Pt-Au/MO$_x$-CeO$_2$ (M = Mn, Fe, Ti) Catalysts for the Co-Oxidation of CO and H$_2$ at Room Temperature

Xiaowei Hong $^{1,†}$, Ye Sun $^{1,†}$, Tianle Zhu $^{1,*}$ and Zhiming Liu $^{2,*}$

$^1$ School of Space and Environment, Beihang University, Beijing 100191, China; hongxiao86@126.com (X.H.); suny@buaa.edu.cn (Y.S.)

$^2$ State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

* Correspondence: zhutl@buaa.edu.cn (T.Z.); liuzm@mail.buct.edu.cn (Z.L.);
Tel.: +86-10-8231-4215 (T.Z.); +86-10-6442-7356 (Z.L.)

$^†$ These authors contributed equally to this work.

Abstract: A series of nanostructured Pt-Au/MO$_x$-CeO$_2$ (M = Mn, Fe, Ti) catalysts were prepared and their catalytic performance for the co-oxidation of carbon monoxide (CO) and hydrogen (H$_2$) were evaluated at room temperature. The results showed that MO$_x$ promoted the CO oxidation of Pt-Au/CeO$_2$, but only the TiO$_2$ could enhance co-oxidation of CO and H$_2$ over Pt-Au/CeO$_2$. Related characterizations were conducted to clarify the promoting effect of MO$_x$. Temperature-programmed reduction of hydrogen (H$_2$-TPR) and X-ray photoelectron spectroscopy (XPS) results suggested that MO$_x$ could improve the charge transfer from Au sites to CeO$_2$, resulting in a high concentration of Ce$^{3+}$ and cationic Au species which benefits for the CO oxidation. In-situ diffuse reflectance infrared Fourier transform spectroscopy (In-situ DRIFTS) results indicated that TiO$_2$ could facilitate the oxidation of H$_2$ over the Pt-Au/TiO$_2$-CeO$_2$ catalyst.

Keywords: CO; H$_2$; Co-oxidation; Pt-Au/MO$_x$-CeO$_2$; Room temperature

1. Introduction

Both H$_2$ and CO co-exist in space capsule. H$_2$ mainly originates from the charge–discharge process of battery and CO is released from processes of human metabolism. H$_2$ and CO, as the typical inflammable and explosive gaseous contaminants, seriously threaten the safety of human and airtight cabin. In addition, long-term exposure to CO causes adverse effects on human health [1]. Therefore, more and more attention has been paid on the simultaneous removal of CO and H$_2$. Catalytic oxidation has been regarded as an effective and green technology to eliminate CO and H$_2$ [2].

Noble metal catalysts for the oxidation of H$_2$ and CO have been extensively studied recently [3–8]. Pt catalysts were considered as the most active catalysts for H$_2$ oxidation at room temperature [9]. Previous studies showed that Pt-Ru/C [10] and Pt-Sn/C [11] electrocatalysts exhibited high catalytic performance for the H$_2$ oxidation, and metallic Pt species were more active than the oxidized Pt species [12,13]. Au catalysts have been reported to be more active than Pt catalysts for CO oxidation [8,14]. CO could be removed at room temperature over Au/CeO$_2$ [15], Au/TiO$_2$ [16], Au/MnO$_x$ [17], and Au/Fe$_2$O$_3$ [18] catalysts. Moreover, cationic Au species were more active than the metallic Au species [18,19].

In order to remove CO and H$_2$ in space capsule, developing novel catalysts with excellent activity for the co-oxidation of CO and H$_2$ is desirable. Recently, a few studies related to the co-oxidation of H$_2$ and CO have been reported [5,6,20–22]. Zhang et al. [21] reported that Pt-Au/CeO$_2$ bimetallic catalysts with ordered macro-porous and meso-porous structure showed superior catalytic performance for
CO oxidation but not for H₂ oxidation. Ru-Pt bimetallic core-shell nanoparticle catalyst has been developed by Eichhorn et al. [23], however, it could not afford the simultaneous removal of CO and H₂. Au-Pd/Fe(OH)x catalyst with separate Au active sites and Pd active sites was excellent for the complete co-oxidation of H₂ and CO at low temperature [5], but the gas hourly space velocity (GHSV) (20,000 h⁻¹) was relatively low. At high GHSV, the oxidation of H₂ was strongly inhibited by the presence of CO [6]. Therefore, the simultaneous removal of H₂ and CO at room temperature at high GHSV still remains challenging. CeO₂ enhanced the oxidation reactions due to its high oxygen storage capacity and redox property [24]. Corma et al. [15] pointed out that nanocrystalline CeO₂ with Ce³⁺ ions could adsorb and activate O₂, thus enhancing the catalyst reactivity. Ordered CeO₂ support with higher surface area could lead to the better dispersion of active sites and also boost oxygen transfer to active platinum species [25]. For the CO and H₂ oxidation, surface diffusion and spillover enhanced oxidation reaction on Pt/CeO₂ [26–28] and Au/CeO₂ catalysts [8,29]. Therefore, CeO₂ nanospheres with meso-structure were promising supports for Au and Pt catalysts. Fe₂O₃ [30–32], TiO₂ [33,34] and MnO₂ [35–38] were proven to be excellent promoters because of their high oxygen storage capacity and redox property. In addition, preparation methods showed significant effect on the catalytic performance of Pt catalysts [12] and urea was an excellent precipitant for Au catalysts [39].

According to the above-mentioned understanding, a series of nanostructured Pt-Au/MOX-CeO₂ (M = Mn, Fe, Ti) bimetallic catalysts were prepared by the reduction-deposition precipitation method and their performance for the co-oxidation of CO and H₂ under the GHSV of 500,000 h⁻¹ at room temperature were evaluated. Physical and chemical properties of the Pt-Au/MOX-CeO₂ (M = Mn, Fe, Ti) bimetallic catalysts were characterized. Based on the characterization, the relationship between the structure and the catalytic performance has been elucidated.

2. Results and Discussion

2.1. Catalytic Activities of the Pt-Au/MOX-CeO₂ Catalysts

Figure 1 presents the activities of the Pt-Au/MOX-CeO₂ catalysts for the catalytic co-oxidation of CO and H₂. For Pt-Au/CeO₂ catalyst, conversions of CO and H₂ are 93% and 25%, respectively, and then gradually decrease. It is attributed to the CO accumulation on Au and Pt active sites. CO can be completely removed while the conversion of H₂ is low over Pt-Au/MnO₂-CeO₂ and Pt-Au/Fe₂O₃-CeO₂ catalysts. It is encouraging that 100% conversions of CO and H₂ are obtained at room temperature over Pt-Au/TiO₂-CeO₂ catalyst. However, the conversion of H₂ decreases over Pt-Au/TiO₂-CeO₂ catalyst due to H₂O accumulation on the Pt and Au active sites [7]. The oxidation of CO is suppressed by H₂O when the H₂O content is over 200 ppm [40]. The inhibiting effect of H₂O is due to the competitive adsorption between H₂O and CO molecules on the surface twofold coordinated oxygen site [41]. On the other hand, a competitive adsorption between H₂O and O₂ molecules also exists due to the accumulation and occupation of H₂O on the Pt and Au active sites [7].

![Figure 1](image-url)  
Figure 1. The activities of Pt-Au/MOX-CeO₂ catalysts for the catalytic co-oxidations of H₂ and CO. Reaction conditions: 100 ppm H₂/100 ppm CO/room air; temperature: 25 °C; GHSV = 500,000 h⁻¹.
2.2. Physicochemical Properties of Catalysts

Figure 2 presents the X-ray diffraction (XRD) patterns of the CeO\textsubscript{2} support and Pt-Au/\textit{MOx-CeO\textsubscript{2}} catalysts. All these samples show typical cubic CeO\textsubscript{2} diffraction peaks (JCPDS 43-1002). The diffraction peaks ascribed to \textit{MOx}, Pt and Au species are absent, which indicates that \textit{MOx}, Pt and Au species are highly dispersed on the support. Figure 3 shows the transmission electron microscope (TEM) images of the CeO\textsubscript{2} support and Pt-Au/\textit{MOx-CeO\textsubscript{2}} catalysts. It can be found that CeO\textsubscript{2} support presents nanosphere that is comprised of many small particles with a crystallite size of 5 nm. The contents of Pt and Au species in energy dispersive spectrometer (EDS) results of the Pt-Au/\textit{MOx-CeO\textsubscript{2}} catalysts are close to the theoretical values (1 wt %). Chemical composition and textural properties of Pt-Au/\textit{MOx-CeO\textsubscript{2}} catalysts are seen in Table 1. Compared with the X-ray photoelectron spectroscopy (XPS) results presented in Table 1, contents of Pt and Au species in EDS results are higher, indicating that parts of Pt and Au species are distributed on the surface of the CeO\textsubscript{2} nanoparticles. Brunauer–Emmett–Teller (BET) surface areas of Pt-Au/\textit{MOx-CeO\textsubscript{2}} catalysts decrease due to the introduction of \textit{MOx}. The dispersions of metal on Pt-Au/\textit{MOx-CeO\textsubscript{2}} catalysts are very close due to the same preparation method.
It indicates that the addition of MOx can promote the redox property of Pt-Au/CeO2 catalyst. The reduction temperatures of Pt species are 70–100 °C [42]; Au species reduction temperatures are usually 100–200 °C [43]; and pure CeO2 reduction temperature is around 553 °C [44]. The peak at 350 °C is attributed to the reduction of CeO2 surface oxygen [45]. Evidently, no reduction peaks ascribed to Pt species are observed for Pt-Au/CeO2 and Pt-Au/TiO2-CeO2 catalysts, suggesting that all the Pt species are metallic Pt species. For Pt-Au/MnO2-CeO2 and Pt-Au/Fe2O3-CeO2 catalysts, the reduction peak at 75 °C is attributed to Pt2+ species. For Pt-Au/CeO2 catalyst, there are two reduction peaks at 160 and 553 °C, which are ascribed to the reduction peaks of Au species and CeO2, respectively [46]. Three reduction peaks at 146, 350 and 465 °C are observed for Pt-Au/TiO2-CeO2 catalyst. It can be observed that three reduction peaks are at 144, 341 and 450 °C for Pt-Au/MnO2-CeO2 catalyst. The reduction peaks are centered at 145, 350 and 464 °C for Pt-Au/Fe2O3-CeO2 catalyst. It is worth noting that the reduction temperature of CeO2 in Pt-Au/MOx-CeO2 is lower than that of Pt-Au/CeO2 nearly by 100 °C, which means that the oxidative performance of CeO2 in Pt-Au/MOx-CeO2 is higher than that of Pt-Au/CeO2. On the other hand, the introduction of MOx influences the reduction temperature of Au species. Lower reduction temperature of Au species indicates the active oxygen species formed on the Pt-Au/MOx-CeO2 catalysts are more active [43]. It is very interesting that, even though the Pt species should be metallic Pt due to the reduction of NaBH4 over the Pt-Au/MnO2-CeO2 and Pt-Au/Fe2O3-CeO2 catalysts, Pt2+ species is observed. The presence of Pt2+ species can be caused by the addition of MnO2 and Fe2O3, both of which improve the electron transfer from Pt sites to CeO2, thus leading to the oxidation of metallic Pt species to Pt2+ species. Metallic Pt species are more active than Pt2+ species for the oxidation reaction, which may clarify the poor activities of Pt-Au/MnO2-CeO2 catalyst and Pt-Au/Fe2O3-CeO2 catalyst for the H2 oxidation. H2 consumed amounts are 0.21, 0.31, 0.38 and 0.39 mmol−1 for the Pt-Au/CeO2, Pt-Au/TiO2-CeO2, Pt-Au/Fe2O3-CeO2, and Pt-Au/MnO2-CeO2 catalysts, respectively. It indicates that the addition of MOx can promote the redox property of Pt-Au/CeO2 catalyst.
XPS measurements are conducted on the Pt-Au/MOx-CeO2 samples and the results are listed in Table 2. The peaks at 83.3–83.6 eV and 84.2–84.5 eV can be assigned to Au0 species and Au+ species, respectively [46,47]. The peaks at 70.2–70.8 eV and 72.4–72.6 eV are attributed to Pt0 species and Pt2+ species [48]. Figures 5 and 6 show that the addition of MOx influences the chemical states of Pt species and Au species due to the electron transfer from Au species and Pt species to CeO2 [49–52]. Cationic Au species possess higher activity than metallic Au species on the CO oxidation [42]. Compared with Pt-Au/CeO2 catalyst, the addition of MOx results in the presence of more cationic Au species over Pt-Au/MOx-CeO2 catalysts. The Ce 3d XPS peaks were fitted by searching for the optimum combination of Gaussian bands with the correlation coefficients (r2) above 0.99. In Figure 7, the Ce 3d core level spectra of the catalyst can be divided into eight components and the content of Ce3+ are listed in Table 2. The bands labeled u′ and v′ represent the 3d104f1 corresponding to Ce3+, and the bands labeled u, u′′, u′′′, v, v′, and v′′′ represent the 3d104f0 corresponding to Ce4+ [53]. Among Pt-Au/MOx-CeO2 catalysts, the content of Ce3+ over Pt-Au/MnO2-CeO2 catalyst is the highest, indicating that more surface oxygen vacancies exist on Pt-Au/MnO2-CeO2 catalyst. Previous researches showed that the formation of Ce3+ over Au/CeO2 catalysts was due to the charge transfer between Au sites and CeO2 [49–51]. Therefore, the introduction of MOx enhances the charge transfer from Au species and Pt species to CeO2 and leads to high content of cationic Au species. O1s XPS spectra of Pt-Au/MOx-CeO2 catalysts are shown in Figure 8 and two peaks at 529.1–529.4 and 531.1–531.4 eV, respectively, appear. The former is ascribed to lattice oxygen (OII) and the latter is attributed to chemisorbed oxygen (OIII) [47]. OII ratios [OII/(OII + OIII)] over Pt-Au/MOx-CeO2 catalysts are higher than that over Pt-Au/CeO2 catalysts due to the presence of higher Ce3+ content.
Table 2. XPS data analysis of Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} catalysts.

| Catalyst       | Pt Species | Content (at. %) | Au Species | Content (at. %) | Ce\textsuperscript{3+} Species Content (at. %) |
|----------------|------------|-----------------|------------|-----------------|-----------------------------------------------|
| Pt-Au/CeO\textsubscript{2} | Pt\textsuperscript{2+} (72.5 eV) | 0              | Au\textsuperscript{0} (83.7 eV) | 66.6 | 34.7 |
|                | Pt\textsuperscript{0} (70.7 eV) | 100             | Au\textsuperscript{+} (84.5 eV) | 33.4 |
| Pt-Au/Fe\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2} | Pt\textsuperscript{0} (70.7 eV) | 77.7            | Au\textsuperscript{0} (83.6 eV) | 44.4 | 40.9 |
|                | Pt\textsuperscript{2+} (72.5 eV) | 23.3            | Au\textsuperscript{+} (84.5 eV) | 55.6 |
| Pt-Au/MnO\textsubscript{2}-CeO\textsubscript{2} | Pt\textsuperscript{0} (70.7 eV) | 67.5            | Au\textsuperscript{0} (83.6 eV) | 18.4 | 41.1 |
|                | Pt\textsuperscript{2+} (72.5 eV) | 32.5            | Au\textsuperscript{+} (84.5 eV) | 81.6 |
| Pt-Au/TiO\textsubscript{2}-CeO\textsubscript{2} | Pt\textsuperscript{2+} (72.5 eV) | 0              | Au\textsuperscript{0} (83.4 eV) | 59.2 | 36.7 |
|                | Pt\textsuperscript{0} (70.7 eV) | 100             | Au\textsuperscript{+} (84.5 eV) | 40.8 |

Figure 5. Au 4f XPS spectra of Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} catalysts: (a) Pt-Au/CeO\textsubscript{2}; (b) Pt-Au/Fe\textsubscript{2}O\textsubscript{3}-CeO\textsubscript{2}; (c) Pt-Au/MnO\textsubscript{2}-CeO\textsubscript{2}; (d) Pt-Au/TiO\textsubscript{2}-CeO\textsubscript{2}.

To further understand the relationship between catalyst activity and catalyst physicochemical property, In-situ diffuse reflectance infrared Fourier transform spectroscopy (In-situ DRIFT) spectra of the Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} catalysts obtained upon exposure to CO, H\textsubscript{2} and synthetic air at 25 °C are shown in Figure 9. Seven distinct bands are observed in the in-situ DRIFT spectra. The bands at 3324–3395, 1640, 3691–3701, 2169, 2083–2084, 1568–1575, and 1282–1298 cm\textsuperscript{-1} are ascribed to isolated hydroxyl groups $\nu$(OH) [29], adsorbed water $\delta$(H-O-H) [43], another hydroxyl groups $\nu$(OH) [54–58], the adsorption of CO on Au sites [59–61], the adsorption of CO on Pt sites [42,62,63], the carbonate species [29], and carbonate species [29], respectively. It has been proposed that isolated hydroxyl groups originated from the decomposition of the OOH species, which were generated from the reaction between the associatively adsorbed oxygen and dissociative adsorbed hydrogen, and the isolated hydroxyl groups further react with dissociative adsorbed hydrogen to generate H\textsubscript{2}O [7,29].
**Figure 5.** Au 4f XPS spectra of Pt-Au/MOx-CeO2 catalysts: (a) Pt-Au/CeO2; (b) Pt-Au/Fe2O3-CeO2; (c) Pt-Au/MnO2-CeO2; (d) Pt-Au/TiO2-CeO2.

**Figure 6.** Pt 4f XPS spectra of Pt-Au/MOx-CeO2 catalysts: (a) Pt-Au/CeO2; (b) Pt-Au/Fe2O3-CeO2; (c) Pt-Au/MnO2-CeO2; (d) Pt-Au/TiO2-CeO2.

**Figure 7.** Ce 3d XPS spectra of Pt-Au/MOx-CeO2 catalysts: (a) Pt-Au/CeO2; (b) Pt-Au/TiO2-CeO2; (c) Pt-Au/Fe2O3-CeO2; (d) Pt-Au/MnO2-CeO2.

To further understand the relationship between catalyst activity and catalyst physicochemical property, In-situ diffuse reflectance infrared Fourier transform spectroscopy (In-situ DRIFT) spectra of the Pt-Au/MOx-CeO2 catalysts obtained upon exposure to CO, H2 and synthetic air at 25 °C are shown in Figure 9. Seven distinct bands are observed in the in-situ DRIFT spectra. The bands at 3324–3395, 1640, 3691–3701, 2169, 2083–2084, 1568–1575, and 1282–1298 cm⁻¹ are ascribed to isolated hydroxyl groups υ(OH) [29], adsorbed water δ(H-O-H) [43], another hydroxyl groups υ(OH) [54–58], the adsorption of CO.
To solve this problem, In-situ DRIFTS test results of Pt-Au/CeO$_2$ best catalytic activity for the co-oxidation of CO and H$_2$ were observed. The intensity of bands at 3386 and 1640 cm$^{-1}$ was almost unchanged, which suggests little H$_2$ is oxidized by CO. For Pt-Au/MnO$_2$ catalyst, the intensity of bands at 2169 and 2084 cm$^{-1}$ was not the oxidation of H$_2$, suggesting little H$_2$ is oxidized by CO. However, the intensity of bands at 3389 and 1640 cm$^{-1}$ was almost unchanged, which indicates that little CO accumulates on Pt-Au/MO$_x$ catalyst due to the close amount of Pt and Au species over Pt-Au/Mo$_x$ catalyst and Pt-Au/MO$_x$-CeO$_2$ catalysts. Little CO accumulation on Pt-Au/MO$_x$-CeO$_2$ catalysts in Figure 9 is because of the enhanced CO oxidation instead of adsorption capability. For Pt-Au/CeO$_2$ catalyst, the intensity of bands at 2169 and 2084 cm$^{-1}$ increases, which means that much CO accumulates on the Au and Pt active sites. The intensity of other bands is almost unchanged, which suggests little H$_2$ is oxidized because Pt active sites are occupied and poisoned by CO. Therefore, CO and H$_2$ cannot be simultaneously removed over Pt-Au/CeO$_2$ catalyst. For Pt-Au/MnO$_2$-CeO$_2$ catalyst, no peaks can be observed at 2169 and 2084 cm$^{-1}$ with the reaction proceeding, which suggests that the introduction of MnO$_2$ enhances the oxidation of CO. However, the intensity of bands at 3389 and 1640 cm$^{-1}$ are seldom unchanged, which indicates that little H$_2$ is oxidized. Therefore, the introduction of MnO$_2$ improves the oxidation of CO but not the oxidation of H$_2$. Over Pt-Au/Fe$_2$O$_3$-CeO$_2$ catalyst, the intensity of the peak at 2084 cm$^{-1}$ suggests that little CO accumulates and the Fe$_2$O$_3$ improves the activity of Pt-Au/CeO$_2$ catalyst for CO oxidation. The intensity of bands at 3386 and 1640 cm$^{-1}$ suggest that little H$_2$ is oxidized to H$_2$O. Consequently, Fe$_2$O$_3$ improves the activity of Pt-Au/CeO$_2$ catalyst for the CO oxidation not for H$_2$ oxidation. Some CO accumulates on the Pt-Au/TiO$_2$-CeO$_2$ catalyst, as confirmed by the presence of the band at 2084 cm$^{-1}$. The intensity change of peaks at 3691, 3395 and 1640 cm$^{-1}$ suggests that many isolated -OH species and H$_2$O are produced, indicating that much H$_2$ is oxidized into H$_2$O. Based on the in-situ DRIFTS results of the Pt-Au/MO$_x$-CeO$_2$ catalysts, Pt-Au/TiO$_2$-CeO$_2$ catalyst presents the best catalytic activity for the co-oxidation of CO and H$_2$.

![Figure 8. O1s XPS spectra and O$_{1s}$ ratios of Pt-Au/OM$_x$-CeO$_2$ catalysts: (a) Pt-Au/CeO$_2$; (b) Pt-Au/Fe$_2$O$_3$-CeO$_2$; (c) Pt-Au/MnO$_2$-CeO$_2$; (d) Pt-Au/TiO$_2$-CeO$_2$.](image)
2017 accumulation amount does not reach the CO saturated adsorption capability over Pt-Au/CeO2 catalyst observed at 2169 and 2084 cm⁻¹ band at 2084 cm⁻¹ unchanged, which indicates that little H₂ is oxidized. Therefore, the introduction of MnO₂ improves the activity for the co-oxidation of CO and H₂.

In-situ DRIFTS test results of Pt-Au/CeO₂ catalyst upon 3000 ppm CO + N₂ and 3000 ppm H₂ + synthetic air can be observed in the Figure 10. The results indicate that the CO oxidation of CO but not the oxidation of H₂. Over Pt-Au/Fe₂O₃-CeO₂ catalyst, the intensity of the peak at 2084 cm⁻¹ is because of the enhanced CO oxidation instead of adsorption capability. For Pt-Au/CeO₂ catalyst, the intensity of bands at 2169 and 2084 cm⁻¹ simultaneously removed over Pt-Au/CeO₂ catalyst.

For Pt-Au/MnO₂-CeO₂ catalyst, no peaks can be observed in the Figure 9, which suggests little H₂ is oxidized into H₂O. Based on the in-situ DRIFTS results of the Pt-Au/MOₓ-CeO₂ catalysts, Pt-Au/TiO₂-CeO₂ catalyst presents the best catalytic activity for the co-oxidation of CO and H₂.

Some CO accumulates on the Pt-Au/TiO₂-CeO₂ catalyst, as confirmed by the presence of the −OH species and H₂O are produced, indicating that much H₂ is oxidized into H₂O. Based on the in-situ DRIFTS results of the Pt-Au/MOₓ-CeO₂ catalysts, Pt-Au/TiO₂-CeO₂ catalyst presents the best catalytic activity for the co-oxidation of CO and H₂.

Figure 9. In-situ DRIFT spectra of the Pt-Au/MOₓ-CeO₂ catalysts after exposed upon 3000 ppm CO + 3000 ppm H₂ + synthetic air for 60 min at 25 °C: (a,b) Pt-Au/CeO₂; (c,d) Pt-Au/Fe₂O₃-CeO₂; (e,f) Pt-Au/MnO₂-CeO₂; (g,h) Pt-Au/ TiO₂-CeO₂.
was dissolved in 13 mL ultra-pure water at room temperature. Then, 13 mL propionic acid and CeO$_2$ nanospheres were added under stirring to form a uniform solution at room temperature. The obtained solid was dried at 100 °C overnight, subsequently it was calcined in air at 400 °C for 4 h. Then CeO$_2$ nanospheres were obtained.

Figure 10 shows the effect of CO concentration on the co-oxidation of CO and H$_2$ through in-situ DRIFTS. The intensity of the bands at 3395 and 1640 cm$^{-1}$ in Figure 11a are stronger than that shown in Figure 11b, indicating that more H$_2$O are produced. Therefore, CO obviously hinders the oxidation of H$_2$ in the co-oxidation of CO and H$_2$, which is in accordance with previous reports [22].

Figure 11 shows the effect of CO concentration on the co-oxidation of CO and H$_2$ through in-situ DRIFTS. The intensity of the bands at 3395 and 1640 cm$^{-1}$ in Figure 11b are stronger than that shown in Figure 11a, indicating that more H$_2$O are produced. Therefore, CO obviously hinders the oxidation of H$_2$ in the co-oxidation of CO and H$_2$, which is in accordance with previous reports [22].

3. Materials and Methods

3.1. Catalyst Preparation

The CeO$_2$ nanospheres were prepared by hydrothermal method. Thirteen grams Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 13 mL ultra-pure water at room temperature. Then, 13 mL propionic acid and 390 mL ethylene glycol were added under stirring to form a uniform solution at room temperature. The uniform solution was transferred to a Teflon-sealed autoclave and heated at 180 °C for 7.5 h. After the hydrothermal treatment, the mixture was centrifuged and washed with ethanol for several times. The obtained solid was dried at 100 °C overnight, subsequently it was calcined in air at 400 °C for 4 h. Then CeO$_2$ nanospheres were obtained.
MO\textsubscript{x}-CeO\textsubscript{2} (M = Mn, Fe, Ti) supports, with a Ce/M molar ratio of 9, were obtained by precipitation method. CeO\textsubscript{2} nanospheres were homogeneously dispersed in Mn(NO\textsubscript{3})\textsubscript{2} or Fe(NO\textsubscript{3})\textsubscript{3} aqueous solution, or tetra-n-butyl titanate ethanol solution, and the suspension was stirred for 2 h at room temperature. Then ammonia solution was added to the above solution under stirring until pH was 10 at room temperature. The suspension was filtered and washed with ultra-pure water. The obtained solid samples were first dried at 105 °C for 12 h and subsequently calcined in air at 400 °C for 4 h to obtain MO\textsubscript{x}-CeO\textsubscript{2} (M = Mn, Fe, Ti) supports.

Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} (M = Mn, Fe, Ti) catalysts were prepared by reduction-deposition precipitation method [49]. Four grams MO\textsubscript{x}-CeO\textsubscript{2} was uniformly dispersed into the H\textsubscript{2}PtCl\textsubscript{6} solution containing 0.04 g Pt at room temperature. After impregnation for 2 h, the pH value of suspension was adjusted to 10. NaBH\textsubscript{4} solution was quickly added into the suspension (NaBH\textsubscript{4}/Pt = 10, molar ratio) while being stirred for 2 h at room temperature. The suspension was filtered and washed with ultra-pure water, then dried under vacuum at 120 °C for 12 h to obtain Pt/MO\textsubscript{x}-CeO\textsubscript{2}. Then 2 g Pt/MO\textsubscript{x}-CeO\textsubscript{2} was uniformly dispersed into the HAuCl\textsubscript{4} solution containing 0.02 g Au at room temperature. Subsequently, urea was added as the precipitant. The mixture was stirred at 80 °C for 8 h and then aged for 12 h at room temperature. Then, the mixture was filtered and washed with ultra-pure water. The resulting powder was dried under vacuum at room temperature for 12 h to yield Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} catalysts.

3.2. Catalyst Characterization

XRD patterns were recorded with a Shimadzu (Tokyo, Japan) XRD-6000 diffractometer operated at 40 kV and 40 mA, using nickel-filtered Cu Kα (λ = 0.1542 nm) radiation. Surface areas of the catalysts were determined by the BET method by a Micromeritics ASAP 2000 instrument (Quantachrome, Boynton Beach, FL, USA). CO chemisorption measurements were measured an Autochem II 2920 (Micromeritics Instrument Corp, Atlanta, GA, USA) automated chemisorption analyzer. The surface chemical states of Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} catalysts were tested by XPS (PHI Quan tro SXM ULVAC-PHI, Tokyo, Japan) using an Al Kα X-ray source (1486.7 eV) at 15 kV and 25 W with the binding energy calibrated by C 1s at 284.8 eV. HRTEM micrographs were obtained with a JEM-2100F (Jeol, Tokyo, Japan) microscope at 200 kV.

H\textsubscript{2}-TPR measurements were carried out in a fixed bed quartz reactor (i.d. = 10 mm) by using 0.36 g catalyst at 25 °C. Before activity evaluation, the Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} catalysts were pretreated under Ar at 120 °C for 0.5 h at a flow rate of 100 mL min\textsuperscript{-1}. The simultaneous reaction gas consisted of 100 ppm CO and 480 ppm H\textsubscript{2}, and air (50% relative humidity) as the balance gas, and the total flow rate was fixed at 3.6 L min\textsuperscript{-1}, corresponding to a GHSV of 500,000 h\textsuperscript{-1}. H\textsubscript{2}, CO and CO\textsubscript{2} were measured by gas chromatograph (GC) equipped with TCD and FID detectors. CO and CO\textsubscript{2} were converted to CH\textsubscript{4} by Ni catalytic converter before the measurement.

4. Conclusions

A series of nanostructured Pt-Au/MO\textsubscript{x}-CeO\textsubscript{2} (M = Mn, Fe, Ti) catalysts were prepared and Pt-Au/TiO\textsubscript{2}-CeO\textsubscript{2} catalyst presented the best catalytic performance for the total co-oxidation of CO.
and H₂ at room temperature. The introduction of MOₓ into CeO₂ can enhance the charge transfer from Pt and Au sites to CeO₂, which improves CO oxidation. The introduction of TiO₂ enhances the decomposition of OOH species into O₂ species and OH species, while the introduction of MnO₂ and Fe₂O₃ cannot. The addition of TiO₂ mainly accounts for the high activity for the co-oxidation of CO and H₂ over the Pt-Au/TiO₂-CeO₂ catalyst.

**Acknowledgments:** This work has been financially supported by the National Natural Science Foundation of China (21177006) and Special Foundation for Environmental Public Sector Research of Ministry of Environmental Protection of People’s Republic of China (No. 201409080).

**Author Contributions:** Tianle Zhu and Zhiming Liu conceived and designed the experiments; Xiaowei Hong and Ye Sun performed the experiments, analyzed the data and wrote the paper.

**References**

1. Seo, P.W.; Choi, H.J.; Hong, S.I.; Hong, S.C. A study on the characteristics of CO oxidation at room temperature by metallic Pt. J. Hazard. Mater. 2010, 178, 917–925. [CrossRef] [PubMed]
2. Tang, X.F.; Chen, J.L.; Huang, X.M.; Xu, Y.; Shen, W.J. Pt/MnOₓ-CeO₂ catalysts for the complete oxidation of formaldehyde at ambient temperature. Appl. Catal. B 2008, 81, 115–121. [CrossRef]
3. Noei, H.; Qiu, H.; Wang, Y.; Muhler, M.; Wöll, C. Hydrogen loading of oxide powder particles: A transmission IR study for the case of zinc oxide. ChemPhysChem 2010, 11, 3604–3607. [CrossRef] [PubMed]
4. Reina, T.R.; Moreno, A.A.; Ivanova, S.; Odriozola, J.A.; Centeno, M.A. Influence of Vanadium or Cobalt Oxides on the CO Oxidation Behavior of Au/MOₓ/CeO₂-Al₂O₃ Systems. ChemCatChem 2012, 4, 512–520. [CrossRef]
5. Qiao, B.; Wang, A.Q.; Takahashi, M.; Zhang, Y.J.; Wang, J.H.; Deng, Y.Q.; Zhang, T. A novel Au & Pd/Fe(OH)ₓ catalyst for CO + H₂ co-oxidations at low temperatures. J. Catal. 2011, 279, 361–365.
6. Liu, P.; Logadottir, A.; Nørskov, J.K. Modeling the electro-oxidation of CO and H₂/CO on Pt, Ru, PtRu and Pt₃Sn. Electrochim. Acta 2003, 48, 3731–3742.
7. Green, I.X.; Tang, W.; Neurock, M.; Yates, J.T. Low-Temperature Catalytic H₂ oxidation over Au Nanoparticle/TiO₂ Dual Perimeter Sites. Angew. Chem. Int. Ed. 2011, 50, 10186–10189. [CrossRef] [PubMed]
8. Javier, G.; Silvio, C.; Fierro-Gonzalez, J.C.; Hao, Y.; Gates, B.C.; Avelino, C. CO oxidation catalyzed by supported gold: cooperation between gold and nanocrystalline rare-earth supports forms reactive surface superoxide and peroxide species. Angew. Chem. Int. Ed. 2005, 117, 4778–4781.
9. Ramírez-Alvarez, E.; Rico-Martínez, R.; Krischer, K. Self-organized reactivity patterns during the oxidation of H₂-CO mixtures on a rotating Pt ring-electrode. Electrochim. Acta 2013, 112, 894–898. [CrossRef]
10. Giorgi, L.; Pozio, A.; Bracchini, C.; Giorgi, R.; Turtù, S. H₂ and H₂/CO oxidation mechanisms on Pt/C, Ru/C and Pt-Ru/C electrocatalysts. J. Appl. Electrochem. 2001, 31, 325–334. [CrossRef]
11. Arenz, M.; Stamenkovic, V.; Blizanac, B.B.; Mayrhofer, K.J.J.; Markovic, N.M.; Ross, P.N. Carbon-supported Pt-Sn electrocatalysts for the anodic oxidation of H₂, CO, and H₂/CO mixtures. Part II: The structure-activity relationship. J. Catal. 2005, 232, 402–410. [CrossRef]
12. Li, Z.H.; Yang, K.; Liu, G.; Deng, G.F.; Li, J.Q.; Li, G.; Yue, R.L.; Yang, J.; Chen, Y.F. Effect of Reduction Treatment on Structural Properties of TiO₂ Supported Pt Nanoparticles and Their Catalytic Activity for Benzene Oxidation. Catal. Lett. 2014, 144, 1080–1087. [CrossRef]
13. Carrettin, S.; Concepcion, P.; Corma, A.; Lopez Nieto, J.M.; Puntes, V.F. Nanocrystalline CeO₂ increases the activity of Au for CO oxidation by two orders of magnitude. Angew. Chem. Int. Ed. 2004, 43, 2538–2540. [CrossRef] [PubMed]
14. Yu, J.; Wu, G.S.; Lu, G.Z.; Mao, D.S.; Guo, Y. Promoting effects of ceria on the catalytic performance of gold supported on TiO₂ for low-temperature CO oxidation. RSC Adv. 2014, 4, 16985–16991. [CrossRef]
17. Wang, L.C.; Huang, X.S.; Liu, Q.; Liu, Y.M.; Cao, Y.; He, H.Y.; Fan, K.N.; Zhuang, J.H. Gold nanoparticles deposited on manganese(III) oxide as novel efficient catalyst for low temperature CO oxidation. *J. Catal.* **2008**, *259*, 66–74. [CrossRef]

18. Qiao, B.; Zhang, J.; Liu, L.; Deng, Y. Low-temperature prepared highly effective ferric hydroxide supported gold catalysts for carbon monoxide selective oxidation in the presence of hydrogen. *Appl. Catal. A* **2008**, *340*, 220–228. [CrossRef]

19. Hutchings, G.; Hall, M.; Carley, A.; Landon, P.; Solsona, B.; Kiely, C.; Herzing, A.; Makkee, M.; Moulijn, J.; Overweg, A. Role of gold cations in the oxidation of carbon monoxide catalyzed by iron oxide-supported gold. *J. Catal.* **2006**, *242*, 71–81. [CrossRef]

20. Avgouropoulos, G.; Ioannides, T. CO tolerance of Pt and Rh catalysts: effect of CO in the gas-phase oxidation of H2 over Pt and Rh supported catalysts. *Appl. Catal. B* **2005**, *56*, 77–86. [CrossRef]

21. Liu, L.Q.; Qiao, B.T.; He, Y.D.; Zhou, F.; Yang, B.Q.; Deng, Y.Q. Catalytic co-oxidation of CO and H2 over FeOx-supported Pd catalyst at low temperatures. *J. Catal.* **2012**, *294*, 29–36. [CrossRef]

22. Liu, L.Q.; Qiao, B.T.; He, Y.D.; Zhou, F.; Yang, B.Q.; Deng, Y.Q. Catalytic co-oxidation of CO and H2 over FeOx-supported Pd catalyst at low temperatures. *J. Catal.* **2012**, *294*, 29–36. [CrossRef]

23. Alayoglu, S.; Nilekar, A.U.; Mavrikakis, M.; Eichhorn, B. Ru–Pt core–shell nanoparticles for preferential oxidation of carbon monoxide in hydrogen. *Nat. Mater.* **2008**, *7*, 333–338. [CrossRef] [PubMed]

24. Laguna, O.H.; Perez, A.; Centeno, M.A.; Odriozola, J.A. Synergy between gold and oxygen vacancies in gold supported on Zr-doped ceria catalysts for the CO oxidation. *Appl. Catal. B* **2015**, *176*, 385–395. [CrossRef]

25. Vaysilov, G.N.; Lykhach, Y.; Migani, A.; Staudt, T.; Petrova, G.P.; Tsud, N.; Skála, T.; Bruix, A.; Illas, F.; Prince, K.C. Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles. *Nat. Mater.* **2011**, *10*, 310–315. [CrossRef] [PubMed]

26. Lykhach, Y.; Staudt, T.; Vorokhta, M.; Skála, T.; Johánek, V.; Prince, K.C.; Matolin, V.; Libuda, J. Hydrogen spillover monitored by resonant photoemission spectroscopy. *J. Catal.* **2012**, *285*, 6–9. [CrossRef]

27. Teschner, D.; Wootsch, A.; Röder, T.; Matusek, K.; Paál, Z. Ceria as a new support of noble metal catalysts for hydrocarbon reactions: Chemisorption and catalytic studies. *Solid State Ionics* **2001**, *141*, 709–713. [CrossRef]

28. Khetan, A.; Pitsch, H.; Han, B. Structure and Reactivity of Sub-Monolayer Pt on CeO2 Surface from First Principles Thermodynamics. *ESC Meet. Abstr.* **2014**, *122*, 153–164.

29. Piccolo, L.; Daly, H.; Valcarcel, A.; Meunier, F.C. Promotional effect of H2 on CO oxidation over Au/TiO2 studied by operando infrared spectroscopy. *Appl. Catal. B* **2009**, *86*, 190–195. [CrossRef]

30. Cao, J.L.; Wang, Y.; Yu, X.L.; Wang, S.R.; Wu, S.H.; Yuan, Z.Y. Mesoporous CuO–Fe3O4 composite catalysts for low-temperature carbon monoxide oxidation. *Appl. Catal. B* **2008**, *79*, 26–34. [CrossRef]

31. Tabakova, T.; Avgouropoulos, G.; Papavasiliou, J.; Manzoli, M.; Boccuzzi, F.; Tenchev, K.; Vindigni, F.; Ioannides, T. CO-free hydrogen production over Au/CeO2–Fe2O3 catalysts: Part 1. Impact of the support composition on the performance for the preferential CO oxidation reaction. *Appl. Catal. B* **2011**, *101*, 256–265. [CrossRef]

32. Zebeda, T.; Martinez-Hernández, A.; Guil-López, R.; Pawelec, B. Preferential CO oxidation in excess of hydrogen over Au/HMS catalysts modified by Ce, Fe and Ti oxides. *Appl. Catal. B* **2010**, *100*, 450–462. [CrossRef]

33. Peza-Ledesma, C.L.; Escamilla-Perea, L.; Nava, R.; Pawelec, B.; Fierro, J.L.G. Supported gold catalysts in SBA-15 modified with TiO2 for oxidation of carbon monoxide. *Appl. Catal. A* **2010**, *375*, 37–48. [CrossRef]

34. Parreira, L.A.; Bogdanchikova, N.; Petstryakov, A.; Zebeda, T.A.; Tuzovskaya, I.; Farias, M.H.; Gusevskaya, E.V. Nanocrystalline gold supported on Fe-, Ti- and Ce-modified hexagonal mesoporous silica as a catalyst for the aerobic oxidative esterification of benzyl alcohol. *Appl. Catal. A* **2011**, *397*, 145–152. [CrossRef]

35. Ayastuy, J.L.; González-Marcos, M.P.; González-Velasco, J.R.; Gutierrez-Ortiz, M.A. MnOx/Pt/Al2O3 catalysts for CO oxidation in H2-rich streams. *Appl. Catal. B* **2007**, *70*, 532–541. [CrossRef]

36. Zhao, Z.; Lin, X.; Jin, R.; Wang, G.; Muhammad, T. MOx (M = Mn, Fe, Ni or Cr) improved supported Co3O4 catalysts on ceria–zirconia nanoparticulate for CO preferential oxidation in H2-rich gases. *Appl. Catal. B* **2012**, *115–116*, 53–62. [CrossRef]
37. Binas, V.D.; Sambani, K.; Maggos, T.; Katsanaki, A.; Kiriakidis, G. Synthesis and photocatalytic activity of Mn-doped TiO$_2$ nanostructured powders under UV and visible light. *Appl. Catal. B* **2012**, *113–114*, 79–86. [CrossRef]

38. Chang, S.M.; Liu, W.S. The roles of surface-doped metal ions (V, Mn, Fe, Cu, Ce, and W) in the interfacial behavior of TiO$_2$ photocatalysts. *Appl. Catal. B* **2014**, *156–157*, 466–475. [CrossRef]

39. Zanella, R.; Giorgio, S.; Henry, C.R.; Louis, C. Alternative methods for the preparation of gold nanoparticles supported on TiO$_2$. *J. Phys. Chem. B* **2002**, *106*, 7634–7642. [CrossRef]

40. Daté, M.; Haruta, M. Moisture Effect on CO Oxidation over Au/TiO$_2$ Catalyst. *J. Catal.* **2001**, *201*, 221–224.

41. Xu, X.L.; Li, J.Q. DFT studies on H$^+$ on TiO$_2$. *Surf. Sci.* **2011**, *605*, 1962–1967. [CrossRef]

42. Na, H.; Zhu, T.; Liu, Z. Effect of preparation method on the performance of Pt–Au/TiO$_2$ catalysts for the catalytic co-oxidation of HCHO and CO. *Cata. Sci. Technol.* **2014**, *4*, 2051–2057.

43. Chen, B.B.; Shi, C.; Crocker, M.; Wang, Y.; Zhu, A.M. Catalytic removal of formaldehyde at room temperature over supported gold catalysts. *Appl. Catal. B* **2013**, *132–133*, 245–255. [CrossRef]

44. Wang, Y.; Zhu, A.; Zhang, Y.; Au, C.T.; Yang, X.; Shi, C. Catalytic reduction of NO by CO over NiO/CeO$_2$ catalyst in stoichiometric NO/CO and NO/CO/O$_2$ reaction. *Appl. Catal. B* **2008**, *81*, 141–149. [CrossRef]

45. Chen, Y.C.; Chen, K.B.; Lee, C.S.; Lin, M.C. Direct Synthesis of Zr-Doped Ceria Nanotubes. *J. Phys. Chem. C* **2009**, *113*, 5031–5034. [CrossRef]

46. Li, H.F.; Zhang, N.; Chen, P.; Luo, M.F.; Lu, J.Q. High surface area Au/CeO$_2$ catalysts for low temperature formaldehyde oxidation. *Appl. Catal. B* **2011**, *110*, 279–285. [CrossRef]

47. Hong, X.; Sun, Y.; Zhu, T.; Liu, Z. Pt–Au/CeO$_2$ catalysts for the simultaneous removal of carbon monoxide and formaldehyde. *Cata. Sci. Technol.* **2016**, *6*, 3606–3615. [CrossRef]

48. An, N.; Yu, Q.; Gang, L.; Li, S.; Jia, M.; Zhang, W. Complete oxidation of formaldehyde at ambient temperature over supported Pt/Fe$_2$O$_3$ catalysts prepared by colloid-deposition method. *J. Hazard. Mater.* **2011**, *186*, 1392–1397. [CrossRef]

49. Lawrence, N.J.; Brewer, J.R.; Wang, L.; Wu, T.S.; Wells-Kingsbury, J.; Ihrig, M.M.; Wang, G.; Soo, Y.L.; Mei, W.N.; Cheung, C.L. Defect engineering in cubic cerium oxide nanostructures for catalytic oxidation. *Nano Lett.* **2011**, *11*, 2666–2671. [CrossRef] [PubMed]

50. Esch, F.; Fabris, S.; Zhou, L.; Montini, T.; Africh, C.; Fornasiero, P.; Comelli, G.; Rosei, R. Electron localization determines defect formation on ceria substrates. *Science* **2005**, *309*, 752–755. [CrossRef] [PubMed]

51. Kim, H.Y.; Lee, H.M.; Henkelman, G. CO oxidation mechanism on CeO$_2$-supported Au nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 1560–1570. [CrossRef] [PubMed]

52. Lykhach, Y.; Kozlov, S.M.; Skala, T.; Tovt, A.; Stetsovych, V.; Tsud, N.; Dvořák, F.; Johánek, V.; Neitzel, A.; Mysliveček, J. Counting electrons on supported nanoparticles. *Nat. Mater.* **2015**, *15*, 284–288. [CrossRef] [PubMed]

53. Shan, W.P.; Liu, F.D.; He, H.; Shi, X.Y.; Zhang, C.B. A superior Ce-W-Ti mixed oxide catalyst for the selective catalytic reduction of NOx with NH$_3$. *Appl. Catal. B* **2012**, *115*, 100–106. [CrossRef]

54. Zhang, C.B.; Liu, F.D.; Zhai, Y.P.; Ariga, H.; Yi, N.; Liu, Y.C.; Asakura, K.; Flytzani-Stephanopoulos, M.; He, H. Alkali-Metal-Promoted Pt/TiO$_2$ Opens a More Efficient Pathway to Formaldehyde Oxidation at Ambient Temperatures. *Angew. Chem. Int. Ed.* **2012**, *51*, 9628–9632. [CrossRef] [PubMed]

55. Sun, S.; Ding, J.; Bao, J.; Gao, C.; Qi, Z.; Li, C. Photocatalytic oxidation of gaseous formaldehyde on TiO$_2$: An in situ DRIFTS study. *Catal. Lett.* **2010**, *137*, 239–246. [CrossRef]

56. Enevoldsen, G.H.; Pinto, H.P.; Foster, A.S.; Jensen, M.C.; Hofer, W.A.; Hammer, B.; Lauritsen, J.V.; Besenbacher, F. Imaging of the hydrogen subsurface site in rutile TiO$_2$. *Phys. Rev. Lett.* **2009**, *102*, 136103. [CrossRef] [PubMed]

57. Park, Y.K.; Aghalayam, P.; Vlachos, D.G. A generalized approach for predicting coverage-dependent reaction parameters of complex surface reactions: Application to H$_2$ oxidation over platinum. *J. Phys. Chem. A* **1999**, *103*, 8101–8107. [CrossRef]

58. Aloisio, S.; Francisco, J. Existence of a Hydroperoxy and Water (HO$_2$·H$_2$O) Radical Complex. *J. Phys. Chem. A* **1998**, *102*, 1899–1902. [CrossRef]

59. Chiorino, A.; Manzoli, M.; Menegazzo, F.; Signoretto, M.; Vindigni, F.; Pinna, F.; Boccuzzi, F. New insight on the nature of catalytically active gold sites: Quantitative CO chemisorption data and analysis of FTIR spectra of adsorbed CO and of isotopic mixtures. *J. Catal.* **2009**, *262*, 169–176. [CrossRef]
60. Comotti, M.; Li, W.C.; Spliethoff, B.; Schüth, F. Support Effect in High Activity Gold Catalysts for CO. *J. Am. Chem. Soc.* **2006**, *128*, 917–924. [CrossRef] [PubMed]

61. Qi, L.; Tang, C.; Zhang, L.; Yao, X.; Cao, Y.; Liu, L.; Gao, F.; Dong, L.; Chen, Y. Influence of cerium modification methods on catalytic performance of Au/mordenite catalysts in CO oxidation. *Appl. Catal. B* **2012**, *127*, 234–245. [CrossRef]

62. Haneda, M.; Suzuki, K.; Sasaki, M.; Hamada, H.; Ozawa, M. Catalytic performance of bimetallic PtPd/Al₂O₃ for diesel hydrocarbon oxidation and its implementation by acidic additives. *Appl. Catal. A* **2014**, *475*, 109–115. [CrossRef]

63. Li, N.; Chen, Q.Y.; Luo, L.F.; Huang, WX.; Luo, M.F.; Hu, G.S.; Lu, J.Q. Kinetic study and the effect of particle size on low temperature CO oxidation over Pt/TiO₂ catalysts. *Appl. Catal. B* **2013**, *142*, 523–532. [CrossRef]

**Sample Availability:** Samples of the compounds are available from the authors.