

Active and stable Pt-Ceria nanowires@silica shell catalyst: design, formation mechanism and total oxidation of CO and toluene

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Abstract:

Cerium oxide is one of the most important rare earth metal oxides in catalysis, however, the sintering problem of noble metals and CeO₂ at higher temperature (e.g., >700°C) is still unresolved. Herein, Pt nanoparticles self-assembled on ultra-thin CeO₂ nanowires (NWs) and then confined inside a thermally robust porous silica shell (Pt-CeO₂NW@SiO₂) were introduced. The thickness of CeO₂ NWs was just ~2.0 nm. Moreover, Pt-CeO₂ NW@SiO₂ showed significantly enhanced catalytic performances for total oxidation of CO and toluene. The increased catalytic properties are attributed to the strong metal-support interaction effect between Pt and CeO₂ NWs at sub-nanoscale. Most importantly, the special core-shell structure also affords excellent sintering resistance retention up to 700 °C for 100 h, due to the guarding effect of porous silica shell. Finally, the formation mechanism of Pt-CeO₂ NW@SiO₂ was investigated in detail. Current strategy should inspire many rational designs of rare-earth metal-based nanocatalysts for real-world catalysts.

1. Introduction

Total oxidation of carbon monoxide (CO)[1-3] and volatile organic compounds (VOCs)[4-9] is an important topic in environmental catalysis, while Pt/CeO₂ is one promising catalyst toward this target.[10-18] From the proof of principle, CeO₂ with high oxygen storage capacity and abundant oxygen vacancy defects between Ce³⁺ and Ce⁴⁺ oxidation states can benefit the charge transfer and oxygen migration,[19-21] meanwhile, Pt species function well for C-C and C-H bond activation, especially at moderate and high temperatures.[22] Generally, a strong interaction exists between CeO₂ and Pt species, which results in highly active sites locating at the interface between CeO₂ and Pt species,[23-26] the so called interfacial catalysis.[27-32] Actually, Pt/CeO₂ hybrids with many well-defined morphologies, such as nanorod, nanocube, have been studied intensively.[33-37] To maximum the active interface, Pt/CeO₂ nanowire with uniform dispersion of Pt and ceria species are of great interest.

Actually, metal nanowires have already shown attractive performance in many processes.[38-40] Whereas their thermal stability is far from ideal, because the nanowires themselves with high surface energy tend to sinter, distort and aggregate into larger nanoparticles under high temperature reaction, leading to loss of the original superior properties. Therefore, developing a strategy to prevent the sintering of the metal nanowires remains a challenging issue for the commercialization of metal nanowire-based catalysts.[41] Although a silica coating strategy has been used in palladium-ceria nanowire system,[42] the formation mechanism—an important study to bring up a new principle—was missed.

Herein, we show an in-situ self-assembly method to prepare, the Pt-CeO₂ nanowire@SiO₂ catalyst, with a core-shell structure that comprises of a self-assembled Pt-CeO₂ nanowire (NW) as the core and microporous silica as the shell. The thickness of ceria nanowires was just 2.0 nm, which could be considered as the thinnest ceria nanowires, to the best of our knowledge. More importantly, the formation mechanism of this novel material was also investigated in detail. Finally, we investigate

the catalytic performance of the core-shell catalyst containing rare earth nanowires self-assembled with Pt NPs, and interestingly Pt-CeO₂ NW@SiO₂ catalyst shows excellent catalytic performance for CO and toluene total combustion. The CO and toluene oxidation reach 100% conversion at 70 °C and 170 °C, respectively, which is far better than the performance of control catalysts by impregnation method. The Pt-CeO₂ NW@SiO₂ also has superior thermal stability due to enclosing the Pt-CeO₂ nanowires in porous silica shell.

2. Experimental

2.1. Catalyst preparation

Synthesis of Pt-CeO₂NW@SiO₂, Pt@SiO₂ and CeO₂NW@SiO₂. Pt-CeO₂ NW@SiO₂ was synthesized in a reverse-micelle emulsion system according to our previous reported literature with some modifications.[42]. The method for synthesis of Pt@SiO₂ and CeO₂NW@SiO₂ was similar with Pt-CeO₂NW@SiO₂ just without adding the precursors of Ce(NO₃)₃·6H₂O and Pt(NH₃)₄(NO₃)₂, respectively. The above method and procedure was also used to synthesize the pure silica nano-spheres by using deionized water in place of aqueous solution of Pt(NH₃)₄(NO₃)₂ and Ce(NO₃)₃·6H₂O. During the synthesis of 2%Pt-CeO₂NW@ SiO₂ and CeO₂NW@SiO₂ catalyst, a few drops of liquid from the round bottom flask before adding TEOS were extracted to investigate its plausible formation mechanism. The detailed procedures could be found in Supporting Information.

Synthesis of Pt-CeO₂/SiO₂ and Pt/SiO₂. For comparison, traditional catalysts with Pt and Pt-CeO₂ supported on SiO₂ nano-spheres were also synthesized through conventional impregnation method (0.02 g Pt(NH₃)₄(NO₃)₂ and 0.02 g Pt(NH₃)₄(NO₃)₂ with 0.03 g Ce(NO₃)₃·6H₂O impregnated with 0.5 g SiO₂ spheres). After impregnation, the samples were dried in a vacuum oven at 80 °C for 12 h, and calcined in air at 500 °C for 4 h, then, reduced in 10%H₂/N₂ at 400 °C for 4 h to obtain the final 2%Pt/SiO₂ and 2%Pt-CeO₂/SiO₂ samples. The Pt contents for all the five samples

are similar to the original values of the catalysts synthesis within the experimental error which determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) method. The Ce contents for three catalysts are the same, which is ~2%(wt) and also confirmed by ICP-OES method.

Synthesis of 1%Pt-CeO₂ NW@SiO₂-HNO₃. To study the effect of CeO₂ on catalytic performance of Pt-CeO₂NW@SiO₂, 1%Pt-CeO₂ NW@SiO₂ sample was treated in a certain amount of concentrated nitric acid at 70 °C for 2 h to remove the CeO₂ nanowires. The resulting sample was calcined in air atmosphere at 500 °C for 4 h, then reduced in 10%H₂/N₂ at 400 °C for 4 h. The final catalyst is denoted as 1%Pt-CeO₂ NW@SiO₂ -HNO₃.

2.2. Catalyst Characterization

X-ray diffraction (XRD) patterns, hydrogen temperature programmed reduction (H₂-TPR), carbon monoxide temperature programmed desorption (CO-TPD), transmission electron microscopy (TEM), scanning TEM (STEM), line scan and elemental mapping images, nitrogen adsorption-desorption analysis, X-ray photoelectron spectrum (XPS), inductively coupled plasma optical emission spectrometry (ICP-OES) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) measurements were performed to characterize the physical, chemical and reaction process of the catalysts. The detailed characterization methods were shown in Supporting Information.

2.3. Catalytic activity test

Carbon monoxide (CO) oxidation. All the catalysts were evaluated for CO oxidation as a model reaction in a continuous flow reactor with a gas composition of 1% CO, 21% O₂ and balanced by high purity N₂. [8, 43] Typically, 50 mg of catalyst was used for each measurement with a flow rate of 30 ml min⁻¹, which corresponds to a weight hourly space velocity (WHSV) of 36000 ml h⁻¹ g⁻¹. The reactants and products were analyzed on-line on a GC9310 gas chromatograph equipped with a TDX-01 column and a TCD detector.

Toluene total oxidation. The catalysts were also evaluated for toluene total oxidation in a quartz tube (Inner Diameter=6 mm) reactor with a continuous flow over 30 mg catalyst, which is similar to our previous report.[7] The detailed activity test process was presented in Supporting Information.

3. Results and discussion

3.1. Characterization of Pt-CeO₂NW@SiO₂

The transmission electron microscope (TEM) images in **Fig. 1(a) and 1(b)** displayed that the Pt-CeO₂ NW@SiO₂ with perfect wormlike core@shell structure was synthesized. It is clearly observed that elongated Pt-CeO₂ NWs are all embedded in silica shell. The dimension of these Pt-CeO₂ nanowires is just around 2.0 nm. HRTEM was adopted to confirm the crystal structure (**Fig. 1(c)**). The Pt-CeO₂ NW@SiO₂ sample shows the typical planes of 0.28 nm and 0.32 nm for the (200) and the (111) lattice planes of CeO₂, respectively. The lattice plane of 0.22 nm agrees well with (111) characteristic plane of Pt metal. The Fast Fourier Transform (FFT) pattern (inset of **Fig. 1(c)**) described three dim rings corresponding to (111) and (200) plane of the CeO₂ phase and the (111) plane of Pt metal, which further proves that the formation of self-assembled Pt-CeO₂ nanowires. Furthermore, high-angle annular dark-field STEM (HAADF-STEM) technique was used to determine the morphology structure. The Pt and Ce species are located in the center of the silica shell networks (see **Fig. 1(d)**). This result was further confirmed by the line scan technique, the self-assembled Pt-CeO₂ nanowires were loaded in the center of the Pt-CeO₂ NW@SiO₂ sample (**Fig. 1(d) inset**).

The HAADF-STEM mapping technique was also used for analysis of the distribution of the Pt, O, Si and Ce components in the nanostructures. As shown in the images presented in **Fig. 2(a-e)**, the Si element spreads in the whole particle. The Ce element signal could not be found in the shell position but only appeared in the core position, and the Pt elements existed in the similar position with Ce

element, thus indicating that Pt nanoparticles deposit on the CeO₂.

Additionally, XPS measurements were performed to identify the surface compositions and chemical valence of Pt-CeO₂ NW@SiO₂ and the control sample (Pt-CeO₂/SiO₂ prepared via impregnation method). XPS result reveals that the Pt-CeO₂NW@SiO₂ and Pt-CeO₂/SiO₂ afford two energy peaks at 71.6 and 75.1eV, which are typical bands for the Pt 4f_{7/2} and Pt 4f_{5/2} electrons of metallic Pt⁰ (**Fig. 1(e)**). No peaks corresponding to Pt²⁺ were observed, which demonstrated that all the Pt²⁺ species had been reduced by H₂. [44] Obviously, the intensity of two peaks for Pt 4f_{7/2} and Pt 4f_{5/2} electrons in Pt-CeO₂NW@SiO₂ catalyst is weaker than that of Pt-CeO₂/SiO₂, indicating that Pt is mainly coated by SiO₂ in core-shell structure. Over Ce 3d XPS spectra, two prominent bands at 884.4 and 904.0 eV in the Pt-CeO₂/SiO₂ catalyst can be ascribed to the Ce 3d_{5/2} and Ce 3d_{3/2}, respectively (**Fig. 1(f)**).

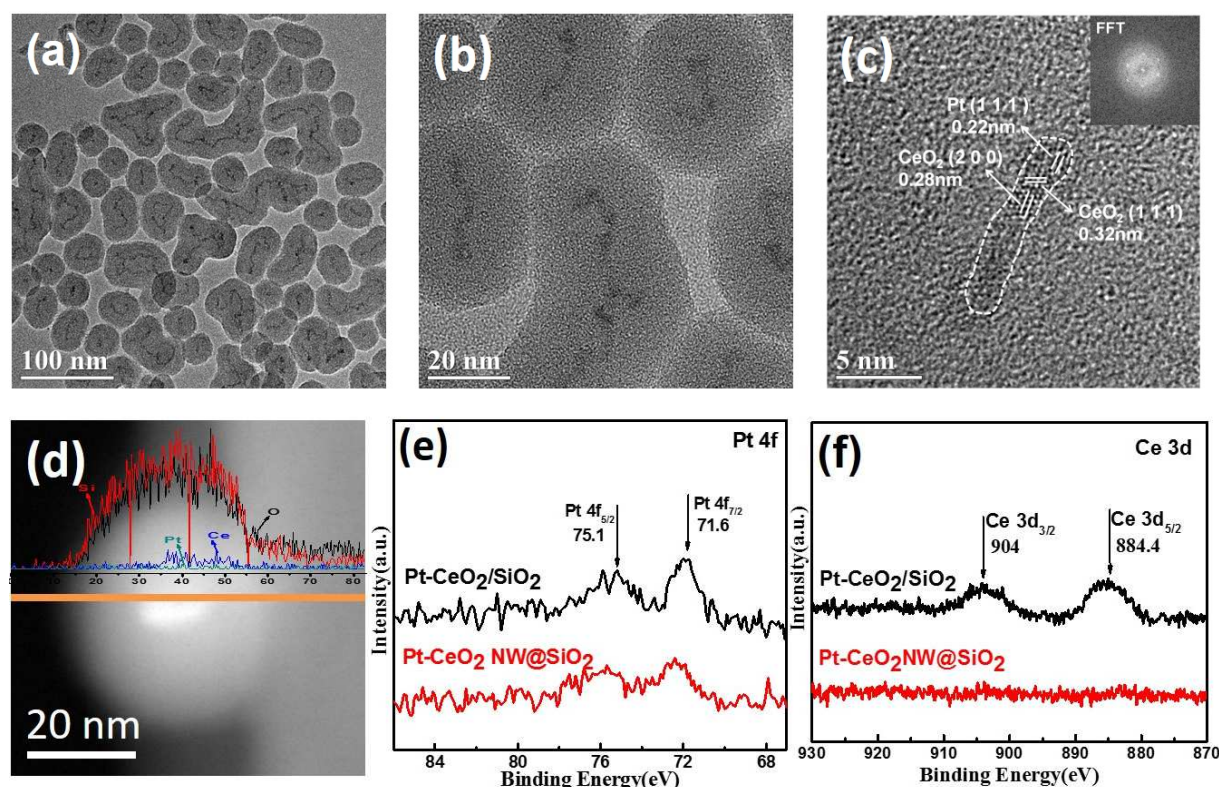


Fig. 1. TEM and HRTEM images (a, b, c) and HAADF-STEM image (inset is line scan) (d) of Pt-CeO₂ NW@SiO₂, XPS profiles of Pt4f and Ce3d for Pt-CeO₂ NW@SiO₂ and Pt-CeO₂/SiO₂ catalysts (e, f).

It is hard to detect the peaks for Ce from the wide scan survey of Pt-CeO₂NW@SiO₂

nanocomposite, which also suggests that the majority of CeO₂ nanowires were really coated by a silica layer, forming a perfect core–shell structure. It is well known that XPS technique is usually applied to characterize the surface composition of materials and its detectable depth is no more than 10 nm.[42] Thus, if Pt-CeO₂ nanowires are embedded by the SiO₂ outer shell and it is thick enough, which is legitimate that no or weak bands of Pt and Ce signals could be detected. Therefore, all the TEM, line scanning and XPS results confirm that the Pt-CeO₂ NW@SiO₂ nanocomposite has been successfully synthesized.

To identify the crystal structure of those catalysts, the XRD analysis was performed. As displayed in **Fig. 2(f) and Fig. S1**, all the samples have one broad peak at 2θ of 15 to 35°, which is the typical pattern of amorphous silica. Another five weak diffraction bands at 2θ of 39.7°, 46.2°, 67.4°, 81.2°, 85.7° are observed, which are assigned to the (111), (200), (220), (311), and (222) facets of Pt⁰ (PDF#04-0802). Apparently, the diffraction peaks of Pt in Pt-CeO₂NW@SiO₂ catalysts is weaker, which is a testimony of their high dispersity, and it will be further confirmed by CO chemisorption. There were no diffraction peaks relating to CeO₂, which is ascribed to the low content loading of CeO₂ and the shield effect of silica shell, thus escaping the detection of XRD. It is reasonable because the Pt- CeO₂ nanowire cores are embedded in SiO₂ shells.

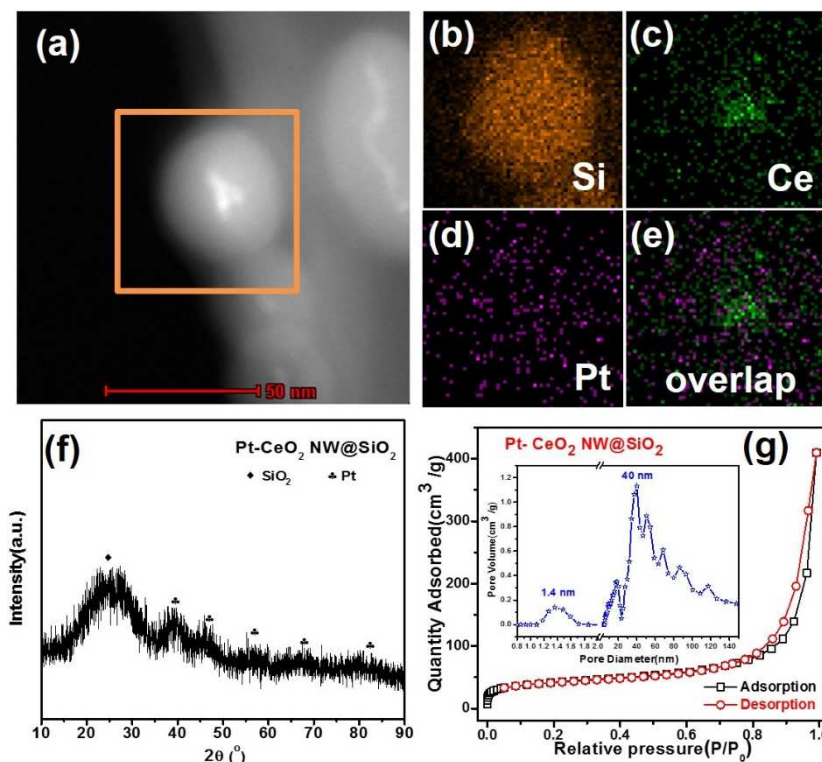


Fig. 2. HAADF-STEM EDX Mapping (a, b, c, d and e), XRD pattern (f) and N₂ adsorption/desorption isotherm and pore size distribution (inset) (g) of Pt-CeO₂ NW@SiO₂.

The texture structures of the samples were then determined by N₂ sorption technique at 77K, and the results are presented in **Fig. 2(g)**, **Fig. S2**, and **Table S1**. All five catalysts show an increasing N₂ uptake in p/p_0 between 0.6 and 0.9, which is characteristic of mesoporous materials. The mesopores in Pt-CeO₂ NW@SiO₂ (6–40 nm) may be derived from the particle assembling, which is in line with the TEM results displayed in **Fig. 1(b)**. The porous silica shell (~1.4 nm) was obviously seen from the N₂ sorption analysis, which is an important channel to make gas reactants access to active Pt-CeO₂ core.

3.2 Plausible formation mechanism of Pt-CeO₂NW@SiO₂

In order to explore the formation mechanism of Pt-CeO₂ NW@SiO₂ with core-shell structure, a part of the liquid suspension before adding the silica source (TEOS) into the synthetic process was extracted to perform the TEM characterization. The TEM images (**Fig. 3. Fig. 3 (a, b)**) clearly show the presence of typical nanowire structure yet without silica layers, which are considered to be

Pt(OH)_x-Ce(OH)_x nanowires. The dark dots on the nanowires indicate the presence of Pt-based nanoparticles. Furthermore, HAADF-STEM technique was adopted to measure the distribution of Pt, Ce and O elements over the self-assembled Pt(OH)_x-Ce(OH)_x nanowires (**Fig. 3 (c-g)**). The Pt, Ce and O elements are spread homogeneously over the nanowires. Thus, we here consider that the formation of Pt(OH)_x-Ce(OH)_x starts with the growth of Ce(OH)_x nanowires.

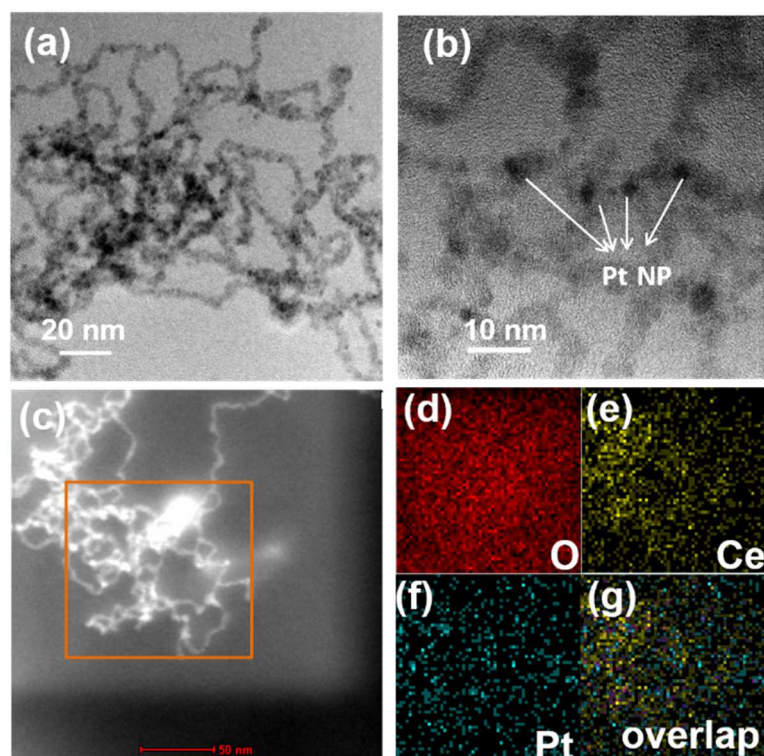


Fig. 3. TEM images (a, b) and HAADF-STEM EDX Mapping of Pt-Ce(OH)_x NW(c ,d, e, f, and g)

In order to figure out this process, we carried out a control experiment to prepare Ce(OH)_x nanowires, namely, keeping the same synthetic conditions yet without the addition of the Pt precursor. Interestingly, we did obtain the relevant products of Ce(OH)_x nanowires (**Fig. 4 (a, b)**). The uniform nanowires without the heavy dark dots indicate the presence of pure Ce(OH)_x nanowires. Moreover, the CeO₂ nanowires can also be embedded in SiO₂ shell (**Fig. 4 (c, d)**), which strongly supported our above-mentioned viewpoint. It should be regarded that the ceria nanowires were synthesized in inverse microemulsion system for the first time. As far as we know, this kind of

ceria nanowire was the thinnest one among the reported literatures (**Table S2**), whose width is only ~2.0 nm. We deduced that the formation mechanism of Pt-CeO₂ nanowires includes: a) Pt nanoparticles supported on Ce(OH)_x nanowires to form Pt(OH)_x-Ce(OH)_x nanowires *via* a self-assembly process; b) The TEOS was hydrolyzed along the nanowires to form the elongated wormlike shell, leading to Pt-CeO₂ nanowires after calcining and reducing.

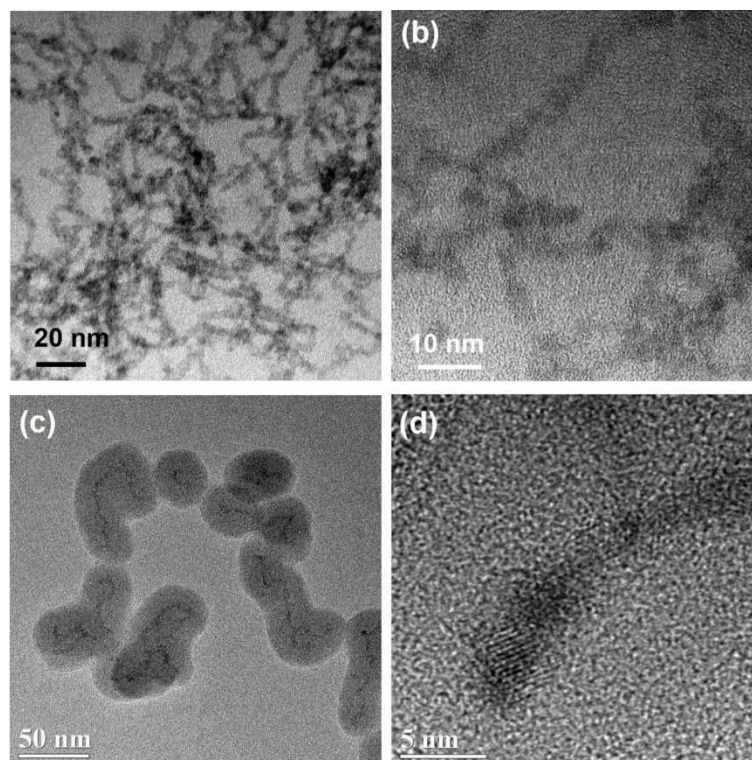
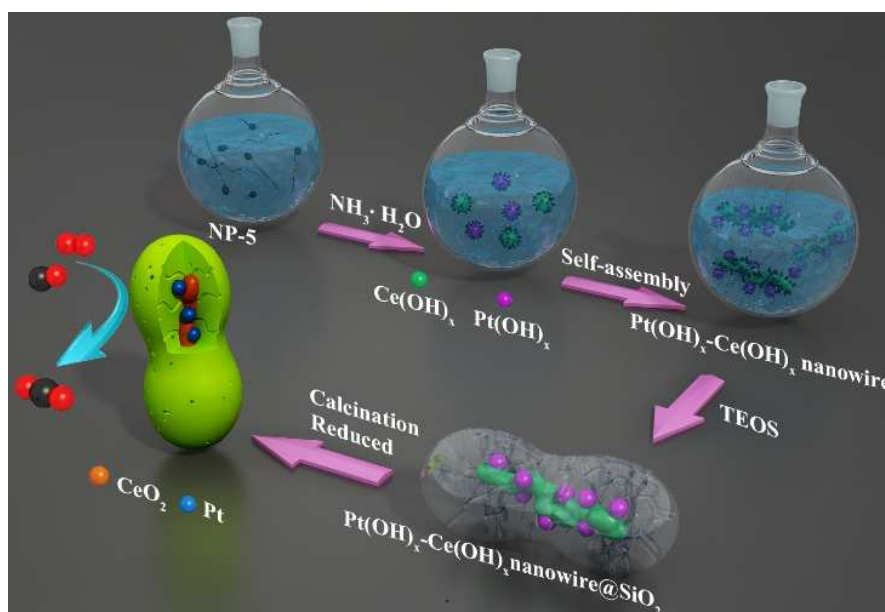


Fig. 4. TEM images of Ce(OH)_x NW (a, b) and CeO₂ NW@SiO₂(c, d).

The plausible formation mechanism of Pt-CeO₂ NW@SiO₂ by the inverse microemulsion method was described in **Scheme 1**. Pt(NH₃)₄(NO₃)₂, Ce(NO₃)₃·6H₂O, and tetraethylorthosilicate (TEOS) were chosen as the core and shell precursors, respectively. In the first step, Pt(NH₃)₄(NO₃)₂ and Ce(NO₃)₃·6H₂O aqueous solution was dropped into the water-in-oil (w/o) reverse micelle system. After adding the aqueous NH₃·H₂O to the above system, the nucleation, growth and self-assembly of Pt(OH)_x NPs and Ce(OH)_x NWs, result in Pt(OH)_x-Ce(OH)_x nanowires in micelle system. When TEOS was added, the hydrolysis of TEOS by aqueous NH₃·H₂O would proceed on the interface

between water and oil, leading to the encapsulation of $\text{Pt}(\text{OH})_x\text{-Ce}(\text{OH})_x$ nanowires in silica shell. Subsequently, the obtained $\text{Pt}(\text{OH})_x\text{-Ce}(\text{OH})_x$ NW@ SiO_2 species were separated by centrifugation, washing and drying. Then, the sample was calcined and reduced in air and H_2 atmosphere. Therefore, the Pt-CeO_2 NW@ SiO_2 catalyst were obtained via embedding the self-assembled Pt-CeO_2 nanowires inside silica shell.



Scheme 1. A plausible formation mechanism of Pt-CeO_2 NW@ SiO_2 .

3.3. Reducibility of Pt-CeO_2 NW@ SiO_2 and related catalysts

Hydrogen temperature programmed reduction (H_2 -TPR) experiments were performed to study the reducibility of the 2% Pt-CeO_2 NW@ SiO_2 , 2% $\text{Pt-CeO}_2/\text{SiO}_2$ and 2% Pt@SiO_2 catalysts. The H_2 -TPR profiles are presented in **Fig. 5**. For the 2% Pt@SiO_2 sample, there was no signal of reduction. Because the three catalysts were reduced in 10% H_2/N_2 at 400 °C for 4 h to completely reduce the Pt species. For the 2% $\text{Pt-CeO}_2/\text{SiO}_2$ sample, the reduction peak at ~415 °C was attributed to the reduction of surface Ce^{4+} to Ce^{3+} species, while the reduction peak centered at ~535 °C was owing to the reduction of the bulk Ce^{4+} species to Ce^{3+} . Over 2% Pt-CeO_2 NW@ SiO_2 , two main reduction peaks are found at 489 °C and 684 °C, respectively. However, in comparison to the 2% $\text{Pt-CeO}_2/\text{SiO}_2$

synthesized *via* impregnation method, the reduction peak of 2%Pt-CeO₂ NW@SiO₂ has moved toward high temperature after optimization of the catalyst structure, which indicates that the encapsulated Pt-CeO₂ NW has a more intimate contact with the microporous silica, compared with the 2%Pt-CeO₂/SiO₂ sample. This phenomenon was also observed by many other related core-shell catalysts.[42, 45-47] In addition, the formation of more Pt-CeO₂ interfaces may also increase their strong metal-support interaction and attribute to its higher reduction temperature.

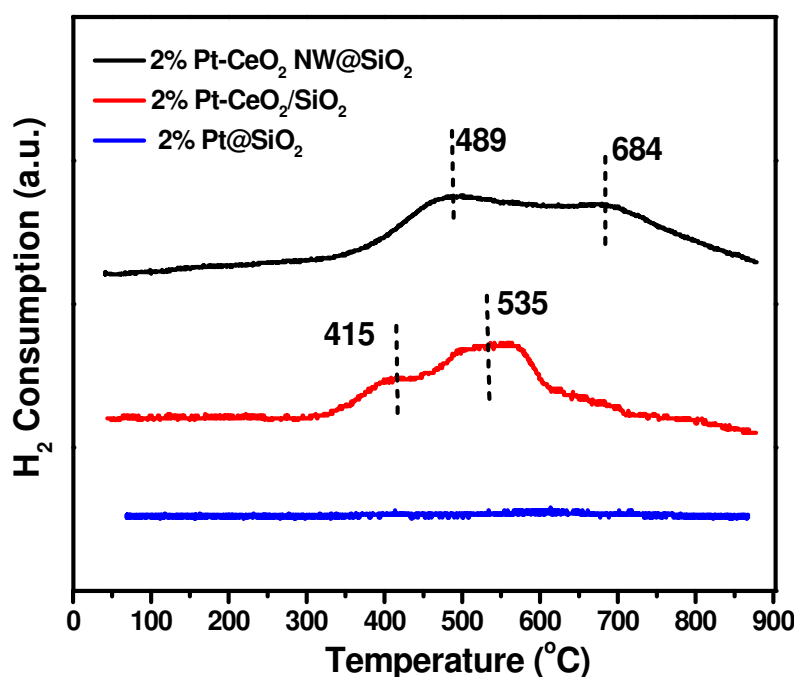


Fig. 5. H₂-TPR profiles of 2%Pt-CeO₂ NW@SiO₂ and related catalysts.

3.4 Catalytic performances of Pt-CeO₂NW@SiO₂

The carbon monoxide (CO) oxidation reaction was chosen as one of the model reactions to test the catalytic performance of Pt-CeO₂NW@SiO₂ and related catalysts. The activity results were displayed in **Fig. 6(a)**. The weight hourly space velocity (WHSV) of the CO oxidation reaction was fixed at 36 000 mL h⁻¹ g⁻¹. It is convenient to compare the catalytic activity of these catalysts by using the reaction temperatures of T₁₀, T₅₀, and T₉₀ (temperatures of CO conversion at 10%, 50% and 90%, respectively), as listed in **Table S2**. For all of the five samples, 2%Pt-CeO₂ NW@SiO₂ is

the most active, followed by 1%Pt-CeO₂NW@SiO₂ and 2%Pt@SiO₂. For example, the temperature of T₅₀ is 51 °C over 2%Pt-CeO₂ NW@SiO₂, 76 °C over 1%Pt-CeO₂ NW@SiO₂, and 103 °C over 2%Pt@SiO₂. For the 2%Pt/SiO₂ and 2%Pt-CeO₂/SiO₂ samples, both of them show low catalytic activity, which can be seen that their T₅₀ reached up to 142 °C and 124 °C, respectively. For converting CO to CO₂, the 100% conversion temperatures of these samples follow the sequence of 2%Pt /SiO₂ (150 °C) < 2%Pt-CeO₂/SiO₂ (130 °C) < 2%Pt@SiO₂ (110 °C) < 1%Pt-CeO₂ NW@SiO₂ (90 °C) < 2%Pt-CeO₂ NW@SiO₂ (70 °C). The BET surface areas of all the catalysts are shown in **Table S1**, However, the slight difference in surface areas seems not responsible for the differences in catalytic performances. Besides specific surface areas, other factors, e.g., metal nanoparticle dispersity, material structure and the interaction between ceria and Pt probably play important effects on their catalytic performances. The high catalytic activity in Pt-CeO₂ NW@SiO₂ may be owing to the existence of more Pt-CeO₂ interfaces, which can maximums the active sites between Pt and CeO₂. [17, 48] The formation of ultra-thin Pt-CeO₂ nanowires can also benefit the dispersion of the Pt species. Though the content of Pt in 1%Pt-CeO₂ NW@SiO₂ is half of that in 2%Pt/SiO₂ and 2%Pt-CeO₂/SiO₂, its catalytic performance is better than the latter two samples.

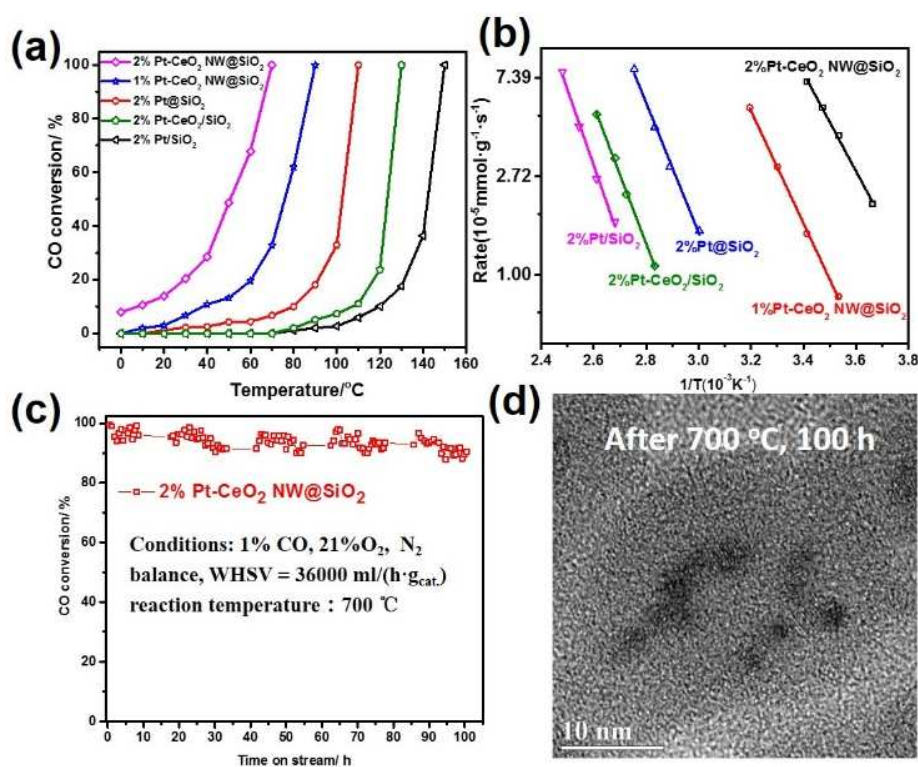


Fig. 6. (a) CO oxidation performance, (b) Arrhenius plots and (c) High temperature stability of Pt-CeO₂ NW@SiO₂; (d) TEM images of spent Pt-CeO₂ NW@SiO₂ after high temperature thermal stability test.

To further investigate the reaction behavior over Pt-CeO₂ NW@SiO₂ and related catalysts, the apparent activation energy (E_a) was calculated. To exclude the mass and heat transfer limitation, the E_a values over various samples were calculated at CO conversion under 20%. The Arrhenius plots and E_a values for each sample were presented in **Fig. 6(b)** and **Table S3**. For 2%Pt-CeO₂NW@SiO₂ catalyst, its E_a value is relatively lower than the other four catalysts, which are consistent with their catalytic activity differences. As displayed in **Table S3**, the reaction rate on 2%Pt-CeO₂NW@SiO₂, the most active catalyst in this work, is $6.7 \times 10^{-2} \text{ mmol g}^{-1} \text{ s}^{-1}$, which is the maximum reaction rate among the samples.

Long-term thermal stability tests of 2%Pt-CeO₂ NW@SiO₂ at 700°C for 100 h were also conducted. As shown in **Fig. 6(c)**, the catalyst activity barely declined. Slight aggregation is observed in TEM images of spent catalyst (**Fig. 6(d)**), and the spent catalyst still maintains core-shell structure with nanowires in the core. Those results indicate that the SiO₂ shell confinement can improve the thermal stability of Pt-CeO₂ NWs, and also decrease metal sintering under the conditions of high-temperature reactions.[49]

Generally speaking, over Pt based catalysts, CO molecules adsorb strongly on the outer surface of Pt NPs at low temperature, whose reaction rate is determined by the desorption of CO. The CO-TPD profiles in **Fig. 7** and **Table S3** demonstrate that the higher catalytic activity of the Pt-CeO₂NW@SiO₂ catalyst leads to their higher CO-desorption capability compared with other control samples. The turnover frequencies (TOF) of the exposed surface Pt active sites determined by CO-TPD method were calculated at 20 °C and the results were presented in **Table S3**. It can be clearly observed that 2%Pt-CeO₂ NW@SiO₂ has the highest TOF values due to the addition of CeO₂,

which are six times higher than that of 2%Pt@SiO₂, and also much higher than that of 2%Pt-CeO₂/SiO₂.

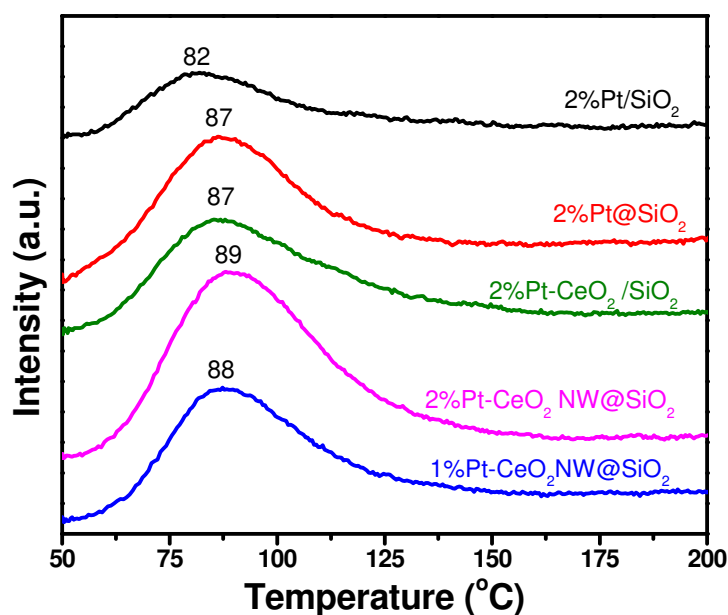


Fig. 7. CO-TPD profiles of Pt-CeO₂NW@SiO₂ and related catalysts.

The constructed Pt-CeO₂ NW@SiO₂ may act as a general catalyst, due to the high dispersion of Pt NPs, the strong Pt and CeO₂ interaction with plenty of Pt-CeO₂ interfaces, and the protection of the silica shell for Pt-CeO₂ nanowires working in high-temperature catalytic reactions. Therefore, these results encourage us to try the self-assembled Pt-CeO₂NW@SiO₂ catalyst in other catalytic reactions.

The catalytic combustion of toluene was then investigated for 2%Pt-CeO₂ NW@SiO₂, 2%Pt-CeO₂/SiO₂ and 2%Pt@SiO₂ catalysts at a temperature range of 90 to 220 °C in 1000 ppm of toluene, 40% O₂, and N₂ with a WHSV of 20,000 ml g⁻¹ h⁻¹. **Fig. 8** shows the catalytic activities of those three catalysts. The toluene conversion increased with the increasing of reaction temperature. For the 2%Pt-CeO₂ NW@SiO₂, 2%Pt-CeO₂/SiO₂ and 2%Pt@SiO₂ samples, the temperatures at toluene conversion of 90% are 167, 177, and 193°C, respectively. Therefore, it can be obtained that the activities of the three catalysts followed the sequence of 2%Pt-CeO₂/SiO₂ < 2%Pt@SiO₂ < 2%Pt-CeO₂ NW@SiO₂. It is further verified that the incorporation of the CeO₂ can enhance the

performances of the catalyst, a synergistic effect between Pt and CeO₂ and forming Pt-CeO₂ nanowires can provide more active sites in Pt-CeO₂ interface.

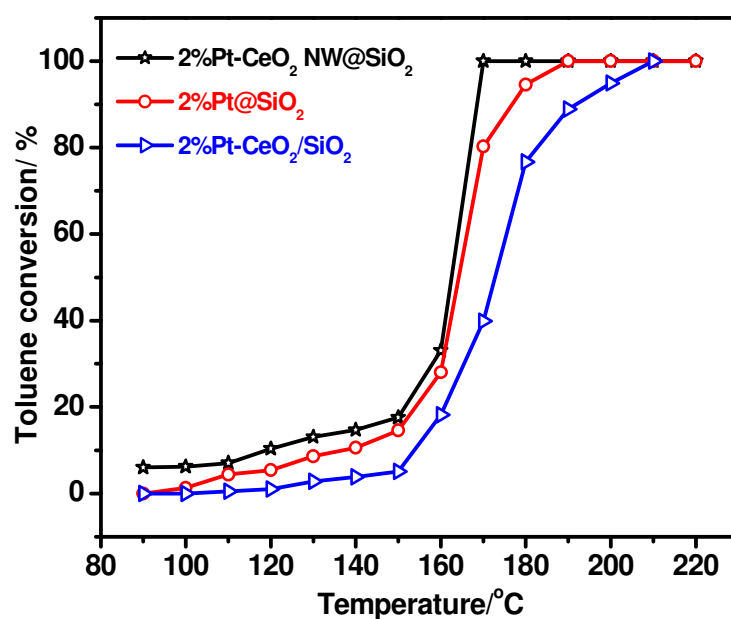


Fig. 8. Catalytic combustion of toluene over 2%Pt-CeO₂ NW@SiO₂ and related catalysts. Reaction conditions: 0.030 g catalyst, 1000 ppm toluene, 40% O₂, balance N₂, total flow rate = 10 ml min⁻¹, GHSV = 20,000 ml g⁻¹ h⁻¹.

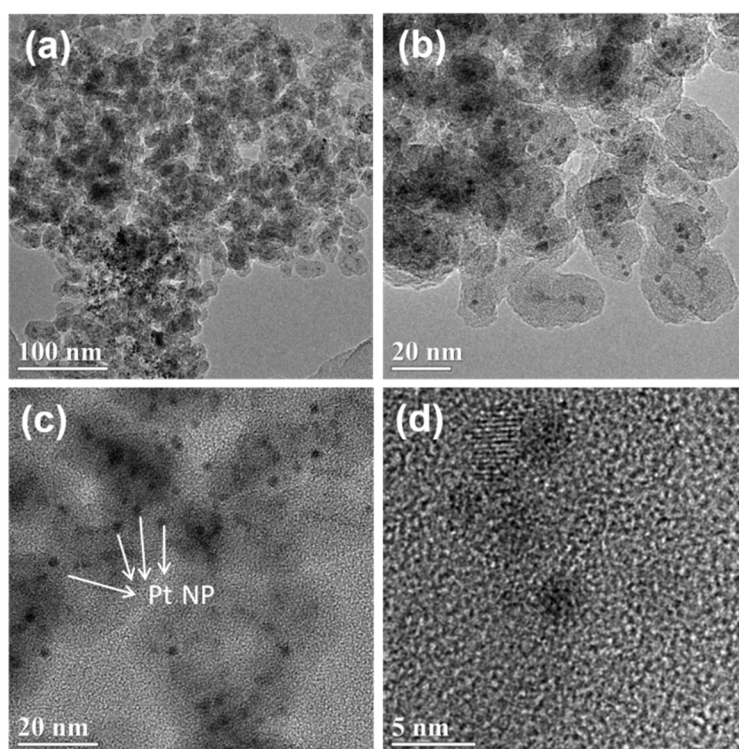


Fig. 9. TEM images of Pt-CeO₂ NW@SiO₂ treated by concentrated HNO₃ (To remove CeO₂ nanowires).

To further investigate the relationship between the special structure and the catalytic performance of these catalysts, the 1%Pt-CeO₂NW@SiO₂ catalyst was treated by concentrated nitric acid. In this trial, the motivation is to remove the CeO₂ nanowire in the core-shell structure. The TEM and HRTEM images of 1%Pt-CeO₂ NW@SiO₂ after treated with concentrated nitric acid are shown in **Fig. 9(a-d)**. Pt-CeO₂ nanowires in 1%Pt-CeO₂NW@SiO₂-HNO₃ catalyst obviously disappeared compared with its pristine sample (**Fig. S3**), while Pt nanoparticles were retained. There is trace amount of Ce in the treated catalyst, which is confirmed by ICP-OES method. The result of Ce content can further demonstrate that CeO₂ nanowires in 1%Pt-CeO₂ NW@SiO₂ were dissolved by the concentrated nitric acid. CO oxidation activity on the 1%Pt-CeO₂ NW@SiO₂ catalysts before and after treated with concentrated nitric acid are shown in **Fig. 10**. 1%Pt-CeO₂ NW@SiO₂ catalyst can achieve 100% CO conversion at 90°C, however, the 1%Pt-CeO₂ NW@SiO₂-HNO₃ catalyst exhibits evidently worse activity than the original catalyst with 100% CO conversion moving higher by 30 °C due to the loss of CeO₂ nanowires, which offers Pt-CeO₂ interface and active sites to reactants, which signifies the importance of the stronger synergistic effect between Pt and CeO₂.

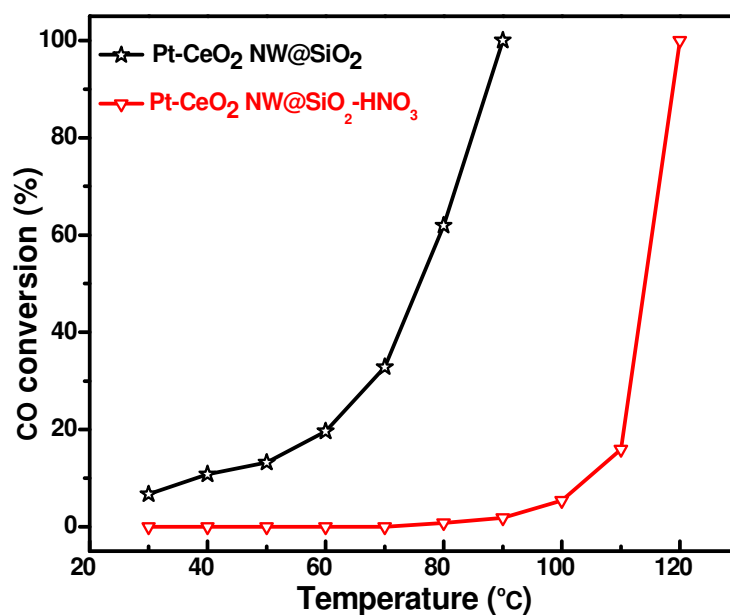


Fig. 10. performance of 1%Pt-CeO₂ NW@SiO₂ before and treated by HNO₃ for CO oxidation.

Conditions: 1% CO, 21%O₂, N₂ balance, WHSV = 36000 ml g_{cat.}⁻¹ h⁻¹.

3.4. In situ DRIFTS analysis

In situ DRIFTS spectroscopy was adopted to study the CO adsorption and oxidation behavior over Pt@SiO₂, Pt-CeO₂NW@SiO₂ and Pt-CeO₂/SiO₂. **Fig. 11** (A), (C) and (E) show the *in situ* DRIFT spectra of CO adsorption at 110 °C (Pt@SiO₂), 70 °C (Pt-CeO₂NW@SiO₂) and 130 °C (Pt-CeO₂/SiO₂), respectively. CO adsorbed onto these samples formed the CO vibration band at 2082 cm⁻¹, which is assigned to linearly bonded CO species on Pt active sites.[50, 51] The intensity of CO adsorption decreased gradually in the sequence of Pt@SiO₂ > Pt-CeO₂ NW@SiO₂ > Pt-CeO₂/SiO₂, demonstrating that the amount of active Pt sites for CO adsorption was reduced with the increase of the Pt particle size over the Pt-CeO₂/SiO₂. CO molecules adsorb strongly with the surface active oxygen and forms various carbonate species between 1000 and 1800 cm⁻¹. [52] The same carbonate species are observed over the surface of the three catalysts, while the corresponding peaks are stronger for the Pt-CeO₂NW@SiO₂ and Pt-CeO₂/SiO₂ samples. It indicates that the Pt-CeO₂NW@SiO₂ and Pt-CeO₂/SiO₂ samples possesses more active adsorption sites. In addition, the bands at 2342 and 2360 cm⁻¹ were also distinguished. The band at 2360 and 2342 cm⁻¹ have been attributed to the asymmetric stretch of physisorbed CO₂, and the intensity of CO₂ decreased gradually with the consumption of surface oxygen species. When O₂ was introduced into the steam, the intensity of the Pt-CO bands at 2082 cm⁻¹ decreased notably with time for these three catalysts.

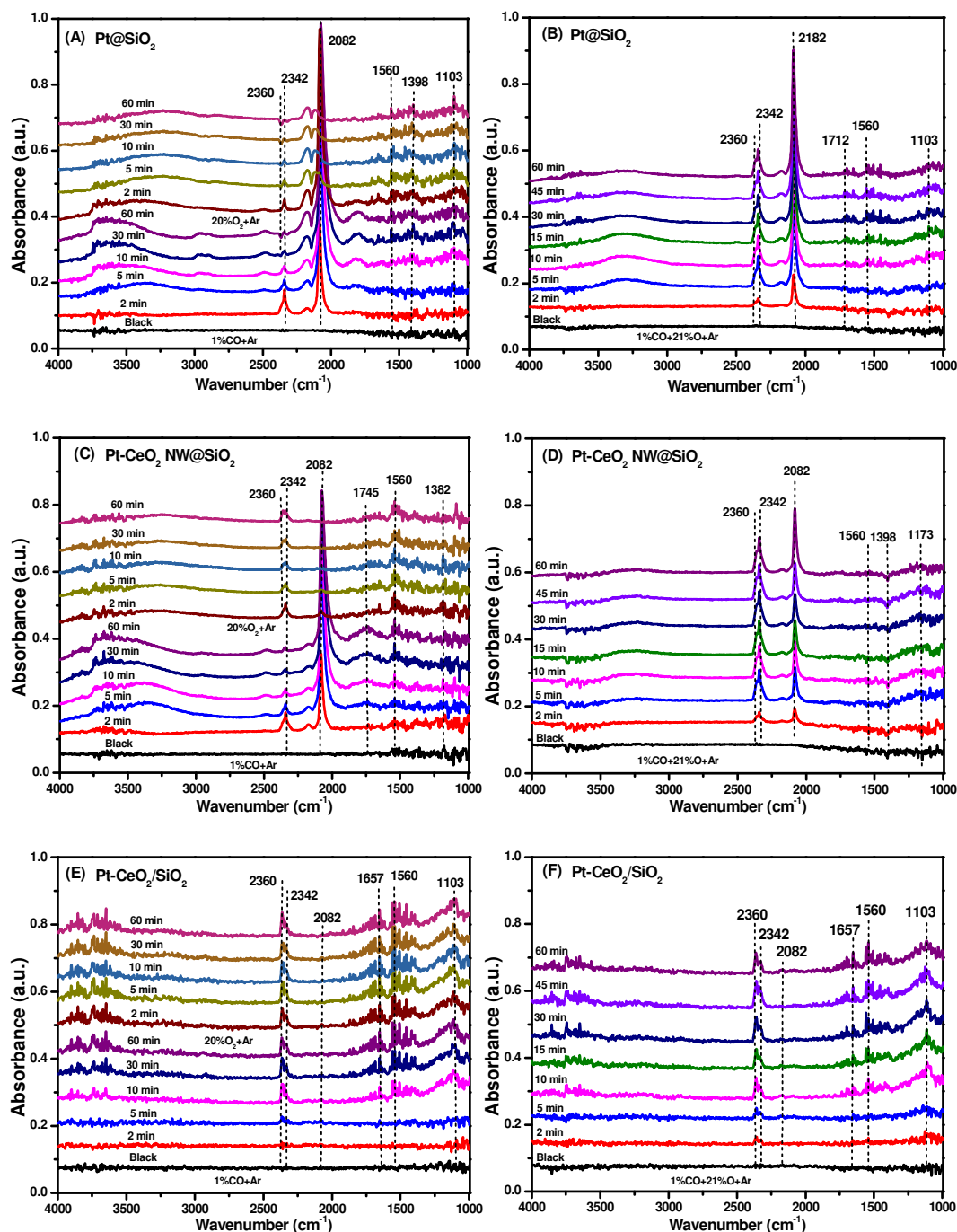


Fig. 11. Evolution of different IR bands in the 1000-2500 cm^{-1} interval for (A) Pt@SiO₂, (C) Pt-CeO₂ NW@SiO₂, and (E) Pt-CeO₂/SiO₂ catalysts at 110 °C, 70 °C and 130 °C, respectively, exposed to 1 vol% CO in Ar while switching the 1 vol% CO to 20 vol% O₂ in Ar at time = 60 min. And evolution of different IR bands in the 1000-2500 cm^{-1} interval for (B) Pt@SiO₂, (D) Pt-CeO₂ NW@SiO₂, and (F) Pt-CeO₂/SiO₂ catalysts at 110 °C, 70 °C and 130 °C, respectively, exposed to 1 vol % CO-21 vol % O₂-78 vol % Ar.

To identify adsorbed species on the three catalysts during CO oxidation reaction, the *in situ* DRIFTS analyses were further carried out to study CO oxidation over the three catalysts. **Fig. 11** (B),

(D) and (F) show DRIFT spectra of adsorbed species over the three catalysts exposed to the gas of 1 vol% CO/21 vol% O₂/78 vol% Ar at 110 °C, 70 °C and 130 °C as a function of time, respectively. When reaction gas was introduced into the stream, it was clearly seen that the linear adsorption of CO on Pt sites soon over Pt-CeO₂ NW@SiO₂ and Pt@SiO₂, importantly, CO adsorption intensity over Pt-CeO₂/SiO₂ was relatively low, compared to that of Pt-CeO₂NW@SiO₂ and Pt@SiO₂. The bands at 2360 and 2342 cm⁻¹ have been attributed to the asymmetric stretch of physisorbed CO₂, and the formation of CO₂ appeared gradually. It is noticed that the intensity of the bands increases in proportion to the time. The *in situ* DRIFT analysis confirmed that the moderate adsorption intensity of CO over Pt-CeO₂NW@SiO₂ was very important to improve its catalytic performances.

4. Conclusions

In summary, a thermally stable catalyst with a novel self-assembled Pt-CeO₂ nanowires as the core and porous silica as the shell (Pt-CeO₂NW@SiO₂) has been successfully fabricated via an *in situ* strategy. Especially, one of the thinnest CeO₂ nanowire (~2 nm) was obtained via the reverse microemulsion method. The final Pt-CeO₂NW@SiO₂ displays not only an enhanced catalytic activity but also a good thermal stability for CO oxidation and toluene combustion. Compared with Pt@SiO₂ and Pt-CeO₂/SiO₂, the thermally stable Pt-CeO₂NW@SiO₂ with special core-shell nanostructure exhibits the characteristics of the high dispersion of Pt nanoparticles, low aggregate of particles, even reacted at 700 °C for 100 h. The stronger synergistic effect between Pt and CeO₂ and plenty of Pt-CeO₂ interfaces attribute to its high catalytic activity in CO oxidation and toluene combustion. The porous SiO₂ shell could offer a physical and energy barrier to prevent the migration and growth of Pt nanoparticles, which contribute to the excellent sinter-resistant ability of the catalyst. This approach is simple and efficient, which can be potentially extended to design other high performances core-shell catalysts applying in harsh reactions.

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Graphic Abstract

Pt nanoparticles self-assembled on ultra-thin CeO_2 nanowires (NWs) and then confined inside a thermally robust porous silica shell ($\text{Pt-CeO}_2\text{NW@SiO}_2$) were introduced. The thickness of CeO_2 NWs was just ~ 2.0 nm, which is the thinnest ceria nanowires among the reported literatures. Moreover, Pt-CeO_2 NW@ SiO_2 showed significantly enhanced catalytic performance for total oxidation of CO and toluene.

