CeO$_2$-Promoted PtSn/SiO$_2$ as a High-Performance Catalyst for the Oxidative Dehydrogenation of Propane with Carbon Dioxide

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Abstract: The oxidative dehydrogenation of propane with CO$_2$ (CO$_2$-ODP) has been extensively investigated as a promising green technology for the efficient production of propylene, but the lack of a high-performance catalyst is still one of the main challenges for its industrial application. In this work, an efficient catalyst for CO$_2$-ODP was developed by adding CeO$_2$ to PtSn/SiO$_2$ as a promoter via the simple impregnation method. Reaction results indicate that the addition of CeO$_2$ significantly improved the catalytic activity and propylene selectivity of the PtSn/SiO$_2$ catalyst, and the highest space-time yield of 1.75 g(C$_3$H$_6$)·g(catalyst)$^{-1}$·h$^{-1}$ was achieved over PtSn/SiO$_2$ with a Ce loading of 6 wt%. The correlation of the reaction results with the characterization data reveals that the introduction of CeO$_2$ into PtSn/SiO$_2$ not only improved the Pt dispersion but also regulated the interaction between Pt and Sn species. Thus, the essential reason for the promotional effect of CeO$_2$ on CO$_2$-ODP performance was rationally ascribed to the enhanced adsorption of propane and CO$_2$ originating from the rich oxygen defects of CeO$_2$. These important understandings are applicable in further screening of promoters for the development of a high-performance Pt-based catalyst for CO$_2$-ODP.

Keywords: oxidative dehydrogenation; propane; carbon dioxide; supported PtSn catalyst; ceria

1. Introduction

Propylene is one of the most important raw materials for the chemical industry [1,2]. It is mainly produced by the steam cracking of naphtha and the byproduct of fluid catalytic cracking (FCC) of heavier oil fractions, which suffer from both low propylene yield and high energy consumption [3]. Moreover, these technologies cannot meet the continuously increased market demand for propylene. As a consequence and owing to the growing alternative supply of propane from the shale gas, the catalytically direct dehydrogenation of propane to propylene (PDH) has been attracting increased attention. However, the currently industrialized PDH process is still challenged by the quick deactivation of commercial PtSn/Al$_2$O$_3$ or CrO$_x$/Al$_2$O$_3$ catalysts, low yields of propylene limited by thermodynamics, and high reaction temperatures [4,5]. To address these issues, the oxidative dehydrogenation of propane to propylene using O$_2$, CO$_2$, N$_2$O, or SO$_2$ as an oxidant is proposed as a more efficient route [6,7]. Among these alternative processes, the oxidative dehydrogenation of propane with greenhouse gas of CO$_2$ (CO$_2$-ODP) is the most attractive from an environmental viewpoint. On the one hand, in comparison with PDH, CO$_2$-ODP can effectively enhance the equilibrium conversion of propane by removing the produced hydrogen [4,8]. On the other hand, a higher selectivity of propylene for CO$_2$-ODP can be achieved in comparison with that achieved by using O$_2$ as an oxidant, for which deep oxidation is an important issue. Moreover, the CO$_2$-ODP process provides an attractively tandem approach via efficient production of propylene with simultaneous conversion of CO$_2$ to
Thus, in this work, a high-performance CO pregnerating the CeO CO selective breaking of C-H bonds in propane with the expedited tandem conversion of Fe oxides, such as CrO and superior stability, outperforming the state-of-the-art catalysts, including the supported of 6 wt%, showed a space-time yield of propene as high as 1.75 g(C with a greater ability to break C-C bonds in alkane molecules, supported PtSn has already been applied as a commercial catalyst for the PDH reaction [17]. This rigorously indicates that the addition of SnO into Pt shifts the selective breaking of C-C bonds to the favorable activation of C-H bonds in propane molecules. Although the action nature of the added SnO on Pt is still not unambiguously revealed, the improved Pt dispersion and the electron transfer between Pt and Sn species are commonly agreed to be key factors in determining the activity and selectivity of propene for the PDH reaction [18,19]. This is further supported by quantitative studies on the interactions between Pt and Sn species, which can be tuned by adding promoters and changing the synthesis methods of the catalyst, including thermal treatment under different atmospheres [20].

In the case of CO activation, CeO with a high oxygen-storage capacity and abundant oxygen defects was extensively investigated as a support/promoter/catalyst for the reactions involving CO as a reactant [21]. In our previous study [22], CeO and CeO-based solid solutions were found to be effective for converting CO into CO during the oxidative dehydrogenation of ethylbenzene with CO, the ability of which is closely connected with oxygen defects over the oxides. Moreover, two functions of CeO as an additive over Pt-based catalysts for the PDH reaction were manifested as stabilizing Pt, suppressing coke deposition [23].

Based on these analyses, the combination of PtSn with CeO may create a good CO ODP catalyst, provided that the assisted activation of CO is achieved by oxygen defects over CeO. Moreover, silica is widely used as a support for the CO ODP reaction [6], the side reactions of which are inhibited in comparison with Al2O3 with a higher acidity [24,25]. Thus, in this work, a high-performance CO ODP catalyst was developed by simply impregnating the CeO precursor into PtSn/SiO2. The PtSn/SiO2 catalyst, with a Ce loading of 6 wt%, showed a space-time yield of propene as high as 1.75 g(C3H8)·g(catalyst) h and superior stability, outperforming the state-of-the-art catalysts, including the supported oxides, such as CrOx, GaOx, and VOx, as well as the supported metals, such as Pd and Fe3Ni. The essence of the high CO ODP performance of CeO2-promoted PtSn/SiO2 is rigorously revealed as the enhanced adsorption of propane and CO, which favors the selective breaking of C-H bonds in propane with the expedited tandem conversion of CO2 to CO.
2. Experimental
2.1. Catalyst Preparation

PtSnCe/SiO$_2$, PtCe/SiO$_2$, PtSn/SiO$_2$, and SnCe/SiO$_2$ catalysts were prepared by the sequential impregnation method, whereby the amounts of Pt, Sn, and Ce were fixed at 0.5, 0.9, and 6 wt%, respectively. The reagents of H$_2$PtCl$_6$·6H$_2$O (Pt ≥ 37.5%, Shanghai Aladdin Biochemical Co., Ltd., Shanghai, China), SnCl$_2$·6H$_2$O (>99.9%, Guangdong Guanghua Sci-Tech Co., Ltd., Shantou, China), and Ce(NO$_3$)$_3$·6H$_2$O (>99.0%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China) were chosen as the precursors of the Pt, Sn, and Ce species, respectively. The SiO$_2$ support, with a specific BET surface area of 580 m$^2$/g and an average pore diameter of 3.0 nm (Fuji Silysia Chemical Ltd., Kasugai Aichi, Japan), was pre-treated in air at 550 °C for 3 h. Impregnation was performed at 80 °C under stirring for 2 h, and the subsequent drying was carried out at 80 °C for 4 h. Following sequential impregnation with the desired amount of aqueous solution of H$_2$PtCl$_6$·6H$_2$O, the acetone solution of SnCl$_2$·2H$_2$O and the aqueous solution of Ce(NO$_3$)$_3$·6H$_2$O, PtSnCe/SiO$_2$, PtCe/SiO$_2$, PtSn/SiO$_2$, and SnCe/SiO$_2$ catalysts were obtained after calcining at 500 °C for 3 h under atmospheric conditions.

2.2. Catalyst Characterizations

N$_2$ physical adsorption/desorption isotherms were measured on a Bel-sorp-Max instrument at −196 °C. Before each experiment, the sample was degassed at 300 °C under vacuum for 10 h. Specific surface area and pore-size distribution (PSD) were calculated by the Brunauer–Emmett–Teller equation (BET) and Barrett–Joyner–Halenda method (BJH), respectively.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker D8 Advance) equipped with Cu-Kα radiation (40 kV, 40 mA). The sample was scanned from the 2θ of 10 to 80° with a rate of 0.2 s/step.

Transmission electron microscopy (TEM) images were obtained with a high-resolution transmission electron microscope (Tecnai G2 F20, FEI) operated at 200 kV. Before measurement, the fresh sample was pre-reduced at 500 °C in 10 vol% H$_2$/Ar for 1 h. Then, about 2 mg of the reduced sample was ultrasonically dispersed in anhydrous ethanol (2 mL). After 1 h, two drops of the suspension were deposited on a carbon-enhanced copper grid and dried at 60 °C in air for 0.5 h.

H$_2$-O$_2$ titration experiments were carried out on a Micromeritics Autochem 2920 instrument to determine the dispersion of Pt. For each test, a total of 150 mg of the sample was pre-reduced at 500 °C for 1 h in 10 vol% H$_2$/Ar (30 mL/min). After cooling to 50 °C in Ar, a flow of 3 vol% O$_2$/Ar (30 mL/min) was pulsed until the consumption peaks became stable. Subsequently, the sample was purged under an Ar flow for 1 h, and consecutive pulses of 10 vol% H$_2$/Ar (0.5 mL) were performed. By assuming that the adsorption stoichiometry factor of Pt/H$_2$ equals to 2/3, according to references [26,27], the dispersion of Pt was calculated using the following Equation (1).

\[
\text{Dispersion (\%)} = \frac{V_{H_2} \times f \times M_{Pt}}{W_{Pt} \times 22,414} \times 100
\]  

where $V_{H_2}$ is the volume of adsorbed H$_2$ (mL), f is the stoichiometry factor, $M_{Pt}$ is the atomic weight of Pt (g/mol), and $W_{Pt}$ is the weight of the supported Pt on the sample (g).

Experiments concerning temperature-programmed reduction of H$_2$ (H$_2$-TPR) were carried out on a Micromeritics Autochem 2920 instrument. About 100 mg of the sample was pre-treated at 350 °C for 0.5 h under an Ar stream. After cooling to 50 °C, H$_2$-TPR was performed from 50 to 800 °C at a heating rate of 10 °C/min under a 10 vol% H$_2$/Ar flow (30 mL/min). H$_2$ consumption was monitored and determined by a pre-calibrated thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) was conducted on an X-ray photoelectron spectrometer (KRATOS Analytical Ltd., Manchester, UK) equipped with an Al-Kα radiation source (1486.6 eV). Before measurements, all the samples were pre-reduced at 500 °C.
for 1 h in 10 vol% H$_2$/Ar. The C 1s spectrum at 284.6 eV was applied to calibrate the binding energy.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO (CO-DRIFTS) was carried out on a Nicolet iS50 instrument (Thermo Scientific) equipped with an in situ cell. Firstly, the sample was reduced in situ at 500 °C for 1 h in 10 vol% H$_2$/Ar with a flow rate of 30 mL/min. After this, the sample was cooled to 30 °C and purged with Ar. Then, 10 vol% CO/Ar with a flow rate of 30 mL/min was introduced in the cell for 0.5 h. Afterwards, the sample was purged with Ar to remove any physically adsorbed CO on the surface of sample, and DRIFTS spectra were recorded. Prior to each experiment, the background spectra were recorded.

Experiments concerning temperature-programmed desorption of C$_3$H$_8$/CO$_2$/C$_3$H$_6$ (C$_3$H$_8$/CO$_2$/C$_3$H$_6$-TPD) were performed on a Micromeritics Autochem 2920 instrument. About 100 mg of the sample was pre-reduced at 500 °C for 1 h in 10 vol% H$_2$/Ar. After this, the sample was cooled to 70 °C and purged with Ar. Then, the pre-treated sample was saturated with pure C$_3$H$_8$, CO$_2$, or C$_3$H$_6$ with a flow rate of 30 mL/min for 1 h. Afterwards, the sample was purged by an Ar stream for 1 h, and temperature-programmed desorption of C$_3$H$_8$/CO$_2$/C$_3$H$_6$ was performed from 70 to 600 °C at a heating rate of 10 °C/min, respectively. The amount of desorbed C$_3$H$_8$/CO$_2$/C$_3$H$_6$ was monitored and determined by a pre-calibrated thermal conductivity detector (TCD).

Thermogravimetric and differential scanning calorimetry analyses (TG-DSC) of the spent catalysts were carried out on a Q600SDT Thermoanalyzer System (TA Instruments). For each test, about 5 mg of the spent catalyst was heated from 50 to 800 °C with a heating ramp of 10 °C/min.

Raman spectra were obtained on a confocal microprobe laser Raman spectrometer (HORIBA Jobin Yvon) with an excitation laser beam of 532 nm. Spectra in the range of 1000–2000 cm$^{-1}$ were recorded at room temperature to study the type of deposited coke over the spent catalysts.

2.3. Catalytic Tests

Catalytic tests for CO$_2$-ODP were carried out in a quartz fixed-bed reactor (6 mm, i.d.) under 550 °C and atmospheric pressure. For each test, 0.25 g of the catalyst (40–60 mesh) diluted with 0.5 g of quartz sand (40–60 mesh) was loaded into the reactor. Firstly, the catalyst was pre-reduced with 20 vol% H$_2$/He at 500 °C for 1 h. After that, the reactor was heated to 550 °C in a He flow, and the gas mixture of Ar/C$_3$H$_8$/CO$_2$/He in a molar ratio of 1/4/4/16 with a total flow rate of 50 mL/min was introduced into the reactor. The products were analyzed by an online gas chromatograph (GC7920, Peking CAUALIGHT) equipped with FID (Porapak Q column) and TCD (TDX-01) detectors. By using Ar as an internal standard, propane and CO$_2$ conversion, selectivity of different gas products (CH$_4$, C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_8$), and propylene yield were calculated by Equations (2)–(5).

$$\text{C}_3\text{H}_8 \text{ conversion} = \frac{[\text{F}_{\text{C}_3\text{H}_8}]_{\text{inlet}} - [\text{F}_{\text{C}_3\text{H}_8}]_{\text{outlet}}}{[\text{F}_{\text{C}_3\text{H}_8}]_{\text{inlet}}} \times 100\%$$  \hspace{1cm} (2)

$$\text{CO}_2 \text{ conversion} = \frac{[\text{F}_{\text{CO}_2}]_{\text{inlet}} - [\text{F}_{\text{CO}_2}]_{\text{outlet}}}{[\text{F}_{\text{CO}_2}]_{\text{inlet}}} \times 100\%$$  \hspace{1cm} (3)

$$\text{Selectivity of products } i = \frac{n_i \times [\text{F}]_{\text{outlet}}}{3 \times ([\text{F}_{\text{C}_3\text{H}_8}]_{\text{inlet}} - [\text{F}_{\text{C}_3\text{H}_8}]_{\text{outlet}})} \times 100\%$$ \hspace{1cm} (4)

$$\text{C}_3\text{H}_6 \text{ yield} = \frac{[\text{F}_{\text{C}_3\text{H}_6}]_{\text{outlet}}}{[\text{F}_{\text{C}_3\text{H}_8}]_{\text{inlet}}} \times 100\%$$ \hspace{1cm} (5)

The carbon balances calculated from Equation (6) were very close to 100% (98.5 ± 1.5%) for all of the experiments (Figure S1), and thus, the C$_3$H$_8$-based selectivity of CO, i.e., CO...
produced from C₃H₈, was calculated by subtracting the sum of the hydrocarbon products (CH₄ + C₂H₄ + C₂H₆ + C₃H₈) from 100% with Equation (7).

\[
\text{Carbon balance} = \frac{\sum_i n_i \times [F_i]_{\text{outlet}} + 3 \times [F_{\text{C}_3\text{H}_8}]_{\text{inlet}}}{3 \times [F_{\text{C}_3\text{H}_8}]_{\text{inlet}} + [F_{\text{CO}_2}]_{\text{inlet}} + [F_{\text{CO}_2}]_{\text{outlet}}} \times 100\%
\]  

(6)

\[
\text{CO selectivity} = \left(1 - \frac{n_i \times [F_i]_{\text{outlet}}}{3 \times ([F_{\text{C}_3\text{H}_8}]_{\text{inlet}} - [F_{\text{C}_3\text{H}_8}]_{\text{outlet}})}\right) \times 100\%
\]  

(7)

where, \(F_{\text{C}_3\text{H}_8}\), \(F_{\text{CO}_2}\), and \(F_{\text{CO}}\) are the volumetric flow rate (mL/min) of C₃H₈, CO₂, and CO, respectively; \(i\) stands for the detected hydrocarbon product, i.e., CH₄, C₂H₄, C₂H₆, and C₃H₈; and \(F_i\) and \(n_i\) represent the flow rate and carbon number of the hydrocarbon product, respectively.

3. Results
3.1. Catalytic Results of CO₂-ODP

The time-on-stream (TOS) results of CO₂-ODP over PtSn/SiO₂, PtCe/SiO₂, and PtSnCe/SiO₂ are shown in Figure 1. Indeed, PtSn/SiO₂ showed a very low propane conversion of 4.4% at a TOS of 5 min (Figure 1a). In contrast, a significantly higher propane conversion was achieved over the Ce-containing catalysts, and PtSnCe/SiO₂ showed the highest initial propane conversion of 55.8%. Taking the activity as the propane conversion at a TOS of 5 min, an increased order of PtSn/SiO₂ < PtCe/SiO₂ < PtSnCe/SiO₂ was observed. Moreover, the blank experimental results of CO₂-ODP indicate a propane conversion of less than 2.5% over SnCe/SiO₂ (Figure S2). Thus, the Pt species over the catalysts are responsible for converting propane, the activity of which is associated with the added SnO₂ and/or CeO₂. Where the initial activity indexed by the CO₂ conversion at a TOS of 5 min (Figure 1b) was concerned, PtSn/SiO₂ showed negligible activity. In contrast, a significantly high initial CO₂ conversion of 26.4% over PtCe/SiO₂ and 25.9% over PtSnCe/SiO₂ was achieved. In the case of stability, Figure 1a,b clearly shows that PtSnCe/SiO₂ was the most stable catalyst at a TOS of 80 min, leading to the concurrently decreased conversions of propane and CO₂ in the same order of PtSnCe/SiO₂ > PtCe/SiO₂ > PtSn/SiO₂ with increasing TOS.

Concerning product distribution, propylene selectivity was varied to a relatively large extent over these catalysts (Figure 1c). In the case of PtSn/SiO₂, the lowest propylene selectivity of 30.9% was observed at a TOS of 5 min. On the contrary, a higher propylene selectivity was achieved over the Ce-containing catalysts, and the highest initial propylene selectivity of 89.1% was reached over PtSnCe/SiO₂. With increasing TOS, propylene selectivity at the end of the reaction was decreased in the order of PtSnCe/SiO₂ (93.4%) >> PtCe/SiO₂ (45.0%) > PtSn/SiO₂ (27.4%). To understand the side reactions, the selectivity of gaseous byproducts originating from C₃H₈ were examined, and the results are shown in Figure 1d and Figure S3. In the case of PtSnCe/SiO₂ and PtCe/SiO₂, CO was the predominant byproduct, while the selectivity of C₂H₆, C₂H₄, and CH₄ was very low. This indicates that CO₂-RP may be the main side reaction over these catalysts in comparison with cracking [13,28]. The significantly higher CO selectivity of 56.9% at a TOS of 5 min was observed over PtCe/SiO₂, indicating the more favorable breaking of C-C bonds in propane. In contrast, PtSnCe/SiO₂ showed a very low CO selectivity of about 10%, coinciding with the significantly high propylene selectivity. Concerning PtSn/SiO₂, although the calculated selectivity of CO was 53.9% at a TOS of 5 min, supporting the occurrence of CO₂-RP, its error may be large due to the very low CO₂ conversion (Figure 1b). Thus, the CO selectivity of PtSn/SiO₂ is not further discussed with that of PtSnCe/SiO₂ and PtCe/SiO₂.
To show the superior performance of the PtSnCe/SiO2 catalyst for CO2-ODP, the calculated space-time yield of propylene (STY\textsubscript{C3H6}) over PtSnCe/SiO2 and those over different types of catalysts with the best performance from the representative literature are summarized in Table S1. Among the reported catalysts, including CrO\textsubscript{x}, VO\textsubscript{x}, GaO\textsubscript{x}, Pd, and Pt, the highest STY\textsubscript{C3H6} of 0.63 g(C\textsubscript{3}H\textsubscript{6})·g(catalyst)\textsuperscript{-1}·h\textsuperscript{-1} was observed at a reaction temperature of 600 °C over CrO\textsubscript{x}-doped mesoporous silica spheres (7.07Cr/MSS-2). In our case, however, the PtSnCe/SiO2 catalyst showed an initial STY\textsubscript{C3H6} as high as 1.75 g(C\textsubscript{3}H\textsubscript{6})·g(catalyst)\textsuperscript{-1}·h\textsuperscript{-1} at a reaction temperature of 550 °C, which is significantly higher than those over the reported catalysts. Moreover, 1.16 g(C\textsubscript{3}H\textsubscript{6})·g(catalyst)\textsuperscript{-1}·h\textsuperscript{-1} was still achieved, even at a TOS of 6 h, indicating a superior catalytic stability. The durability of PtSnCe/SiO2 was further investigated by the reaction/regeneration cycles, the regeneration of which is performed at 500 °C in an air flow for 30 min. As shown in Figure 1e, the CO2-ODP performance of the catalyst regenerated for two times was very...
similar to that of the fresh catalyst, indicating the good durability of PtSnCe/SiO2. Thus, the catalytic results clearly reflect the superiority of the PtSnCe/SiO2 catalyst for CO2-ODP.

3.2. Textural and Structural Properties

The N2 adsorption-desorption isotherms of PtSn/SiO2, PtCe/SiO2, and PtSnCe/SiO2 are shown in Figure S4. According to the IUPAC classification, all of the catalysts exhibited a similar type-IV isotherm, indicating the presence of mesopores. Moreover, the appearance of an H1-type hysteresis loop over these catalysts occurred at p/p0 = 0.4–0.6 characterizing the uniform spherical pores. These observations were more directly reflected from the PSD patterns determined by the BJH method. As indicated by Figure S4b, a very narrow and sharp PSD peak at about 3 nm was observed for all of these catalysts. From the calculated textural parameters summarized in Table 1, the BET specific surface area was slightly decreased from 568.9 to 527.3 m2/g in the order of PtSn/SiO2 > PtCe/SiO2 > PtSnCe/SiO2. In the case of mean pore size and total pore volume, the changes were also very limited. These results suggest very similar textural properties of the samples due to the minimal loadings of Pt, Sn, and/or Ce species over the same silica support.

Table 1. Textural properties, crystallite size, and metal dispersion of the different catalysts.

| Catalyst          | Specific Surface Area (m2/g) | Mean Pore Size (nm) | Total Pore Volume (cm3/g) | Crystallite Size (nm) | Metal Dispersion *** (%) |
|-------------------|-------------------------------|---------------------|---------------------------|-----------------------|--------------------------|
| PtSn/SiO2         | 568.9                         | 3.19                | 0.42                      | 8.5 ± 0.2             | 13.4                     |
| PtCe/SiO2         | 536.4                         | 3.25                | 0.43                      | 3.4 ± 0.2             | 20.9                     |
| PtSnCe/SiO2       | 527.3                         | 3.16                | 0.41                      | 2.1 ± 0.3             | 41.3                     |

*: The average size of 100 particles randomly selected in the TEM images was measured using Nano Measurer 1.2.5 software. **: calculated from Scherrer’s equation and the (111) diffraction of the cubic CeO2, as given in the XRD patterns. ***: calculated from Equation (1) in Section 2.2 and the H2-O2 titration results.

XRD patterns of the catalysts are shown in Figure 2. All of the catalysts exhibited a broad XRD peak at ~22.6°, corresponding to the amorphous nature of the SiO2 support [29]. In the case of PtSn/SiO2, the characteristic diffractions at 2θ of 39.8, 46.2, and 67.4° were clearly observed, which were assigned to (111), (200), and (220) crystal planes of the cubic Pt metal, respectively [30,31]. In contrast, when CeO2 was present, the XRD peaks ascribed to Pt metal disappeared, and only the characteristic diffractions at 2θ of 28.5, 33.1, 47.5, and 56.3° conclusively attributed to the (111), (200), (220), and (311) crystal planes of the cubic fluorite structure of CeO2, respectively [22,32], were clearly observed over PtCe/SiO2 and PtSnCe/SiO2. This indicates that the addition of Ce can significantly improve the dispersion of Pt metal, and the SnO2 species is present as the amorphous or highly dispersed nature.

Figure 2. XRD patterns of the PtSn/SiO2, PtCe/SiO2, and PtSnCe/SiO2 catalysts.

To directly observe the Pt particles, the catalysts pre-reduced in 10 vol% H2/Ar at 500 °C for 1 h were investigated by TEM analysis. As shown in Figure 3a, Pt particles were...
clearly observed over all of the catalysts. PtSn/SiO2 showed the largest Pt particles, while the significantly smaller Pt particles were present over PtCe/SiO2 and PtSnCe/SiO2, which supports the XRD results. To make a quantitative comparison, statistics analysis was performed; the Pt particle-size distribution histograms are given in Figure 3b, and the average diameter of Pt is summarized in Table 1. The metallic Pt size was continuously decreased from 8.5 ± 0.2 to 2.1 ± 0.3 nm in the order of PtSn/SiO2 >> PtCe/SiO2 > PtSnCe/SiO2, indicating that the addition of CeO2 can significantly improve the dispersion of Pt metal. This is further supported by the H2-O2 titration results, in which the calculated Pt dispersion was continuously increased from 13.4 to 41.3% in the order of PtSn/SiO2 < PtCe/SiO2 < PtSnCe/SiO2 (Table 1). Generally, the addition of SnO2 can effectively improve the Pt dispersion. However, this is contradictory to the observations over PtSn/SiO2, in which a Pt size as high as 8.5 ± 0.2 nm was observed. As for the reason, it has been reported that PtSn/SiO2 catalysts directly calcined in an oxidative atmosphere during the preparation process show poor Pt dispersion [33] due to the weak interaction between Pt and SnO2 on the SiO2 support. This is in agreement with our experimental results, in which all of the catalysts were obtained by calcining in air at 500 °C after impregnation, as described in Section 2.1. In contrast, when CeO2 was introduced, the Pt size was significantly decreased over PtCe/SiO2 and PtSnCe/SiO2. Taking these results into account, the lower Pt size of 2.1 nm for PtSnCe/SiO2, compared to that of PtCe/SiO2, indicates that in addition to increasing the Pt dispersion, the presence of CeO2 can improve the interaction between Pt and SnO2, leading to the highest Pt dispersion over PtSnCe/SiO2.

3.3. Reduction Behavior

The redox properties of the catalysts were analyzed by H2-TPR. As shown in Figure 4, for the PtSn/SiO2 catalyst, a weak and broad reduction peak was observed at ~450 °C, which can be can be attributed to the reduction of SnO2 [34,35]. In the case of PtCe/SiO2, two reduction peaks were observed at 279 °C and 733 °C. The first peak at 279 °C was attributed to the reduction of active oxygen species over the CeO2 surface, while the very weak peak at 733 °C corresponded to the reduction of the lattice oxygen over the bulk CeO2 [22,36]. Concerning PtSnCe/SiO2, only one reduction peak was observed at 233 °C, attributed to the reduction of surface oxygen species. The reduction-peak temperature below 600 °C was continuously decreased in the order of PtSn/SiO2 >> PtCe/SiO2 > PtSnCe/SiO2, while the amount of the H2 consumption calculated from the reduction peak during H2-TPR below 600 °C (Table 2) was increased in the order of PtSn/SiO2 << PtCe/SiO2 < PtSnCe/SiO2, leading to the greatest reducibility of PtSnCe/SiO2. It has been reported that the hydrogen spillover effect induced from the interaction between the Pt and SnO2/CeO2 can accelerate the reduction of oxygen over the catalyst, and a higher dispersion of Pt commonly leads to a greater reducibility [37,38]. Based on this explana-
According to references [41, 42], the presence of Pt commonly leads to a greater reducibility [37, 38]. Based on this explanation, the reduction of active oxygen species over the CeO$_2$ surface, while the very weak peak at 733 °C corresponded to the reduction of the lattice oxygen over the bulk CeO$_2$ [22, 36]. Concerning PtSnCe/SiO$_2$, only one reduction peak was observed at 233 °C, which can be attributed to the reduction of SnO$_2$ [34, 35]. In the case of PtCe/SiO$_2$, a weak and broad reduction peak was observed at ~450 °C, indicating the formation of more oxygen defects after the reduction. This is consistent with the significantly greater amount of H$_2$ consumption during the H$_2$-TPR over the fresh PtSnCe/SiO$_2$ than that over PtCe/SiO$_2$ (Table 2), resulting from the stronger hydrogen spillover effect due to the greater dispersion of Pt (Table 1).

As shown in Figure 5a, the binding energies at around 71.4 eV for 4f$_{5/2}$ and 74.7 eV for 4f$_{7/2}$ were clearly observed over PtSn/SiO$_2$, indicating the presence of metallic Pt$^0$ [40]. In contrast, when CeO$_2$ was added, the binding energies of Pt 4f were clearly increased, and the XPS peaks at 72.8 eV for 4f$_{7/2}$ and 76.1 eV for 4f$_{5/2}$ assigned to Pt$^{2+}$ species [40] were clearly observed over PtCe/SiO$_2$ and PtSnCe/SiO$_2$. Following the results of deconvolution of the Pt 4f peaks (Figure 5a), the relative content of Pt$^0$ and Pt$^{2+}$ was calculated by respective peak area. As shown in Table 2, PtSn/SiO$_2$ showed the exclusively metallic Pt species, which is consistent with XRD results (Figure 2). Contrarily, the relative content of Pt$^{2+}$ was as high as 69.5% and 66.9% for PtCe/SiO$_2$ and PtSnCe/SiO$_2$, respectively. According to references [41, 42], the presence of Pt$^{2+}$ over the CeO$_2$-containing catalysts originates from the strong interaction between Pt and CeO$_2$, which may be the key reason for the greater dispersion of Pt over PtCe/SiO$_2$ and PtSnCe/SiO$_2$ than over PtSn/SiO$_2$.

3.3. Reduction Behavior

The redox properties of the catalysts were analyzed by H$_2$-TPR. As shown in Figure 4, the H$_2$ consumption during H$_2$-TPR below 600 °C and XPS peak-fitting results of different catalysts.

| Catalyst     | H$_2$ Consumption (mol/g) | Pt$^0$ (%) | Pt$^{2+}$ (%) | Sn$^0$ (%) | Ce$^{3+}$ (%) |
|--------------|----------------------------|------------|---------------|------------|---------------|
| PtSn/SiO$_2$ | 23.5                       | 100.0      | 0             | 0          | -             |
| PtCe/SiO$_2$ | 78.5                       | 30.5       | 69.5          | -          | 31.9          |
| PtSnCe/SiO$_2$ | 140.6                     | 33.1       | 66.9          | 12.0       | 43.2          |

Figure 4. H$_2$-TPR profiles of the PtSn/SiO$_2$, PtCe/SiO$_2$, and PtSnCe/SiO$_2$ catalysts.

3.4. Chemical States

XPS analysis was used to study the surface chemical states of the catalysts. Before measurements, all of the catalysts were pre-reduced in 10 vol% H$_2$/Ar at 500 °C for 1 h. Ce 3d spectra are usually fitted with eight Gaussian-Lorentzian peaks corresponding to two pairs of spin-orbit doubles [32, 39]. As shown in Figure S5, the peaks labeled as $v$, $v''$, and $u$, $u''$ were assigned to the ionization of Ce$^{4+}$ 3d$_{5/2}$ and Ce$^{4+}$ 3d$_{3/2}$, respectively, while the peaks marked with $v'$ and $u'$ were originated from Ce$^{3+}$ 3d$_{5/2}$ and Ce$^{3+}$ 3d$_{3/2}$, respectively. Based on those peak areas, the relative content of Ce$^{3+}$ was calculated, defined as the ratio of Ce$^{3+}/$(Ce$^{3+} + $ Ce$^{4+}$). As shown in Table 2, the relative content of Ce$^{3+}$ over PtSnCe/SiO$_2$ is clearly higher than that of PtCe/SiO$_2$, indicating the formation of more oxygen defects after the reduction. This is consistent with the significantly greater amount of H$_2$ consumption during the H$_2$-TPR over the fresh PtSnCe/SiO$_2$ than that over PtCe/SiO$_2$ (Table 2), resulting from the stronger hydrogen spillover effect due to the greater dispersion of Pt (Table 1).
This is supported by the TEM and H$_2$-O$_2$ titration results (Figure 3 and Table 1). As shown in Figure 5b, the Sn 3d$_{5/2}$ at about 487.0 eV was deconvoluted to analyze the chemical state of Sn. In the case of PtSn/SiO$_2$, a symmetric Sn 3d$_{5/2}$ XPS peak with a binding energy of 487.2 eV was observed, indicating the presence of only SnO$_2$ species, as reported in [28]. However, besides oxide species, a small amount of Sn$^0$ species located at 485.7 eV was observed over PtSnCe/SiO$_2$. As for the reason, it is noteworthy that PtSnCe/SiO$_2$ showed a slightly higher content of Pt$^0$ than PtCe/SiO$_2$ (Table 2), which may originate from the improved interaction between SnO$_2$ and Pt due to the presence of CeO$_2$. This coincides well with the presence of Sn$^0$ species, indicating the possible formation of Pt-Sn bimetallic nanoparticles [28,43].

![Figure 5. Pt 4f (a) and Sn 3d (b) XPS spectra of the reduced catalysts.](image)

3.5. CO-DRIFTS Studies

To further investigate the structural and electronic properties of Pt, DRIFTS experiments were performed by using CO as a probing molecule since its adsorption on Pt surfaces has been well studied. As shown in Figure 6, two overlapping bands were clearly observed in the case of PtSn/SiO$_2$ at 2000 and 2024 cm$^{-1}$, assigned to Si-H stretching vibrations in the different SiO$_2$ configuration [44]. Moreover, a very weak peak was detected at about 2074 cm$^{-1}$, assigned to the linearly bonded CO on Pt$^0$ terraces, indicating the presence of large, highly coordinated nanoparticles [45,46]. When PtCe/SiO$_2$ and PtSnCe/SiO$_2$ were considered, significantly weakened and even disappeared peaks were observed for the Si-H stretching vibrations, which may be due to the coverage of CeO$_2$ on the SiO$_2$ surface. Moreover, strong band was observed at ~2060 cm$^{-1}$, ascribed to the linearly bonded CO on Pt$^0$, with intermediate coordination sites, such as edges or steps sites [47], indicating the high dispersion of Pt over these two Ce-containing catalysts [48,49]. This is supported by the results of TEM and H$_2$-O$_2$ titration (Figure 3 and Table 1). Noteworthy, besides the band at 2060 cm$^{-1}$, a weak adsorption band was detected over PtCe/SiO$_2$ at 1820 cm$^{-1}$, ascribed to the bridge-bonded CO on two neighboring Pt atoms [24]. However, it disappeared in the case of PtSnCe/SiO$_2$, accompanying a decreased intensity of the linear adsorption peak at 2060 cm$^{-1}$. The disappeared bridge-bonded CO over PtSnCe/SiO$_2$ suggests that the SnO$_2$ breaks the ensemble of Pt atoms and forms a checkerboard Pt-Sn surface structure [24,50] because CO does not adsorb at the bridge sites between Sn and Pt. The decreased intensity of the peak at 2060 cm$^{-1}$, in comparison with PtCe/SiO$_2$, can be explained as the reduced surface coverage of CO due to the presence of SnO$_2$ [51]. These results indicate that the presence of CeO$_2$ on a PtSn/SiO$_2$ catalyst can not only improve the Pt dispersion but also improve the interaction between Pt and SnO$_2$. 
TOS of 5 min was increased in the order of PtSnCe/SiO$_2$ >> PtCe/SiO$_2$ >> PtSn/SiO$_2$, coinciding well with the dispersion of Pt over the catalysts. This indicates that the amount of active Pt species is the key factor determining the activation of propane in the course of CO$_2$-ODP, which is consistent with the reported results for PDH [52]. When the activation of CO$_2$ was considered, the significant conversion of CO$_2$ was only observed over the Ce-containing catalysts of PtSnCe/SiO$_2$ and PtCe/SiO$_2$, while CO$_2$ conversion for PtSn/SiO$_2$ was negligible. This indicates that the introduced CeO$_2$ plays a key role in the activation of CO$_2$, which is supported by our previous work for oxidative dehydrogenation of ethylbenzene with CO$_2$ [53]. To shed some light on these observations, C$_3$H$_8$- and CO$_2$-TPD experiments were performed over the catalysts. In the case of C$_3$H$_8$-TPD (Figure 7a), a very broad curve was observed for all of the catalysts in the temperature range of 100–400 °C, indicating the varied strength of adsorbed propane [54,55]. For PtSn/SiO$_2$, two overlapping peaks were clearly observed at about 118 °C and 236 °C, respectively. When PtCe/SiO$_2$ and PtSnCe/SiO$_2$ were considered, the peak maxima were shifted toward higher temperatures in comparison with those of PtSn/SiO$_2$. Moreover, the peak areas of desorbed propane were significantly increased. This indicates the intensified adsorption of propane over the Ce-containing catalysts. The amount of desorbed propane was calculated below 400 °C during C$_3$H$_8$-TPD, and the results are given in Table 3. It was increased in the order of PtSn/SiO$_2$ << PtCe/SiO$_2$ < PtSnCe/SiO$_2$, which coincides well with the propane conversion. This clearly reveals that the amount of adsorbed propane plays a key role in determining the activity of these catalysts for CO$_2$-ODP, which can be reasonably associated with Pt dispersion. As for the adsorption of CO$_2$, a broad CO$_2$-TPD pattern similar to that of C$_3$H$_8$-TPD was obtained for all of the catalysts (Figure 7b). For PtSn/SiO$_2$, only a small peak was observed at about 126 °C, indicating the very weak adsorption of CO$_2$, which is consistent with references [56,57]. In contrast, the peak temperature of desorbed CO$_2$ increased to 141 °C over PtCe/SiO$_2$ and PtSnCe/SiO$_2$. Moreover, a shoulder peak could be observed at a higher temperature of 242 °C, which can be explained by the stronger adsorbed CO$_2$ on the surface of CeO$_2$. This indicates the presence of CeO$_2$-enhanced CO$_2$ adsorption. As shown in Table 3, the amount of desorbed CO$_2$ was calculated below 400 °C during CO$_2$-TPD. It was increased in the order of PtSn/SiO$_2$ << PtCe/SiO$_2$ < PtSnCe/SiO$_2$, the changing pattern of which coincides well with that of CO$_2$ conversion at the steady state of TOS (Figure 1b). It has been reported that CeO$_2$ with richer oxygen defects commonly leads to enhanced adsorption and activation of CO$_2$ [21,32]. Following this understanding, the greater amount of adsorbed CO$_2$ in the case of PtSnCe/SiO$_2$ than that of PtCe/SiO$_2$ can be reasonably ascribed to the presence of more oxygen defects of CeO$_2$, as revealed by the Ce 3d XPS results (Table 2). These results indicate that the amount of adsorbed CO$_2$ plays a
key role in determining the activation of CO$_2$ over the catalysts, which can be connected with the introduced CeO$_2$.

![Figure 7. C$_3$H$_8$ (a) and CO$_2$-TPD (b) profiles over the reduced catalysts.](image)

| Catalyst       | C$_3$H$_8$ (mmol/g) * | CO$_2$ (mmol/g) * | C$_3$H$_6$ (wt%) | Coke Content (wt%) | ID/IG | Coking Rate (g/mol) |
|----------------|------------------------|-------------------|-----------------|-------------------|-------|-------------------|
| PtSn/SiO$_2$   | 0.09                   | 0.04              | 0.10            |                   | -     | -                 |
| PtCe/SiO$_2$   | 0.22                   | 0.11              | 0.23            | 1.71              | 0.73  | 2.09              |
| PtSnCe/SiO$_2$ | 0.30                   | 0.14              | 0.26            | 2.53              | 0.81  | 0.07              |

*: Amounts of desorbed C$_3$H$_8$, CO$_2$, and C$_3$H$_6$ were determined from the TPD patterns given in Figures 6 and 7.

4.2. Insights into Product Selectivity

As indicated by the results in Section 3.1, the selectivity of propylene varied to a relatively large extent over the PtSn/SiO$_2$, PtCe/SiO$_2$, and PtSnCe/SiO$_2$ catalysts (Figure 1c). According to the analysis of product distribution (Figure 1d), this is explained by the simultaneous occurrence of CO$_2$-RP in the course of CO$_2$-ODP. By correlating the characterization results of Sections 3.2–3.5, the significant propylene selectivity over PtSnCe/SiO$_2$ can be explained as the Ce promoted interaction between Sn and Pt, which favors the breaking of C-H bonds in propane [23,58]. However, in addition to the side reaction of CO$_2$-RP induced from propane, the selectivity of propylene is also determined by its possible secondary reactions, including successive polymerization (coke deposition) and further cracking, owing to the difficult desorption of propylene from the surface of catalysts [59]. For further insight, C$_3$H$_6$-TPD experiments were performed, and the results are given in Figure 8. A very broad desorption signal was observed in the temperature range of 100 to 450 °C for all of the catalysts, indicating the varied strength of propylene adsorption on the surface of the catalyst [54]. In the case of PtSn/SiO$_2$, two overlapping peaks were observed at about 123 °C and 204 °C. In contrast, both the peak temperature and amount of desorbed propylene over PtCe/SiO$_2$ and PtSnCe/SiO$_2$ were clearly higher than over PtSn/SiO$_2$, indicating a stronger adsorption of propylene. Furthermore, as given in Table 3, the amount of adsorbed propylene was calculated below 450 °C during C$_3$H$_6$-TPD and was found to increase in the order of PtSn/SiO$_2$ < PtCe/SiO$_2$ < PtSnCe/SiO$_2$. When propylene selectivity is compared with the amount of propylene adsorption, exactly the same trend is found, i.e., the greater the amount of propylene adsorption, the higher the propylene selectivity. This result is contradictory to the common expectation. Considering the dominant byproduct of CO in the course of CO$_2$-ODP (Figure 1d), it can be concluded that the simultaneous occurrence of CO$_2$-RP plays a key role in determining the propylene selectivity in comparison with the secondary reaction of propylene.
TG-DSC was performed to analyze the amount and kind of deposited coke over the spent catalysts after a TOS of 2 h, and the results are shown in Figure S6 and Table 3. For all of the catalysts, a clear weight loss was observed at about 30–200 °C, induced from the physical desorption of water (Figure S6a), accompanying the clearly endothermic peak of DSC curves at around 74 °C (Figure S6b). With a further increase in temperature from 200 to 800 °C, the TG signal commonly assigned to the burning of deposited coke was almost steady in the case of PtSn/SiO2, indicating a negligible amount of coke formed on the surface. This coincides well with the significantly low propane conversion (Figure 1a). Contrary to this, a weight loss of 1.71% and 2.53% was clearly observed over PtCe/SiO2 and PtSnCe/SiO2, respectively, at about 300–600 °C, ascribed to the burning of coke. This was further revealed by the exothermic peak of DSC curves. Moreover, the peak temperature of DSC for PtSnCe/SiO2 (400 °C) was clearly lower than that for PtCe/SiO2 (452 °C), suggesting a difference in the degree of graphitization of the deposited coke. To further confirm this, visible Raman characterization was performed. As given in Figure S7, typical Raman shifts were observed over PtCe/SiO2 and PtSnCe/SiO2 at 1340 and 1600 cm⁻¹, assigned to the disordered (D band) and graphitic carbon (G band), respectively. To quantify the extent of graphitization of the deposited coke, the intensity ratio of the D and G bands, i.e., I_D/I_G, was calculated. As shown in Table 3, PtSnCe/SiO2 showed a higher value of I_D/I_G (0.81) than PtCe/SiO2 (0.73), indicating a lesser extent of graphitization of coke species [32]. This is in agreement with the DSC results (Figure S6b). The difference in the species of deposited coke can be explained by the fact that PtCe/SiO2 is favorable to CO2-RP, while PtSnCe/SiO2 is promising for CO2-ODP. The lesser extent of graphitization of coke species on the surface of PtSnCe/SiO2 mainly originated from the polymerization of the produced C3H6. However, PtCe/SiO2 led to the formation of more graphitic carbon species due to the severe breaking of the C-C bond in propane through CO2-RP. The coking rate (g/mol) of PtCe/SiO2 and PtSnCe/SiO2, defined as grams of deposited coke, was calculated following references [54,60] by converting 1 mole of propane after a TOS of 2 h. In the case of PtSnCe/SiO2, the coking rate was 0.07 g/mol, which is clearly lower than that of PtCe/SiO2 (2.09 g/mol). This indicates that coke deposition over PtSnCe/SiO2 is significantly inhibited, which may result from the lesser extent of graphitization of coke species for CO2-ODP.

5. Conclusions

In summary, a highly efficient CO2-ODP catalyst was developed with STY₃H₆ as high as 1.75 g(C₃H₆)g(catalyst)⁻¹h⁻¹ by simply impregnating Ce (6 wt%) into PtSn/SiO2. Moreover, CO2-ODP performance was essentially restored after the regeneration of the catalyst at 500 °C for 30 min in an air flow. Additionally, the promotional effect of CeO2 on PtSn/SiO2 played a key role in determining the initial CO2-ODP performance, leading to the same increased order of PtSn/SiO2 < PtCe/SiO2 < PtSnCe/SiO2 for the initial propane.
conversion of 4.4%, 20.6%, and 55.8% and propylene selectivity of 31.0%, 39.7%, and 89.1%. Physical, chemical, and spectra characterizations reveal that the addition of CeO$_2$ led to an increased Pt dispersion of 13.4% for PtSn/SiO$_2$ < 20.9% for PtCe/SiO$_2$ < 41.3% for PtSnCe/SiO$_2$ and strong interactions between Pt and Sn species over the PtSnCe/SiO$_2$ catalyst, which favors the synchronized activation of C-H bonds in propane and the C=O bonds in CO$_2$ molecules. This was explained as the enhanced adsorption of propane and CO$_2$ in the order of PtSn/SiO$_2$ < PtCe/SiO$_2$ < PtSnCe/SiO$_2$, essentially originated from the rich oxygen defects over the added CeO$_2$. With these understandings, the modification of catalysts with improved oxygen defects over oxides, as well as the search for promoters with richer oxygen defects than CeO$_2$, is expected to produce a more effective Pt-based catalyst for CO$_2$-ODP, with additional studies still in progress in our laboratory.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/nano12030417/s1](https://www.mdpi.com/article/10.3390/nano12030417/s1). Figure S1: Carbon balances of CO$_2$-ODP over the PtSn/SiO$_2$, PtCe/SiO$_2$, and PtSnCe/SiO$_2$ catalysts at different times on stream, Figure S2: Time-on-stream catalytic activity for CO$_2$-ODP over SnCe/SiO$_2$, Figure S3: Time-on-stream selectivity of CH$_4$, C$_2$H$_4$, and C$_2$H$_6$, Figure S4: N$_2$ adsorption/desorption isotherms and pore-size distributions determined by the BJH method for PtSn/SiO$_2$, PtCe/SiO$_2$ and PtSnCe/SiO$_2$ catalysts, Figure S5: Ce 3d XPS spectra of the reduced PtCe/SiO$_2$ and PtSnCe/SiO$_2$ catalysts, Figure S6: TG and DSC patterns of the catalysts after CO$_2$-ODP for a time on stream of 2 h, Figure S7: Raman spectra of the catalysts after CO$_2$-ODP for a time on stream of 2 h, Table S1: List of the reaction conditions and the main results of CO$_2$-ODP over different catalysts [13,16,54,61–68].

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