

Article

Formic Acid Modified Co_3O_4 - CeO_2 Catalysts for CO Oxidation

Ruishu Shang ^{1,†}, Yiping Duan ^{1,†}, Xinyan Zhong ¹, Wei Xie ¹, Yan Luo ¹ and Lihong Huang ^{1,2,*}

¹ Department of Chemical and Pharmaceutical Engineering, Chengdu University of Technology, Chengdu 610059, China; shangruishu0917@163.com (R.S.); duanyipingyznu@163.com (Y.D.); xinyan_zhong@yahoo.com (X.Z.); xiewei0403@yahoo.com (W.X.); luoyan0419@yahoo.com (Y.L.)

² Richard G. Lugar Center for Renewable Energy, Indiana University-Purdue University, Indianapolis, IN 46224, USA

* Correspondence: huanglihong06@cdut.cn or lihhuang@iupui.edu; Tel.: +86-28-84078939; Fax: +86-28-84079074

† These authors contributed equally to this work.

Academic Editor: Keith Hohn

Received: 13 January 2016; Accepted: 10 March 2016; Published: 17 March 2016

Abstract: A formic acid modified catalyst, Co_3O_4 - CeO_2 , was prepared via facile urea-hydrothermal method and applied in CO oxidation. The Co_3O_4 - CeO_2 -0.5 catalyst, treated by formic acid at 0.5 mol/L, performed better in CO oxidation with T_{50} obtained at 69.5 °C and T_{100} obtained at 150 °C, respectively. The characterization results indicate that after treating with formic acid, there is a more porous structure within the Co_3O_4 - CeO_2 catalyst; meanwhile, despite of the slightly decreased content of Co, there are more adsorption sites exposed by acid treatment, as suggested by CO-TPD and H_2 -TPD, which explains the improvement of catalytic performance.

Keywords: Co_3O_4 - CeO_2 catalyst; urea-hydrothermal synthesis; CO oxidation; formic acid treatment

1. Introduction

Removal of CO has been studied extensively because CO is toxic and poses health concerns in fields of exhaust emission control and air purifications. Low temperature oxidation of carbon monoxide is considered to be the most efficient and cost-effective method for removal of CO [1,2].

For CO oxidation at low temperature, catalyst with high activity is a key factor. Noble metal catalysts, such as Pt, Ru, Rh, Au, *etc.*, show high activity and stability in CO oxidation [2]. However, the high cost of noble materials is a concern. As alternatives, transition metal oxides and their mixed oxides have then been studied for CO oxidation, such as MnO_x and CuO-CeO_2 [3,4].

Among the transition metal oxides, Co_3O_4 has been studied in the field of air pollution control, and has also been considered as a promising non-noble metal oxide catalysts for CO oxidation [2]. Meanwhile, in oxidation processes, CeO_2 is widely used for its abundant oxygen vacancy defects, oxygen storage capacity, and its redox property [5,6]; even in a lean oxygen atmosphere, CeO_2 can release oxygen and produce oxygen vacancy via the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle [2,7].

It is reported that the core@shell structure with a high interface area of Co_3O_4 - CeO_2 can be an effective way to improve catalytic performance, such as $\text{Co}_3\text{O}_4@\text{CeO}_2$ core@shell cubes with optimized CeO_2 shell thickness, which produced a 100% conversion of CO at 190 °C in CO oxidation tests, as reported by Zhen *et al.* [2]. The relatively low activity of the $\text{Co}_3\text{O}_4@\text{CeO}_2$ catalysts can be attributed to the large particle size (about 300 nm) and the coating shell of CeO_2 , which constrains the diffusion of reactants to core of Co_3O_4 [8].

Meanwhile, with respect to synthesis strategy, hydrothermal synthesis is an efficient approach to prepare porous materials [9], while additives, such as urea, are helpful to synthesize well

crystallized particles [10,11]. In the urea-hydrothermal synthesis process, ultrasonics can be also employed for the improvement of dispersion via cavitation bubbles produced to agitate materials from agglomeration [12].

Herein, a facile method using urea-hydrothermal synthesis was used to fabricate composite structures of $\text{Co}_3\text{O}_4\text{-CeO}_2$ with a smaller particle size and high surface area to address the concerns of the core@shell structure. The obtained $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalyst was further treated using formic acid to modify the composite structure and facilitate the diffusion of reactants, and was then tested in CO oxidation. To the best of the authors' knowledge, this formic-acid-treated $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalyst for CO oxidation has not been reported. The relationship between structure-reactivity has also been studied using characterizations of XRD, TPR, HRTEM, XPS, BET, ICP-AES, CO-TPD, and H_2 -TPD. The prepared composite catalysts were listed in Table 1, in which the catalysts of $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$ and $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-1.0}$ were treated using formic acid with 0.5 mol/L and 1.0 mol/L, respectively; meanwhile, for comparison, the Co_3O_4 catalyst was tested in CO oxidation as well.

Table 1. The list of the $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts as prepared.

Catalysts	Surface Area, m ² /g	Average Pore Volume, mL/g	Average Pore Size, nm	Particle Size		Co ₃ O ₄ Content, wt % ^c
				Estimated by XRD, nm		
				Precursors ^a	Calcined ^b	
CeO ₂	79.8	0.087	4.4	26.2	20.7	-
Co ₃ O ₄	19.3	0.064	12.7	19.4	29.0	-
Co ₃ O ₄ -CeO ₂	53.0	0.126	8.9	16.4	23.9	52.00
Co ₃ O ₄ -CeO ₂ -0.5	68.3	0.146	8.1	15.8	23.6	42.74
Co ₃ O ₄ -CeO ₂ -1.0	73.4	0.142	7.2	16.6	23.8	37.56

^a Estimated by the peak near 20.5 degree of $\text{CoO}(\text{OH})$; ^b Estimated by the peak near 37.0 degree of Co_3O_4 ;

^c Determined by ICP-AES.

2. Results and Discussion

2.1. Catalytic Performance Tests

To evaluate the catalytic activities, CO oxidation experiments were conducted. As shown in Figure 1, over CeO_2 , only 20.5% of CO was oxidized at 250 °C, suggesting that CeO_2 was not active for CO oxidation at low temperatures. For Co_3O_4 , the temperature at 50% of CO conversion (T_{50}) was 137.3 °C, while the conversion of CO reached 98% at 250 °C. By contrast, the catalyst of $\text{Co}_3\text{O}_4\text{-CeO}_2$ showed improved catalytic activity: T_{50} was obtained at 75.4 °C, while T_{100} was recorded at 200 °C. After treatment with formic acid, the $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$ catalyst produced T_{50} of 69.5 °C and T_{100} of 150 °C, respectively; this activity is higher than the $\text{Co}_3\text{O}_4\text{-CeO}_2$ core@shell catalysts with optimized CeO_2 shell thickness, which produced a 100% conversion of CO (T_{100}) at 190 °C, as shown by Zhen *et al.* [2]. Similar higher activity was also obtained for 25 mg of $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$ for CO oxidation, as listed in Figure S2. Meanwhile, for $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-1.0}$, T_{50} was increased slightly to 79.7 °C and T_{100} was recorded at 225 °C. The higher activity observed for the $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$ catalyst suggests that there could be variation in the textures and structures using treating with formic acid, and need to be confirmed.

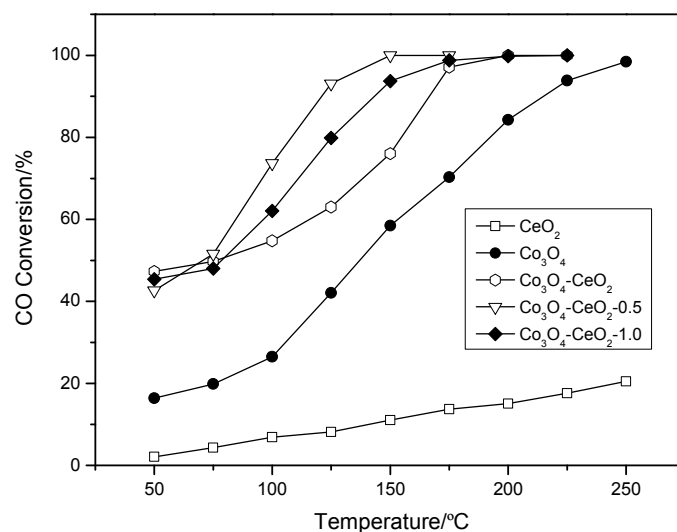


Figure 1. CO conversions over Co-based catalysts.

The stability test on the Co₃O₄-CeO₂-0.5 catalyst was conducted at 150 °C for 30 h, as listed in Figure S1. The results showed that the conversion of CO was recorded near 100% for 18 h, and then dropped slightly and remained stable near 97%, suggesting that the Co₃O₄-CeO₂-0.5 catalyst was stable for CO oxidation.

2.2. Characterizations

2.2.1. XRD

To investigate the structures using processes of urea-hydrothermal synthesis, loading of CeO₂, and acid treatment, the precursors and oxides of these Co-based catalysts were scanned using XRD.

As shown in Figure 2A, there are two main structures in the precursors of catalysts, after hydrothermal synthesis and before calcination. The peaks at 20.3°, 37.1°, 39.2°, 50.7°, 65.4°, and 69.1° can be assigned to reflections of CoO(OH) (PDF#: 07-0169) in the precursors of Co₃O₄ (Line 1 in Figure 2A). For the other precursors catalysts with CeO₂, peaks emerged at 28.5°, 33.0°, 47.4°, and 56.3° can be assigned to CeO₂ (PDF#: 34-0394), while the peaks of CoO(OH) became weaker with treatment using formic acid. The particle sizes of CoO(OH) in the Co₃O₄-CeO₂ precursors were estimated, which varied within 15.6–16.8 nm, as shown in Table 1.

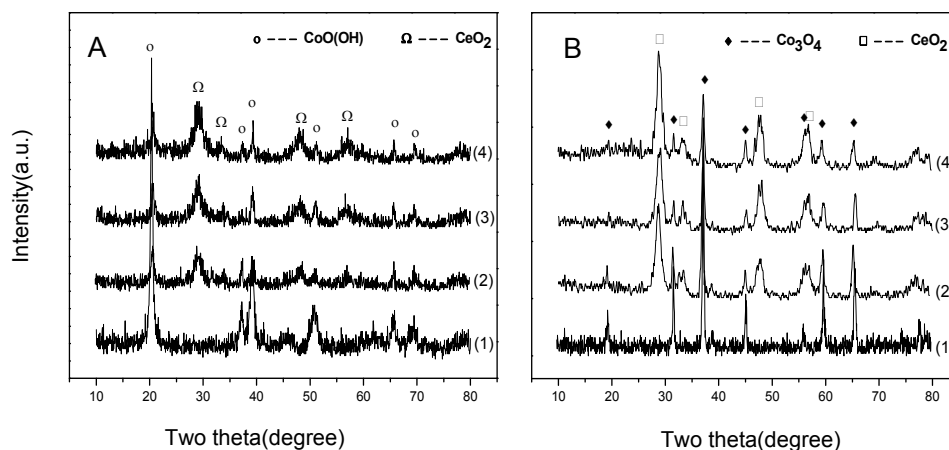


Figure 2. XRD patterns of (A) precursors; (B) calcined catalysts of (1) Co₃O₄; (2) Co₃O₄-CeO₂; (3) Co₃O₄-CeO₂-0.5; and (4) Co₃O₄-CeO₂-1.0.

For the catalysts after calcination and treatment with formic acid, as shown in Figure 2B, peaks of CeO_2 were found, and the species of $\text{CoO}(\text{OH})$ was transformed into Co_3O_4 near 19.1° , 31.4° , 36.9° , 45° , 59.6° , and 65.5° [2], suggesting that there could be two separate phases of CeO_2 and Co_3O_4 . Meanwhile, the peaks of Co_3O_4 became weak with treatment using formic acid, and particle size varied within 23.6–23.9 nm, as shown in Table 1.

2.2.2. HRTEM

HRTEM was employed to confirm the two phases. As shown in Figure 3A, two phases can be found using HRTEM. In Figure 3B, by measuring the lattice distance, the lattice distances of 0.27 nm and 0.31 nm can be indexed into the faces of (200) and (111) of CeO_2 , respectively; in Figure 3C, the lattice distance of 0.28 nm can be indexed into the face of (220) in Co_3O_4 [13,14]. This is consistent with the two phases of Co_3O_4 and CeO_2 using XRD (Figure 2B).

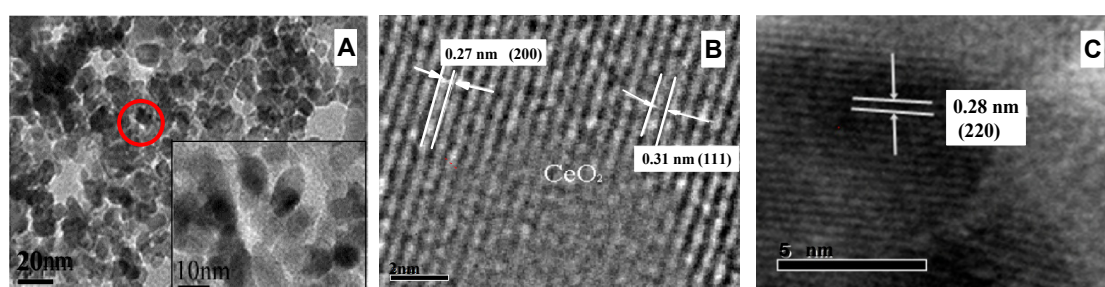


Figure 3. HR-TEM images of (A), Co_3O_4 - CeO_2 catalyst; (B,C), enlarged part from (A).

2.2.3. ICP-AES

ICP-AES was used to measure the weight percentage of Co_3O_4 before and after formic acid treatment. As shown in Table 1, the weight percentage of Co_3O_4 decreased with increasing concentration of formic acid, and is consistent with the weakened peaks of Co_3O_4 from XRD measurements (Figure 2B), suggesting that the acid treatment leads to a dissolving of Co_3O_4 and may result in variation of the textures of these catalysts.

2.2.4. N_2 Physisorption

To investigate the textual properties of these catalysts, N_2 adsorption–desorption isotherms experiments were recorded, while the surface area (SA), pore size, and pore volume of these Co-based oxide catalysts were measured using the BET method and the BJH method. It can be observed that there are hysteresis loops in the adsorption isotherms in Figure 4, and the average pore size falls into a mesoporous range of 7.2–8.9 nm (Table 1). After treatment using formic acid, the SA increases from $53.0 \text{ m}^2/\text{g}$ for Co_3O_4 - CeO_2 to $68.3 \text{ m}^2/\text{g}$ for Co_3O_4 - CeO_2 -0.5 and $73.4 \text{ m}^2/\text{g}$ for Co_3O_4 - CeO_2 -1.0; concurrently, the pore volume increases from 0.126 mL/g for Co_3O_4 - CeO_2 to 0.146 mL/g for Co_3O_4 - CeO_2 -0.5, suggesting that, with formic acid treatment, the Co_3O_4 - CeO_2 catalysts became more porous, which can be attributed to the dissolving of Co species during formic acid treatment, as suggested by ICP-AES.

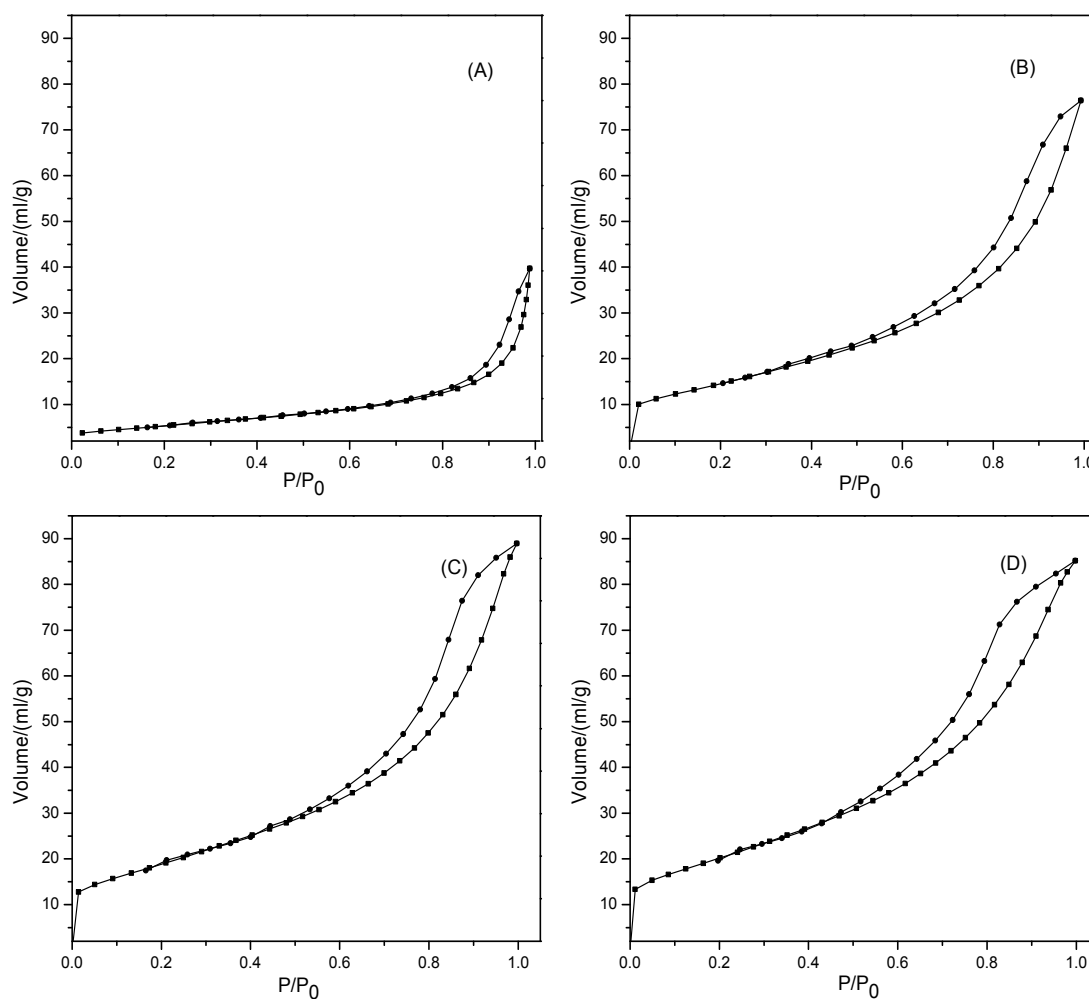


Figure 4. N_2 adsorption–desorption isotherms for catalysts of (A) Co_3O_4 ; (B) $Co_3O_4-CeO_2$; (C) $Co_3O_4-CeO_2-0.5$; and (D) $Co_3O_4-CeO_2-1.0$.

2.2.5. Temperature-Programmed Reduction (TPR)

To study the reduction properties of these $Co_3O_4-CeO_2$ catalysts, temperature-programmed reduction (TPR) was conducted. As shown in Figure 5 (A1), the pure CeO_2 showed two weak reduction peaks at 524 °C and 896 °C, which can be attributed to the reduction of surface and bulk species of CeO_2 , respectively [15]. For the Co-based catalysts, the reduction peak near 350 °C and 500 °C can be attributed to the reduction from Co^{3+} to Co^{2+} and to Co^0 , respectively [13,16]. For the $Co_3O_4-CeO_2$ catalyst, the reduction peaks become weak, while shoulder peaks can be found near 600 °C, which can be attributed to the interaction between Co and Ce [17]. For catalysts treated with formic acid, the reduction peaks become weaker, suggesting that the content of Co species decreased and is consistent with the results of ICP-AES; meanwhile, the reduction peaks move to lower temperatures, which can be attributed to the porous structures and higher surface areas, as suggested by BET.

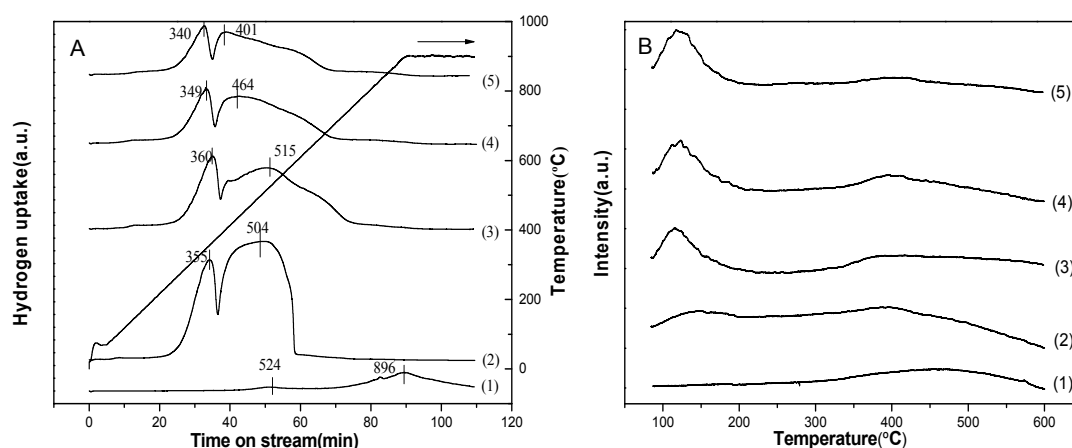


Figure 5. TPR profiles (A) and CO-TPD (B) profiles of the calcined catalysts: (1) CeO_2 in TPR or blank in TPD; (2) Co_3O_4 ; (3) $\text{Co}_3\text{O}_4\text{-CeO}_2$; (4) $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$; (5) $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-1.0}$.

2.2.6. X-ray Photoelectron Spectra (XPS)

To find the valence state of the Co and Ce species, XPS was recorded. As shown in Figure 6A–C, for the Co 2p spectra, there is a main peak at 779.9 eV, which can be assigned to the species of Co^{2+} and Co^{3+} [18], while the satellite peak at 782.2 eV can be attributed to the Co^{2+} species [19], suggesting that the Co species mainly exist as Co_3O_4 , and this is consistent with the results from XRD. In Figure 6D,E for Ce 3d spectra, the peaks near 882.5 eV, 898.1 eV, 901.0 eV, and 916.5 eV can be attributed to Ce^{3+} of Ce 3d_{5/2}, while the peaks near 888.0 eV and 906.8 eV can be attributed to Ce^{4+} of Ce 3d_{3/2} [20,21]. The XPS results confirm the species of Co_3O_4 and CeO_2 in these $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts.

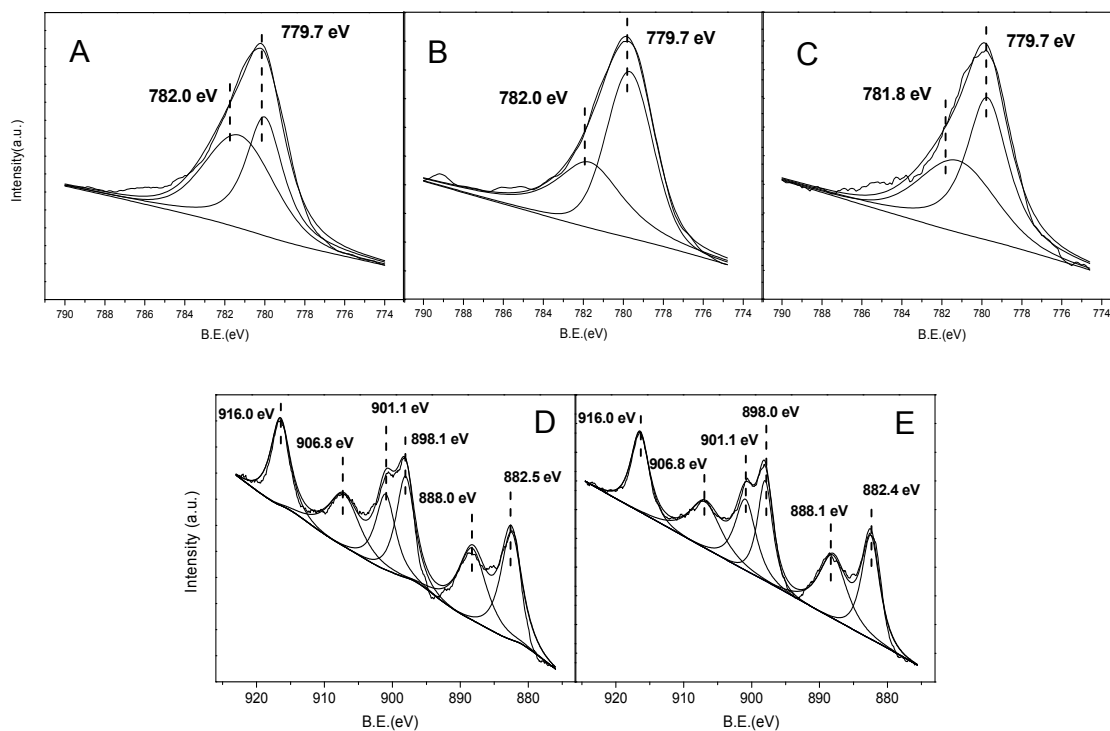


Figure 6. XPS of Co-based catalysts: Co_{2p} of (A) Co_3O_4 , (B) $\text{Co}_3\text{O}_4\text{-CeO}_2$, and (C) $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$; Ce_{3d} of (D) $\text{Co}_3\text{O}_4\text{-CeO}_2$ and (E) $\text{Co}_3\text{O}_4\text{-CeO}_2\text{-0.5}$.

2.2.7. Temperature-Programmed Desorption (TPD) of CO

To find the adsorption properties of CO for these core-shell catalysts, CO-TPD was carried out. As shown in Figure 5B, there is a weak CO desorption peak near 150 °C for Co₃O₄ [22]. For the Co₃O₄-CeO₂ catalyst, the peak of CO desorption intensifies, suggesting that the addition of CeO₂ was helpful to increase CO adsorption capacity. After treatment using formic acid, the peak of CO desorption becomes stronger, suggesting that there were more adsorption sites exposed by formic acid.

The spent catalysts were scanned using XRD and XPS, as shown in Figures S3 and S4. There are no obvious differences in terms of intensities, binding energies, and particle size, indicating that these Co₃O₄-CeO₂ catalysts were stable during CO oxidation, and are consistent with the stability in CO oxidation.

2.2.8. Temperature-Programmed Desorption (TPD) of H₂

H₂-TPD was conducted and used to measure the H₂ adsorption behavior of these cobalt-based catalysts. As shown in Table S1, the hydrogen adsorption amount of Co₃O₄ was recorded near 0.120 mmol/g-catalyst; with the promotion of CeO₂ in Co₃O₄-CeO₂, the adsorption amount increased and reached 0.191 mmol/g-catalyst. After treatment using formic acid in Co₃O₄-CeO₂-0.5, there is a high hydrogen adsorption near 0.382 mmol/g-catalyst, indicating that there are more adsorption sites created using formic acid treatment with a high surface area and pore volume. Over Co₃O₄-CeO₂-1.0 with a higher formic acid amount at 1.0 mol/L, the hydrogen adsorption amount dropped slightly to 0.349 mmol/g-catalyst, which can be attributed to the dissolving of Co species and loss of adsorption sites. The H₂ adsorption sites can be related to the active sites for CO oxidation, and were then used to calculate TOFs at 50 °C [23]. As shown in Table S1, similar to the hydrogen adsorption, the highest TOF at 50 °C was observed for Co₃O₄-CeO₂-0.5, while the corresponding specific reaction rate was recorded near 64.353 mol_{CO} h⁻¹ g_{catalyst}⁻¹. According to the activity results of Co₃O₄-CeO₂-0.5, the treatment using formic acid created more porous structures with higher surface areas and more active sites, thus, the activity was improved. Meanwhile, the decrease of activity for Co₃O₄-CeO₂-1.0 can be attributed to the dissolving of Co species and the loss of active sites.

2.3. Discussion

Based on the reaction results, the CeO₂ catalyst possesses a very weak adsorption capacity, as suggested by CO-TPD, and transformed only 15.6% of CO at 250 °C, suggesting that CeO₂ alone was not active for CO oxidation at low temperatures.

For the Co₃O₄ catalyst, because of the low surface area at 19.3 m²/g, there was a weak CO adsorption peak, suggesting there was a small amount of active sites within the Co₃O₄ catalyst. As a result, T₅₀ was recorded at 137.3 °C, and the CO conversion only reached 93% at 250 °C in the test range of 50–250 °C.

For the catalyst of Co₃O₄-CeO₂, the surface area increased to 53.0 m²/g; meanwhile, the results of CO-TPD indicate that the capacity for CO adsorption was increased, suggesting that there were more active sites consisting of Co and CeO₂ with redox capacity for CO and O₂ activation. As a result, T₅₀ and T₁₀₀ were obtained around 74.8 °C and 250 °C.

With formic acid treatment at 0.5 mol/L for the Co₃O₄-CeO₂-0.5 catalyst, because of the dissolving of Co species, the composite structure became more porous with a higher surface area and pore volume, as indicated by N₂ physisorption; meanwhile, despite the decreased content of Co, the CO adsorption capacity was increased, suggesting that there could be more active sites exposed by acid treatment, as indicated by CO-TPD and H₂-TPD. As a result, the reactivity was further increased: T₅₀ and T₁₀₀ were obtained close to 68.5 °C and 150 °C, respectively. These species remained stable, as suggested by the XRD and XPS for the spent catalyst.

For the Co₃O₄-CeO₂-1.0 catalyst treated with a higher concentration of formic acid at 1.0 mol/L, the content of Co further decreased via the dissolving of Co₃O₄ and the loss of active sites, as suggested

by ICP-AES, XRD, H₂-TPD, CO-TPD, and TPR; despite the slight increase of surface area and pore volume, the reactivity was slightly decreased, with the T_{50} and T_{100} recorded near 83.5 °C and 200 °C, respectively.

3. Experimental Section

3.1. Catalysts Preparation

All chemicals were AR and purchased from KESHI Chemicals (Chengdu, China).

3.1.1. Synthesis of Co₃O₄

Co₃O₄ was synthesized using the urea-hydrothermal method. Aqueous solutions of Co(NO₃)₂·6H₂O:(NH₂)₂CO = 1:9 (molar) were firstly prepared at pH = 12 with NaOH as a pH adjuster. The obtained mixture was then transferred to an autoclave and remained at 180 °C in an oven for 12 h, then it was filtered and washed with deionized water three times.

3.1.2. Synthesis of CeO₂

CeO₂ was prepared using the same procedure described in Section 3.1.1. with Ce(NO₃)₃·6H₂O as reagent.

3.1.3. Synthesis of Co₃O₄-CeO₂

The cobalt precipitate obtained in Section 3.1.1 was ultrasonically dispersed in a mixed solution of ethanol:water = 1 (volume). Then an aqueous solution of Ce(NO₃)₃·6H₂O:CTAB = 1:0.2 (molar) was added to the former solution at Co₃O₄:Ce(NO₃)₃·6H₂O = 4:1 (molar) with pH = 12, stirred at 70 °C for 12 h in an ultrasonic bath, and then filtered and washed with deionized water three times.

3.1.4. Treatment with Formic Acid

The precipitate obtained in Section 3.1.3 was treated with a formic acid solution at 0.5 mol/L and 1.0 mol/L, respectively, for 30 min, and then filtered and washed with deionized water three times. The obtained oxides are denoted as Co₃O₄-CeO₂-0.5 and Co₃O₄-CeO₂-1.0, respectively.

All the precipitates obtained in the previous sections were dried at 105 °C for 12 h and calcined at 500 °C for 4 h in air, and are listed in Table 1.

3.2. Catalytic Performance Evaluation

The CO oxidation test was conducted in a fixed-bed reactor. First, 300 mg of catalyst (20–40 mesh) was loaded in the reactor, and the feed gas, a mixture of 2 mol % CO and 28 mol % O₂ with He as balance at 4000 h^{−1}, was introduced into the reactor. The CO oxidation reaction was carried out, increasing temperature from 50 °C to different temperatures when the conversion of CO reached 100%. The tail gas was analyzed online using a gas chromatograph (SC-200G, Chuanyi Instrument, Chongqing, China). The conversion of CO (X_{CO}) was calculated based on the molar flow rate of CO ($F_{CO, in}$ or $F_{CO, out}$), as follows:

$$X_{CO} = \frac{F_{CO, in} - F_{CO, out}}{F_{CO, in}} \quad (1)$$

where F_{in} or F_{out} are the molar flow rates of CO in the inlet or the outlet of the reactor.

3.3. Characterizations

X-ray diffraction (XRD) was carried out with an X-ray diffractometer (DX-2700, Haoyuan Instrument, Dandong, China) with Cu K α radiation at 40 kV and 30 mA.

Specific surface areas and pore sizes of the whole calcined samples were measured at −196 °C on an automatic adsorption instrument (JWBK-112, JWGB Instrument, Beijing, China).

TEM experiments were performed using a high-resolution transmission electron microscope (JEM-2010, JEOL, Tokyo, Japan).

X-ray photoelectron spectroscopy (XPS) was recorded using a Kratos Axis-Ultra DLD spectrometer using Al K α radiation (1486.6 eV). The binding energies were calibrated relative to the C_{1s} peak from the carbon contamination at 284.6 eV.

Temperature-programmed reduction (TPR) was performed using a fixed-bed reactor with a flow of 5.0% H₂ in N₂ at 10 °C/min.

The composition of catalysts was measured by elemental analysis with an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (IRIS1000, Thermo Electron, Waltham, MA, USA).

CO-temperature-programmed desorption (CO-TPD) was carried out in a fixed-bed reactor. First, 100 mg of catalyst was stabilized in helium at 300 °C, cooled down to 50 °C, and then switched to a CO flow for 30 min. Then, the feed gas was switched back to helium to purge the samples until the baseline was stable; then, the CO desorption was carried out from 50 °C to 700 °C at 10 °C/min.

Hydrogen chemisorption was conducted using the temperature-programmed desorption (TPD) technique. Each catalyst sample was first pretreated in an N₂ flow at 300 °C, and then H₂ was adsorbed, 30 mL/min at 50 °C for 30 min. The feed gas was switched to N₂ to purge the samples until the baseline was stable, and H₂ desorption was conducted in an N₂ flow at 50–750 °C. The turnover frequency (TOF) was calculated using Equation (2), in which X_{CO} is the conversion of CO at 50 °C, N_{CO} is the molecular amount of CO in the feed gas, and N_{Co} is the surface active sites with Co, calculated via H₂ chemisorption by assuming H/Co = 1/1.

$$\text{TOF} = \frac{X_{\text{CO}} N_{\text{CO}}}{N_{\text{Co}}} \quad (2)$$

4. Conclusions

Formic acid modified catalysts of Co₃O₄-CeO₂ were prepared via a urea-hydrothermal synthesis, and the Co₃O₄-CeO₂-0.5 catalyst performed well in CO oxidation: T₅₀ obtained at 69.5 °C and T₁₀₀ obtained at 150 °C, respectively. Based on characterization results, after treatment with formic acid at 0.5 mol/L, the structure became more porous with a higher surface area and pore volume; meanwhile, despite the decreased content of Co, the CO adsorption capacity was increased, suggesting that there could be more adsorption sites exposed by the acid treatment to activate CO, which may explain the improved reactivity.

Acknowledgments: This work was partly supported by the National Natural Science Foundation of China (21276031), and the International Cooperation Program of S&T Department of Sichuan Province (2015HH0013).

Author Contributions: The experimental work was designed by L.H. and R.S.; R.S., Y.D., X.Z., and W.X. performed the experiments; R.S., Y.D., and L.H. analyzed the data; W.X. and Y.L. contributed reagents/materials/analysis tools; R.S., Y.D., and L.H. drafted the paper. The manuscript was amended using the comments of all authors. All authors have given approval for the final version of the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Do, Y.; Cho, I.; Park, Y.; Pradhan, D.; Sohn, Y. CO Oxidation Activities of Ni and Pd-TiO₂@SiO₂ Core-Shell Nanostructures. *Bull. Korean Chem. Soc.* **2013**, *34*, 3635–3640. [[CrossRef](#)]
2. Zhen, J.; Wang, X.; Liu, D.; Song, S.; Wang, Z.; Wang, Y.; Li, J.; Wang, F.; Zhang, H. Co₃O₄@CeO₂ core@shell cubes: Designed synthesis and optimization of catalytic properties. *Chemistry* **2014**, *20*, 4469–4473. [[CrossRef](#)] [[PubMed](#)]
3. Iablokov, V.; Frey, K.; Geszti, O.; Kruse, N. High Catalytic Activity in CO Oxidation over MnOx Nanocrystals. *Catal. Lett.* **2009**, *134*, 210–216. [[CrossRef](#)]
4. Wojciech, G. Acid-base properties of Ni-MgO-Al₂O₃ materials. *Appl. Surface Sci.* **2011**, *257*, 2875–2880.
5. Sasirekha, N.; Sangeetha, P.; Chen, Y.-W. Bimetallic Au-Ag/CeO₂ Catalysts for Preferential Oxidation of CO in Hydrogen-Rich Stream: Effect of Calcination Temperature. *J. Phys. Chem. C* **2014**, *118*, 15226–15233. [[CrossRef](#)]

6. Gil, S.; Garcia-Vargas, J.; Liotta, L.; Pantaleo, G.; Ousmane, M.; Retailleau, L.; Giroir-Fendler, A. Catalytic Oxidation of Propene over Pd Catalysts Supported on CeO₂, TiO₂, Al₂O₃ and M/Al₂O₃ Oxides (M = Ce, Ti, Fe, Mn). *Catalysts* **2015**, *5*, 671–689. [CrossRef]
7. Yan, C.-F.; Chen, H.; Hu, R.-R.; Huang, S.; Luo, W.; Guo, C.; Li, M.; Li, W. Synthesis of mesoporous Co-Ce oxides catalysts by glycine-nitrate combustion approach for CO preferential oxidation reaction in excess H₂. *Int. J. Hydrogen. Energy* **2014**, *39*, 18695–18701. [CrossRef]
8. Gao, W.; Zhao, Y.F.; Chen, H.R.; Chen, H.; Li, Y.W.; He, S.; Zhang, Y.K.; Wei, M.; Evans, D.G.; Duan, X. Core-shell Cu@(CuCo-alloy)/Al₂O₃ catalysts for the synthesis of higher alcohols from syngas. *Green Chem.* **2015**, *17*, 1525–1534. [CrossRef]
9. Schuh, K.; Kleist, W.; Høj, M.; Trouillet, V.; Beato, P.; Jensen, A.D.; Grunwaldt, J.D. Bismuth molybdate catalysts prepared by mild hydrothermal synthesis: Influence of pH on the selective oxidation of propylene. *Catalysts* **2015**, *5*, 1554–1573. [CrossRef]
10. Velu, S.; Suzuki, K.; Vijayaraj, M.; Barman, S.; Gopinath, C.S. *In situ* XPS investigations of Cu_{1-x}Ni_xZnAl-mixed metal oxide catalysts used in the oxidative steam reforming of bio-ethanol. *Appl. Catal. B* **2005**, *5*, 287–299. [CrossRef]
11. Guil-López, R.; Navarro, R.M.; Peña, M.A.; Fierro, J.L.G. Hydrogen production by oxidative ethanol reforming on Co, Ni and Cu ex-hydrotalcite catalysts. *Int. J. Hydrogen Energy* **2011**, *36*, 1512–1523. [CrossRef]
12. Sesis, A.; Hodnett, M.; Memoli, G.; Wain, A.J.; Jurewicz, I.; Dalton, A.B.; Carey, J.D.; Hinds, G. Influence of acoustic cavitation on the controlled ultrasonic dispersion of carbon nanotubes. *J. Phys. Chem. B* **2013**, *117*, 15141–15150. [CrossRef] [PubMed]
13. Wang, F.; Wang, X.; Liu, D.; Zhen, J.; Li, J.; Wang, Y.; Zhang, H. High-performance ZnCo₂O₄@CeO₂ core@shell microspheres for catalytic CO oxidation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 22216–22223. [CrossRef] [PubMed]
14. Kuo, C.H.; Li, W.; Song, W.; Luo, Z.; Poyraz, A.S.; Guo, Y.; Ma, A.W.; Suib, S.L.; He, J. Facile synthesis of Co₃O₄@CNT with high catalytic activity for CO oxidation under moisture-rich conditions. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11311–11317. [CrossRef] [PubMed]
15. Li, H.; Lu, G.; Qiao, D.; Wang, Y.; Guo, Y.; Guo, Y. Catalytic Methane Combustion over Co₃O₄/CeO₂ Composite Oxides Prepared by Modified Citrate Sol-Gel Method. *Catal. Lett.* **2010**, *141*, 452–458. [CrossRef]
16. Xue, L.; Zhang, C.; He, H.; Teraoka, Y. Teraoka. Catalytic decomposition of N₂O over CeO₂ promoted Co₃O₄ spinel catalyst. *Appl. Catal. B* **2007**, *75*, 167–174. [CrossRef]
17. Qu, Z.; Gao, K.; Fu, Q.; Qin, Y. Low-temperature catalytic oxidation of toluene over nanocrystal-like Mn-Co oxides prepared by two-step hydrothermal method. *Catal. Commun.* **2014**, *52*, 31–35. [CrossRef]
18. Huang, L.; Liu, Q.; Chen, R.; Chu, D.; Hsu, A.T. Layered double hydroxide derived Co_{0.3}Mg_{2.7}Al_{1-x}Fe_xO_{4.5±δ} catalysts for hydrogen production via auto-thermal reforming of bio-ethanol. *Catal. Commun.* **2010**, *12*, 40–45. [CrossRef]
19. Baek, J.H.; Park, J.Y.; Hwang, A.R.; Kang, Y.C. Spectroscopic and Morphological Investigation of Co₃O₄ Microfibers Produced by Electrospinning Process. *Bull. Korean Chem. Soc.* **2012**, *33*, 1242–1246. [CrossRef]
20. Li, S.; Zhu, H.; Qin, Z.; Wang, G.; Zhang, Y.; Wu, Z.; Li, Z.; Chen, G.; Dong, W.; Wu, Z.; *et al.* Morphologic effects of nano CeO₂-TiO₂ on the performance of Au/CeO₂-TiO₂ catalysts in low-temperature CO oxidation. *Appl. Catal. B* **2014**, *144*, 498–506. [CrossRef]
21. Qi, L.; Yu, Q.; Dai, Y.; Tang, C.; Liu, L.; Zhang, H.; Gao, F.; Dong, L.; Chen, Y. Influence of cerium precursors on the structure and reducibility of mesoporous CuO-CeO₂ catalysts for CO oxidation. *Appl. Catal. B* **2012**, *119–120*, 308–320. [CrossRef]
22. Wang, T.; Ding, Y.; Lü, Y.; Zhu, H.; Lin, L. Influence of lanthanum on the performance of Zr-Co/activated carbon catalysts in Fischer-Tropsch synthesis. *J. Nat. Gas Chem.* **2008**, *17*, 153–158. [CrossRef]
23. Lin, W.; Cheng, H.; He, L.; Yu, Y.; Zhao, F. High performance of Ir-promoted Ni/TiO₂ catalyst toward the selective hydrogenation of cinnamaldehyde. *J. Catal.* **2013**, *303*, 110–116. [CrossRef]

