Hybrid Composite of Subnanometre CoPd Cluster-Decorated Cobalt Oxide-Supported Pd Nanoparticles Give Outstanding CO Production Yield in CO₂ Reduction Reaction

Che Yan 1*, Dinesh Bhalothia 1, Shou-Shiun Yang 1, Amisha Benival 1, You-Xun Chang 1, Pin-Chieh Wang 1, Yu-Chia Cheng 1, Chi-Liang Chen 2, Shun-Chi Wu 1 and Tsan-Yao Chen 1,3,*

1 Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan
2 National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
3 Hierarchical Green-Energy Materials (Hi-GEM) Research Centre, National Cheng Kung University, Tainan 70101, Taiwan
* Correspondence: chencaeser@gmail.com; Tel.: +886-3-5715131 (ext. 34271); Fax: +885-3-5720724
† These authors contributed equally to this work.

Abstract: Catalytic carbon dioxide (CO₂) hydrogenation to carbon monoxide (CO) via reverse water–gas shift (RWGS) reaction is of particular interest due to its direct use in various industrial processes as feedstock. However, the competitive CO methanation process severely limits the RWGS reaction in a lower temperature range. In this context, we propose a novel nanocatalyst (NC) comprising oxygen vacancy-enriched subnanometer-scale CoPd hybrid cluster (CoOxVPd)-anchored Pd nanoparticles (NPs) on cobalt oxide support underneath (denoted as CP-CoOx/VPd) by using a galvanic replacement reaction-assisted wet chemical reduction method. As-developed CP-CoOx/VPd NC initiated the RWGS reaction at 423 K temperature while showing an optimum CO production yield of ~341 μmol g⁻¹catalyst and a CO selectivity as high as ~99% at 523 K in the reaction gas of CO₂:H₂ = 1:3. The results of physical characterizations along with electrochemical and gas chromatography (GC) suggest that abundant oxygen vacancies in the surface-anchored CoOxVPd clusters are vital for CO₂ adsorption and subsequent activation, while neighboring Pd domains facilitate the H₂ dissociation. The obtained results are expected to provide a feasible design of Co-based NCs for the RWGS reaction.

Keywords: Hybrid composite; CO₂ hydrogenation; Carbon monoxide; CO selectivity; Oxygen vacancies

1. Introduction

The extensive consumption of conventional fossil fuels results in massive CO₂ emissions, which later cause alarming energy and environmental issues. To this end, CO₂ sequestration is crucial for global sustainability; however, technological and economic bottlenecks are prompting the scientific community to recycle CO₂ into value-added fuels or chemicals [1]. CO₂ is a potential one-carbon (C₁) source for producing commodity fuels such as formic acid (HCOOH), methane (CH₄), and carbon monoxide (CO), etc. via CO₂ hydrogenation [2]. Nevertheless, CH₄ is closest to meeting the commercial demands due to its well-explored industrial application [3]. Multidirectional engineering steps have been demonstrated for direct conversion of CO₂ into methane via CO₂ methanation (i.e., CO₂ to CH₄ conversion); however, due to the high activation temperature of CO₂ molecules, the production yield is severely limited [4]. Alternatively, the catalytic transformation of CO₂ to CO via reverse water–gas shift (RWGS) reaction has gained more attention, because unlike CO₂, which is thermodynamically more stable, CO is highly active and its further conversion to value-added commodities is well known [5,6]. It is a
well-known fact that the RWGS reaction is endothermic and thus more favored at higher temperatures, while the CO\textsubscript{2} methanation is thermodynamically more favored at lower temperatures due to its exothermic nature. Therefore, it can be concluded that the competitive CO\textsubscript{2} methanation process suppresses the CO production yield at lower temperatures [7]. Consequently, developing highly efficacious catalysts for RWGS reaction with high CO selectivity and low-temperature operation is needed.

It is an undeniable fact that understanding reaction mechanisms is imperative before designing high-performance catalysts. Therefore, the in-depth study of RWGS reaction carried out in past decades and two possible reaction mechanisms (redox and association) have been proposed [8]. The redox mechanism is a reaction step, where hydrogen molecules (H\textsubscript{2}) dissociate in the first step to *H atoms, which further react with surface *O to create oxygen vacancies (O\textsuperscript{v}). In the second step, the CO\textsubscript{2} molecule dissociates at the O\textsuperscript{v} sites to produce *CO. The *H-assisted reduction of surface oxygen species is the rate-determining step (RDS) in the redox mechanism [9]. Generally, the reducible oxides follow the redox mechanism [10]. On the other hand, in the associative mechanism, the adsorbed CO\textsubscript{2} molecules react with dissociated *H atoms to form intermediate species such as carboxyl (*COOH), and formate (*HCOO), etc., finally decomposing to produce CO and H\textsubscript{2}O, where, the adsorption and dissociation, respectively, of CO\textsubscript{2} and H\textsubscript{2} molecules are determined as key elementary steps [11,12]. The association mechanism is mainly followed by the reducible oxide-supported noble metal nanoparticles (NPs) [13]. The aforementioned discussion suggests that catalyst material has a direct influence on the pathway of RWGS reaction. In addition, it can be concluded that two essential reaction sites for CO\textsubscript{2} adsorption and H\textsubscript{2} dissociation are required in an ideal RWGS reaction catalyst. It is frequently reported in the literature that noble-metal NPs, such as Pd or Pt, facilitate the H\textsubscript{2} dissociation, while O\textsuperscript{v} sites favour CO\textsubscript{2} adsorption [14,15]. For instance, Arenas et al. elucidated the role of O\textsuperscript{v} in CO\textsubscript{2} methanation. They carried out CO\textsubscript{2} methanation on two different catalyst systems: one with O\textsuperscript{v} (Ni-CeO\textsubscript{2}) and the other without O\textsuperscript{v} (Ni-Al\textsubscript{2}O\textsubscript{3}), where the O\textsuperscript{v}-enriched Ni/CeO\textsubscript{2} catalyst achieved higher methanation yield and selectivity. They demonstrated that CO\textsubscript{2} molecules are reduced at the O\textsuperscript{v} sites of CeO\textsubscript{2} support, while H\textsubscript{2} molecules dissociated at the metallic Ni sites [16]. Bahmanpour et al. also found that O\textsuperscript{v} sites are vital for CO\textsubscript{2} adsorption and activation [17].

Our previous works have outlined the role of synergistic collaboration between two or more reaction sites in bimetallic and trimetallic catalyst systems for CO\textsubscript{2} methanation and RWGS reactions, respectively. Pd domains promoted CO\textsubscript{2} dissociation and late transition metal oxides (Ni, Cu, Co) were reduced by H\textsubscript{2} at higher temperature range [18,19].

In line with recent advancements, herein we prepared a heterogeneous nanocatalyst (NC) comprising cobalt oxide-supported Pd NPs with O\textsuperscript{v}-enriched Co/Pd hybrid cluster (denoted CoO\textsuperscript{v}/Pd) decoration (CP-CoO\textsuperscript{v}Pd) using a galvanic replacement-assisted wet chemical reduction method. Such a material delivers a CO production yield of ~3414 μmol g\textsuperscript{-1}\textsubscript{catalyst} with CO selectivity of ~99% at 523 K in the ambient of the CO\textsubscript{2} and H\textsubscript{2} mixture. Results of the physical inspections along with the electrochemical analysis ambiguously suggest that the impressive CO production yield and high CO selectivity of CP-CoO\textsuperscript{v}Pd NC can be attributed to the presence of O\textsuperscript{v} reaction sites on the material’s surface, which are vital for CO\textsubscript{2} adsorption and subsequent activation. On top of that, adjacent Pd atoms facilitate the H\textsubscript{2} dissociation. Consequently, multiple reaction sites in the CP-CoO\textsuperscript{v}Pd simultaneously facilitate all the reaction pathways.
2. Results and Discussion

Physical Characterizations

Figure 1 demonstrates the high-resolution transmission electron microscope (HRTEM) images of Pd/AC and CP-CoOₓPd NCs with the corresponding digital image-processing results (Figure a-1/b-1). Forward Fourier transform (FFT) patterns (Figure a-2/b-2), the inverse Fourier transform (IFT) images (Figure a-3/b-3), and the line histograms of selected fringes (insets) are analyzed for in-depth analysis. The low-magnification TEM images of Pd/AC and CP-CoOₓPd NCs are shown in Figure S1. For easy clarification, an HRTEM image of carbon-supported CoO. NPs (i.e., CoOₓ/AC) is shown in Figure S2. Accordingly, the CoO. NPs are grown with short-range ordered polycrystalline structure and can be consistently confirmed by the presence of ring-like FFT patterns [20]. Figure 1a shows an HRTEM image of bare Pd NPs (i.e., Pd/AC), where Pd NPs are grown in a drop-like structure with severe surface defects (denoted by the yellow circles in the digital image-processing results in Figure a-1) and a typical size range of ~3 to 4 nm. An even closer inspection of Figure 1a reveals that Pd NPs exhibit a long-range ordered atomic structure in three-dimensional space that is consistently confirmed with the hexagonally symmetric FFT pattern (Figure a-2). The fuzzy surface (denoted by the red triangles) can be attributed to some extent of surface oxidation in the absence of steric protection. These rationales can be further confirmed by the IFT (Figure a-3)-derived line histograms (insets) of interplanar spacing of Pd NPs at the surface, as well as subsurface regions. Accordingly, the Pd NPs exhibit random lattice spacing of 0.253 nm and 0.222 nm in the surface and subsurface regions, respectively. These observations integrally indicate a certain extent of lattice expansion at the Pd surface due to possible oxidation. Figure 1b presents the HRTEM image of CoOₓ-supported Pd NPs with CoPd hybrid cluster decoration (i.e., CP-CoOₓPd NC), where it can be seen that the surface and subsurface atomic arrangements and the particle size of the Pd NPs (denoted by blue circle) are severely changed compared to that of bare Pd NPs. The size of CoOₓ-supported Pd NPs is increased by 30% (~4–5 nm) compared to that of Pd NPs on the carbon support (Figure 1a), and can be attributed to the limited extent of heteroatomic intermixing (i.e., CoPd alloy formation) at the CoOₓ-to-Pd interface, as well as surface-anchored CoPd species. These scenarios are consistently confirmed by the increased lattice spacing of 0.246 nm (i.e., lattice relaxation), which is a typical trademark of alloy formation and consistently proved by spectroscopic analysis in later sections. Of utmost importance, the reduced surface defects (Figure b-2) along with the FFT pattern exhibiting symmetric bright spots in lateral spaces (Figure b-3) implies that the decorated CoPd clusters are accommodated in the defect sites of the Pd crystal without disturbing the local structure ordering.
Figure 1. HRTEM images of as-prepared (a) Pd/AC and (b) CP-CoO₃Pd NCs. The digital image-processing results, forward Fourier transformation (FFT) patterns and inverse Fourier transform (IFT) images of the selected areas in HRTEM images are depicted in (a-1/b-1), (a-2/b-2), and (a-3/b-3), respectively, for Pd/AC and CP-CoO₃Pd NCs. The d-spacing values of experimental NCs are calculated using IFT images and their corresponding line histograms (insets).

Figure 2a shows the X-ray diffraction (XRD) patterns of CP-CoO₃Pd NC and reference samples (AC, CoOₓ/AC and Pd/AC), where the diffraction peaks “O₁,” “O₂,” and “O₃,” respectively, centered at ~8.45°, ~11.44°, and ~19.18° correspond to the carbon support. The suppressed and broad diffraction (blue lines) confirm the formation of short-range ordered polycrystalline structure, consistent with former HRTEM observations. The Pd/AC and CP-CoO₃Pd NCs show three characteristic peak—A, B, and C—centered at about ~17.50°, 20.10°, and 28.80°. These peaks can be assigned to the diffraction signals from (111), (200), and (220) facets of metallic face-centered cubic Pd crystal [21]. Notably, compared to Pd/AC, the diffraction peaks of CP-CoO₃Pd NC are significantly broadened, showed higher background (i) and shifted to lower angles (i.e., left side) (Figure 2b), suggesting reduced coherent length (particle size), considerable out-of-phase scattering from its surface with high roughness (due to presence of decorated CoPd species) and higher lattice constant (i.e., expansive strain), respectively. These observations are in good agreement with former HRTEM findings. The presence of peak X (corresponding to the Co₃O₄(311)) in the XRD pattern of CP-CoO₃Pd NC confirms that the Co is present in form of Co₃O₄ and exposed to the surface. In addition, the CP-CoO₃Pd NC demonstrates a suppressed peak Y, corresponding to the Co₃Pd (1 0 -1 3) plane, implying the existence of subnanometer Co₃Pd alloys.
To get more insights into the local atomic and electronic structure of Co atoms in CP-CoO.\textsuperscript{VPd} NC, X-ray absorption spectroscopy (XAS) at Co K-edge was performed. Figure 3a shows the normalized X-ray absorption near edge structure (XANES) spectra of CP-CoO.\textsuperscript{VPd} NC compared with reference samples (CoO/AC), while the XANES spectra of standard CoO and CoO\textsubscript{4} are also compared. In the Co K-edge XANES spectra, the pre-edge "M" and the absorption edge "N" are corresponding to the 1s-to-3d and 1s-to-4p electron transitions, respectively [22]. Generally, the pre-edge elucidates the local symmetry of target atoms. Accordingly, the suppressed pre-edge intensities of standard samples (i.e., CoO and CoO\textsubscript{4}) suggest their octahedral Co-configuration. CoO/AC and CP-CoO.\textsuperscript{VPd} NCs exhibit intense pre-edge intensity, suggesting tetrahedral coconfiguration (i.e., loss of O-atoms (presence of O\textsuperscript{2-}) in these samples [22]. The inflection point (X) position indicates the oxidation state of the target atoms [23]. Notably, the inflection point of CP-CoO.\textsuperscript{VPd} NC undergoes the lowest energy position among the samples under investigation, implying the lowest oxidation state of Co atoms in CP-CoO.\textsuperscript{VPd} NC and therefore increased O\textsuperscript{2-} [24]. With the steric protection of Pd atoms to Co domains underneath, the higher white-line intensity (H\textsubscript{SL}) of CP-CoO.\textsuperscript{VPd} NC compared to CoO/AC indicates the electron relocation from Co-to-Pd atoms. The Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) analysis further confirms the existence of O\textsuperscript{2-} sites in CP-CoO.\textsuperscript{VPd} NC. Figure 3b shows the FT-EXAFS spectra of experimental samples at Co K-edge, while the model-simulated fitting curves are shown in Figure S3 and corresponding structural parameters summarized in Table 1. Accordingly, compared to the coordination number (CN) of the Co-Co bond pair (CN\textsubscript{Co-Co} = 1.29), the Co-O bond pair exhibits higher CN (CN\textsubscript{Co-O} = 2.55). Such a scenario indicates the severe oxidation of Co-atoms in CP-CoO.\textsuperscript{VPd} NC. The CP-CoO.\textsuperscript{VPd} NC shows lower CN for the Co-O bond pair (CN\textsubscript{Co-O} = 0.32 + 2.23 = 2.55) compared to CoO/AC (CN\textsubscript{Co-O} = 2.94). The similar Co content and reduced CN for the Co-O bond pair confirms the presence of O\textsuperscript{2-} in CP-CoO.\textsuperscript{VPd} NC [25]. In addition, the existence of a small CN for the Co-Pd bond pair (CN\textsubscript{Co-Pd} = 0.43) reveals a certain extent of Co-to-Pd heteroatomic intermixing and is consistent with former observations.

The results of Pd K-edge XAS analysis complementarily confirm the aforementioned scenarios. Figure 3c shows the normalized XANES spectra of experimental NCs at Pd K-edge, where the similar position of inflection point to Pd foil confirms the metallic state of Pd atoms in Pd/AC and CP-CoO.\textsuperscript{VPd} NC. The two absorption edges "A" and "B" correspond to the electron transition from 1s to unoccupied 5p and 4f orbitals, respectively [25]. Accordingly, compared to Pd/AC, the suppressed intensity of peak "A" implies a
slight extent of electron relocation from Co-to-Pd atoms in CP-CoOₓPd NC and is consistent with Co-K-edge XANES analysis. The FT-EXAFS spectra of CP-CoOₓPd NC are shown in Figure 3d, while the corresponding structural parameters are listed in Table 1 and the fitting curves shown in Figure S4. Consistent with XRD and Co K-edge FT-EXAFS results, the presence of a small CN for the Pd-Co bond pair (CNₚ₋₉ = 0.55) confirms the formation of subnanometer CoPd alloys CP-CoOₓPd NC. In addition, the higher CN for the Pd-Pd bond pair compared to Pd-O complementarily proves the metallic characteristic of Pd atoms in CP-CoOₓPd NC. These scenarios are further confirmed by wavelet transformation (WT) patterns of the EXAFS spectrum at Co (Figure S5) and Pd K-edges (Figure S6) and discussed in the supplementary information.

Figure 3. X-ray absorption spectroscopy of the experimental NCs compared with reference samples. (a) XANES and (b) FT-EXAFS spectra of the experimental NCs at Co K-edge. (c) XANES and (d) FT-EXAFS spectra of the experimental NCs at Pd K-edge. In the FT-EXAFS spectra at Co K-edge, peak Co⁴⁰⁰⁻⁴⁰⁰₋₉⁻⁴⁰⁰ is the contribution of coordinated Co atoms at octahedral symmetry from the 2nd coordination shell in CoO lattice. The peak of Co⁴⁰⁰⁻⁴⁰⁰₋₉₋₉₋₉ is the contribution of coordinated Co atoms (tetrahedral symmetry) in the 2nd coordination shell of CoO. latttice. *The intensity of Pd foil is reduced by 50% for better representation.

Table 1. Quantitative results of X-ray absorption spectroscopy model analysis at Co and Pd K-edges of experimental and reference NCs.

| Sample  | Pd K-Edge | Co K-Edge |
|---------|-----------|-----------|
|         | Bond Pair | CN       | R (Å) | Bond Pair | CN | R (Å) |
| Pd foil | Pd-Pd     | 11.03    | 2.744 |         |    |       |
| Pd/AC   | Pd-O      | 0.68     | 2.005 |         |    | N/A   |
|         | Pd-Pd     | 4.39     | 2.742 |         |    |       |
X-ray photoelectron spectroscopy (XPS) was used to elucidate the oxidation states of constituting elements and to prove the presence of O\textsuperscript{v} in CP-CoO\textsubscript{x}Pd NC. The XPS spectra of CoO\textsubscript{x}/AC and CP-CoO\textsubscript{x}Pd NC at Co-2p orbital are, respectively, shown in Figure 4a,b, whereas the corresponding deconvolution results are shown in Table S2. Previously published literature reported that a higher Co\textsuperscript{ii}/Co\textsuperscript{iii} ratio implies the presence of O\textsuperscript{v} [26]. Accordingly, compared to CoO\textsubscript{x}/AC (1.11), the higher Co\textsuperscript{ii}/Co\textsuperscript{iii} (1.29) confirms the abundant O\textsuperscript{v} sites in CP-CoO\textsubscript{x}Pd NC. Notably, with the similar Co content, a higher Co\textsuperscript{ii}/Co\textsuperscript{iii} ratio indicates that the majority of O\textsuperscript{v} sites are present in surface-anchored CoO\textsubscript{x}Pd clusters. The XPS spectra at the O-1s orbital further confirm these observations. Figure 4c,d, respectively, show the XPS spectra at the O-1s orbital of CoO\textsubscript{x}/AC and CP-CoO\textsubscript{x}Pd NC. The XPS spectra of the O-1s orbital are further deconvoluted to distinguish the signals from O\textsuperscript{v} and lattice oxygen (denoted by O\textsuperscript{\delta\textsubscript{\text{air}}}), while the corresponding results are summarized in Table S2. Accordingly, the higher area under O\textsuperscript{v} peak suggests the high density of O\textsuperscript{v} sites in CP-CoO\textsubscript{x}Pd NC. The XPS analysis at Pd-3d orbital confirms these characteristics. Figure S7a,b, respectively, depict the XPS spectra of Pd/AC and CP-CoO\textsubscript{x}Pd NC at the Pd-3d orbital. Accordingly, the high Pd\textsuperscript{0}/Pd\textsuperscript{ii} ratio (Table S2) confirms the metallic state of Pd atoms in Pd/AC and CP-CoO\textsubscript{x}Pd NC, which is in good agreement with XAS results. In contrast to XAS observations, the binding energies of Pd\textsuperscript{0} and Pd\textsuperscript{ii} are higher in CP-CoO\textsubscript{x}Pd NC than CoO\textsubscript{x}/AC (Table S2); however, this can be attributed to the electron transfer to surface O\textsuperscript{v} sites.

Cyclic voltammetry (CV) and CO-stripping analysis have been used to confirm the surface chemical identities and geometric configuration of CP-CoO\textsubscript{x}Pd NC. As shown in Figure 5a, the two characteristic peaks O\textsuperscript{ads}\textsuperscript{1} and O\textsuperscript{ads}\textsuperscript{2} at the higher potential region in the forward sweep, respectively, correspond to the formation of Co hydroxide and oxide in CoO\textsubscript{x}/AC, while the presence of the broad O\textsuperscript{ads}\textsuperscript{1} peak in the backward sweep can be assigned to the desorption of oxygenated species from these reaction sites. The smeared peak profile (H\textsuperscript{ads-Pd}) in the forward sweep of the hydrogen underpotential deposition (H\textsubscript{UPD}) region confirms the high affinity towards proton adsorption for Pd/AC [27]. Notably, the CP-CoO\textsubscript{x}Pd NC shows a similar (smeared) peak profile to Pd/AC in H\textsubscript{UPD} region and to CoO\textsubscript{x}/AC (presence of peaks O\textsuperscript{ads}\textsuperscript{1} and O\textsuperscript{ads}\textsuperscript{2} in the forward sweep and peaks O\textsuperscript{ads}\textsuperscript{1} in the backward sweep) in higher potential regions, which confirms the formation of CoO\textsubscript{x}-supported Pd NPs and is consistent with our experimental design. In addition, both the Pd/AC and CP-CoO\textsubscript{x}Pd NC show an obvious oxide reduction peak O\textsuperscript{ads-Pd} in the backward sweep, which corresponds to the oxide reduction from the Pd surface [28].

Figure 5b shows the CO-stripping curves of CP-CoO\textsubscript{x}Pd NC compared with reference samples, where the flat CO-stripping curve of CoO\textsubscript{x}/AC shows its inert nature.
towards CO oxidation. The strong CO oxidation peak (O) indicates a high density of reaction sites for CO adsorption and its subsequent reduction on the surface of Pd/AC [29]. For CP-CoOₓPd NC, an offset of the CO oxidation peak O* to lower potential indicates the reduced energy barrier for CO oxidation and can be attributed to the certain extent of charge localization (i.e., electron transfer) from Co-to-Pd atoms, which is consistent with former findings. The presence of a suppressed and broad peak “P” at lower potentials can be assigned to the current response due to the CO oxidation at the low-energy barrier reaction sites of the Co/Pd alloy. Of utmost importance, compared to Pd/AC, the suppression of the main CO oxidation peak “O” indicates the reduced reaction sites for CO oxidation on the surface of CP-CoOₓPd NC and can be attributed to the presence of inert CoOₓ species in form of CoPd hybrid clusters on the surface of CP-CoOₓPd NC. Based on the aforementioned physical and electrochemical results, the geometric configuration of CP-CoOₓPd NC is proposed and represented in Figure 5c.

Figure 4. X-ray photoelectron spectroscopy of (a) CoOₓ/AC and (b) CP-CoOₓPd NCs at Co-2p orbital. (c) CoOₓ/AC and (d) CP-CoOₓPd NCs at O-1s orbital.
Inspired by the potential geometric and electronic properties, the CO$_2$ hydrogenation performance of CP-CoO$_x$Pd NC was evaluated by a previously reported protocol [18,19], where the gaseous products were analyzed at ambient pressure using a gas chromatography (GC) system equipped with a PDHID detector. Figure 6a shows the CO production yield of CP-CoO$_x$Pd NC and reference samples in the reaction gas (CO$_2$:H$_2$ = 1:3), while corresponding performance parameters are listed in Table S3. Accordingly, CoO$_x$/AC, Pd/AC, and the physical mixture of CoO$_x$+Pd are chemically inert toward CO$_2$ below 423 K temperature, while the CO production yield for CP-CoO$_x$Pd NC is 68.2 μmol g$^{-1}$catalyst at 423 K, which continuously increased with raising the temperature to 573 K, and the highest CO production yield is ~3414 μmol g$^{-1}$catalyst at 573 K. This value is ~90% and ~57% improved compared to the CoO$_x$/AC (~348 μmol g$^{-1}$catalyst) and Pd/AC (~1466 μmol g$^{-1}$catalyst), respectively. In addition, the CP-CoO$_x$Pd NC achieved CO selectivity as high as ~99%. Such high activity and CO selectivity of CP-CoO$_x$Pd NC can be attributed to the presence of O$^v$ sites and adjacent Pd domains in subnanometer-scale CoPd clusters. Previously published literature reported that Pd atoms weakly adsorb CO$_2$, while O$^v$ sites...
are favorable for adsorption and subsequent reduction of CO₂ molecules [14,15]. These scenarios are consistently proved by assessing the CO₂ hydrogenation performance of experimental NCs in the pure CO₂ ambient. As shown in Figure S8a, both the CoOx/AC and Pd/AC are inactive toward CO₂ in the pure CO₂ ambient across the temperature range, while the CP-CoOxVPd NC shows a significant CO production yield in the high-temperature range, confirming that O²⁻ sites promote CO₂ activation. These observations confirm that the O²⁻ and Pd sites synergistically trigger the CO production yield of CP-CoOxVPd NC, where O²⁻ sites and adjacent Pd domains, respectively, boost the CO₂ activation and H₂ dissociation. Finally, the much lower CH₄ production yield in pure CO₂ ambient (Figure S8b) and the reaction gas (Figure 6b) confirms the suppression of the competitive CO₂ methanation process and thus high CO selectivity. The proposed mechanism of CO₂ hydrogenation on the CP-CoOxVPd NC is shown in Figure 6c.

![Figure 6. Gas chromatography (GC)-determined (a) CO and (b) CH₄ production yields of CP-CoOxVPd NC compared with CoOx/AC, Pd/AC and physical mixture of CoOx/AC+Pd/AC in the ambient of CO₂ and H₂ mixture with CO₂:H₂ ratio of 1:3. (c) The proposed mechanism of CO₂ hydrogenation on the CP-CoOxVPd NC.]
3. Experimental

Materials and Methods

Cobalt oxide-supported Pd NPs with O⁺-enriched CoPd hybrid cluster decoration were prepared via a galvanic replacement reaction-assisted wet chemical reduction method. Before synthesis, the catalyst carrier (i.e., carbon black; UR-XC72, UniRegion Bio-Tech, Taipei, Taiwan) was surface-functionalized with an adequate protocol for increasing the metal-support interaction [30]. The surface-functionalized carbon black was denoted as active carbon (AC) in the following of this article. Subsequently, 12 g (0.5 wt.% solution in D.I. water; i.e., the actual amount of AC is 60 mg) of AC was dispersed in 3.06 g of 0.1 M aqueous solution of cobalt (III) chloride (99%, CoCl₃, Sigma-Aldrich Co, St. Louis, MO, USA) and stirred at 400 rpm for 4 h at room temperature (solution A) in the 1st step. Solution A (i.e., Co⁺⁺ adsorbed AC) contains a 30 wt.% weight ratio of Co to AC. In the 2nd step, 0.12 g of sodium borohydride (NaBH₄; 99%, Sigma-Aldrich Co, St. Louis, MO, USA) dissolved in 20 mL of D.I. water was instantly dropped into solution A and stirred at 400 rpm for 10 s to grow Co NPs on the AC surface (solution B). These Co NPs were partially oxidized in the ambient and resulting in a mixed metallic and oxide phase of Co (i.e., Co/CoOₐ). After that, in the 3rd step, 3.06 g of 0.1 M Pd precursor solution was mixed into solution B to grow the Pd NPs over CoO support. In this step, the Pd²⁺ ions were reduced by the excessive amount of NaBH₄ added in the 2nd step. The Pd precursor solution was prepared by dissolving palladium chloride (PdCl₂, 99%, Sigma-Aldrich Co, St. Louis, MO, USA) in 1.0 M of HCl(aq). Herein, it is worth noting that the electronegativity of Pd atoms is higher than Co atoms and thus the galvanic reaction between Pd²⁺ ions and metallic Co atoms is obvious. In this event, subnanometer-scale CoPd hybrid clusters are formed on the surface of Pd NPs due to galvanic replacement between Pd²⁺ ↔ Co followed by spontaneous deposition of residual Pd²⁺ and Co³⁺ ions. Generally, the galvanic replacement reaction is dominated by the electronegativity difference between two atoms. In this case, the electronegativity of Pd is higher than Co and thus, the galvanic replacement reaction between Pd²⁺ ions and Co³⁺ is obvious. Finally, the as-prepared material was washed with acetone and D.I. water, centrifuged, and dried at 100 °C overnight. In the last step, the O⁺ sites in the as-prepared sample were created by exposure to the ambient environment. Hereafter, the cobalt oxide-supported Pd NPs with O⁺-enriched CoPd hybrid cluster decoration are denoted as CP-CoO⁺⁴Pd.

4. Conclusions

We have reported a novel heterogeneous nanocatalyst (NC) consisting of CoO⁻ supported Pd nanoparticles decorated with an oxygen vacancy-enriched subnanometer CoPd hybrid cluster (CP-CoO⁺⁴Pd). The prepared material actively suppressed the competitive CO₂ methanation reaction and thus achieved CO selectivity as high as 99%. CP-CoO⁺⁴Pd NC initiated the CO production at 423 K temperature and achieved an optimum CO production yield of 3414 µmol g⁻¹catalyst at 573 K in the reaction gas of CO₂:H₂ = 1:3. The cross-referencing results of physical characterizations, electrochemical analysis, and gas chromatography (GC) indicate that such a high CO₂ hydrogenation performance of CP-CoO⁺⁴Pd NC at low onset temperature originated from the synergistic cooperation between oxygen vacancies and adjacent Pd domains, where oxygen vacancies promoted the CO₂ adsorption and neighboring Pd sites favored H₂ splitting. In addition, the CoPd alloys at the heterogeneous interface of CoO-to-Pd offered ideal desorption energy for subsequent reaction steps.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101127/s1, Figure S1: Low magnification TEM image of (a) Pd/AC and (b) CP-CoO⁺⁴VPd NCs.; Figure S2: HRTEM images of CoOx/AC. The Forward Fourier Transformed (FFT), Inverse Fourier Transformed (IFT) and the line histogram of are depicted in insets.; Figure S3: Model analysis fitting curves compared with experimental FT-EXAFS spectra at Co K-edge of (a) CoO, (b) CoOₐ, (c) CoOx/AC and (d) CP-CoO⁺⁴Pd NCs. Figure S4: Model
analysis fitting curves compared with experimental FT-EXAFS spectra at Pd K-edge of (a) Pd foil, (b) Pd/AC and (c) CP-CoOx/Pd NCs; Figure S5: The WT for FT-EXAFS spectrum at Co K-edge. (a) CoO4, (b) CoOx/AC, (c) CoO and (d) CP-CoOx/Pd NPs. The intensity of CoO4 and CoO are normalized by 0.4-fold as in FE-EXAFS; Figure S6: The WT for EXAFS spectrum at Pd K-edge. (a) Pd foil, (b) Pd/AC and (c) CP-CoOxVPd NCs; figure S7: X-ray photoelectron spectroscopy of (a) Pd/AC and (b) CP-CoOxVPd NCs at Pd 3d orbital.; Figure S8: The gas chromatography (GC) determined CO:RR results.; Table S1: Benchmark of catalysts for RWGS application. Table S2: Quantitative results of X-ray photoemission spectroscopy model analysis at Co-2p, O-1s and Pd-3d orbitals of experimental and control NCs.; Table S3: Calibrated product concentration of CO and CH4.

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