Pt nanoparticles encapsulated in CeO₂ over-layers synthesized by controlled reductive treatment to suppress CH₄ formation in high-temperature water-gas shift reaction

Jaeha Lee a, Chengbin Li b, Sungsu Kang a, Jungwon Park a, Ji Man Kim c, Do Heui Kim a,⇑

a School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Seoul 08826, Republic of Korea
b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
c Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea

Abstract

Pt supported on CeO₂ (Pt/CeO₂) is known to be a good catalyst for the water-gas shift (WGS) reaction. However, Pt catalyzes the methanation reaction as a side reaction, which limits the usefulness of Pt/CeO₂ as a catalyst in the high-temperature (HT) WGS reaction. In this study, Pt nanoparticles (Pt NPs) were encapsulated in CeO₂ over-layers (Pt in CeO₂) by using controlled reductive treatments to suppress the methanation reaction on Pt NPs. Pt in CeO₂ catalyst demonstrated the much lower CH₄ selectivity while showing the same high activity in the HT-WGS reaction compared to the conventional Pt on CeO₂ catalyst. Detailed characterizations revealed that the underlying Pt NPs promoted the WGS reaction on thin (<1 nm) CeO₂ over-layers by facilitating the formation of active oxygen vacancies. The present contribution to catalyst modification via simple thermal treatments will provide additional way to control metal-support interactions to improve catalytic performance.

© 2021 Elsevier Inc. All rights reserved.

1. Introduction

The main purpose of the water-gas shift (WGS) reaction is to produce additional H₂ by converting CO with H₂O in H₂-rich feed (CO + H₂O = CO₂ + H₂). High-purity H₂ (free of CO) has many uses: it is used, for example, to produce NH₃ or to operate fuel cells (e.g. proton-exchange membrane (PEM) fuel cells) [1,2]. Industrial-scale WGS reactions proceed in two stages: the high-temperature (HT) WGS reaction (350–500 °C) followed by the low-temperature (LT) WGS reaction (200–250 °C) [1,2]. The HT-WGS reaction takes advantage of the high reaction rate, although it has two major disadvantages. (i) The HT-WGS reaction is thermodynamically limited, resulting in incomplete CO conversion [1–3]. For this reason, a LT-WGS reactor must be employed after the HT-WGS reactor [1–3]. The LT-WGS reaction can compensate for the thermodynamic constraints and further reduce the CO concentration below 1 vol% [1–3]. (ii) Methanation is significantly promoted as the side reaction (CO + 3H₂ = CH₄ + H₂O) during the HT-WGS reaction, leading to the loss of H₂ fuel [4–7]. In particular, since the WGS reaction is exothermic, even if the inlet temperature of the HT-WGS reactor is fixed at 350 °C, the outlet temperature of the HT-WGS reactor may exceed 500 °C [1]. At high temperatures (>450 °C), the methanation reaction is significantly promoted [4–7]. Since this disadvantage limits the types of catalyst that can be used in the HT-WGS reaction, suppressing the CH₄ formation during the HT-WGS reaction becomes important [5,6,8–11]. Currently, CuO-Cr₂O₃-Fe₂O₃ catalyst is commercially used in the HT-WGS reaction [3]. However, because of the toxicity of Cr, the development of alternative catalysts for the HT-WGS reaction is needed [3]. Platinum/cerium(IV) oxide (Pt/CeO₂) catalysts (or catalysts with similar formulations, such as Pt/CeO₂-TiO₂) have received considerable attention as candidate catalysts in the LT-WGS reaction [12–18]. Atomically dispersed Pt²⁺ species or interfacial regions between Pt nanoparticles (NPs) and CeO₂ have been reported to serve as the active sites in the WGS reaction [12,17,19–21]. It would be meaningful if Pt/CeO₂ catalyst having the high intrinsic activity in the WGS reaction could be used in the high-temperature domain. However, Pt/CeO₂ catalysts have an intrinsic drawback in the HT-WGS reaction because Pt greatly promotes the methanation reaction at high temperatures [4]. Therefore, in order to use Pt/CeO₂ as the catalyst in the HT-WGS reaction, a control is needed to suppress the methanation reaction on Pt [4,22,23]. One intuitive strategy to achieve this goal is to block the exposed Pt on the surface to suppress the methanation reaction at high temperature while preserving high activity toward...
the HT-WGS reaction. Tsang et al. reported that by synthesizing Pt\(\text{CeO}_2\) core-shell catalysts with a Pt core and CeO\(_2\) shell, in which all Pt sites are covered with CeO\(_2\) shells, the methanation reaction on Pt is significantly suppressed while high activity in the HT-WGS reaction is maintained [4,22,23]. The results of Tsang et al. have two important implications. (i) Beyond the major role of Pt/\(\text{CeO}_2\) as a catalyst in the LT-WGS reaction, Pt/\(\text{CeO}_2\) can also be used as the catalyst in the HT-WGS reaction with high activity and selectivity. (ii) The metal-support interaction between Pt and CeO\(_2\) can grant catalytic activity to the CeO\(_2\) surface of a Pt@CeO\(_2\) core-shell catalyst to achieve high activity in the HT-WGS reaction even if the Pt is completely protected by the CeO\(_2\) shell [4,22,23].

Although Pt@\(\text{CeO}_2\) catalysts suggest a new route for the use of the high-activity Pt/\(\text{CeO}_2\) system in the HT-WGS reaction without promoting the methanation side-reaction, the synthetic conditions for Pt@\(\text{CeO}_2\) limit its practical use. For example, the micro-emulsion technique used to synthesize Pt@\(\text{CeO}_2\) catalysts involves several steps that require sophisticated control mechanisms [4]. In addition, expensive cetyltrimethylammonium bromide (CTAB) is required to synthesize the catalyst with the micro-emulsion technique [4]. Therefore, in this contribution, we tried to prepare a ‘Pt in CeO\(_2\)’ catalyst by simple controlled reductive treatments to the ‘Pt on CeO\(_2\)’ catalyst to modify its structure. CeO\(_2\) is known to undergo agglomeration at high temperature (e.g. 800 °C) under the reducing conditions [24], and the CeO\(_2\) over-layers are expected to form on Pt NPs during the process. In this context, we hypothesized that the ‘Pt in CeO\(_2\)’ catalyst for the HT-WGS reaction could be synthesized simply by controlled reductive treatments at high temperature. It is noteworthy that CeO\(_2\)-encapsulated Pt catalysts are successfully synthesized by utilizing facile and convenient thermal treatments. We found that the ‘Pt in CeO\(_2\)’ catalyst displayed a comparable CO conversion rate in the HT-WGS reaction to the ‘Pt on CeO\(_2\)’ catalyst, while the methanation reaction was significantly suppressed. The catalytic nature of CeO\(_2\) over-layers in interaction with Pt NPs on the ‘Pt in CeO\(_2\)’ catalyst was also studied in detail by combining CO chemisorption, HAADF-STEM, XRD, XPS, and in-situ DRIFTS analysis.

2. Materials and methods

2.1. Catalyst synthesis

\(\text{CeO}_2\) (Rhodia) has a surface area of 135 m\(^2\)/g. Pt (2 wt%) was impregnated on CeO\(_2\) with the incipient wetness impregnation method with aqueous Pt\(\text{(NH}_3\text{)}_2\)\(_2\)(NO\(_3\))\(_2\) solution (Sigma Aldrich, 99.99% grade, metal basis) as a metal precursor at room temperature. After impregnation, the catalysts were dried in an oven at 100 °C for 24 hr. Dried catalysts were oxidized under 15 vol\% O\(_2\)/N\(_2\) at 500 or 800 °C for 2 hr. For example, Pt(2)/\(\text{CeO}_2\) 500C indicates that dried Pt(2)/\(\text{CeO}_2\) was oxidized at 500 °C. The catalytic structure of Pt(2)/\(\text{CeO}_2\) 500C was modified using two different methods. In the first method, samples were reduced under 10 vol\% H\(_2\)/N\(_2\) at 500 or 800 °C for 2 hr (R treatment). For example, Pt(2)/\(\text{CeO}_2\) 800R indicates that Pt(2)/\(\text{CeO}_2\) 500C was reduced at 800 °C. In the second method, after reduction at 250 °C for 2 hr with 10 vol\% H\(_2\)/N\(_2\), the sample was treated with N\(_2\) at 800 °C for 2 hr (NC treatment). For example, Pt(2)/\(\text{CeO}_2\) 800NC indicates that Pt(2)/\(\text{CeO}_2\) 500C was first reduced at 250 °C and then N\(_2\) treated at 800 °C. Reduced catalysts were stabilized under 1 vol\% O\(_2\)/N\(_2\) at 35 °C for 24 hr. In all cases, the flow rate was 100 ml/min and the ramping rate was 10 °C/min.

2.2. H\(_2\) temperature programmed reduction (TPR)

H\(_2\)-TPR analysis was performed in a BET-CAT-BASIC (BEL Japan Inc.) with a thermal conductivity detector (TCD). The catalysts were treated with a He flow (50 ml/min) at 350 °C for 2 hr prior to analysis. After cooling to room temperature, the catalysts were exposed to 5 vol\% H\(_2\)/Ar (50 ml/min) for 30 min and heated from room temperature to 900 °C at a heating rate of 2 or 10 °C/min.

2.3. Powder X-ray diffraction (XRD)

XRD patterns were taken with a Rigaku (mode 1 smartlab) diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 0.1542\) nm). The X-ray voltage and current were 40 kV and 30 mA, respectively. The patterns were collected in a 20 range from 5 to 90° with a scanning step size of 0.02° at a speed of 2.5°/min.

2.4. Surface area measurement

N\(_2\) adsorption/desorption isotherms were measured on a Micromeritics ASAP 2010 apparatus at the temperature of liquid N\(_2\) (-196 °C). Before analysis, all catalysts were pretreated at 300 °C for 4 hr under a vacuum to remove impurities. The pore size distribution and specific surface area were calculated using the Barrett-Joyner-Halenda (BJH) and Brunauer-Emmet-Teller (BET) methods, respectively.

2.5. CO chemisorption

Pulsed CO chemisorption was performed on a BET-CAT-II (BEL Japan Inc.) at ~78 and 50 °C using the experimental procedures put forth by Tanabe et al. [25]. First, 0.05 g of sample was oxidized at 500 °C for 15 min. After purging with He, the sample was reduced at the same temperature for 15 min under a 10 vol\% H\(_2\)/N\(_2\) flow. After cooling to ~78 or 50 °C, CO pulses were introduced until adsorption reached saturation. In addition, static CO chemisorption was performed on CeO\(_2\) 500C with a Micromeritics ASAP 2010 following previously reported procedures [24]. Briefly, 0.2 g of sample was reduced at 200, 350, or 500 °C under pure H\(_2\) for 2 hr, and CO chemisorption was performed at 35 °C. The Pt dispersion was estimated from CO chemisorption by assuming 1 to 1 stoichiometry of CO to Pt.

2.6. O\(_2\) chemisorption

Pulsed O\(_2\) chemisorption was performed on a BET-CAT-II (BEL Japan Inc.) at 100 °C. After the reductive treatment at 500 °C with 10 vol\% H\(_2\)/N\(_2\) for 30 min, samples were purged with He at 500 °C for another 30 min. After cooling the sample temperature to 100 °C, O\(_2\) pulses (5 vol\% O\(_2\)/He in He flow) were introduced until adsorption reached saturation. 0.05 g of sample was used for the analysis. The amount of O\(_2\) adsorbed on Pt was excluded based on the nominal Pt dispersion estimated from CO chemisorption at ~78 °C to measure the amount of O\(_2\) adsorbed on CeO\(_2\). Each Pt atom was assumed to adsorb one O atom (O/Pe = 1.0).

2.7. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) study

In-situ DRIFTS experiments were conducted in a diffuse reflectance cell (Praying Mantis, Harrick) installed in a Fourier transform infrared (FT-IR) spectrometer (IS-50, Thermo Fisher Scientific) with an MCT detector. 10 vol\% H\(_2\)/N\(_2\) or 20 vol\% O\(_2\)/H\(_2\) or N\(_2\) were used to pretreat the sample at 500 °C for 30 min. After the reductive or oxidative pretreatments, the samples were purged with N\(_2\) for another 30 min at 500 °C. Background spectra were obtained after cooling the sample to the CO adsorption temperature and before CO adsorption. 2 vol\% CO/N\(_2\) was used for CO adsorption H\(_2\)O (1.5 μl/min) was added to the sample with the syringe pump.
The total flow rate was maintained at 50 mL/min with N₂ balance gas.

2.8. TEM

High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were obtained with a JEM-2100F (JEOL) electron microscope equipped with a field emission gun at an accelerating voltage of 200 kV. Bright-field TEM images of the samples were also obtained to precisely distinguish lattice fringes and determine the thickness of the CeO₂ over-layers on Pt NPs. To obtain the size distribution curves of the Pt NPs, ~200 Pt NPs from several HAADF-STEM images were counted with ImageJ software. Pt dispersion was estimated from size distribution curves according to the following equation [26]:

\[
D(\%) = \frac{115.4}{d_p^{31}}
\]

where \( D \) is Pt dispersion and \( d_p \) is the average size of Pt NPs. \( d_p \) is calculated as follows:

\[
d_p = \left( \frac{\sum nd^3}{\sum nd^{19}} \right)^{1/3}
\]

Here, \( d \) is the diameter of Pt NPs, and \( n \) is the number of Pt NPs with diameter \( d \).

2.9. X-ray photoelectron spectroscopy (XPS)

XPS analysis was conducted on an AXIS-HSi (Kratos) instrument with Mg Kα radiation (450 W). The charging effects were corrected with respect to the C 1s binding energy of 284.5 eV and the Ce 4f binding energy (\( u^0 \)) of 916.7 eV [27]. The spectra were processed using casaXPS. Depth-profiling XPS analysis was conducted on a K-alpha instrument (Thermo VG, U.K.) with monochromated Al Kα X-ray radiation (360 W). XP spectra were collected sequentially after the Ar sputtering treatments. (500 eV, raster size 2 mm × 2 mm). The chemical compositions were calculated using the integral intensities of lines of each component considering the atomic sensitivity factors [28]. In addition, XPS spectra were measured five times to calculate the standard deviation of Pt-to-Ce molar ratio.

2.10. Catalytic activity evaluation

The HT-WGS reaction was performed in a fixed bed reactor at atmospheric pressure with 0.06 g of catalyst. The feed mixtures were prepared using mass flow controllers (MKS Instruments, Inc.). The reaction was conducted at 450 °C with (i) simple feed containing 3 vol% CO and 24 vol% H₂O or (ii) full feed containing 3 vol% CO, 24 vol% H₂O, 3 vol% CO₂, and 20 vol% H₂. The WGS reaction was also conducted at 200 °C with simple feed or full feed to compare the catalytic activities under the differential reaction condition (at CO conversion < 15%). The total flow rate was 70 mL/min with He as the balance gas. The inlet and outlet gas streams were analyzed online using a TCD and a parallel gas chromatograph (GC, Younglin, Inc.) equipped with a Carboxen 1000 column and a flame ionization detector (FID). A methanizer was used to convert CO and CO₂ to CH₄ for quantification by FID. The conversion data were measured when steady-state operation was reached. Before reaction, the catalysts were pretreated with 5 vol% H₂/He at 500 °C for 1 hr. The WGS reaction rate per exposed Pt atom on catalysts was calculated by using the following formula:

\[
\text{WGS reaction rate per exposed Pt} = \frac{\text{moles of CO}}{\text{moles of Pt} \times \text{sec}} \times \frac{\text{CO conversion (\%) \times CO flow rate (mol)}}{\text{Moles of exposed Pt on catalysts (mol)}}
\]

Here, the moles of exposed Pt on catalysts was estimated from CO chemisorption at −78 °C. In addition, the WGS reaction rate per surface area of catalysts was also calculated to evaluate the WGS activity of the CeO₂ surface of ‘Pt in CeO₂’ catalysts by using the following formula:

\[
\text{WGS reaction rate per surface area of catalysts} = \frac{\left( \frac{\text{moles of CO}}{\text{m}^2 \text{ of catalysts} \times \text{sec}} \right) \times \text{CO conversion (\%)} \times \text{CO flow rate (mol)}}{\text{Surface area of catalysts (m}^2\text{)}}
\]

Here, the BET surface area of catalysts was used to calculate the WGS reaction rate.

The catalytic stability of Pt(2)/CeO₂ 800NC was investigated by performing the WGS reaction at 450 °C for 47 hr under the full feed. Samples were sieved to 150–180 μm size, and 0.05 g of sample was mixed with 0.1 g of α-Al₂O₃. CO conversion and CH₄ yield were estimated by using mass spectroscopy. The total flow rate was 100 mL/min. The selectivity of catalyst for CH₄ during the WGS reaction was also investigated in the temperature range of 400–500 °C. The experimental conditions were the same as those used for the stability test.

3. Results and discussion

3.1. Synthesis of ‘Pt in CeO₂’ with controlled reductive treatment

As mentioned in Introduction, we tried to cover Pt NPs with CeO₂ over-layers by inducing CeO₂ agglomeration via two controlled reductive treatments (NC and R methods). Under oxidizing conditions, Pt forms strong Pt–O–Ce bonds with the CeO₂ surface, which is known to suppress both Pt sintering and CeO₂ agglomeration at high temperature [24,29–31]. Indeed, the crystalline size of CeO₂ in Pt/CeO₂ was smaller than that of CeO₂ after oxidative treatment at 800 °C as evidenced by XRD patterns in Fig. S1. In addition, a high-Pt dispersion was maintained on Pt/CeO₂ 800NC since an XRD peak corresponding to metallic Pt NPs at 39.5 °C is not observed in Fig. S1. However, when Pt–O–Ce bonds are reduced (Pt–O–Ce bonds are completely reduced at 250 °C as shown in Fig. S2), both Pt sintering and CeO₂ agglomeration could occur at high temperature (>600 °C) [24]. Hence, Pt(2)/CeO₂ 500C was reduced at 250 °C and then treated with N₂ at 800 °C to induce CeO₂ agglomeration (NC method). In addition, H₂ treatment at high temperature (>600 °C) accelerates CeO₂ aggregation by reducing CeO₂ bulk. Since the bulk oxygen of CeO₂ is surrounded by Ce atoms, its reduction is thermodynamically unfavorable [29]. For this reason, H₂ can reduce CeO₂ bulk only at temperatures above 600 °C (Fig. S2) [29]. When CeO₂ bulk is reduced at high temperature, vacancies that form in the lattice destabilize the structure of CeO₂ to accelerate CeO₂ aggregation [24]. Thus, Pt(2)/CeO₂ 500C was reduced at 800 °C to accelerate CeO₂ agglomeration (R method).

To selectively chemisorb CO on Pt and to avoid CO chemisorption on CeO₂, pulsed CO chemisorption was performed at −78 °C after H₂ pretreatment at 500 °C [25]. Fig. 1 and Table S1 display the amount of CO chemisorbed on the Pt(2)/CeO₂ 500C, 800R, and 800NC samples. The amount of CO chemisorbed on Pt(2)/CeO₂ 500C decreased from 64 to 1 and 5 μmol/g after 800R and 800NC treatments, respectively. Such a huge decrease in CO chemisorption on Pt(2)/CeO₂ after 800R or 800NC treatments might result from either severe Pt sintering or the coverage of Pt
NPs with CeO$_2$ over-layers. According to CO chemisorption results, the nominal Pt dispersion of Pt(2)/CeO$_2$ 500C, 800R, and 800NC samples are 61, 1 and 5%, respectively, which corresponds to the nominal average Pt NP size of 2, 110, and 22 nm, respectively (Table S1). However, no Pt NPs larger than 10 nm were observed in HAADF-STEM images of the Pt(2)/CeO$_2$ 800R (Fig. 2a) and 800NC (Fig. 2b) samples (more HAADF-STEM images are provided in Fig. S3). According to the particle size distribution curves in Fig. 2c obtained from HAADF-STEM images, the average size of Pt NP is 4.0 and 2.4 nm on Pt(2)/CeO$_2$ 800R and Pt(2)/CeO$_2$ 800NC samples, respectively. Note also that the size of Pt NPs on Pt(2)/CeO$_2$ 500C was about 2 nm according to the HAADF-STEM images of the Pt(2)/CeO$_2$ 500C (Fig. S3). The XRD patterns in Fig. 5a indicate that no large Pt NPs exist in the Pt(2)/CeO$_2$ 800R and 800NC samples, since the intensity of the XRD peak at 39.5° from metallic Pt NPs is small. The Pt dispersions of Pt(2)/CeO$_2$ 800R and 800NC samples, as assessed by CO chemisorption and particle size distribution curves, are compared in Fig. 2d. The Pt dispersions estimated from the Pt size distribution curves were 37 and 56% on Pt(2)/CeO$_2$ 800R and 800NC samples, respectively, which were much higher than those estimated from CO chemisorption, 1 and 5% on Pt(2)/CeO$_2$ 800R and 800NC samples, respectively (Fig. 2d). This indicates that the CeO$_2$ over-layers deposited on Pt NPs inhibit CO chemisorption on Pt, resulting in underestimation of Pt dispersion of the ‘Pt in CeO$_2$’ samples. The combined results imply that the ‘Pt in CeO$_2$’ samples were successfully prepared from the ‘Pt on CeO$_2$’ sample (Pt(2)/CeO$_2$ 500C) without significant Pt sintering by two different methods (R and NC methods).

According to the Pt NP size distribution curves in Fig. 2c obtained from HAADF-STEM images, all Pt NPs in Pt(2)/CeO$_2$ 800NC were smaller than 5 nm in size, while some Pt NPs in Pt(2)/CeO$_2$ 800R were larger than 5 nm in size. The XRD patterns in Fig. 5b also indicate that a small portion of the Pt NPs in Pt(2)/CeO$_2$ 800R are larger than 5 nm in size. Such a difference could be caused by the more severe change in the structure of Pt/CoO$_2$ after R treatment than after NC treatment as discussed in the beginning of Section 3.1. Indeed, the XRD patterns in Fig. S5a show that the crystallite size of CeO$_2$ is 31.1 and 48.4 nm on Pt(2)/CeO$_2$ 800NC and 800R samples, respectively (Table S2). However, it should be stressed that the majority of Pt NPs are around 2 nm in size on both samples (Fig. 2c). It would be also worth to discuss whether the coverage of Pt NP by CeO$_2$ over-layers as observed in the present work is related to the Strong-Metal-Support-Interaction (SMSI) phenomena. SMSI phenomena is the reversible loss of the CO adsorption ability of PGM NP supported on reducible oxides after the reductive treatment at high temperature (> 500 °C) [32,33]. Tauster et al. first reported that the CO adsorption ability of Pt/TiO$_2$ disappeared after the reductive treatment at 500 °C, which recovered after the oxidative treatment at 400 °C [32,34–36]. When oxygen vacancies are formed on reducible oxides, reducible oxides migrate to the surface of PGM NP to minimize the surface energy, resulting in the blockage of CO adsorption sites on PGM NP [37–39]. However, reducible oxides reduce from the surface of PGM NP when the oxygen vacancies are replenished by the oxidative treatment at high temperature (> 400 °C) to restore the CO adsorption ability of PGM NP [37–39]. To verify whether the suppression of CO adsorption ability after the 800R and 800NC treatments is related to SMSI phenomena, the CO adsorption ability of Pt(2)/CeO$_2$ 800R and 800NC samples were investigated after the oxidative treatment at 400 °C. Table S3 shows that the oxidative treatment at 400 °C has little effect on the CO adsorption abilities of Pt(2)/CeO$_2$ 800R and 800NC samples. Since the suppression of CO adsorption ability is not reversible, the formation of CeO$_2$ over-layers on Pt NP during the CeO$_2$ agglomeration is not related to SMSI phenomena. While core-shell synthetic strategies, inverse-catalyst synthetic strategies or SMSI phenomena have been implemented to form metal-oxide over-layers on PGM NP surface [37,40,41], we believe that the present synthetic approach would provide simple alternative to the field.

3.2. Comparison of HT-WGS reaction activity of the ‘Pt on CeO$_2$’ and ‘Pt in CeO$_2$’ catalysts

In this section, the catalytic performances of CeO$_2$, ‘Pt on CeO$_2$’ and ‘Pt in CeO$_2$’ samples in the HT-WGS reaction are comparatively investigated. Table 1 summarizes the HT-WGS reaction activities of high-surface area CeO$_2$ (135 m$^2$/g), ‘Pt on CeO$_2$’ (Pt(2)/CeO$_2$ 500C) and ‘Pt in CeO$_2$’ (Pt(2)/CeO$_2$ 800R and 800NC) catalysts evaluated at 450 °C with simple feed (CO and H$_2$O) and full feed (CO, H$_2$, H$_2$O, and CO$_2$). Note that CeO$_2$ and Pt(2)/CeO$_2$ 800NC catalysts displayed negligible HT-WGS reaction activity even with the simple feed (Table 1). However, Pt(2)/CeO$_2$ 500C and 800NC catalysts displayed comparable CO conversion during the HT-WGS reaction with both the simple feed and the full feed (Table 1). With the simple feed, the CO conversion during the HT-WGS reaction was 98.1 and 97.1% on Pt(2)/CeO$_2$ 500C and 800NC catalysts, respectively. In addition, with the full feed, the CO conversion during the HT-WGS reaction was 51.7 and 51.1% on Pt(2)/CeO$_2$ 500C and 800NC catalysts, respectively. Note that the addition of H$_2$ and CO$_2$ to the reactant feed is well known to decrease CO conversion during the HT-WGS reaction by reaching the thermodynamic limit at high temperature [42,43]. Table 1 also compares the CH$_4$ yield on ‘Pt on CeO$_2$’ (Pt(2)/CeO$_2$ 500C) and ‘Pt in CeO$_2$’ (Pt(2)/CeO$_2$ 800NC) catalysts. CH$_4$ is produced from the reaction between H$_2$ and CO [7]. For this reason, only a small amount of CH$_4$ is produced in the simple feed (without H$_2$ and CO$_2$) on both Pt(2)/CeO$_2$ 500C and 800NC catalysts (CH$_4$ yield < 0.5% on both samples, Table 1). However, in the full feed (with the inclusion of H$_2$ and CO$_2$), the CH$_4$ yields on Pt(2)/CeO$_2$ 500C and 800NC catalysts were 8.7 and 0.9%, respectively (Table 1). This corresponds to a selectivity towards CH$_4$ of 16.8 and 1.4% on Pt(2)/CeO$_2$ 500C and 800NC catalysts during the WGS reaction, respectively. While Pt(2)/CeO$_2$ 500C and 800NC catalysts displayed the comparable CO conversion during the HT-WGS reaction with the full feed, Pt(2)/CeO$_2$ 800NC produced much less amount of CH$_4$ during the HT-WGS reaction (Table 1). It should be also mentioned that ‘Pt in CeO$_2$’ (Pt(2)/CeO$_2$ 800NC) catalyst was non-selective to CH$_4$ formation during the WGS reaction in the temperature region of 400–500 °C (Fig. 3a). Similar to the Pt@CeO$_2$ core-co-

![Fig. 1. The amount of CO chemisorbed on Pt at 78°C (μmol/g)](image-url)
shell catalysts reported by Tsang et al., the CeO$_2$ over-layers on Pt NPs appear to have suppressed the methanation reaction on Pt NPs during the HT-WGS reaction [4]. The catalytic stability of Pt(2)/CeO$_2$ 800NC was also investigated by performing the HT-WGS reaction at 450 °C for 47 hr under the full feed. Pt(2)/CeO$_2$ 800NC displayed the stable performance, maintaining the equilibrium CO conversion (~51%) throughout 47 hr (Fig. 3b). In addition, the CH$_4$ yield was only approximately 0.4% during the entire time period, confirming the usefulness of Pt(2)/CeO$_2$ 800NC catalyst (Fig. 3b).

The WGS reaction activities of ‘Pt on CeO$_2$’ (Pt(2)/CeO$_2$ 500C) and ‘Pt in CeO$_2$’ (Pt(2)/CeO$_2$ 800NC) catalysts were also evaluated at 200 °C to compare the catalytic activity under the differential reaction condition (CO conversion < 15%). Under the simple feed, the CO conversion over ‘Pt on CeO$_2$’ and ‘Pt in CeO$_2$’ catalysts were 12.7 and 6.1%, respectively (Table 2). The CO conversion of ‘Pt on CeO$_2$’ catalyst decreased from 12.7 to 2.5% when H$_2$ and CO$_2$ were added to the feed. The inhibitory effect of H$_2$ and

![Figure 2](image-url)
CO₂ on the LT-WGS reaction activity of Pt-based catalysts has been reported several times [43–45]. Interestingly, the CO conversion of Pt in CeO₂ catalyst increased from 6.1 to 12.0% with the addition of H₂ and CO₂ to the feed. While further study is needed to understand the working chemistry of this phenomenon, the presence of H₂ in the feed may have promoted the catalytic activity of Pt in CeO₂ by facilitating the formation of oxygen vacancies on CeO₂ over-layers, which will be discussed in section 3–4.

According to previous reports, the role of Pt in the WGS reaction is to adsorb CO molecules to react with surface hydroxyls on the CeO₂ surface [17,46]. It is interesting that, although Pt is not exposed to reactants on Pt in CeO₂ (Pt(2)/CeO₂ 800NC) catalyst, it can still catalyze the HT-WGS reaction. It is essential to identify the active sites on Pt in CeO₂ catalyst to understand how the HT-WGS reaction can be promoted without producing CH₄ in other words, without exposed Pt sites on the surface. In section 3–3, the WGS reaction activity of Pt on CeO₂ (Pt(2)/CeO₂ 500C), Pt in CeO₂ (Pt(2)/CeO₂ 800NC), and CeO₂ samples are comparatively investigated to unravel the change in active sites when Pt on CeO₂ catalyst becomes Pt in CeO₂ catalyst. In addition, although Pt NPs are covered with CeO₂ over-layers on both Pt(2)/CeO₂ 800R and 800NC catalysts, only the latter displayed the activity in the HT-WGS reaction. In section 3–4, Pt(2)/CeO₂ 800R and 800NC catalysts are analyzed to understand the factors that determine the catalytic activity of Pt in CeO₂.

3.3. How the interaction between Pt NPs and CeO₂ over-layers influences the catalytic activity of the CeO₂ surface on the ‘Pt in CeO₂’ catalyst

In-situ DRIFTS experiments could provide useful information to distinguish between different active sites on the ‘Pt on CeO₂’ and ‘Pt in CeO₂’ catalysts. The reactivity of CO adsorbed on the ‘Pt on CeO₂’ (Pt(2)/CeO₂ 500C), ‘Pt in CeO₂’ (Pt(2)/CeO₂ 800NC), and CeO₂ samples with H₂O was investigated with in-situ DRIFTS analysis. After pretreatment at 500 °C with H₂, CO was adsorbed at 100 °C for 1 hr, followed by N₂ purging at 100 °C for 1 hr to ensure that only strongly adsorbed CO remains on the samples’ surface. After that, H₂O was supplied to the sample at 100 °C to react with the adsorbed CO. Note that in-situ DRIFTS spectra were collected at 100 °C to prevent the thermal desorption of CO adsorbed on the samples’ surfaces at the higher temperature.

After CO adsorption followed by N₂ purging, DRIFTS peaks from monodentate formate were observed on the CeO₂ 500C, Pt(2)/CeO₂ 500C, and 800NC samples at ~1300 and ~1570 cm⁻¹ (Fig. 4) [46]. Additional peak at ~1390 cm⁻¹ was observed on Pt(2)/CeO₂ 800NC. Although the peak at ~1390 cm⁻¹ should be related to the O—C—O stretching vibrational mode of carboxyl, bicarbonate or carbonate species [47], the origin of its formation has not been strictly analyzed in the literature (Fig. 4). In the case of CeO₂ 500C, CO would adsorb on the CeO₂ surface. On the other hand, on Pt(2)/CeO₂ 500C

Table 2

WGS reaction activities of CeO₂, Pt(2)/CeO₂ 500C, 800R and 800NC catalysts are compared under the differential reaction condition. The catalytic activity was evaluated at 200 °C under simple feed (CO + H₂O) or full feed (CO + H₂O + H₂ + CO₂). Catalysts were pretreated with H₂ at 500 °C for 1 hr before reaction. Reaction rate was calculated either per exposed Pt on catalyst estimated from CO chemisorption at −78 °C (μmol of CO/μmol of Pt/s) or per BET surface area of catalyst (μmol of CO/m² of catalyst/s).

<table>
<thead>
<tr>
<th>Reactant composition</th>
<th>WGS reaction, @200 °C</th>
<th>CO + H₂O</th>
<th>CO conversion (%)</th>
<th>Reaction rate per exposed Pt (μmol of CO/μmol of Pt/s)</th>
<th>CH₄ yield (%)</th>
<th>Reaction rate per surface area (μmol of CO/m² of catalyst/s)</th>
<th>CO + H₂O + H₂ + CO₂</th>
<th>CO conversion (%)</th>
<th>Reaction rate per exposed Pt (μmol of CO/μmol of Pt/s)</th>
<th>CH₄ yield (%)</th>
<th>Reaction rate per surface area (μmol of CO/m² of catalyst/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(2)/CeO₂ 500C ('Pt on CeO₂')</td>
<td>12.7</td>
<td>0.05</td>
<td>0.027</td>
<td>0</td>
<td>2.5</td>
<td>0.01</td>
<td>0.005</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(2)/CeO₂ 800R ('Pt in CeO₂')</td>
<td>0.4</td>
<td>0.10</td>
<td>0.006</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(2)/CeO₂ 800NC ('Pt in CeO₂')</td>
<td>6.1</td>
<td>0.32</td>
<td>0.048</td>
<td>0</td>
<td>12.0</td>
<td>0.63</td>
<td>0.095</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO₂ (135 m²/g)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
with 2 nm-sized Pt NPs loaded on the CeO2 surface (see HAADF-STEM images in Fig. S4), CO could also adsorb on the Pt NP surface or Pt NP-CeO2 interfacial regions in addition to the CeO2 surface. In-situ CO-DRIFTS spectra of the CeO2 500C and Pt(2)/CeO2 500C samples were collected after CO adsorption at 35 °C for 90 min following pretreatment with H2 at 500 °C (Fig. S6). The intensities of DRIFTS peaks assigned to monodentate formate at ~1300 and ~1570 cm⁻¹ were similar on both samples (Fig. S6). However, the DRIFTS peaks at ~1390, ~2080 and ~1840 cm⁻¹ were only observed on Pt(2)/CeO2 500C (Fig. S6). While the peaks at ~2080 and ~1840 cm⁻¹ could be assigned to linear-bonded CO and bridge-bonded CO on Pt NPs, respectively [48-50], the peak at ~1390 cm⁻¹ should be assigned to the O–C–O stretching vibrational mode of carbonyl, bidentate or carbonate species that are formed by the adsorption of CO at the interface between Pt NP and CeO2. Such assignment could explain the absence of the DRIFTS peak at ~1390 cm⁻¹ on the ‘Pt on CeO2’ samples (Fig. 4), since the Pt NP-CeO2 interface may not exist on the surface when CeO2 over-layers fully cover Pt NPs.

The monodentate formate (at ~1300 and ~1570 cm⁻¹) on Pt(2)/CeO2 500C did not react with H2O according to the DRIFTS spectra in Fig. 5a. Instead, the intensity of the peak at ~1390 cm⁻¹, assigned to the O–C–O stretching vibrational mode of carboxyl, bidentate or carbonate species formed by the adsorption of CO at the Pt NP-CeO2 interface, significantly decreased in intensity upon H2O exposure (Fig. 5a). At the same time, evolution of CO2 was observed in the DRIFTS spectra upon H2O exposure (data not shown). These findings indicate that CO adsorbed on the Pt NP-CeO2 interfacial regions reacted with H2O actively to produce CO2. This agrees with previous reports that Pt NP-CeO2 interfacial regions catalyze the WGS reaction [17,46]. The DRIFTS peaks from monodentate formate in the WGS reaction mechanism [47,53]. This agrees with our observation that monodentate formate on Pt(2)/CeO2 catalyst did not react with H2O (Fig. 5b). Therefore, the enhanced reactivity of monodentate formate on Pt(2)/CeO2 catalyst as observed in Fig. 5c would be the meaningful change. The reactivity of monodentate formate on ‘Pt in CeO2’ catalysts evaluated at 100 °C with in-situ DRIFTS experiment would differ from that under the practical reaction condition. However, Fig. 5 clearly demonstrate that the reaction path may have changed when ‘Pt on CeO2’ catalyst transformed into ‘Pt in CeO2’ catalyst by the controlled reductive treatment.

To gain more insight into the active sites on the ‘Pt on CeO2’ (Pt(2)/CeO2 500C) and ‘Pt in CeO2’ (Pt(2)/CeO2 800NC) catalysts, kinetic analysis was performed. The WGS reaction was performed at 150, 200, 250 and 300 °C under the full feed, and the apparent activation energies (Ea) were obtained by assuming the plug flow reactor model (raw data as well as calculation details are provided in Fig. S7, and results are displayed in Fig. 6) [54]. The activation energies were calculated to be 19.2 and 6.5 kcal/mol on the Pt(2)/CeO2 500C and 800NC catalysts, respectively (Fig. 6). Note that the Ea of Pt(2)/CeO2 500C estimated in this work (19.2 kcal/mol) is comparable (within 10%) to the values reported in the literature, confirming the validity of the current work [43,47,55,56]. Here, Ea represents the algebraic sum of intrinsic activation energies of elementary steps and heats of adsorption for equilibrium steps, associated with the prevailing reaction mechanism. Therefore, the large difference in Ea between Pt(2)/CeO2 500C and 800NC catalysts indicates that some critical steps in the WGS reaction mechanism differ on these two catalysts. This is intuitive considering that both CO and H2O should be activated on the CeO2 surface of ‘Pt in CeO2’ catalyst, unlike the case of ‘Pt on CeO2’ catalyst where Pt and CeO2 could activate CO and H2O, respectively. Transformation of inert CeO2 surface into the catalytically active one by the interaction with Pt NP enabled the HT-WGS reaction to proceed without the formation of CH4 on Pt.

3.4. Why does only Pt(2)/CeO2 800NC have the activity, and not Pt(2)/CeO2 800R?

Although Pt NPs are fully covered with CeO2 over-layers in both Pt(2)/CeO2 800R and 800NC catalysts, only Pt(2)/CeO2 800NC was active in the HT-WGS reaction (Table 1). While the CeO2 surface should catalyze the WGS reaction in ‘Pt in CeO2’ catalysts, the dif-
ference in BET surface area of Pt(2)/CeO₂ 800R (17 m²/g) and 800NC (33 m²/g) catalysts cannot explain the large difference in the catalytic activity (Table S2). Therefore, the intrinsic catalytic activity of CeO₂ over-layers of Pt(2)/CeO₂ 800R and 800NC catalysts would be very different.

To catalyze the WGS reaction, both H₂O and CO should be activated on the catalysts' surface. Here, H₂O can be activated on the oxygen vacancies formed on CeO₂ surface [46,47]. In addition, since ‘Pt in CeO₂’ catalysts do not expose Pt to the surface, CeO₂ surface should adsorb CO instead of Pt to catalyze the WGS reaction. It can be hypothesized that the presence of oxygen vacancies on CeO₂ surface may alter the CO adsorption ability of CeO₂ surface. The CO adsorption abilities of an oxidized CeO₂ surface and a reduced CeO₂ surface with oxygen vacancies were investigated with static CO chemisorption after the reductive treatments at different temperature (200, 350 and 500 °C). The H₂-TPR spectrum of CeO₂ 500°C (Fig. S8a) shows that the CeO₂ surface is fully reduced at 500°C. Some surface reduction occurs at 350°C, while no reduction occurs at 200°C. Fig. S8b displays the amount of CO chemisorbed on CeO₂ 500°C after 200R, 350R, or 500R pretreatments. After 200R treatment, CO chemisorption did not occur. After 350R and 500R treatments, 41 and 133 l mol/g of CO chemisorbed on CeO₂, respectively. Fig. S8 indicates that oxygen vacancies on the reduced CeO₂ surface facilitate CO chemisorption [24]. The role of oxygen vacancies in promoting CO chemisorption was also verified by the in-situ CO-DRIFTS spectra of CeO₂ 500°C (Fig. S9), which was obtained by adsorbing CO at 35 °C for 30 min after pretreat-

Fig. 5. After CO chemisorption (Fig. 4), in-situ DRIFTS spectra were collected while flowing H₂O at 100 °C on (a) Pt(2)/CeO₂ 500C, (b) CeO₂ 500C, and (c) Pt(2)/CeO₂ 800NC samples. (d) The change in intensity of the DRIFTS peak from monodentate formate (νs(OCO) at 1300 cm⁻¹) was monitored while flowing H₂O to the samples.

Fig. 6. The activation energies in WGS reaction of the Pt(2)/CeO₂ 500C and 800NC catalysts (see Fig. S7 in SI for the detailed derivation).
ment with H₂ or O₂ at 500 °C. The DRIFTS peak intensities grew much larger after the reductive pretreatment, indicating that oxygen vacancies promoted the CO adsorption on CeO₂ surface (Fig. S9). Hence, oxygen vacancies formed on the CeO₂ overlayers of ‘Pt in CeO₂’ catalyst would catalyze the WGS reaction by activating both H₂O and CO. Therefore, to understand the difference in the HT-WGS reaction activities of Pt(2)/CeO₂ 800R and 800NC catalysts, the concentration of oxygen vacancies on the CeO₂ over-layers of two catalysts should be compared.

In order to quantitatively estimate the concentration of oxygen vacancies formed on CeO₂ over-layers of Pt(2)/CeO₂ 800R and 800NC catalysts, O₂ chemisorption was performed at 100 °C. Indeed, the CeO₂ surface of Pt(2)/CeO₂ 800NC adsorbs the much larger amount of O₂ than the CeO₂ surface of Pt(2)/CeO₂ 800R; CeO₂ of Pt(2)/CeO₂ 800R and 800NC catalysts adsorbed 0.3 and 22.6 μmol/g of O₂, respectively, which corresponds to 0.02 and 0.69 μmol/m² of O₂, respectively (Fig. 7a). In addition, the O 1s XP spectra in Fig. 7b also indicate a high concentration of oxygen vacancies on Pt(2)/CeO₂ 800NC (C 1s, Pt 4f, and Ce 4f XP spectra of the catalysts are provided in Fig. S10.) The XP peak from oxygen vacancies is clearly observed in the region between 529 and 531 eV of Pt(2)/CeO₂ 800NC [57–59]. Such a peak was not clearly detected in Pt(2)/CeO₂ 500C (not reduced), nor in Pt(2)/CeO₂ 800R. Only XP peaks from lattice oxygen (528–530 eV) and surface oxygen or OH groups (531–534 eV) are visible in these samples [57,58]. In summary, both O₂ chemisorption and XP spectra indicate that the concentration of oxygen vacancies formed on CeO₂ over-layers of Pt(2)/CeO₂ 800NC is much higher than that formed on CeO₂ over-layers of Pt(2)/CeO₂ 800R.

To verify whether the different concentration of oxygen vacancy indeed affects the CO adsorption ability of differently prepared ‘Pt in CeO₂’ catalysts, the CO adsorption ability of the CeO₂ surface of Pt(2)/CeO₂ 800R and 800NC catalysts was evaluated. CO selectively adsorbs on Pt at −78 °C, while CO adsorbs on both Pt and a CeO₂ surface at 50 °C [25]. Hence, the amount of CO adsorbed on the CeO₂ surface of Pt/CeO₂ catalysts could be evaluated by subtracting the amount of CO adsorbed at −78 °C from that adsorbed at 50 °C. Fig. 7c shows that the CeO₂ surface of Pt(2)/CeO₂ 800NC (37 μmol/g, or 1.12 μmol/m²) adsorbs the larger amount of CO than the CeO₂ surface of Pt(2)/CeO₂ 800R (12 μmol/g, or 0.70 μmol/m²). The in-situ CO-DRIFTS spectra in Fig. 7d, obtained by adsorbing CO at 100 °C for 90 min after pretreatment with H₂ at 500 °C, also show a larger amount of CO adsorbed on Pt(2)/CeO₂ 800NC than on Pt(2)/CeO₂ 800R. Fig. 7c and 7d clearly show that the higher concentration of oxygen vacancy on ‘Pt in CeO₂’ catalyst facilitates the CO adsorption.

Based on the discussion in Fig. 7, it can be speculated that the WGS reaction rate is much higher on Pt(2)/CeO₂ 800NC than on...
Pt(2)/CeO₂ 800R (CO conversion, 97.1 vs 3.6% at 450 °C under the simple feed, Table 1), because the former catalyst has the much higher concentration of oxygen vacancy on its CeO₂ over-layers that can activate both CO and H₂O. Analogously to the present work, Hardacre et al. reported that CeO₂ film on a Pt(111) surface could catalyze CO oxidation reaction, because Pt surface promoted the formation of oxygen vacancies on CeO₂ film [60]. They also suggested that the CeO₂ film should be thin to allow the effective interaction between Pt and CeO₂ to occur [60]. Tsang et al. also reported that the WGS reaction activity of Pt@CeO₂ decreased when the CeO₂ layer became too thick [4]. As we discussed in Section 3.1, structural modification was less severe on Pt(2)/CeO₂ 800NC than on Pt(2)/CeO₂ 800R. Therefore, the thinner CeO₂ over-layers would have formed on Pt NPs in Pt(2)/CeO₂ 800NC than in Pt(2)/CeO₂ 800R to possess distinct catalytic activity.

Fig. 8a-d display the bright-field TEM images of Pt(2)/CeO₂ 800R and 800NC catalysts. Fig. 8a and b show low- and high- magnification images of Pt(2)/CeO₂ 800R, respectively. The CeO₂ over-layers thicker than 1 nm encapsulating Pt NPs could be clearly observed when the periphery of a CeO₂ particle was closely observed (Fig. 8b). Fig. 8c and 8d show low- and high- magnification images of Pt(2)/CeO₂ 800NC, respectively. The CeO₂ over-layers thinner than 0.5 nm encapsulating Pt NPs could be clearly observed when the periphery of a CeO₂ particle was closely observed (Fig. 8d) (more TEM images of each sample are provided in Fig. S11). TEM images in Fig. 8a-d strongly indicate that the CeO₂ over-layer is much thicker on Pt(2)/CeO₂ 800R than on Pt(2)/CeO₂ 800NC.

Fig. 8e displays the depth profiling XP spectra of Pt(2)/CeO₂ 500°C, 800R, and 800NC samples. The samples were ion sputtered with an Ar gun before each spectrum was taken. Normalized Pt/ Ce decreased most rapidly with increasing the number of Ar sputtering in Pt(2)/CeO₂ 500°C, because Ar could readily remove Pt from ‘Pt on CeO₂’ samples. On the other hand, normalized Pt/ Ce decreased more slowly on ‘Pt in CeO₂’ samples, which can be explained by the delayed removal of Pt due to the CeO₂ over-layers on Pt NPs (Fig. 8e). In addition, normalized Pt/ Ce decreased more slowly on Pt(2)/CeO₂ 800R than on Pt(2)/CeO₂ 800NC. This is another evidence which indicates that thicker CeO₂ over-layers are formed on the former sample. In summary, although Pt NPs were covered with CeO₂ over-layers after both 800R and 800NC treatments, thinner CeO₂ over-layers are formed on the Pt(2)/CeO₂ 800NC. Thin CeO₂ over-layers would interact with Pt NPs to possess the high concentration of oxygen vacancies necessary to catalyze the WGS reaction [60]. It would be worth to mention that while the treatment gas condition determined the thickness of CeO₂ over-layers on Pt NP in this study, the treatment temperature or the surface concentration of Pt (that is, Pt loading) could also influence the thickness of CeO₂ over-layers on Pt NP.

As the last remark, it should be emphasized that the catalytic activities of oxygen vacancies formed on CeO₂ and ‘Pt in CeO₂’ samples would be completely different. Fig. 9 compares the amount of O₂ chemisorbed at 100 °C after the reductive pretreatment at 500 °C (that would represent the amount of oxygen vacancies

Fig. 9. The amount of O₂ chemisorbed at 100 °C (unit: μmol of O₂/m² of catalyst), which would represent the amount of oxygen vacancies formed, is compared to the number of CO converted under the simple feed at 200 °C (data from Table 2, unit: μmol of CO/m² of catalyst) on the CeO₂ surface of CeO₂, Pt(2)/CeO₂ 800NC and 800R catalysts.
formed on the surface) to the number of CO converted under the simple feed at 200 °C (data from Table 2) on the CeO₂ surface of CeO₂ and ‘Pt in CeO₂’ (Pt(2)/CeO₂ 800NC and 800R) catalysts. The amount of O₂ chemisorbed on CeO₂, Pt(2)/CeO₂ 800NC and 800R catalysts are 0.56, 0.69 and 0.02 μmol/m², respectively. Meanwhile, the number of CO converted on the CeO₂ surface of CeO₂, Pt(2)/CeO₂ 800NC and 800R catalysts are 0, 0.048 and 0.006 μmol/m²/s, respectively. Although the large amount of oxygen vacancies was formed after the reductive treatment at 500 °C, Pt-free CeO₂ surface could not catalyze the WGS reaction (Fig. 9). Indeed, while the oxygen vacancies enabled the adsorption of CO on CeO₂ surface (Fig. 59), the monodentate formate formed on CeO₂ did not react with H₂O (Fig. 5b). On the contrary, Pt(2)/CeO₂ 800NC catalyst with thin CeO₂ over-layers on Pt NP not only chemisorbed the large amount of O₂ (0.69 μmol/m²) but it also displayed high WGS activity (0.048 μmol/m²/s) (Fig. 9). In line with such observations, monodentate formate formed on Pt(2)/CeO₂ 800NC did react with H₂O (Fig. 5c). Meanwhile, Pt(2)/CeO₂ 800R catalyst with thick CeO₂ over-layers on Pt NP chemisorbed only little amount of O₂ (0.02 μmol/m²), and it also displayed low WGS activity (0.006 μmol/m²/s) (Fig. 9). Therefore, the high catalytic activity of thin CeO₂ over-layers on Pt NP should be resulting from the unique interaction between thin CeO₂ over-layers and Pt NP. Rodriguez et al. demonstrated in their series of publications that the interface between PGM and CeO₂ has the high catalytic activity in the WGS reaction [15,41,61]. However, it should be stressed that little or no interfaces would exist in ‘Pt in CeO₂’ catalyst. Instead, the fully covered Pt NPs seem to have promoted the intrinsic activity of CeO₂ over-layers in the WGS reaction through the unique metal-support interaction. Recently, Yan et al. reported that hetero-structured MoO₃/γ-Mo₂N greatly promoted the formation of oxygen vacancies on MoO₃ surface to accomplish the high catalytic activity of Pt/γ-Mo₂N catalyst in the LT-WGS reaction [44]. They reported that MoO₃ thin layers on γ-Mo₂N exhibit a very small formation energy of oxygen vacancies due to the stress induced by the mismatch of lattices of MoO₃ and γ-Mo₂N [44]. Similarly, the lattice mismatch between thin CeO₂ over-layers and Pt NP would lower the formation energy of oxygen vacancies to grant the high catalytic activity to CeO₂ over-layers.

Various strategies have been devised to tailor the metal-support interactions to improve the catalytic performance in several reactions [37,48,62,63]. In this study, the intrinsic WGS reaction activity of CeO₂ was significantly enhanced by tailoring the metal-support interactions between Pt NPs and CeO₂ over-layers without using complex procedures and expensive structure directing agents. We succeeded in preparing the ‘Pt in CeO₂’ catalyst with simple thermal treatments that have high activity in the HT-WGS reaction and does not produce CH₄ during the reaction. We believe that the current contribution will broaden the horizon of research into ways to manipulate metal-support interactions to develop better catalysts.

4. Conclusion

‘Pt in CeO₂’ catalysts were synthesized from ‘Pt on CeO₂’ catalyst by controlled reductive treatments to suppress the methanation reaction while maintaining high activity in the HT-WGS reaction. The structure of Pt(2)/CeO₂ was modified by two different methods: 1. reductive treatment to reduce CeO₂ bulk (R treatment) and 2. reductive treatment at 250 °C followed by thermal treatment with N₂ (NC treatment). The HT-WGS reaction activity of Pt/CeO₂ was completely lost after 800R treatment. However, CO conversion during the HT-WGS reaction with the ‘Pt in CeO₂’ catalyst prepared by 800NC treatment was comparable to that of the ‘Pt on CeO₂’ catalyst. More importantly, the methanation reaction during HT-WGS was almost completely suppressed on the ‘Pt in CeO₂’ catalyst. Detailed HAADF-STEM, XPS, CO chemisorption, and in-situ DRIFTS studies indicate that thin CeO₂ over-layers formed by 800NC treatment could catalyze the WGS reaction while thick CeO₂ over-layers formed by 800R treatment could not. Therefore, the ‘Pt in CeO₂’ catalyst prepared by 800NC treatment in this study would be a good candidate catalyst for the HT-WGS reaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (NRF-2016R1A5A1009592).

Appendix A. Supplementary material

Appendix supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2021.01.021.

References
