores (36.3 nm) and some intraparticle micropores (1.4 nm). The micropores attributed to the structure directing agent (NP-5) were also existed in the SiO₂ and Pd@SiO₂ samples (**Figure S4**). The reactants (CH₄ and O₂) and products (CO₂ and H₂O) were able to easily access and leave the active Pd-Ce-O sites through these micropores. The mesopores resulting from the accumulation of the silica nanospheres show a slight difference, which may be due to the addition of Pd or Ce precursors that changed the size and morphology of the silica shell.



Figure 3. (a) Heating and cooling (5°C min⁻¹) light-off curves of CH₄ conversion against temperature for Pd-CeNW@SiO₂ (1.5 wt.Pd%), Pd@SiO₂ (1.5 wt.Pd%), and a commercial Pd/Al₂O₃ catalyst (2.0 wt.Pd%); (b) Arrhenius plots, (c) high-temperature stability, and (d) water resistance of Pd-CeNW@SiO₂. Conditions: 1% CH₄, 21% O₂, balanced with N₂, WHSV = 36000 mL g_{cat}⁻¹ h⁻¹.

PdO_x is a high-performance catalyst for the CH₄ combustion reaction,^[3b, 11] and CeO_x has been used successfully as a support for PdO_x to enhance catalytic performance owing to its high oxygen storage capacity.^[2c, 4a, 10] These features motivated us to explore the CH₄ combustion application by current Pd-CeNW@SiO₂ catalyst. For comparison, Pd@SiO₂, Pd/Al₂O₃ (a commercial catalyst with 2.0 wt.% Pd), and Pd-Ce/SiO₂ were also studied; the results are shown in **Figure 3a and Figure S5**. Pd-Ce/SiO₂ shows the worst activity due to relatively large Pd or Pd-Ce particle size; thus, the commercial catalyst (2 wt.% Pd/Al₂O₃) was selected as the reference. In detail, the temperatures corresponding to 100% conversion of CH₄ to CO₂ and H₂O

for Pd-CeNW@SiO₂ (red curve), Pd@SiO₂ (pink curve), and the commercial Pd/Al₂O₃ catalyst (blue curve) catalysts were 350, 375, and 425 °C, respectively (Figure 3 a). Note that the temperature of 50% methane conversion is only 290 °C for Pd-CeNW@SiO2, which means that it is an excellent low-temperature methane combustion catalyst. The activity details are listed in Table S3 and Figure S6. Pd-CeNW@SiO2 and the reference samples showed stable activity for CH₄ combustion over the entire range of temperatures studied (200 - 800 °C) (Figure 3a), with no decrease in activity during either heating or cooling curves. By contrast, Pd-CeNW@SiO2 afforded better activity than Pd@SiO₂ and the commercial catalyst (2 wt.%Pd/Al₂O₃) during the cooling stage. The enhanced activity of the Pd-CeNW@SiO₂ catalyst may be the result of the strong Pd-CeO₂ interaction and the excellent oxygen donation capability of CeO₂.[6d, 6e]

For comparison, the catalytic performances of Pd-based catalysts for CH_4 total combustion compared with the state of the art are presented in **Table S4**. It can be clearly observed that Pd-CeNW@SiO₂ is one of the best materials for CH_4 combustion.

Kinetic rate data verified the very high intrinsic activity of the catalyst compared with the related catalysts (**Figure 3b**); the quantification results are listed in **Table S3**. The reaction rates at 275 °C on the Pd-CeNW@SiO₂ sample were about 2.8 times higher than those on Pd@SiO₂ and 10.5 times higher than on the commercial catalyst, under conditions of 1% CH₄, 21% O₂, balanced with N₂, WHSV = 36000 mL g_{cat}⁻¹ h⁻¹.

Carbon monoxide temperature programmed desorption (CO-TPD) tests (**Figure S8**) were used to quantify the metal dispersion and the number of exposed active sites on the Pd. The turnover-frequency (TOF) values derived from the dispersion of Pd were listed in Table S3. The TOF values at 275 °C for the Pd-CeNW@SiO₂ sample were 2.74 times higher than those for the Pd@SiO₂ sample without ceria.

H₂-TPR (temperature programmed reduction) experiments (Figure S9) were performed to study the redox properties and strong metal-oxide interactions of Pd-CeNW@SiO2. Pd@SiO2 showed a major reduction peak at 88 °C, which was attributed to the reduction of PdO_x to metallic Pd.^[12] This reduction peak observed for the Pd-CeNW@SiO₂ sample shifts to a higher temperature (120 °C) owing to the strong Pd-CeO₂ interaction.^[6d] The Pd-CeNW@SiO₂ sample showed two additional H₂-consumption peaks. These two peaks at 300-400 °C and 700-900 °C can be assigned to the reduction of Ce4+ to Ce3+ of the surface and lattice Ce species, respectively.^[13] The H₂-TPR of Pd-Ce/SiO₂ consists of two peaks at 60-120 °C. The peak at 60 °C is attributed to the reduction of the individual PdO species, while the peak at 105 °C belongs to the reduction of the Pd species interacting with CeOx. O2-TPD experiments (Figure S10) were performed to further study the oxygen properties of Pd-CeNW@SiO₂ and Pd@SiO₂. Pd-CeNW@SiO₂ possessed more active oxygen species than Pd@SiO2. In brief, the H2-TPR and O2-TPD results demonstrated that both the activity and the amount of active oxygen species were higher in Pd-CeNW@SiO2. These factors are believed to be favorable to accelerate CH₄ oxidation.^[14] *In situ* DRIFT spectra of CH₄ combustion on Pd-CeNW@SiO₂ (**Figures S11 and S12**) showed that the bands (1120 cm⁻¹) assigning to bicarbonate^[5d] increased after CH₄ adsorption with time and disappeared after O₂ introduction. Thus, it is clear that CO₂ and H₂O is produced from the intermediate of adsorbed bicarbonate.

High-temperature stability and water and SO₂ tolerance are crucial parameters for determining the application potential of a methane combustion catalyst. Therefore, Pd-CeNW@SiO2 was examined under conditions of high temperature, moisture or SO₂ for an extended time, with the results shown in Figure 3 (c and d) and Figures S18-19. The catalyst displayed outstanding longterm stability at 310 or 800 °C for 50 hours, during which the methane conversion remained essentially unchanged. Thus, the Pd-CeNW@SiO₂ displayed superior high temperature thermal stability. Interestingly, the TEM image (Figure S13) of the spent catalyst at 800 °C after 50 hours maintains the initial core-shell structure, and the core Pd-Ce-O solid solution nanowire is not sintered clearly. Moreover, the pore volume and pore size of the catalyst barely changed under the harsh reaction conditions, as shown by the N₂ adsorption/desorption isotherm (Figure S14). Even more exciting, Pd-CeNW@SiO₂ also displayed a preferred SO₂ and water resistance. With 5 vol. % water vapor in methane, for Pd-CeNW@SiO₂, the temperature corresponding to total conversion of CH₄ was 450 °C (Figure S15). No evident CH₄ conversion decrease was observed during the 24 hours test at 375 or 445 °C, indicating the catalyst was structurally stable with excellent water tolerance (Figure 3d and Figure S16). The TEM image (Figure S17) of the spent catalyst at 445 °C after 24 hours with 5 vol. % water vapor further proved the point.

In the presence of 20 ppm SO₂, the catalytic performance followed the sequence of Pd-CeNW@SiO₂ > Pd@SiO₂ > Pd-Ce/SiO₂ (**Figures S18 and S19**). *In situ* DRIFT spectra of SO₂ adsorption at 450 °C (**Figures S20-S22**) showed typical bands at around 1255 and 1110 cm⁻¹ corresponding to palladium sulfate^[5c] on Pd-Ce/SiO₂ and Pd@SiO₂, which was the main factor deactivating Pd-based catalysts when SO₂ is contained in the reaction gas. Obviously, the formation rate and amount of palladium sulfate followed the sequence of Pd-CeNW@SiO₂ < Pd@SiO₂ < Pd-Ce/SiO₂, which is in agreement with SO₂ resistance sequence. Thus, it is clear that the porous shell has the shielding effect for SO₂ poison and a protective role for CeO₂ on Pd^[15] leading to Pd-CeNW@SiO₂ catalyst with excellent SO₂ tolerance.

Even with simultaneous addition of SO₂ and water vapor to the feed gas at 450 °C, methane conversion remained at 100% during the 10 h test for Pd-CeNW@SiO₂ (**Figure S23**). It seems fair to say that the catalyst showed superior thermal, H₂O stability and sulfur tolerance. In addition, methane catalytic combustion activity over Pd-CeNW@SiO₂ at a higher weight hourly space velocity (WHSV) was tested, and the CH₄ conversion at 72000 mL g_{cat}.⁻¹ h⁻¹ (Figure S24).

In summary, a Pd-CeNW@SiO₂ core-shell catalyst with ultrathin Pd-Ce-O solid solution or highly dispersed mixed oxide nanowire as the core and microporous silica as the shell was

designed and synthesized for the first time and used for methane total combustion. The catalyst showed outstanding catalytic performance for methane combustion because of the shielding effect of SiO₂ shell, which prevented the sintering of active phases, and the strong Pd-CeO₂ interaction. In addition, the Pd-Ce-O_x cores remained isolated even after reacting for 50 hours at 800 °C. Pd-CeNW@SiO₂ also showed superior water vapor and SO₂ tolerance. These results give it potential for natural gas vehicle and power station emissions control. The synthesis strategy developed in this work should encourage the development of many high-performance catalysts under harsh conditions (e.g., vehicle emissions control, reforming, and water gas shift reaction).

Acknowledgements

This work is supported by the National Key R&D Program of China (2016YFC0205900), the National Natural Science Foundation of China (21503106, 21567016 and 21773106), the Natural Science Foundation of Jiangxi Province (20171BCB23016 and 20171BAB203024), and the Foundation of State Key Laboratory of Coal Clean Utilization and Ecological Chemical Engineering (Grant No. 2016-15). The authors gratefully acknowledge Dr. Yuan Wang from the University of New South Wales and Duanjian Tao from the Jiangxi Normal University for their constructive suggestions during revising this manuscript.

Keywords: solid solutions \bullet core-shell \bullet CH₄ total oxidation \bullet strong metal-support interactions \bullet thermal-, vapor- and SO₂-tolerance

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Entry for the Table of Contents

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One plus one is greater than two. Double confinement strategy was introduced to design a methane combustion catalyst with ultra-high water and sulphur tolerance.



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