Research Article

Synthesis of $\text{CoO}_x\text{-TiO}_2$ Catalysts and Its Application for Low-Temperature CO Oxidation

Der-Shing Lee and Yu-Wen Chen

Department of Chemical and Materials Engineering, National Central University, Chung-Li 320, Taiwan

Correspondence should be addressed to Yu-Wen Chen; ywchen@ncu.edu.tw

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A series of $\text{Au/CoO}_x\text{-TiO}_2$ with various Co/Ti ratios prepared. $\text{CoO}_x/\text{TiO}_2$ was prepared by incipient wetness impregnation with aqueous solution of cobalt nitrate. Au catalysts were prepared by deposition-precipitation (DP) method at pH 7 and 338 K. The catalysts were characterized by inductively coupled plasma-mass spectrometry, temperature programming reduction, X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, and X-ray photoelectron spectroscopy. The reaction was carried out in a fixed bed reactor with a feed containing 1% CO in air at weight hourly space velocities of 120,000 mL/h g and 180,000 mL/h g. High gold dispersion and narrow particle size distribution were obtained by DP method. The addition of CoO_x into Au/TiO_2 enhanced the activity of CO oxidation significantly. $\text{Au/5\% CoO}_x\text{-TiO}_2$ had the highest catalyst among all the catalysts. CoO_x was mainly in the form of nanosize Co_3O_4 which could stabilize the Au nanoparticles. CoO_x donated partial electrons to Au. The interactions among Au, CoO_x , and TiO_2 account for the high catalytic activity for CO oxidation.

1. Introduction

Carbon monoxide is a toxic, colorless, and tasteless gas. It can cause human being to die in short time. Low-temperature CO oxidation has been extensively studied because it plays an important role in gas purification in CO_2 lasers, CO gas sensors, air purification devices, and removing trace quantity of CO from ambient air in enclosed atmospheres such as submarines and aircrafts [1–3]. When gold is deposited as nanoparticles on metal oxides, it exhibits surprisingly high catalytic activity for CO oxidation at a temperature as low as 100 K. The activity of gold catalysts also depends on support, preparation method and condition. Haruta and coworkers [1–4] found the high activity of supported gold catalysts for low-temperature CO oxidation. It is believed to occur on the metal-support interface. Cobalt oxides are good in removing the CO, NO_x , and VOC_s in the air. The cobalt oxides have different oxidation states, such as CoO_2 , Co_2O_3 , Co_3O_4 , and CoO. The Co_3O_4 and CoO are more stable than the others. For the activity of CO oxidation reaction, the Co_3O_4 has a higher activity than CoO [5–8]. The Co_3O_4 has been reported to be an effective catalyst in the oxidation reaction.

Furthermore, it has also been used as a support for gold. CoO_x was reported to be active for CO oxidation, but not very active at room temperature. Although CO oxidation on Au catalysts has been extensively studied [9–13], none the of researchers has used $\text{CoO}_x\text{-TiO}_2$ binary oxide as the support.

In this study, the effect of the content of CoO_x in $\text{Au/CoO}_x\text{-TiO}_2$ on the activity of CO oxidation was elucidated. The catalysts were characterized by various techniques.

2. Experimental

2.1. Catalysts Preparation. Reagents used here were analytical grade. P25 TiO_2 was obtained from Evonik Degussa Company. $\text{CoO}_x\text{-TiO}_2$ was prepared by incipient wetness impregnation method. Various amounts of aqueous $\text{Co}(\text{NO}_3)_2$ solution were added into TiO_2 powder under stirring. The traditional incipient wetness impregnation was used in the preparation. The pore volume of TiO_2 was $0.6 \text{ cm}^3/\text{g}$. It was calcined in air at 473 K for 4 h. The temperature was not too high to have Crystalline phase of Co_3O_4 . Au was then added by deposition-precipitation (DP) technique. An aqueous

FIGURE 1: XRD of patterns Au/CoO_x-TiO₂, (a) Au/TiO₂, (b) Au/1% CoO_x-TiO₂, (c) Au/3% CoO_x-TiO₂, (d) Au/5% CoO_x-TiO₂, (e) Au/8% CoO_x-TiO₂, and (f) Au/10% CoO_x-TiO₂.

TABLE 1: Actual gold loading on support of the catalysts.

Catalyst	Nominal (wt.%)		Actual (wt.%)	
	Au	Co	Au	Co
Au/TiO ₂	1	0	0.744	0.00
Au/1% CoO _x -TiO ₂	1	1	0.427	0.45
Au/3% CoO _x -TiO ₂	1	3	0.721	3.24
Au/5% CoO _x -TiO ₂	1	5	0.701	5.25
Au/8% CoO _x -TiO ₂	1	8	0.710	8.89
Au/10% CoO _x -TiO ₂	1	10	0.791	10.6

solution of HAuCl₄ was added into the solution containing suspended CoO_x-TiO₂ support at a rate of 10 mL/min. The temperature of the solution was maintained at 338 K. 1 M NH₄OH solution was used to adjust the pH value to 7. After aging for 2 h, the precipitate was filtered and washed with hot water until no chloride ions were detected. Finally, the sample was dried overnight in air at 353 K and then calcined at 453 K for 4 h. This temperature was high enough to reduce cationic gold to metallic gold, but not too high to cause the sintering of gold particles.

2.2. Characterization. The catalysts were characterized by inductively coupled plasma-mass spectrometry (ICP-MS), X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS).

The exact gold content was analyzed by ICP-MS (PE-SCIEX ELAN 6100 DRC). The cross flow pneumatic nebulizer and double-pass-scott-type spray chamber were used to nebulize the samples. The solution was transferred by peristaltic pump, and the nebulizer used to nebulize the samples into spray chamber detected by DRC-ICP-MS. A CEM MDS-2000

(CEM, Matthews, NC, USA) microwave apparatus equipped with Teflon vessels was used to digest the powder samples.

XRD analysis was performed on a Siemens D5000 powder diffractometer using CuKα1 radiation (0.15405 nm) at a voltage and current of 40 kV and 40 mA, respectively. The sample was scanned over the range of $2\theta = 20-70^\circ$ at a rate of $0.05^\circ/\text{min}$ to identify the crystalline structure. The sample was prepared as a thin layer on a sample holder.

The morphologies and particle sizes of the samples were determined by TEM on a JEM-2000 EX II operated at 160 kV and HRTEM on a JEOL JEM-2010 operated at 160 kV. Initially, a small amount of the sample was placed into a sample tube filled with a 95% methanol solution, and after agitating under ultrasonic environment for 10 min, one drop of the dispersed slurry was dipped onto a carbon-coated copper mesh (no. 300) (Ted Pella Inc., CA, USA), and dried in an oven for 1 h. Images were recorded digitally with a Gatan slow scan camera (GIF). Based on the several images of TEM or HRTEM, more than 100 particles were counted and the size distribution graph was obtained.

The XPS spectra were recorded with a Thermo VG Scientific Sigma Probe spectrometer. The XPS spectra were collected using AlK_α radiation at a voltage and current of 20 kV and 30 mA, respectively. The base pressure in the analyzing chamber was maintained in the order of 10^{-7} Pa. The spectrometer was operated at 23.5 eV pass energy and the binding energy was corrected by contaminant carbon (C_{1s} = 284.5 eV) in order to facilitate the comparisons of the values among the catalysts and the standard compounds. Peak fitting was done using XPSPEAK 4.1 with Shirley background and 30 : 70 Lorentzian/Gaussian convolution product shapes. The full width at half maximum (FWHM) in the entire spectra was 1.3 eV.

2.3. CO Oxidation. The catalytic activities of CO oxidation in air were carried out in a downward, fixed-bed continuous-flow, Pyrex glass tubular reactor loaded with 0.05 g of catalyst. The reactant gas containing 1% CO in air was fed into a reactor with a flow rate of 100 mL/min (WHSV = 120,000 mL/h·g) or 150 mL/min (WHSV = 180,000 mL/h·g). The outlet gas was analyzed by a gas chromatograph (China Chromatography 8700T) equipped with a MS-5A column and a thermal conductivity detector. Calibration of the gases was done with a standard gas containing the known concentration of the components. The CO conversion was calculated as follows:

$$\text{CO conversion } (X_{\text{CO}}\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} * 100\%, \quad (1)$$

where [CO] is the concentration of CO.

3. Results and Discussion

3.1. ICP-MS. The elemental analysis results in Table 1 show the real gold and cobalt loadings in the catalysts. In this study, the original amount of gold in the solution was 1 wt.%, and the content of cobalt was between 1 and 10 wt.%. Only about 70% of Au was deposited by DP process, in agreement

FIGURE 2: The TEM image and Au particle size distribution of Au/CoO_x-TiO₂.

with the literature data. Au/10 wt.% CoO_x-TiO₂ catalyst had the highest Au loading among all catalysts, inferring that adding CoO_x could change the isoelectric point of TiO₂. It is known [4] that the amount of Au deposit in DP process was influenced by the isoelectric point of the support.

3.2. XRD. Figure 1 shows the XRD patterns of Au/CoO_x-TiO₂. All catalysts containing TiO₂ support showed intense XRD peaks for anatase and rutile, as expected. It is known that TiO₂ P-25 has both anatase and rutile structures. Adding cobalt and Au and pretreatment did not change its

FIGURE 3: The TEM diffraction pattern of Au/3% CoO_x-TiO₂.TABLE 2: XPS of binding energy in Au/CoO_x-TiO₂.

Catalyst	Au		Co		Ti		O
	4f7/2	4f5/2	2p3/2	2p1/2	2p3/2	2p1/2	1s
1% CoO _x -TiO ₂	—	—	782.9	798.5	458.9	464.7	533.0
5% CoO _x -TiO ₂	—	—	781.3	796.3	459.1	465.0	530.4
Au/TiO ₂	84.2	87.9	—	—	459.3	465.0	530.3
Au/1% CoO _x -TiO ₂	83.9	87.6	781.8	797.4	458.6	464.4	530.0
Au/3% CoO _x -TiO ₂	83.4	87.1	780.3	795.5	458.4	463.9	529.9
Au/5% CoO _x -TiO ₂	82.9	86.6	779.4	794.7	458.5	464.0	529.9
Au/TiO ₂ *	84.1	87.8	—	—	458.8	464.5	530.3
Au/1% CoO _x -TiO ₂ *	83.9	87.5	781.8	797.4	458.4	464.2	530.1
Au/3% CoO _x -TiO ₂ *	84.1	87.8	779.8	796.0	458.8	464.4	530.1
Au/5% CoO _x -TiO ₂ *	84.7	88.4	781.2	796.5	458.2	463.9	529.7

* After reaction.

crystallinity, because the condition was not harsh. The peaks at $2\theta = 36.85^\circ$ (311), 59.35° (511), and 65.27° (440) corresponding to Co₃O₄ were observed in the XRD patterns, but the peaks were very weak even in the sample with 10 wt.%CoO_x, indicating that CoO_x was a very small particle of Co₃O₄. No distinct gold peaks at $2\theta = 38.2^\circ$ and 44.5° were observed, because the particle size of gold was too small to detect.

3.3. TEM. Figure 2 shows the TEM images and the gold particle size distributions of various Au/CoO_x-TiO₂ catalysts. The gold particles in images were observed as dark spots. The TEM images clearly show that the average particle size of Au in these catalysts was around 3 nm. The results are in accordance with the XRD results, which showed that Au particle sizes were less than 4 nm. The electron diffraction pattern of Au/3%CoO_x-TiO₂ catalyst is shown in Figure 3. It shows many diffraction rings corresponding to the crystalline lattices of TiO₂, Co₃O₄, and Au, in agreement with XRD results.

3.4. HRTEM. The HRTEM images on the sample Au/3% CoO_x-TiO₂ in different spots are shown in Figure 4. Figure 4(a) shows that CoO_x aggregated on TiO₂ surface. The gold particles were well dispersed on both CoO_x and TiO₂. Figure 4(b) shows that CoO_x and TiO₂ had a strong interaction with each other. Figure 4(c) shows that the gold particle deposited on CoO_x, and had strong interaction with CoO_x-TiO₂. Figure 4(d) shows that the gold particle deposited on TiO₂. It can be observed that the particle size of Au was very small. The Au particle size was about 3 nm. Both TEM and HRTEM diffraction images show the diffraction ring of Co₃O₄ (220), confirming the formation of Co₃O₄ in these samples.

3.5. XPS. The XPS analysis was carried out on all the samples, and the binding energies and compositions of all the samples were tabulated in Tables 2 and 3. Au 4f is characterized by the doublet of two spin-orbit components, namely, Au 4f_{7/2} and Au 4f_{5/2} as shown in Figure 5. The binding energies of

FIGURE 4: The HRTEM image of Au/3% CoO_x-TiO₂.

Au⁰ and Au⁺ in Au 4f_{7/2} are 84.0 and 85.5 eV, respectively. The binding energy of Au 4f shifted to a lower one by adding CoO_x in Au/TiO₂, but there was no regular trend with the content of CoO_x. The composition of Au⁰ and Au⁺ did not have the relationship with CoO_x content. The binding energy of Au 4f_{7/2} on all of the catalysts shifted to a higher binding energy after reaction. The composition of Au⁰ and Au⁺ was changed after reaction as shown in Figure 6. The presence of Au⁺ species seems to be effective in promoting activity for CO oxidation [10, 13]. The Au⁺ species in Au/3% CoO_x-TiO₂ was abundant compared to other catalysts.

The XPS spectra of Co 2p of various samples are shown in Figure 7. Co 2p is characterized by the doublet of two spin-orbit components, namely, Co 2p_{3/2} and Co 2p_{1/2}. The binding energies of Co 2p_{3/2} and Co 2p_{1/2} were 778 and 793 eV [14]. The binding energy shifted to a lower energy when gold was on the support. The binding energy decreased with increasing the content of CoO_x. The XRD results and

TEM diffraction images showed that the CoO_x was in the form of Co₃O₄. The XPS spectra of Co 2p of various samples after reaction are shown in Figure 8.

As shown in Figure 9, the binding energy of lattice oxygen in TiO₂ was 529 eV [12–15], and the binding energy of OH[−] group in TiO₂ was 531.8 eV [12–15]. The O 1s spectra showed no distinction between Au/TiO₂ and Au/CoO_x-TiO₂. Figure 9(a) shows that O 1s spectrum of 1%CoO_x-TiO₂ shifted to higher a position, due to the SMSI effect on Co and TiO₂, and the binding energy was ~533 eV. The binding energy of O 1s did not change with the content of CoO_x. There is no distinction between the samples before and after reaction, as shown in Figure 10.

Ti 2p is characterized by the doublet of two spin-orbit components, namely, Ti 2p_{3/2} and Ti 2p_{1/2}. The gap between Ti 2p_{3/2} and Ti 2p_{1/2} is 5–6 eV, it is ascribed to Ti⁴⁺ (458.9 eV) [16]. As shown in Figure 11, the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} of Au/CoO_x-TiO₂ shifted to lower ones than

TABLE 3: XPS analysis in Au/CoO_x-TiO₂.

Catalyst	Au		Co		O	
	Au ⁰	Au ⁺	Co ²⁺	Co ³⁺	O ²⁻	OH ⁻
1% CoO _x -TiO ₂	—	—	72.6	27.4	84.1	15.9
5% CoO _x -TiO ₂	—	—	35.2	64.8	82.1	17.9
Au/TiO ₂	68.5	31.5	—	—	64.5	35.5
Au/1% CoO _x -TiO ₂	83.4	16.6	50.8	41.2	76.9	23.1
Au/3% CoO _x -TiO ₂	56.3	43.7	49.6	50.4	89.8	10.2
Au/5% CoO _x -TiO ₂	70.2	29.8	41.7	58.3	91.4	8.6
Au/TiO ₂ *	92.9	7.1	—	—	81.5	18.5
Au/1% CoO _x -TiO ₂ *	72.9	27.1	41.2	58.8	80.4	19.6
Au/3% CoO _x -TiO ₂ *	71.8	28.2	47.8	52.2	69.5	30.5
Au/5% CoO _x -TiO ₂ *	72.4	28.6	58.3	41.7	68.5	31.5

* After reaction.

FIGURE 5: XPS of Au 4f spectra of the catalysts before reaction: (a) Au/TiO₂, (b) Au/1% CoO_x-TiO₂, (c) Au/3% CoO_x-TiO₂, and (d) Au/5% CoO_x-TiO₂ (Au⁰ is the dash line, and Au⁺ is the short-dash line). FIGURE 7: XPS of Co 2p spectra of the catalysts before reaction: (a) 1% CoO_x-TiO₂, (b) 5% CoO_x-TiO₂, (c) Au/1% CoO_x-TiO₂, (d) Au/3% CoO_x-TiO₂, and (e) Au/5% CoO_x-TiO₂, (Co²⁺ is the dash line, and Co³⁺ is the short dash line). FIGURE 6: XPS of Au 4f spectra of the catalysts after reaction: (a) Au/TiO₂, (b) Au/1% CoO_x-TiO₂, (c) Au/3% CoO_x-TiO₂, and (d) Au/5% CoO_x-TiO₂ (Au⁰ is the dash line, and Au⁺ is the short dash line). FIGURE 8: XPS of Co 2p spectra of the catalysts after reaction: (a) Au/1% CoO_x-TiO₂, (b) Au/3% CoO_x-TiO₂, and (c) Au/5% CoO_x-TiO₂ (Co²⁺ is the dash line, and Co³⁺ is the short dash line).

FIGURE 9: XPS of O 1s spectra of the catalysts before reaction: (a) 1% CoO_x - TiO_2 , (b) 5% CoO_x - TiO_2 , (c) Au/TiO_2 , (d) $\text{Au/1\% CoO}_x$ - TiO_2 , (e) $\text{Au/3\% CoO}_x$ - TiO_2 , and (f) $\text{Au/5\% CoO}_x$ - TiO_2 (O^{2-} is the blue dash line and OH^- is the red dash line).

FIGURE 11: XPS of Ti 2p spectra of the catalysts before reaction: (a) 1% CoO_x - TiO_2 , (b) 5% CoO_x - TiO_2 , (c) Au/TiO_2 , (d) $\text{Au/1\% CoO}_x$ - TiO_2 , (e) $\text{Au/3\% CoO}_x$ - TiO_2 , and (f) $\text{Au/5\% CoO}_x$ - TiO_2 .

FIGURE 10: XPS of O 1s spectra of the catalysts after reaction: (a) Au/TiO_2 , (b) $\text{Au/1\% CoO}_x$ - TiO_2 , (c) $\text{Au/3\% CoO}_x$ - TiO_2 , and (d) $\text{Au/5\% CoO}_x$ - TiO_2 (O^{2-} is the blue dash line and OH^- is the red dash line).

FIGURE 12: XPS of Ti 2p spectra of the catalysts after reaction: (a) Au/TiO_2 , (b) $\text{Au/1\% CoO}_x$ - TiO_2 , (c) $\text{Au/3\% CoO}_x$ - TiO_2 , and (d) $\text{Au/5\% CoO}_x$ - TiO_2 .

those of Au/TiO_2 , indicating the interaction of CoO_x with TiO_2 . The Ti 2p spectra of the samples did not change after reaction as shown in Figure 12.

3.6. CO Oxidation. All of the Au/CoO_x - TiO_2 catalysts were very active for CO oxidation. Figure 13 shows that the addition of CoO_x to Au/TiO_2 could enhance the activity of the catalyst significantly. At weight hourly space velocity (WHSV) of 120,000 mL/g h, CO conversions on all Au/CoO_x - TiO_2 catalysts reach 100% even at 308 K. In contrast, Au/TiO_2 was not active at room temperature. It should be noted that only 0.7 wt.% Au was used in this study. In order to differentiate the activities of these catalysts, a higher WHSV of 180,000 mL/h g was used. Figure 14 shows that the best catalyst was $\text{Au/3\% CoO}_x$ - TiO_2 . $\text{Au/3\% CoO}_x$ - TiO_2 could

oxidize CO completely at low temperature, and the result was similar with Cunningham et al. [17]. It contained the highest gold loading and the highest content of active sites (Au^+). Our results were different from that reported by Haruta [1] for Au/TiO_2 , because they used a different amount of gold. 1 wt.% Au/TiO_2 was used in this study, and 10 wt.% Au/TiO_2 was used in their study [1]. It should be noted that Co_3O_4 is an active catalyst for CO oxidation [18, 19], but not at ambient condition. By adding Au on the Co_3O_4 , the catalyst became very active at ambient condition. The results clearly demonstrated that Au/CoO_x - TiO_2 catalyst is a promising catalyst for CO oxidation at ambient condition. The small Au particle size, narrow Au particle size distribution, and well Au dispersions on CoO_x - TiO_2 support play the key roles. The presence of CoO_x could stabilize the nano Au particles, resulting in high activity of the catalyst [20–25].

FIGURE 13: The CO conversion on Au/CoO_x-TiO₂ Reaction condition: 1% CO in air, WHSV = 120,000 mL/hg.

FIGURE 14: The CO conversion on Au/CoO_x-TiO₂ Reaction condition: 1% CO in air, WHSV = 180,000 mL/hg.

4. Conclusion

CoO_x-TiO₂ supports were prepared by incipient wetness impregnation method. Au catalysts were prepared by DP method to load Au on these supports. The results showed small Au particle size (2.4–3.3 nm), narrow Au particle size distribution, and well Au dispersions on these catalysts. Au/10% CoO_x-TiO₂ had the maximum gold loading. CoO and TiO₂ had interactions between each other. Adding Co into Au/TiO₂ could increase the activity of CO oxidation. CO chemisorbed on octahedrally coordinated cobalt sites, while tetrahedrally coordinated cobalt sites were inactive for CO adsorption. It could enhance the activity of CO

oxidation. Comparing the other catalysts in this study, the Au/3% CoO_x-TiO₂ catalyst had the highest CO conversion at a low temperature. It contained the highest gold loading and the highest content of active sites (Au⁺).

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