An Efficient Support-Free Nanoporous Co Catalyst for Reverse Water–Gas Shift Reaction

Yongli Shen, Zhen Cao and Zihui Xiao *

Tianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New Energy Materials & Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China; ylshen@tjut.edu.cn (Y.S.); cczz250@163.com (Z.C.)
* Correspondence: zhxiao@email.tjut.edu.cn

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Abstract: A Co-based catalyst is a great candidate for the hydrogenation of CO$_2$. Herein, a support-free nanoporous Co catalyst with high surface area and hierarchical pores was prepared by chemical dealloying, which exhibited excellent performance in the reverse water–gas shift (RWGS) reaction. High conversion of 54.2% and RWGS reaction rate of 812 µmolCO$_2$/g$_\text{cat}$/s could be obtained at a high weight hourly space velocity.

Keywords: nanoporous Co; CO$_2$ hydrogenation; hierarchical pores; dealloying

1. Introduction

Recycling carbon dioxide (CO$_2$) as a renewable and environmentally friendly source is considered an effective way to reduce our dependence on petrochemicals. However, there are only a few industrial processes that utilize CO$_2$ because of its high kinetic and thermodynamic stability with high oxidation state of carbon. Among the proposed utilization processes, CO$_2$ hydrogenation for producing high added-value chemicals and fuels is of special interest [1]. In recent years, hydrogenation of CO$_2$ to carbon monoxide (reverse water–gas shift reaction, RWGS) is an attractive approach, as CO can serve as a versatile building block in Fischer–Tropsch synthesis [2,3].

To date, many catalysts have been used for the hydrogenation of CO$_2$ to CO, such as metal catalysts including Pt [4], Pd [5], Au [6], Cu [7], Ni [8], Co [9], Fe [10] as active component, metal carbide (Mo$_2$C) catalyst [11], and metal oxide (BaZr$_{0.8}$Y$_{0.16}$Zn$_{0.04}$O$_3$) catalyst [12]. The noble metal catalysts were reported as efficient catalysts, which exhibited great CO$_2$ conversion, while relatively low weight hourly space velocity (WHSV) was employed, resulting in a low RWGS reaction rate. Additionally, the high cost of it limits its application. For the other transition metal and metal oxide catalysts, low CO$_2$ conversion was obtained at a high WHSV. Among these, Co-based catalysts have attracted widespread attention due to high activity even at high WHSV; while the activity and selectivity of the RWGS reaction was sensitive to the particle size of Co and metal dispersion. Small particle size and high dispersion of Co were beneficial to the RWGS reaction. As reported, the Co–CeO$_2$ catalyst with small Co particles was found to be selective for the RWGS reaction [9]. Large Co particles (over 10 nm) were favorable to methanation rather than RWGS reaction [13–15]. Moreover, it was found that the mesoporous Co–CeO$_2$ catalyst with high surface area and high dispersion of Co possessed high activity in RWGS reaction [16]. As observed, an increase in loadings of Co was beneficial to enhance the activity of supported catalysts [16], while high loadings led to large particle size and low surface area of active Co, and consequently low selectivity of RWGS reaction. On the basis of this, exploiting a novel support-free Co catalyst with high surface area is an effective method to further enhance activity in the RWGS reaction.
Compared to the conventional nanoparticle catalysts, nanoporous (NP) metal catalysts with a three-dimensional and bicontinuous structure have gained much attention due to their unique physical and chemical properties, such as high surface area, abundant surface coordination, unsaturated atoms, and nanoscale ligaments [17]. Moreover, it is well known that a high density of surface steps and kinks for the nanoporous catalysts are active for various chemical reactions. Herein, a nanoporous Co (NP-Co) catalyst with hierarchical pores was prepared by chemical dealloying of CoAl alloy, which exhibited excellent activity and selectivity for the RWGS reaction.

2. Results and Discussion

The formation process of the NP-Co catalyst is shown in Figure 1a. During the dealloying, active element Al could be removed in alkaline solution, subsequently, the reconstruction of residual Co led to the formation of NP-Co with hierarchical pores. The Brunauer–Emmett–Teller (BET) surface area of it was calculated to be 22 m²/g. The addition of NaBH₄ was intended to prevent the oxidation of Co, although it could not be avoided completely. The Co₃O₄ oxide layer on the surface of NP-Co was formed as displayed in Figure 1b. The hydrogen temperature-programmed reduction (H₂-TPR) profile of the fresh NP-Co showed two main reduction peaks and a shoulder peak centered at about 280, 400, and 620 °C, respectively [18]. The first and shoulder peak could be assigned to the reduction of Co₃O₄ to CoO, and the second one to the subsequent reduction of CoO to Co⁰. Accordingly, reduction pretreatment temperatures of 400 and 600 °C were employed in this work. As displayed in Figure 1c, a homogeneous, bicontinuous, interpenetrating ligament-channel, hierarchical pores structure was obtained after dealloying, while there was unobvious change in morphology after reduction pretreatment compared to NP-Co. The XRD pattern of the original Co₃O₄Al₈₅ phase (Figure 1d). After dealloying, only a weak diffraction peak assigned to Co (111) (JCPDS 15-0806) for all catalysts could be identified as shown in the enlarged figure, suggested low crystallinity of Co.

![Figure 1](image-url)
For a detailed view of surface properties of the catalysts, the chemical states of Co species were investigated by X-ray photoelectron spectroscopy (XPS) analysis. Figure 1e illustrates the XPS spectra of Co 2p for the NP-Co catalysts with different pretreatment. For the NP-Co catalyst, it was clearly found that the peaks of Co 2p were non-stoichiometric in nature, suggesting that the Co atom in Co$_3$O$_4$ had two types of cobalt ions (Co$^{3+}$ in a octahedral coordination and Co$^{2+}$ in a tetrahedral coordination) [19]. The peaks at about 780.6 and 796.6 eV were ascribed to Co$^{3+}$ in octahedral coordination, while the peaks at about 782.7 and 789.5 eV were ascribed to Co$^{2+}$ in tetrahedral coordination. Meanwhile, a weak shoulder peak corresponding to Co$^0$ could be observed at the binding energy (BE) of 778.0 eV. After reduction, the Co-400R catalyst was characterized by the BE of the Co 2p$_{3/2}$ component of 780.9 eV and a low intensity of the shake-up satellite peak at ca. 786.0 eV, which was typical for Co$^{2+}$ ions in the CoO phase [20]. Additionally, the BE centered at 778.0 eV assigned to Co$^0$ could be also observed. Elevating the reduction temperature, the content of surface Co was significantly increased for the Co-600R catalyst. Meanwhile, the BE of it shifted upward compared to the Co-400R catalyst, indicating that the chemical environment of the Co species had changed with the increase of reduction temperature, which was likely related to the surface reconstruction at high temperature, and therefore needs further examination.

The catalytic performance and stability of the NP-Co catalysts in RWGS reaction was investigated. Figure 2a displays the catalytic performance of the Co-400R catalyst at different reaction temperatures. Obviously, the CO$_2$ conversion was significantly increased on elevating the reaction temperature from 300 to 700 °C. Meanwhile, high temperature was also beneficial to the selectivity of the RWGS reaction. This is because the methanation of CO$_2$ is an exothermic reaction, but endothermic for the RWGS reaction, which is favored at high reaction temperatures [21]. Unexpected, higher selectivity of CO was observed at 300 °C compared to that at 400 °C, which was in agreement with the observation on the 10% Co–CeO$_2$ and Ru/SDC catalyst [9,22], although the underlying reasons were not clear. It was speculated that this might be related to the competitive adsorption activation of CO$_2$ and H$_2$ at different temperatures. Thus, additional work is necessary to gain an understanding of the mechanisms of CO$_2$ hydrogenation at low reaction temperature.

Based on the CO$_2$ conversion, the RWGS reaction rate could be calculated as listed in Table 1. Compared to the reported catalysts, the NP-Co catalysts exhibited excellent performance in terms of RWGS reaction rate even superior to noble metal catalysts. Moreover, as for the Co-based catalysts, the highest conversion could be also obtained over the NP-Co catalyst under almost the same reaction conditions even without the dispersion of supports. This high performance could be attributed to abundant surface coordination unsaturated atoms and high surface area. This provides a foundation for developing more NP-Co-based catalysts with better performance in the RWGS reaction.

Table 1. Comparison of reverse water–gas shift (RWGS) reaction rate and CO selectivity for the NP-Co and literature-reported catalysts.

| Catalysts                | H$_2$:CO$_2$ | Temp. (°C) | WHSV (mL/g/h) | Conv. (%) (µmolCO$_2$/g/s) | Sel. of CO (%) | Ref. |
|--------------------------|--------------|------------|---------------|-----------------------------|----------------|-----|
| Pt/K/Mullite             | 1:1          | 550        | 30,000        | 30.9 (52)                   | 99.2           | [23]|
| Pd-In/SiO$_2$            | 1:1          | 600        | 60,000        | 29.4 (44)                   | 100            | [24]|
| K80-Pt/L                 | 1:1          | 400        | 30,000        | 13 (21.9)                   | 100            | [4] |
| Au/CoO$_2$               | 1:1          | 400        | 6000          | 21 (15.7)                   | 100            | [25]|
| Mn–CoO$_2$               | 4:1          | 400        | 60,000        | 8.1 (6.1)                   | 100            | [13]|
| BaZr$_{0.8}$Y$_{0.16}$Zn$_{0.04}$O$_3$ | 1:1          | 600        | 2400          | 37.5 (5.6)                  | 97             | [12]|
| Cu–Fe/SiO$_2$            | 1:1          | 600        | 120,000       | 15 (112)                    | N/A            | [26]|
| Ni/InSiO$_2$             | 4:1          | 400        | 400,000       | 25 (13)                     | 96             | [8]  |
| Co–CeO$_2$               | 1:1          | 600        | 300,000       | 38 (711)                    | 100            | [9]  |
| Co–CeO$_2$               | 4:1          | 400        | 60,000        | 35 (26.2)                   | 62             | [13]|
| Mesoporous Co–CeO$_2$    | 1:1          | 600        | 600,000       | 34.5 (1749)                 | 99.8           | [16]|
| Fe$_2$O$_3$              | 1:1          | 510        | 120,000       | 28 (84)                     | 100            | [10]|
| Cu/β-Mo$_3$C             | 2:1          | 600        | 300,000       | (477)                       | 99.2           | [27]|
| Co-400R                  | 1:1          | 400        | 300,000       | 12.3 (184)                  | 71.6           | This work |
| Co-400R                  | 1:1          | 500        | 300,000       | 29.4 (440)                  | 80.9           | This work |
was gradually declined in the stability testing at high reaction temperature, while a great stability for XPS and H pretreatment, reaction, and even at high temperature [28,29]. After reaction, the characterization of the pretreatments is nearly identical at 600 °C. Nevertheless, the stability of those was significantly changed in reaction. This was because the surface of nanoporous metal catalysts could be restructured during pretreatment, reaction, and even at high temperature [28,29]. After reaction, the characterization of the recycled catalysts by means of XRD, XPS, and SEM was carried out as shown in Figures S1 and S2, and Figure 2e. Through a long time reaction, the surface Co could be oxidized to CoO by formed H2O [30], resulting in the absence of surface Co phase in the recycled catalysts as displayed in the XPS and H2-TPR results (Figure S3). As reported, the formation of surface CoO might be beneficial to the adsorption of acidic CO2 molecules [31], which consequently enhanced the activity. From SEM images, it was found that a certain amount of carbon nanofibers was formed during reaction for the Co-400R catalyst, which was consistent with the observation in previous work [9], where catalytic decomposition of CH4 to carbon was more favorable at higher temperature. However, there was no carbon nanofiber formation, and the coarsening of ligaments could be observed for the Co-600R-S catalyst. This might be related to the low content of CH4 in the reaction atmosphere (Figure 2b, lowest selectivity of CH4 for the Co-600R catalyst). Moreover, the coarsening of ligaments might lead to the decline of activity for the decomposition of CH4. The activity of the Co-400R and Co-600R catalysts was gradually declined in the stability testing at high reaction temperature, while a great stability for the Co-400R catalyst at the relatively low reaction temperature (400 °C) was observed as shown in Figure 2c. This might be related to the low degree of reconstitution and carbon formation, which needs to be further confirmed.

Table 1. Cont.

| Catalysts  | H2:CO2  | Temp. (°C) | WHSV (mL/g/h) | Conv. (%) (umolCO2/g/s) | Sel. of CO (%) | Ref.          |
|------------|---------|------------|----------------|-------------------------|----------------|---------------|
| Co-400R    | 1:1     | 600        | 300,000        | 45.8 (686)              | 97.2           | This work     |
| Co-400R    | 1:1     | 700        | 300,000        | 54.2 (812)              | 99.9           | This work     |

In Figure 2b, it is noteworthy that the initial activity of the NP-Co catalysts with different pretreatments is nearly identical at 600 °C. Nevertheless, the stability of those was significantly changed in reaction. This was because the surface of nanoporous metal catalysts could be restructured during pretreatment, reaction, and even at high temperature [28,29]. After reaction, the characterization of the recycled catalysts by means of XRD, XPS, and SEM was carried out as shown in Figures S1 and S2, and Figure 2e. Through a long time reaction, the surface Co could be oxidized to CoO by formed H2O [30], resulting in the absence of surface Co phase in the recycled catalysts as displayed in the XPS and H2-TPR results (Figure S3). As reported, the formation of surface CoO might be beneficial to the adsorption of acidic CO2 molecules [31], which consequently enhanced the activity. From SEM images, it was found that a certain amount of carbon nanofibers was formed during reaction for the Co-400R-S catalyst, which was consistent with the observation in previous work [9], where catalytic decomposition of CH4 to carbon was more favorable at higher temperature. However, there was no carbon nanofiber formation, and the coarsening of ligaments could be observed for the Co-600R-S catalyst. This might be related to the low content of CH4 in the reaction atmosphere (Figure 2b, lowest selectivity of CH4 for the Co-600R catalyst). Moreover, the coarsening of ligaments might lead to the decline of activity for the decomposition of CH4. The activity of the Co-400R and Co-600R catalysts was gradually declined in the stability testing at high reaction temperature, while a great stability for the Co-400R catalyst at the relatively low reaction temperature (400 °C) was observed as shown in Figure 2c. This might be related to the low degree of reconstitution and carbon formation, which needs to be further confirmed.

Figure 2. Catalytic performance and stability of the NP-Co catalysts in RWGS reaction. (a) Catalytic performance of the Co-400R catalyst at different temperature; (b,c) the stability of the NP-Co catalysts with different pretreatments at different temperatures (reaction conditions: Atmospheric pressure, H2/CO2 = 1:1, weight hourly space velocity (WHSV) = 300,000 mL/g/h); (d) illustration of the NP-Co catalysts structure changes in pretreatment and reaction; (e) SEM images of the recycled NP-Co catalysts.
Combined with the characterization of the recycled catalysts, the difference of stability could be explained as shown in Figure 2d. In the case of the Co-600R catalyst, the surface restructuring of it occurred at high reduction temperature, resulting in a decrease in methanation activity and production of CH$_4$. Afterward, gradual coarsening of ligaments in reaction became the main reason for poor stability. Better stability was achieved for the Co-400R catalyst compared to the Co-600R catalyst, but a large amount of carbon nanofibers was formed, leading to the coverage of active sites and decline of activity. Moreover, the formation of carbon nanofibers could also not efficiently restrain the coarsening of ligaments. At low reaction temperature, the ligament coarsening of the NP-Co catalyst and the formation of carbon on it were suppressed, leading to a great stability, while the selectivity of CO$_2$ hydrogenation was relatively low. Thus, enhancing the selectivity of CO$_2$ hydrogenation with high activity at low temperature is the aim for developing novel NP-Co-based catalysts.

3. Materials and Methods

3.1. Catalyst Preparation

High-purity Co and Al (Co:Al = 15:85) ingots (99.99 wt.%, Zhongnuoxincai, Beijing, China) were smelted in a high-frequency vacuum induction furnace and the alloy melts were transferred through gravity pouring onto a single copper roller with a rotation speed of 3000 r/min. Afterward, the obtained ribbons were further treated by the dealloying strategy in 10% NaOH solution containing NaBH$_4$ at 25 °C for 24 h until no bubbles were released. At last, the product was washed with deionized water, and dried in a vacuum oven at 60 °C for 24 h. Before reaction, the NP-Co catalyst was in situ pretreated in 10% H$_2$/Ar (50 mL/min) at 400 °C or 600 °C for 2 h, which was defined as the Co-400R or Co-600R catalyst. After reaction at 600 °C, the recycled catalysts were defined as the Co-400R-S and Co-600R-S catalyst. In addition, the Co-400R-S1 catalyst was obtained after reaction at 400 °C for the Co-400R catalyst.

3.2. Catalyst Characterization

A SmartLab 9 KW diffractometer equipped with a Cu Kα monochromatized radiation source (λ = 1.5418 Å) was employed for collecting the powder X-ray diffraction (XRD, Rigaku, Tokyo, Japan) data, which was operated at 40 KV and 30 mA. The morphology of samples was observed by scanning electron microscopy (SEM, FEI Verios 460L, FEI, Hillsboro, OR, USA) equipped with an X-ray energy dispersive spectroscope (EDS).

Using a Quantachrome Instruments Autosorb-iQ-C automated gas sorption analyzer (Boynton Beach, FL, USA), the nitrogen adsorption–desorption isotherms were measured by static N$_2$ physisorption at 77 K. The specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method.

Hydrogen temperature-programmed reduction (H$_2$-TPR) of the samples was carried out in a stream of 10% H$_2$/Ar with a flowing rate of 50 mL/min at 400 °C or 600 °C for 2 h. A pretreatment was conducted at 200 °C in Ar for 2 h before analysis. Subsequently the TPR analysis was performed from room temperature to 800 °C with a heating rate of 10 °C/min. The amount of the hydrogen consumption during the reduction was estimated with a thermal conductivity detector.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a ThermoFisher ESCALAB 250Xi (Waltham, MA, USA). A monochromatic Al Kα (1486.6 eV) X-ray source was used as incident radiation. For making overall energy resolution better than 0.5 eV, the analyzer slit was set to 0.4 mm and a pass energy of 200 eV was used. The binding energies were calibrated using the C1s peak at 285 eV as a reference. Based on a mixed Gaussian/Lorentzian peak shape, the experimental data are analyzed by a Shirley-type background and a nonlinear least-squares fitting.
3.3. Activity Tests

The catalytic performance evaluation was performed in a continuous-flow fixed-bed quartz reactor at atmospheric pressure. Ten milligrams of NP-Co catalyst (40–60 mesh) diluted with SiO$_2$ (190 mg) was placed in the quartz tube reactor with an inner diameter of 10 mm. After pretreatment, the catalysts were exposed to the feed gas (a stream of H$_2$/CO$_2$/Ar (40/40/20 vol.%) at 50 mL/min). The weight hourly space velocity (WHSV) was calculated on the basis of total flow rate. At each temperature, the products were analyzed after 30 min of steady-state reaction. The product was analyzed by using a gas chromatograph (Agilent 7890B) with an FID (Flame Ionization Detector) and two TCD (Thermal Conductivity Detector) detectors. The conversion of CO$_2$ and CO selectivity was defined as follows:

$$\text{CO}_2 \text{ conversion} = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100\%$$

$$\text{CO selectivity} = \frac{[\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{out}} + [\text{CH}_4]_{\text{out}}} \times 100\%$$

4. Conclusions

In summary, the support-free nanoporous Co catalyst with an open bicontinuous network structure and hierarchical pores was prepared by dealloying. Due to high surface area and abundant surface coordination unsaturated atoms, it exhibited excellent performance in the RWGS reaction. The decline of activity in stability testing was mainly due to the surface reconstruction and coarsening of ligaments at high temperature. Meanwhile, a certain amount of carbon nanofibers was formed during reaction, which was originated from the catalytic decomposition of CH$_4$. Nevertheless, these could be restrained, and a great stability was obtained at relative low reaction temperature. In short, the synthesis of NP-Co catalysts provides a promising route for developing other catalysts with high reactivity in CO$_2$ hydrogenation.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/5/423/s1, Figure S1: XRD patterns of the recycled NP-Co catalysts, Figure S2: XPS spectra of Co 2p for the recycled NP-Co catalysts, Figure S3: H$_2$-TPR profile of the Co-400R-S1 catalyst.

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References

1. Porosoff, M.D.; Yan, B.; Chen, J.G. Catalytic reduction of CO$_2$ by H$_2$ for synthesis of CO, methanol and hydrocarbons: Challenges and opportunities. *Energy Environ. Sci.* **2016**, *9*, 62–73. [CrossRef]
2. Daza, Y.A.; Kuhn, J.N. CO$_2$ conversion by reverse water gas shift catalysis: Comparison of catalysts, mechanisms and their consequences for CO$_2$ conversion to liquid fuels. *RSC Adv.* **2016**, *6*, 49675–49691. [CrossRef]
3. Saeidi, S.; Amin, N.A.S.; Rahimpour, M.R. Hydrogenation of CO$_2$ to value-added products—A review and potential future developments. *J. CO$_2$ Util.* **2014**, *5*, 66–81. [CrossRef]
4. Yang, X.; Su, X.; Chen, X.; Duan, H.; Liang, B.; Liu, Q.; Liu, X.; Ren, Y.; Huang, Y.; Zhang, T. Promotion effects of potassium on the activity and selectivity of Pt/zeolite catalysts for reverse water gas shift reaction. *Appl. Catal. B Environ.* **2017**, *216*, 95–105. [CrossRef]
5. Kwak, J.H.; Kovarik, L.; Szanyi, J. Heterogeneous catalysis on atomically dispersed supported metals: CO$_2$ reduction on multifunctional Pd catalysts. *ACS Catal.* **2013**, *3*, 2094–2100. [CrossRef]
6. Xu, H.; Li, Y.; Luo, X.; Xu, Z.; Ge, J. Monodispersed gold nanoparticles supported on a zirconium-based porous metal-organic framework and their high catalytic ability for the reverse water-gas shift reaction. *Chem. Commun.* 2017, 53, 7953–7956. [CrossRef] [PubMed]

7. Ronda-Lloret, M.; Rico-Frances, S.; Sepulveda-Escribano, A.; Ramos-Fernandez, E.V. CuOx/CeO2 catalyst derived from metal organic framework for reverse water-gas shift reaction. *Appl. Catal. A Gen.* 2018, 562, 28–36. [CrossRef]

8. Gonçalves, R.V.; Vono, L.L.R.; Wojcieszak, R.; Dias, C.S.B.; Wender, H.; Teixeira-Neto, E.; Rossi, L.M. Selective hydrogenation of CO2 into CO on a highly dispersed nickel catalyst obtained by magnetron sputtering deposition: A step towards liquid fuels. *Appl. Catal. B Environ.* 2017, 209, 240–246. [CrossRef]

9. Wang, L.; Liu, H.; Chen, Y.; Yang, S. Reverse water-gas shift reaction over co-precipitated Co-CeO2 catalysts: Effect of Co content on selectivity and carbon formation. *Int. J. Hydrog. Energy* 2017, 42, 3682–3689. [CrossRef]

10. Fishman, Z.S.; He, Y.; Yang, K.R.; Lounsbury, A.W.; Zhu, J.; Tran, T.M.; Zimmerman, J.B.; Batista, V.S.; Wojcieszak, R.; Dias, C.S.B.; Wender, H.; Teixeira-Neto, E.; Rossi, L.M. Selective hydrogenation of CO2 to CO conversion: Via the reverse water-gas shift reaction. *MRS Bull.* 2017, 42(9), 12984–12995. [CrossRef] [PubMed]

11. Liu, X.; Kunkel, C.; Ramirez De La Piscina, P.; Homs, N.; Viñes, F.; Illas, F. Effective and Highly Selective CO Generation from CO2 Using a Polycrystalline α-Mo2C Catalyst. *ACS Catal.* 2017, 7, 4323–4335. [CrossRef]

12. Kim, D.H.; Park, J.L.; Park, E.J.; Kim, Y.D.; Uhm, S. Dopant Effect of Barium Zirconate-Based Perovskite-Type Catalysts for the Intermediate-Temperature Reverse Water Gas Shift Reaction. *ACS Catal.* 2014, 4, 3117–3122. [CrossRef]

13. Dai, B.; Zhou, G.; Ge, S.; Xie, H.; Jiao, Z.; Zhang, G.; Xiong, K. CO2 reverse water-gas shift reaction on mesoporous M-Co2O3 catalysts. *Can. J. Chem. Eng.* 2017, 95, 634–642. [CrossRef]

14. Zhou, G.; Wu, T.; Xie, H.; Zheng, X. Effects of structure on the carbon dioxide methanation performance of Co-based catalysts. *Int. J. Hydrog. Energy* 2013, 38, 10012–10018. [CrossRef]

15. Diez-Ramirez, J.; Sánchez, P.; Kyriakou, V.; Zafeiratos, S.; Marnellos, G.E.; Konsolakis, M.; Dorado, F. Effect of support nature on the cobalt-catalyzed CO2 hydrogenation. *J. CO Util.* 2017, 21, 562–571. [CrossRef]

16. Wang, L.; Liu, H. Mesoporous Co-CeO2 catalyst prepared by colloidal solution combustion method for reverse water-gas shift reaction. *Catal. Today* 2018, 316, 155–161. [CrossRef]

17. Chen, Q.; Ding, Y.; Chen, M. Nanoporous metal by dealloying for electrochemical energy conversion and storage. *MRS Bull.* 2018, 43, 43–48. [CrossRef]

18. Prieto, G.; Martínez, A.; Concepción, P.; Moreno-Tost, R. Cobalt particle size effects in Fischer-Tropsch synthesis: Structural and in situ spectroscopic characterisation on reverse micelle-synthesised Co/ITQ-2 model catalysts. *J. Catal.* 2009, 266, 129–144. [CrossRef]

19. Wang, F.; Zhang, L.; Xu, L.; Deng, Z.; Shi, W. Low temperature CO oxidation and CH4 combustion over Co3O4 nanosheets. *Fuel* 2017, 203, 419–429. [CrossRef]

20. Ibrahim, M.; Marcelot-Garcia, C.; Ait Atmane, K.; Berrichi, E.; Lacroix, L.M.; Zwick, A.; Warot-Fonrose, B.; Lachaize, S.; Decorse, P.; Piquemal, J.Y.; et al. Carbon coating, carburization, and high-temperature stability improvement of cobalt nanorods. *J. Phys. Chem. C* 2013, 117, 15808–15816. [CrossRef]

21. Su, X.; Xu, J.; Liang, B.; Duan, H.; Hou, B.; Huang, Y. Catalytic carbon dioxide hydrogenation to methane: A review of recent studies. *J. Energy Chem.* 2016, 25, 553–565. [CrossRef]

22. Panaritis, C.; Edake, M.; Courillard, M.; Einakchi, R.; Baranova, E.A. Insight towards the role of ceria-based supports for reverse water gas shift reaction over RuFe nanoparticles. *J. CO2 Util.* 2018, 26, 350–358. [CrossRef]

23. Liang, B.; Duan, H.; Su, X.; Chen, X.; Huang, Y.; Chen, X.; Delgado, J.J.; Zhang, T. Promoting role of potassium in the reverse water gas shift reaction on Pt/mullite catalyst. *Catal. Today* 2017, 281, 319–326. [CrossRef]

24. Ye, J.; Ge, Q.; Liu, C.J. Effect of PdIn bimetallic particle formation on CO2 reduction over the Pd-In/SiO2 catalyst. *Chem. Eng. Sci.* 2015, 135, 193–201. [CrossRef]

25. Zhu, X.; Qu, X.; Li, X.; Liu, J.; Liu, J.; Zhu, B.; Shi, C. Selective reduction of carbon dioxide to carbon monoxide over Au/Co3O4 catalyst and identification of reaction intermediate. *Chin. J. Catal.* 2016, 37, 2053–2058. [CrossRef]

26. Chen, C.S.; Cheng, W.H.; Lin, S.S. Study of iron-promoted Cu/SiO2 catalyst on high temperature reverse water gas shift reaction. *Appl. Catal. A Gen.* 2004, 257, 97–106. [CrossRef]
27. Zhang, X.; Zhu, X.; Lin, L.; Yao, S.; Zhang, M.; Liu, X.; Wang, X.; Li, Y.W.; Shi, C.; Ma, D. Highly Dispersed Copper over $\beta$-Mo$_2$C as an Efficient and Stable Catalyst for the Reverse Water Gas Shift (RWGS) Reaction. *ACS Catal.* **2017**, *7*, 912–918. [CrossRef]

28. Zugic, B.; Wang, L.; Heine, C.; Zakharov, D.N.; Lechner, B.A.J.; Stach, E.A.; Biener, J.; Salmeron, M.; Madix, R.J.; Friend, C.M. Dynamic restructuring drives catalytic activity on nanoporous gold-silver alloy catalysts. *Nat. Mater.* **2016**, *16*, 558–564. [CrossRef]

29. Biener, M.M.; Biener, J.; Wichmann, A.; Wittstock, A.; Baumann, T.F.; Bäumer, M.; Hamza, A.V. ALD Functionalized Nanoporous Gold: Thermal Stability, Mechanical Properties, and Catalytic Activity. *Nano Lett.* **2011**, *11*, 3085–3090. [CrossRef]

30. Jacobs, G.; Patterson, P.M.; Das, T.K.; Luo, M.; Davis, B.H. Fischer-Tropsch synthesis: Effect of water on Co/Al$_2$O$_3$ catalysts and XAFS characterization of reoxidation phenomena. *Appl. Catal. A Gen.* **2004**, *270*, 65–76. [CrossRef]

31. Yin, G.; Yuan, X.; Du, X.; Zhao, W.; Bi, Q.; Huang, F. Efficient Reduction of CO$_2$ to CO Using Cobalt–Cobalt Oxide Core–Shell Catalysts. *Chem. Eur. J.* **2018**, *24*, 2157–2163. [CrossRef] [PubMed]