

Article

Pt/MO_x/SiO₂, Pt/MO_x/TiO₂, and Pt/MO_x/Al₂O₃ Catalysts for CO Oxidation

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Abstract: Conventional supported Pt catalysts have often been prepared by loading Pt onto commercial supports, such as SiO₂, TiO₂, Al₂O₃, and carbon. These catalysts usually have simple metal-support (*i.e.*, Pt-SiO₂) interfaces. To tune the catalytic performance of supported Pt catalysts, it is desirable to modify the metal-support interfaces by incorporating an oxide additive into the catalyst formula. Here we prepared three series of metal oxide-modified Pt catalysts (*i.e.*, Pt/MO_x/SiO₂, Pt/MO_x/TiO₂, and Pt/MO_x/Al₂O₃, where M = Al, Fe, Co, Cu, Zn, Ba, La) for CO oxidation. Among them, Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃ showed the highest catalytic activities. Relevant samples were characterized by N₂ adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), H₂ temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS), CO temperature-programmed desorption (CO-TPD), O₂ temperature-programmed desorption (O₂-TPD), and CO₂ temperature-programmed desorption (CO₂-TPD).

Keywords: Pt catalysts; cobalt oxide; CO oxidation

1. Introduction

Supported metal catalysts have been widely used in a number of reactions for the synthesis of chemicals, the ablation of environmental pollutants, and the processing of fossil, hydrogen, and biomass fuels [1]. These catalysts are usually prepared by impregnating solid supports with soluble and decomposable metal salts followed by calcination (thermal decomposition) and appropriate reduction. Alternatively, metal colloids (nanoparticles) can be deposited onto supports. The commonly used supports include SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , CeO_2 , and carbon. These supported metal catalysts usually have simple metal-support (*i.e.*, Pt- SiO_2) interfaces.

A way to tune the local structure and functionality of supported metal catalysts is to put an additive such as a small amount of metal oxide, either before or after loading metals onto supports. In many circumstances, the properties (e.g., thermal stability, redox property, acid-base property) of supported metal catalysts can be changed accordingly [2–4].

One case in point is the development of metal oxide-promoted Au catalysts. It is often recognized that Au nanoparticles supported on TiO_2 support can sinter under elevated temperatures, thus leading to decreased catalytic activity. To circumvent this problem, Yan *et al.* modified TiO_2 support with some Al_2O_3 additives, and then loaded Au onto the modified support ($\text{Al}_2\text{O}_3/\text{TiO}_2$) via deposition-precipitation [5]. The resulting $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ showed better thermal stability than the conventional Au/TiO_2 , and therefore retained significant catalytic activity after being treated at 500 °C. Ma extended this modification to the development of a series of $\text{Au}/\text{M}_x\text{O}_y/\text{TiO}_2$ ($\text{M} = \text{Ca}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Ga}, \text{Y}, \text{Zr}, \text{Mo}, \text{W}, \text{Bi}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) catalysts, and found that some additives can stabilize Au nanoparticles and lead to better catalytic activity in CO oxidation [6] and the water-gas shift reaction [7]. This modification strategy is general, as demonstrated in numerous studies on the development of modified Au catalysts [8–12].

Supported Pt catalysts are useful in various reactions related to chemical synthesis, environmental catalysis, and fuel conversions. The previous research has focused on the influence of preparation methods and details on the performance of Pt catalysts in a wide range of reactions. There are numerous papers on the application of modified Pt catalysts in many reactions [13–19]. For instance, Nieuwenhuys and co-workers developed a number of promoted Pt catalysts for automotive pollution control [20–22]. Kondarides and co-workers developed $\text{Pt}/\text{MO}_x/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{MO}_x/\text{TiO}_2$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Y}, \text{Zr}, \text{La}, \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Er}, \text{Tm}$) catalysts, and found that most of these composite catalysts are more active than the corresponding $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/TiO_2 in the water-gas shift reaction [23]. However, there are few comprehensive reports on the development of several series of modified Pt catalysts for CO oxidation.

In this work, we modified commercial SiO_2 , TiO_2 , and Al_2O_3 supports with metal oxide (MO_x , $\text{M} = \text{Al}, \text{Fe}, \text{Co}, \text{Cu}, \text{Zn}, \text{Ba}, \text{La}$) additives, and then loaded Pt onto the modified supports by conventional impregnation. These catalysts were screened using catalytic CO oxidation as a probe reaction. Among them, $\text{Pt}/\text{CoO}_x/\text{SiO}_2$, $\text{Pt}/\text{CoO}_x/\text{TiO}_2$, and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ catalysts showed the highest activities and were subjected to detailed characterization.

2. Results and Discussion

2.1. Effect of Pretreatment in 4% H₂/He

All the Pt catalysts reported here were prepared using H₂PtCl₆ as the precursor via impregnation. H₂PtCl₆ is a relatively cheap Pt precursor, and has been commonly used in the preparation of supported Pt catalysts. Impregnation is a convenient way to prepare supported metal catalysts in the laboratories and in industry. In the literature, as-prepared Pt catalysts (prepared by calcining H₂PtCl₆/supports) were sometimes pretreated in H₂ at elevated temperatures to reduce cationic Pt and remove residual Cl [24–26].

Results from our initial experiments involving Pt/SiO₂, Pt/TiO₂, and Pt/Al₂O₃ indeed show that it is necessary to pretreat the catalysts in H₂ prior to catalytic testing. As shown in Figure S1 in the Supporting Information, Pt/SiO₂, Pt/TiO₂, and Pt/Al₂O₃ catalysts pretreated in 4% H₂ at 300 °C are active in CO oxidation, achieving 50% CO conversion at 176, 142, and 117 °C, respectively. On the other hand, Pt/SiO₂, Pt/TiO₂, and Pt/Al₂O₃ (prepared by calcining H₂PtCl₆/SiO₂, H₂PtCl₆/TiO₂, and H₂PtCl₆/Al₂O₃ at 500 °C) not pretreated in 4% H₂ are much less active. Therefore, in the flowing experiments, all the catalysts were pretreated in 4% H₂ prior to reaction testing.

2.2. Pt/MO_x/SiO₂ Catalysts

Figure 1 shows the CO conversions on Pt/MO_x/SiO₂ catalysts as a function of reaction temperature. Pt/SiO₂ starts to show CO conversion above 75 °C, and achieves 50% and 100% CO conversion at 141 and 150 °C, respectively. The catalytic activities of various catalysts, in terms of their *T*₅₀ (temperature required for 50% conversion) values, follow the sequence of Pt/CoO_x/SiO₂ (*T*₅₀ = 32 °C) > Pt/BaO/SiO₂ (*T*₅₀ = 121 °C) > Pt/La₂O₃/SiO₂ (*T*₅₀ = 136 °C) > Pt/SiO₂ (*T*₅₀ = 141 °C) > Pt/CuO_x/SiO₂ (*T*₅₀ = 143 °C) > Pt/Al₂O₃/SiO₂ (*T*₅₀ = 151 °C) ~ Pt/ZnO/SiO₂ (*T*₅₀ = 151 °C) > Pt/FeO_x/SiO₂ (*T*₅₀ = 170 °C). The trend is also clearly seen from the positions of the conversion curves in Figure 1. In particular, Pt/CoO_x/SiO₂ is the most active and can achieve complete CO conversion at 55 °C.

Figure 2 shows the XRD patterns of Pt/MO_x/SiO₂ catalysts collected after reaction testing. These catalysts are referred to as spent Pt/MO_x/SiO₂ catalysts. We picked out spent catalysts for XRD characterization because they are closer to the working catalysts after being exposed to the reaction ambient. Pure SiO₂ (reference sample) shows a broad peak centered at 22°, indicating its amorphous nature. For Pt/SiO₂, five additional peaks appear at 2θ = 39.7°, 46.2°, 67.4°, 81.2°, and 85.7°, assigned to metallic Pt. The Pt peaks are sharp, indicating the presence of big Pt particles. As shown in Figure 2, the addition of FeO_x or ZnO does not decrease the intensities of Pt peaks obviously, whereas the addition of Al₂O₃, CoO_x, CuO_x, BaO, or La₂O₃ attenuates the Pt peaks significantly, indicating the stabilization of Pt nanoparticles on the latter MO_x/SiO₂ supports.

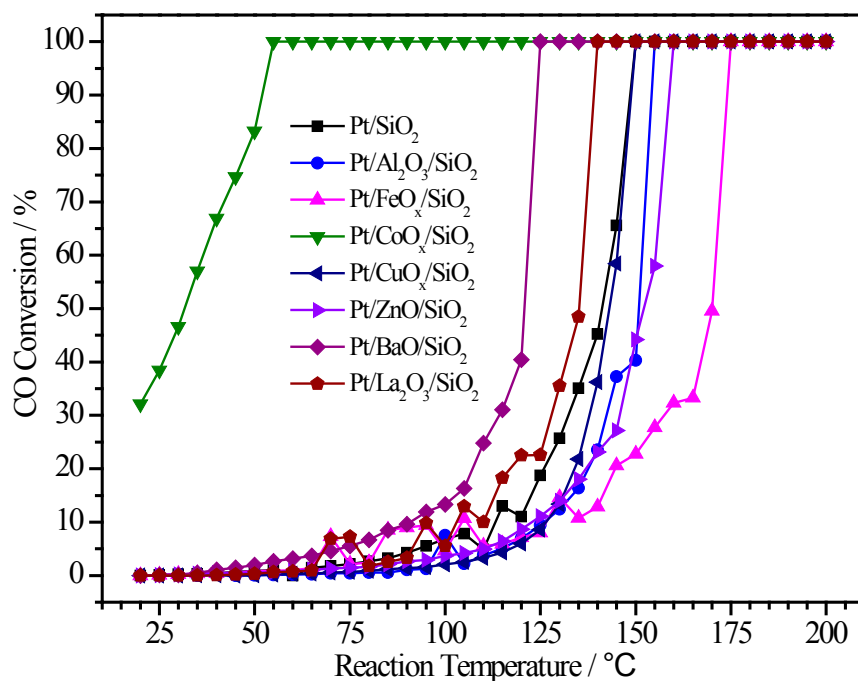


Figure 1. CO conversions on Pt/MO_x/SiO₂ catalysts as a function of reaction temperature.

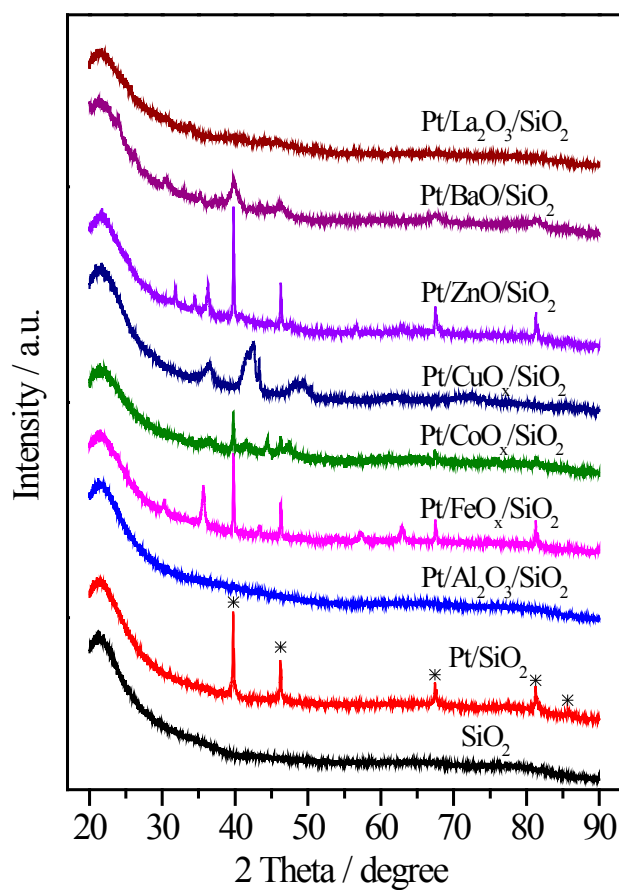


Figure 2. XRD patterns of Pt/MO_x/SiO₂ catalysts collected after reaction testing. The XRD pattern of SiO₂ support is shown for comparison. (*: Pt).

From Figure 2, some peaks other than the characteristic peaks of Pt and SiO₂ can be seen. Therefore, these data were analyzed more carefully. As shown in Figure S2, the Pt/FeO_x/SiO₂ collected after 4% H₂ pretreatment and reaction testing has three sets of peaks corresponding to Pt, Fe₂O₃, and SiO₂. The spent Pt/CoO_x/SiO₂ contains Pt, CoO, Co₃O₄, and SiO₂. The spent Pt/CuO_x/SiO₂ contains Cu₃Pt, Cu₂O, Cu, and SiO₂. The spent Pt/ZnO/SiO₂ contains Pt, ZnO, and SiO₂.

The MO_x content of MO_x/SiO₂ supports prepared by incipient wetness impregnation was intended to be fixed at 0.05 g MO_x per g SiO₂, *i.e.*, the content of MO_x in the catalyst was intended to be 4.76 wt.%. The Pt content of the catalysts prepared by incipient wetness impregnation was intended to be 2 wt.%. However, some loss of Pt was found to occur during the calcination of the H₂PtCl₆/MO_x/SiO₂ precursors in porcelain crucibles. The inner walls of porcelain crucibles become shinny in some cases, indicating the coating of the inner walls by metallic Pt. In addition, after drying the slurry containing H₂PtCl₆ and MO_x/SiO₂ in a beaker, some dried H₂PtCl₆ may adhere to the bottom or wall of the beaker. A similar phenomenon can happen for the preparation of MO_x/SiO₂ supports.

We then analyzed the Pt and M contents of Pt/MO_x/SiO₂ catalysts by ICP. Here the contents of M rather than MO_x were presented due to the oxidation states of some MO_x are unknown at this stage. As shown in Table 1, the M contents of Pt/MO_x/SiO₂ catalysts are in the range of 1.14–4.4 wt.%, and the Pt contents are in the range of 0.31–1.78 wt.%. The atomic Pt:M ratios are in the range of 1:3.3 and 1:24. From Figure 1 and Table 1, it is clear that the addition of CoO_x can dramatically increase the catalytic activity in CO oxidation. We will present more characterization data in later sections.

Table 1. ICP results, T_{50} , and T_{100} for Pt/MO_x/SiO₂ catalysts.

Sample	Pt (wt.%)	M (wt.%)	Atomic Pt:M	T_{50} (°C)	T_{100} (°C)
Pt/SiO ₂	0.90	-	1:0	141	150
Pt/Al ₂ O ₃ /SiO ₂	1.78	2.34	1:9.5	151	155
Pt/FeO _x /SiO ₂	0.95	1.14	1:4.2	170	175
Pt/CoO _x /SiO ₂	0.48	1.80	1:12.4	32	55
Pt/CuO _x /SiO ₂	0.31	2.42	1:24	143	150
Pt/ZnO/SiO ₂	0.96	2.65	1:8.2	151	160
Pt/BaO/SiO ₂	0.46	4.40	1:13.6	121	125
Pt/La ₂ O ₃ /SiO ₂	1.00	2.34	1:3.3	136	140

2.3. Pt/MO_x/TiO₂ Catalysts

Figure 3 shows the CO conversions on Pt/MO_x/TiO₂ catalysts as a function of reaction temperature. Pt/TiO₂ begins to show some activity above 120 °C, and achieves 50% and 100% CO conversions at 176 and 180 °C, respectively. Apparently, Pt/TiO₂ is less active than Pt/SiO₂ reported above. From Figure 3, it is also clear that all the MO_x additives promote the catalytic activity, and the most effective promoter is still CoO_x. Pt/CoO_x/TiO₂ achieves 50% and 100% CO conversion at 91 and 115 °C, respectively.

Figure 4 shows the XRD patterns of spent Pt/MO_x/TiO₂ catalysts. Comparing the XRD patterns of Pt/TiO₂ and TiO₂, it is clear that Pt/TiO₂ shows additional peaks at $2\theta = 39.7^\circ$, 46.2° , 67.4° , 81.2° , and 85.7° , corresponding to metallic Pt. In particular, the peak at $2\theta = 39.7^\circ$ is the sharpest. These metallic Pt peaks are not as obvious as those shown in Figure 2, because the SiO₂ support in Figure 2 is amorphous and its XRD peaks have low intensities, whereas the TiO₂ support in Figure 4 is crystalline (mainly

anatase) and its XRD peaks have high intensities. As seen from Figure 4, the addition of FeO_x does not attenuate the metallic Pt peaks, and the addition of CoO_x attenuates the metallic Pt peaks slightly, whereas the addition of other oxide additives lead to obviously attenuated Pt peaks, indicating the stabilization of Pt nanoparticles. No additional peaks can be observed.

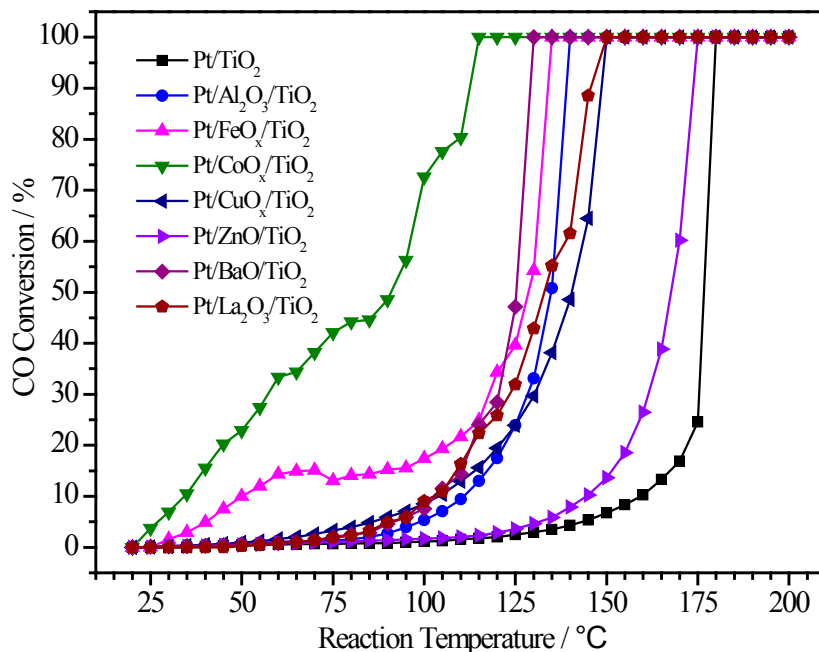


Figure 3. CO conversions on $\text{Pt}/\text{MO}_x/\text{TiO}_2$ catalysts as a function of reaction temperature.

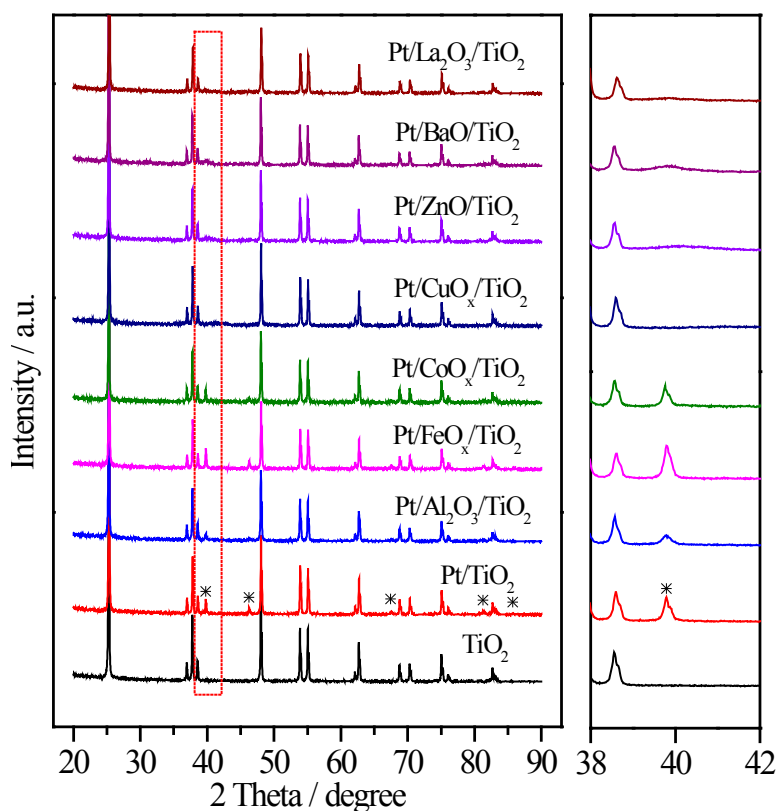


Figure 4. XRD patterns of $\text{Pt}/\text{MO}_x/\text{TiO}_2$ catalysts collected after reaction testing. The XRD pattern of TiO_2 support is shown for comparison. (*: Pt).

The Pt and M contents of Pt/MO_x/TiO₂ catalysts are shown in Table 2. The M contents of Pt/MO_x/TiO₂ catalysts are in the range of 2.4–3.66 wt.%, and the Pt contents are in the range of 0.9–1.74 wt.%. From Figure 3 and Table 2, it is clear that the addition of CoO_x can dramatically increase the catalytic activity in CO oxidation.

Table 2. ICP results, T_{50} , and T_{100} for Pt/MO_x/TiO₂ catalysts.

Sample	Pt (wt.%)	M (wt.%)	Atomic Pt:M	T_{50} (°C)	T_{100} (°C)
Pt/TiO ₂	1.20	-	1:0	176	180
Pt/Al ₂ O ₃ /TiO ₂	1.50	2.40	1:11.6	135	140
Pt/FeO _x /TiO ₂	1.74	2.90	1:5.8	128	135
Pt/CoO _x /TiO ₂	0.90	2.79	1:10.2	91	115
Pt/CuO _x /TiO ₂	1.64	3.66	1:6.8	140	150
Pt/ZnO/TiO ₂	1.68	3.26	1:5.8	167	175
Pt/BaO/TiO ₂	1.67	3.54	1:3.0	126	130
Pt/La ₂ O ₃ /TiO ₂	1.20	3.02	1:3.5	133	150

2.4. Pt/MO_x/Al₂O₃ Catalysts

Figure 5 shows the CO conversions on Pt/MO_x/Al₂O₃ catalysts as a function of reaction temperature. Pt/Al₂O₃ starts to show some activity above 75 °C, and achieves 50% and 100% CO conversions at 121 and 125 °C, respectively. Apparently, Pt/Al₂O₃ is more active than Pt/SiO₂ and Pt/TiO₂. For the Pt/MO_x/Al₂O₃ catalysts, the activities follow the sequence Pt/CoO_x/Al₂O₃ > Pt/BaO/Al₂O₃ > Pt/Al₂O₃ > Pt/CuO_x/Al₂O₃ ~ Pt/FeO_x/Al₂O₃ > Pt/ZnO/Al₂O₃ > Pt/La₂O₃/Al₂O₃. In particular, Pt/CoO_x/Al₂O₃ shows complete CO conversion at room temperature (RT).

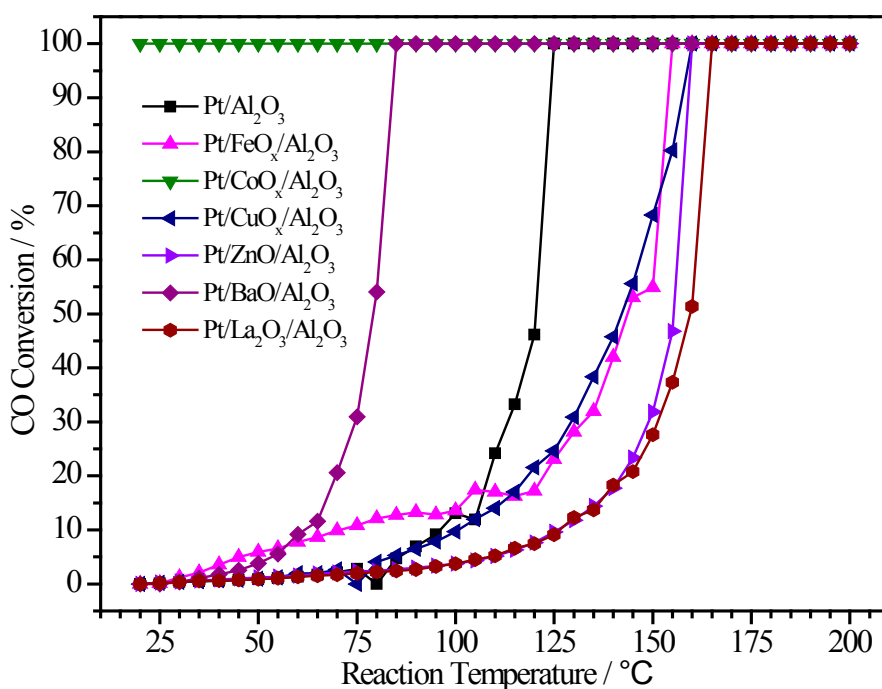


Figure 5. CO conversions on Pt/MO_x/Al₂O₃ catalysts as a function of reaction temperature.

Figure 6 shows the XRD patterns of Pt/MO_x/Al₂O₃. The Al₂O₃ used in this study is crystalline (α -Al₂O₃). Pt/Al₂O₃ shows characteristic α -Al₂O₃ and metallic Pt peaks. The addition of Fe₂O₃ does not lead to attenuated metallic Pt peaks, whereas the addition of other metal oxide additives can attenuate the metallic Pt peaks, indicating the stabilization of Pt nanoparticles.

The Pt and M contents of Pt/MO_x/Al₂O₃ catalysts are shown in Table 3. The M contents of these catalysts are in the range of 0.08–4.00 wt.%, and the Pt contents are in the range of 0.33–0.92 wt.%, indicating that the Pt contents are relatively low on the MO_x/Al₂O₃ supports.

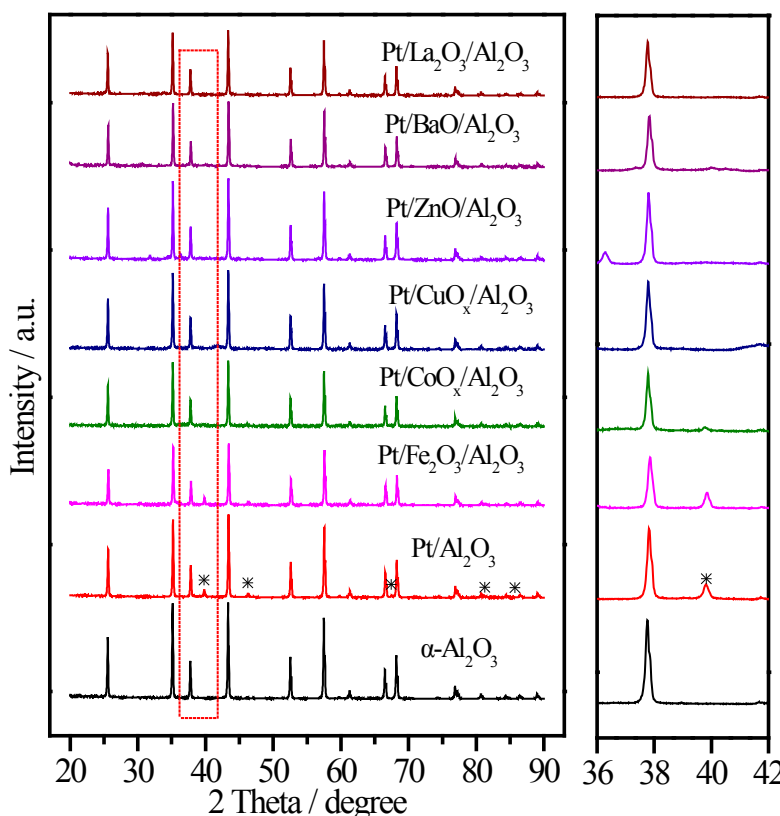


Figure 6. XRD patterns of Pt/MO_x/Al₂O₃ catalysts collected after reaction testing. The XRD pattern of α -Al₂O₃ support is shown for comparison. (*: Pt).

Table 3. ICP results, T_{50} , and T_{100} for Pt/MO_x/Al₂O₃ catalysts.

Sample	Pt (wt.%)	M (wt.%)	Atomic Pt:M	T_{50} (°C)	T_{100} (°C)
Pt/Al ₂ O ₃	0.75	-	1:0	121	125
Pt/FeO _x /Al ₂ O ₃	0.69	0.08	1:0.4	143	155
Pt/CoO _x /Al ₂ O ₃	0.33	0.39	1:3.9	<RT	<RT
Pt/CuO _x /Al ₂ O ₃	0.38	3.73	1:30.1	142	160
Pt/ZnO/Al ₂ O ₃	0.92	2.79	1:9.0	156	160
Pt/BaO/Al ₂ O ₃	0.41	4.00	1:13.9	79	85
Pt/La ₂ O ₃ /Al ₂ O ₃	0.80	2.42	1:4.2	159	165

2.5. Control Experiments

It is clear from Figures 1, 3, and 5 that the addition of certain MO_x additives can significantly enhance the activity in CO oxidation. To see whether the activity is due to MO_x/SiO₂, MO_x/TiO₂, and MO_x/SiO₂

alone (without Pt), these modified supports were tested in CO oxidation. As shown in Figure S3, among MO_x/SiO_2 supports, only $\text{CoO}_x/\text{SiO}_2$ shows some activity above 140 °C. Among MO_x/TiO_2 supports, only $\text{CoO}_x/\text{TiO}_2$ and $\text{CuO}_x/\text{TiO}_2$ show some activity above 130 °C. Among $\text{MO}_x/\text{Al}_2\text{O}_3$ supports, only $\text{CoO}_x/\text{Al}_2\text{O}_3$ and $\text{CuO}_x/\text{TiO}_2$ show some activity above 75 and 100 °C, respectively. These data underscore the importance of integrating three components (Pt, MO_x , and oxide support) in improving the catalytic activity.

Figure 7 compares the catalytic activities of $\text{Pt}/\text{CoO}_x/\text{SiO}_2$, $\text{Pt}/\text{CoO}_x/\text{TiO}_2$, $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ and their corresponding supports. Although $\text{CoO}_x/\text{SiO}_2$, $\text{CoO}_x/\text{TiO}_2$, and $\text{CoO}_x/\text{Al}_2\text{O}_3$ show significant activities, the high activities of $\text{Pt}/\text{CoO}_x/\text{SiO}_2$, $\text{Pt}/\text{CoO}_x/\text{TiO}_2$, and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ are not contributed from $\text{CoO}_x/\text{SiO}_2$, $\text{CoO}_x/\text{TiO}_2$, and $\text{CoO}_x/\text{Al}_2\text{O}_3$ alone.

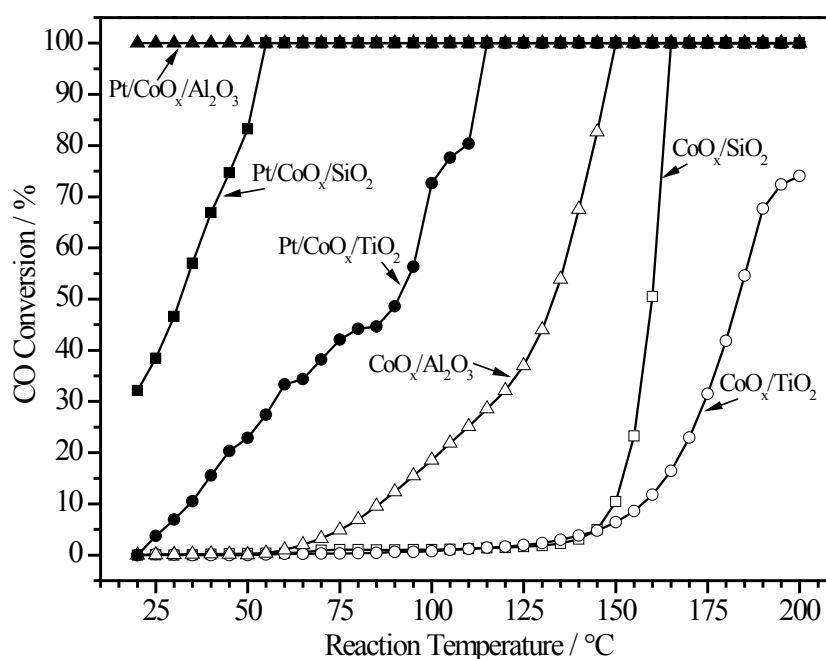


Figure 7. CO conversions on $\text{Pt}/\text{CoO}_x/\text{SiO}_2$, $\text{Pt}/\text{MO}_x/\text{TiO}_2$ and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ catalysts as a function of reaction temperature.

To put the work in perspective, an additional sample, Pt/CoO_x was synthesized by decomposing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 500 °C followed by loading Pt via impregnation. The CoO_x prepared by thermal decomposition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has a BET surface area of 4.5 m^2/g , and the Pt content of Pt/CoO_x is determined by ICP as 0.30 wt.%. The catalyst was tested after being pretreated in 4% H_2 at 300 °C. As seen in Figure S4, $\text{Pt}/\text{Co}_3\text{O}_4$ starts to show CO conversion above 25 °C, and reaches 50% and 100% conversions at 126 and 135 °C, respectively.

2.6. More Characterization of CoO_x -Promoted Pt Catalysts

2.6.1. TEM Data

Figure 8A,B shows the TEM images of Pt/SiO_2 collected after reaction testing. The majority of the amorphous SiO_2 spheres are micrometer-sized. There are a portion of small-sized SiO_2 spheres. This feature is consistent with the low surface area of the SiO_2 support (0.4 m^2/g). In addition, some wind-like

amorphous SiO_2 substances attach to SiO_2 spheres. Pt/SiO_2 contains a wide range of Pt particles sizes, normally on the order of 5–20 nm. The average Pt particle size is 13.0 nm.

Figure 8C,D shows the TEM images of spent $\text{Pt}/\text{CoO}_x/\text{SiO}_2$. The BET surface area of $\text{CoO}_x/\text{SiO}_2$ support is $1.4 \text{ m}^2/\text{g}$. It seems that Pt nanoparticles tend to attach to the wind-like amorphous features rather than SiO_2 spheres. In addition, Pt nanoparticles on $\text{CoO}_x/\text{SiO}_2$ support are quite small and the mean particle size is 2.4 nm. The size distributions of Pt particles are shown in Figure 8E,F.

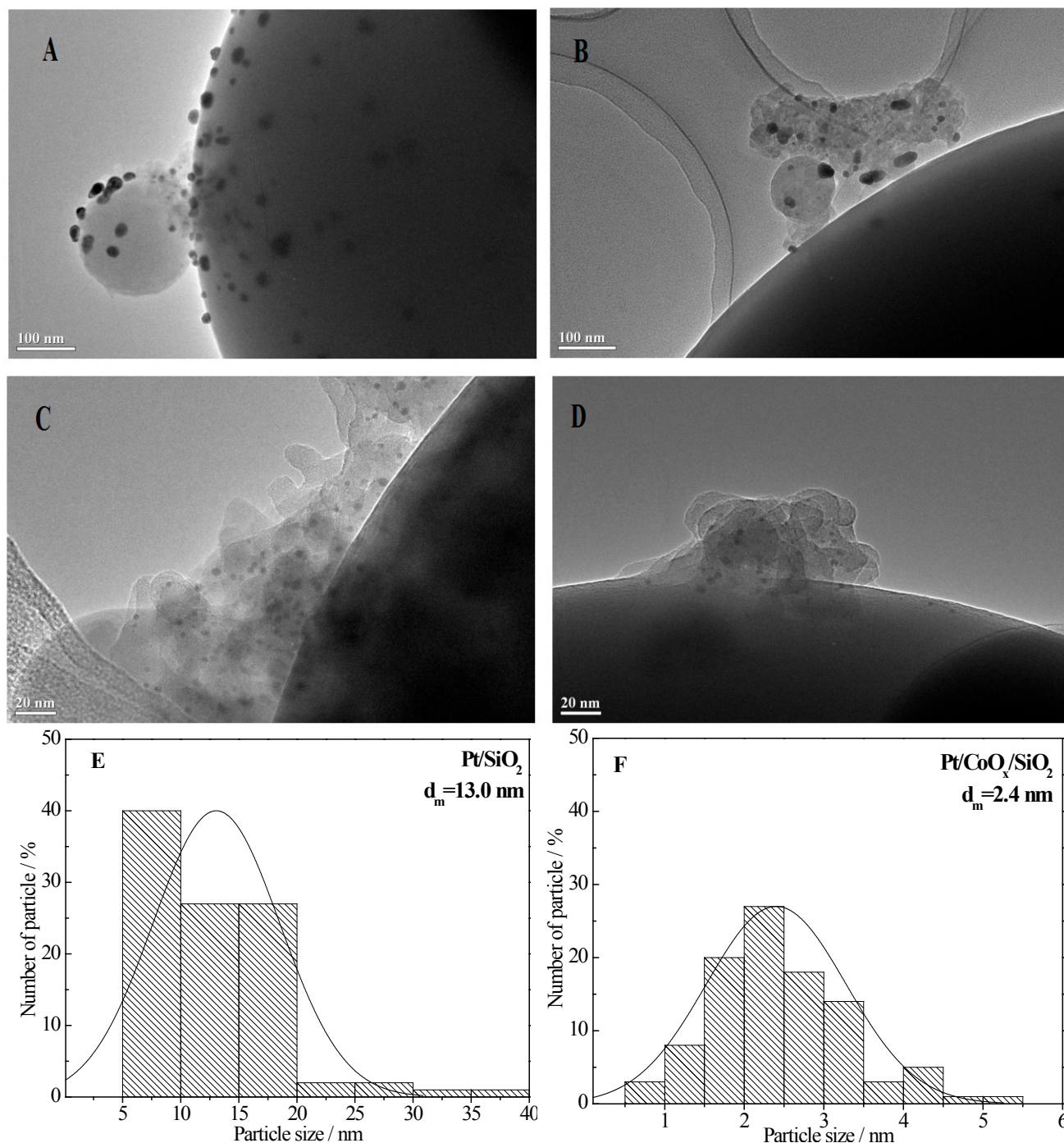


Figure 8. TEM images of the spent Pt/SiO_2 (A,B) and $\text{Pt}/\text{CoO}_x/\text{SiO}_2$ (C,D) catalysts. Size distributions of Pt particles of spent Pt/SiO_2 (E) and $\text{Pt}/\text{CoO}_x/\text{SiO}_2$ (F).

Figure 9A,B shows the TEM images of spent Pt/TiO₂. The TiO₂ support is crystalline (mainly anatase) and has a particle-like morphology. The BET surface area of TiO₂ support is determined by N₂ adsorption-desorption as 9.5 m²/g. Pt nanoparticles on TiO₂ are usually large. The addition of CoO_x into the catalyst leads to additional amorphous phase on the catalyst. The BET surface area of CoO_x/TiO₂ support is 8.4 m²/g. Some of the Pt nanoparticles are adjacent to the amorphous substances (Figure 9C,D). The size distributions of Pt particles are shown in Figure 9E,F.

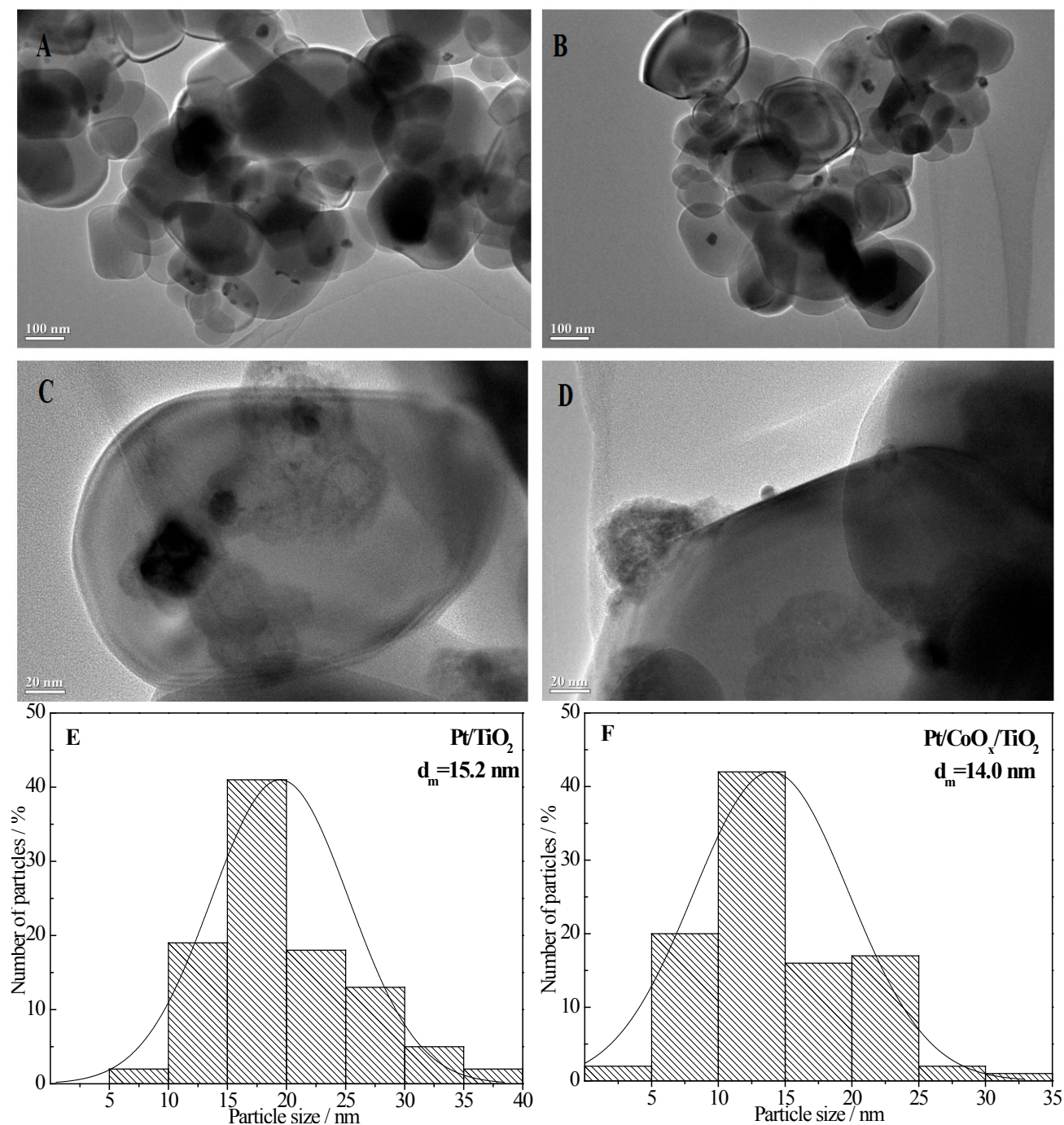


Figure 9. TEM images of the spent Pt/TiO₂ (A,B) and Pt/CoO_x/TiO₂ (C,D) catalysts. Size distributions of Pt particles of spent Pt/TiO₂ (E) and Pt/CoO_x/TiO₂ (F).

Figure 10 shows the TEM images of spent $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$. Here the Al_2O_3 refers to $\alpha\text{-Al}_2\text{O}_3$ support with a BET surface area of $5.7\text{ m}^2/\text{g}$, and the BET surface area of $\text{CoO}_x/\text{Al}_2\text{O}_3$ is $5.4\text{ m}^2/\text{g}$. As shown in Figure 10, $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ both exhibit very small Pt nanoparticles with sizes of $\sim 2\text{ nm}$. There are occasionally some bigger Pt particles (Figure S5), which explains the appearance of small XRD peaks corresponding to metallic Pt (Figure 6). Normally CoO_x coatings or amorphous substances are not clear to see. The size distributions of Pt particles are shown in Figure 10E,F.

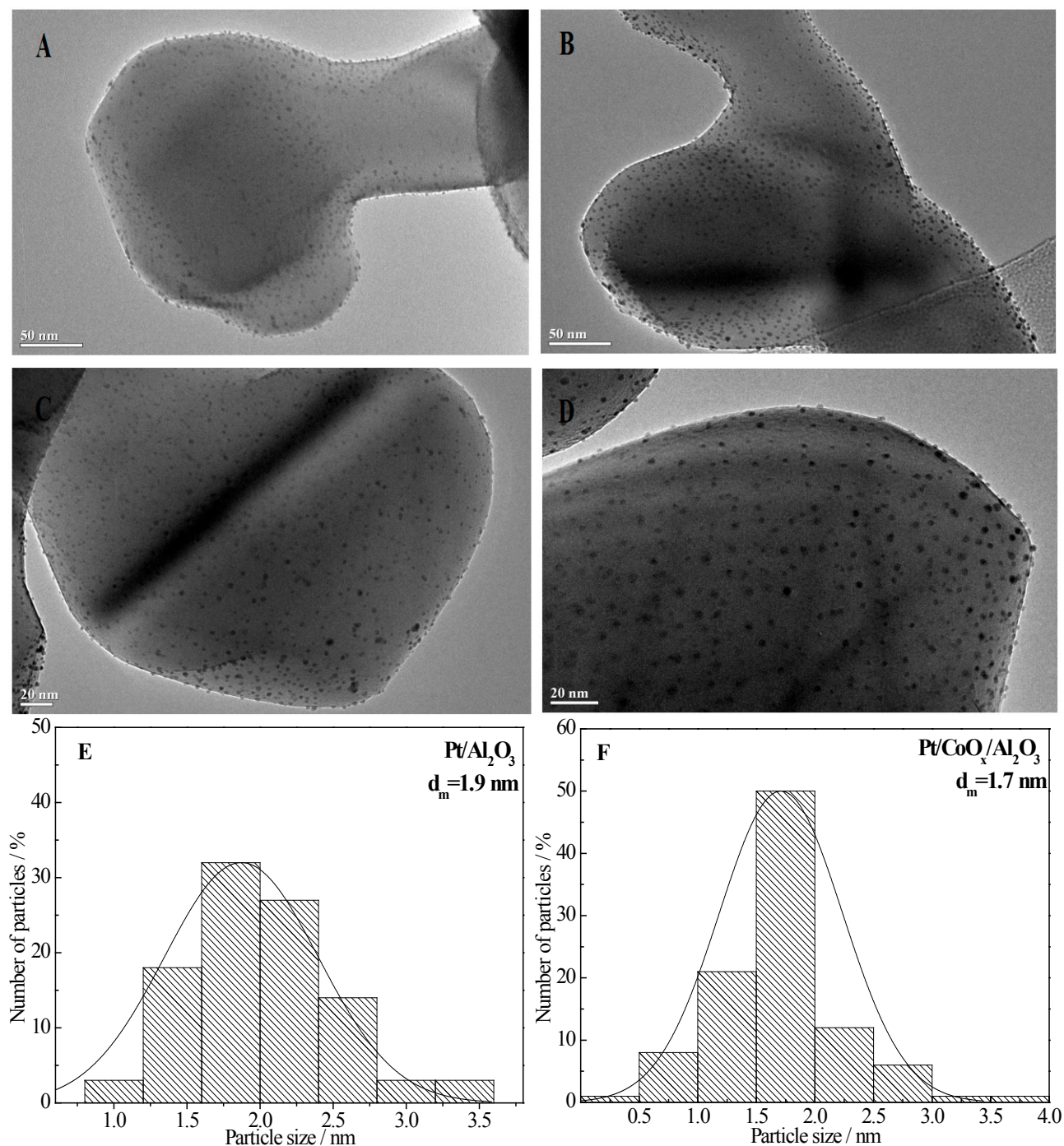


Figure 10. TEM images of the spent $\text{Pt}/\text{Al}_2\text{O}_3$ (A,B) and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ (C,D) catalysts. Size distributions of Pt particles of spent $\text{Pt}/\text{Al}_2\text{O}_3$ (E) and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ (F).

2.6.2. H₂-TPR

Figure 11 shows the TPR profiles of the Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃ catalysts and some reference samples. There is no obvious H₂ consumption peak on Pt/SiO₂, Pt/TiO₂, and Pt/Al₂O₃, probably due to the low Pt loading on these catalysts. The reduction peaks on CoO_x/SiO₂, CoO_x/TiO₂, and CoO_x/Al₂O₃ can be attributed to the reduction of CoO_x to metallic Co [27]. For Pt/CoO_x/SiO₂, the first peak at 110 °C can be attributed to the reduction of Pt species [28] and the second peak is due to the reduction of CoO_x to metallic Co. Two peaks appear for Pt/CoO_x/TiO₂; the first small peak is contributed to the reduction of Pt species and Co³⁺ to Co²⁺, and the second one is caused by the reduction of Co²⁺ [29–32]. Pt/CoO_x/Al₂O₃ has much closer peaks at the lowest temperature around 150 °C. By comparing the peak positions, it is clear that the presence of Pt can facilitate the reduction of CoO_x at lower temperatures.

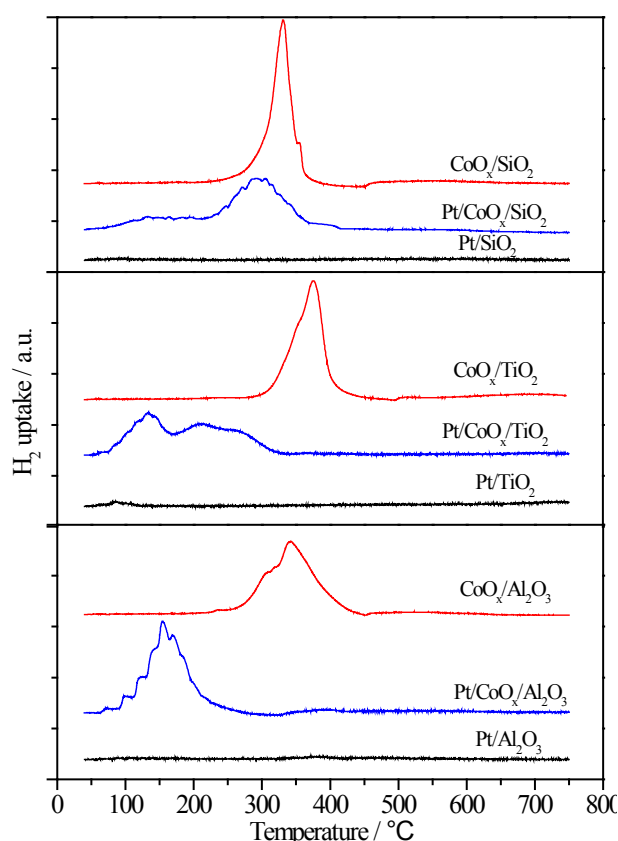


Figure 11. H₂-TPR profiles of SiO₂, TiO₂, and Al₂O₃-based samples.

2.6.3. XPS Characterization of Pt Species

The oxidation states of Pt species of the calcined, reduced, and spent Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃ were studied by XPS. Here, the calcined sample refers to the sample calcined in air at 500 °C, the reduced sample refers to the sample obtained by reducing the calcined sample in 4% H₂ at 300 °C, and the spent sample refers to the catalyst collected after reaction testing.

Figure 12 shows the XPS data of Pt/CoO_x/SiO₂ samples. The Pt_{4f} profiles were deconvoluted into three peaks centered at around 74.3, 72.5, and 71.2 eV, corresponding to Pt⁴⁺ [33], Pt²⁺ [34–36], and Pt⁰ [37], respectively. As seen from Figure 12 and Table 4, the Pt species in the calcined Pt/CoO_x/SiO₂ mainly exist in the form of Pt²⁺ (60.5%, relative proportion among Pt species) and Pt⁴⁺ (39.5%).

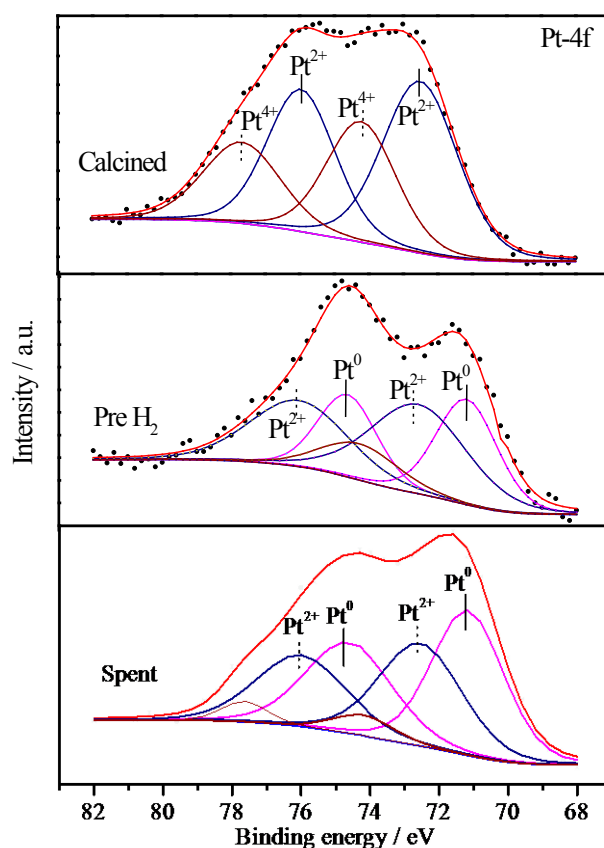


Figure 12. Pt-4f XPS spectra of the calcined, reduced, and spent Pt/CoO_x/SiO₂.

Table 4. The relative proportions (peak areas) of different Pt species as observed from the Pt-4f/Pt-4d XPS spectra of the calcined (I), H₂ pretreated (II) and spent (III) Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, Pt/CoO_x/Al₂O₃.

Sample	Treatment State	Relative Proportions (%)		
		Pt ⁰	Pt ²⁺	Pt ⁴⁺
Pt/CoO _x /SiO ₂	I	-	60.5	39.5
	II	35.9	48.1	16.0
	III	51.6	42.2	6.2
Pt/CoO _x /TiO ₂	I	7.6	60.5	31.9
	II	46.2	46.1	7.7
	III	8.8	27.2	64.0
Pt/CoO _x /Al ₂ O ₃	I	-	7.3	92.7
	II	16.6	65.5	17.9
	III	14.8	66.9	18.3

After reduction in 4% H₂ at 300 °C, the Pt species mainly exist in the form of Pt⁰ (35.9%) and Pt²⁺ (48.1%), whereas the relative proportion of Pt⁴⁺ is 16.0%, indicating the transformation of significant portions of Pt²⁺ and Pt⁴⁺ to Pt⁰.

For Pt/CoO_x/SiO₂ collected after reaction testing, the relative proportions of Pt⁰, Pt²⁺, and Pt⁴⁺ are 51.6%, 42.2%, and 6.2%, respectively, indicating the further reduction of small portions of Pt²⁺ and Pt⁴⁺ during the course of CO oxidation.

Figure 13 shows the XPS data of the calcined, reduced, and spent Pt/CoO_x/TiO₂. For calcined Pt/CoO_x/TiO₂, the relative proportions of Pt⁰, Pt²⁺, and Pt⁴⁺ are 7.6%, 60.5%, and 31.9%, respectively.

After reduction in 4% H₂ at 300 °C, the relative proportions change to 46.2%, 46.1%, and 7.7%, respectively, indicating the reduction of part of Pt²⁺ and Pt⁴⁺ to Pt⁰. The trend is consistent with the trend in the case of Pt/CoO_x/SiO₂.

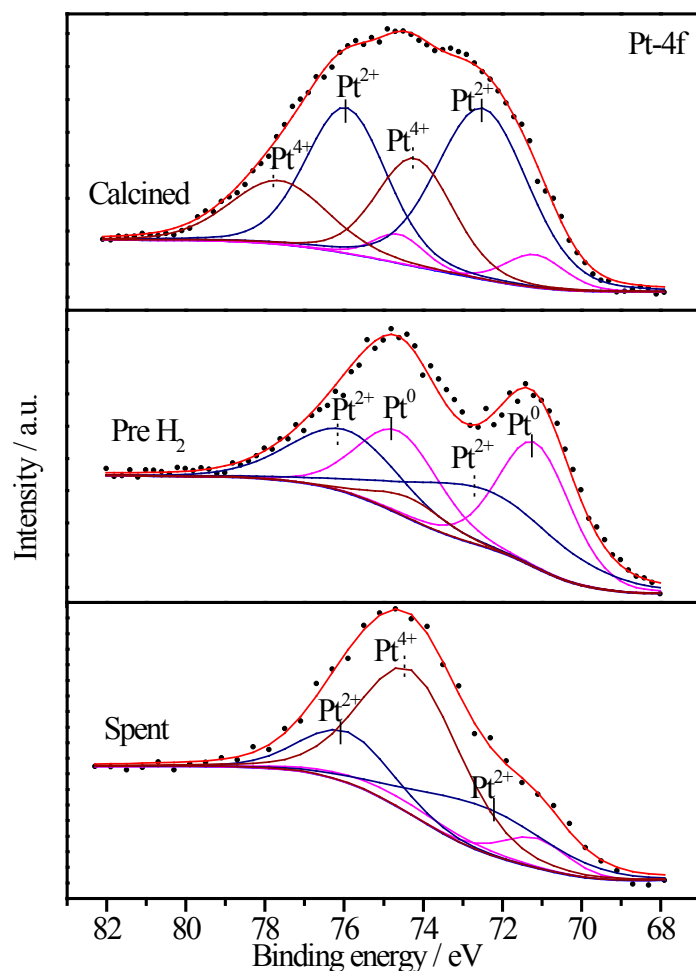


Figure 13. Pt-4f XPS spectra of the calcined, reduced, and spent Pt/CoO_x/TiO₂.

After reaction testing, the relative proportions of Pt⁰, Pt²⁺, and Pt⁴⁺ of Pt/CoO_x/TiO₂ are 8.8%, 27.2%, and 64.0%, respectively, indicating the oxidation of significant portions of Pt⁰ and Pt²⁺ during CO oxidation.

Figure 14 shows the XPS data of the calcined, reduced, and spent Pt/CoO_x/Al₂O₃. Here, Pt_{4d} rather than Pt_{4f} data were analyzed, due to the strong interference caused by the Al_{2p} peak [15,38]. The raw data were deconvoluted into three peaks assigned to Pt⁴⁺ [39–41], Pt²⁺ [42], and Pt⁰ [40]. As shown in Figure 14 and Table 4, the calcined Pt/CoO_x/Al₂O₃ contains Pt²⁺ (7.3%) and Pt⁴⁺ (92.7%), but no Pt⁰. The reduced sample contains Pt⁰ (16.6%), Pt²⁺ (65.5%), and Pt⁴⁺ (17.9%), indicating the significant reduction of Pt⁴⁺ to Pt²⁺ and Pt⁰. For the spent catalyst, the relative proportions of Pt⁰, Pt²⁺, and Pt⁴⁺ become 14.8%, 66.9%, and 18.3%, respectively, indicating the partial oxidation of Pt⁰ during the course of CO oxidation.

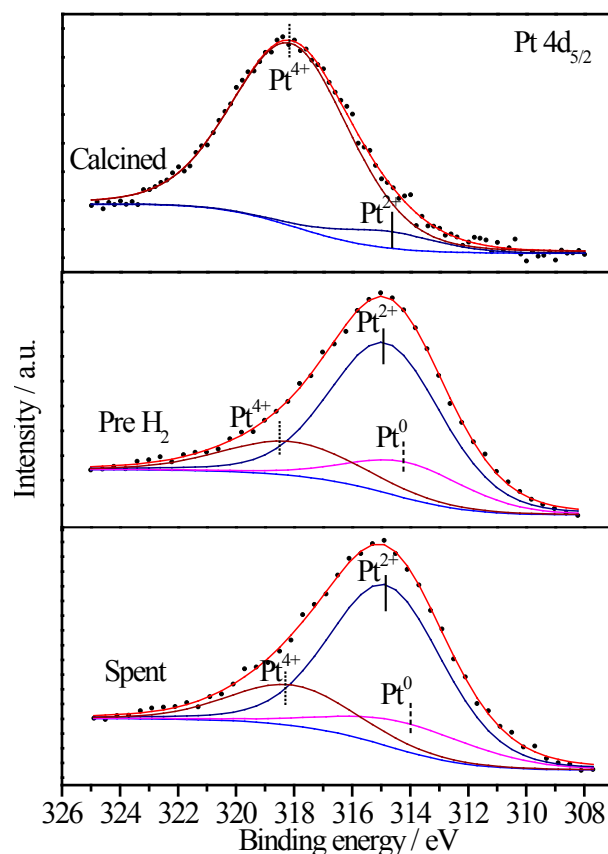


Figure 14. Pt-4d XPS spectra of the calcined, reduced, and spent Pt/CoO_x/Al₂O₃.

2.6.4. XPS Characterization of Co Species

The Co-2p regions of the XPS spectra were analyzed. The XPS spectra contain Co-2p_{3/2} and Co-2p_{1/2} regions with relatively low and high binding energies. The Co-2p_{3/2} region contains the peaks due to Co³⁺ (780.2 eV), Co²⁺ (781.8 eV), and a Co²⁺ satellite located at 786.3 eV [43,44]. The energy difference between the corresponding Co-2p_{3/2} and Co-2p_{1/2} peaks is approximately 15 eV [43–47].

As seen from Figure 15 and Table 5, the Co species in the calcined Pt/CoO_x/SiO₂ are Co³⁺ (57.4%) and Co²⁺ (42.6%), which means that the CoO_x in this sample is in the form of Co₃O₄. After reduction in 4% H₂ at 300 °C, the proportions of Co³⁺ and Co²⁺ are 40.5% and 59.5%, respectively, indicating the reduction of a portion of Co³⁺ to Co²⁺. For spent Pt/CoO_x/SiO₂, the relative proportions of Co³⁺ and Co²⁺ are 50.2% and 49.8%, indicating the oxidation of a small portion of Co²⁺ during the course of CO oxidation.

Figure 16 shows the XPS data of the calcined, reduced, and spent Pt/CoO_x/TiO₂. For the calcined Pt/CoO_x/TiO₂, the relative proportions of Co³⁺ and Co²⁺ are 64.5% and 35.5%. After reduction in 4% H₂ at 300 °C, the relative proportions change to 18.8% and 81.2%, indicating the reduction of a significant portion of Co³⁺ to Co²⁺. After reaction testing, the relative proportions of Co³⁺ and Co²⁺ are 26.0% and 74.0%, indicating the oxidation of part of Co²⁺ to Co³⁺ during CO oxidation.

Figure 17 shows the XPS data of the calcined, reduced, and spent Pt/CoO_x/Al₂O₃. The calcined Pt/CoO_x/Al₂O₃ contains Co³⁺ (65.0%) and Co²⁺ (35.0%). The reduced sample contains Co³⁺ (26.4%) and Co²⁺ (73.6%), indicating the reduction of a significant portion of Co³⁺ to Co²⁺. For the spent catalyst, the relative proportions of Co³⁺ and Co²⁺ become 44.3% and 55.7%, respectively, indicating the partial oxidation of Co²⁺ during the course of CO oxidation. This trend is consistent with the trend seen above.

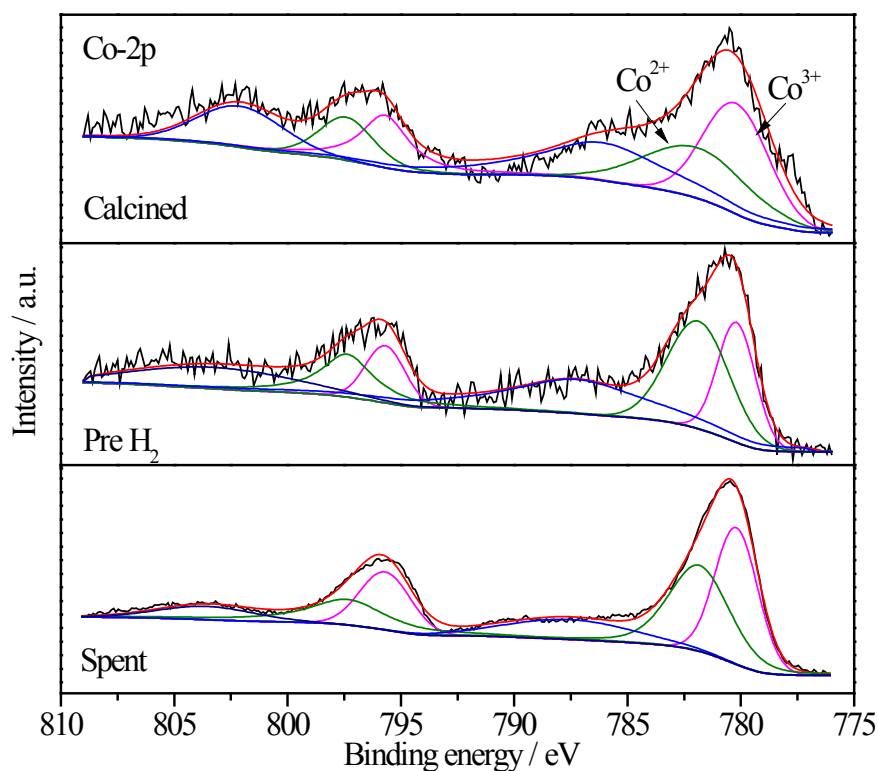


Figure 15. Co-2p XPS spectra of the calcined, reduced, and spent Pt/CoO_x/SiO₂.

Table 5. The binding energies and relative proportions (peak areas) of different Pt species as observed from the Co-2p XPS spectra of the calcined (I), H₂ pretreated (II) and spent (III) Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, Pt/CoO_x/Al₂O₃.

Sample	Treatment State	Relative Proportions (%)	
		Co ³⁺	Co ²⁺
Pt/CoO _x /SiO ₂	I	57.4	42.6
	II	40.5	59.5
	III	49.8	50.2
Pt/CoO _x /TiO ₂	I	64.5	35.5
	II	18.8	81.2
	III	26.0	74.0
Pt/CoO _x /Al ₂ O ₃	I	65.0	35.0
	II	26.4	73.6
	III	44.3	55.7

2.6.5. CO-TPD

Figure 18 shows the CO-TPD profiles of Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, Pt/CoO_x/Al₂O₃ and some reference samples. These samples were all pretreated in 4% H₂ at 500 °C prior to CO adsorption and temperature-programmed desorption.

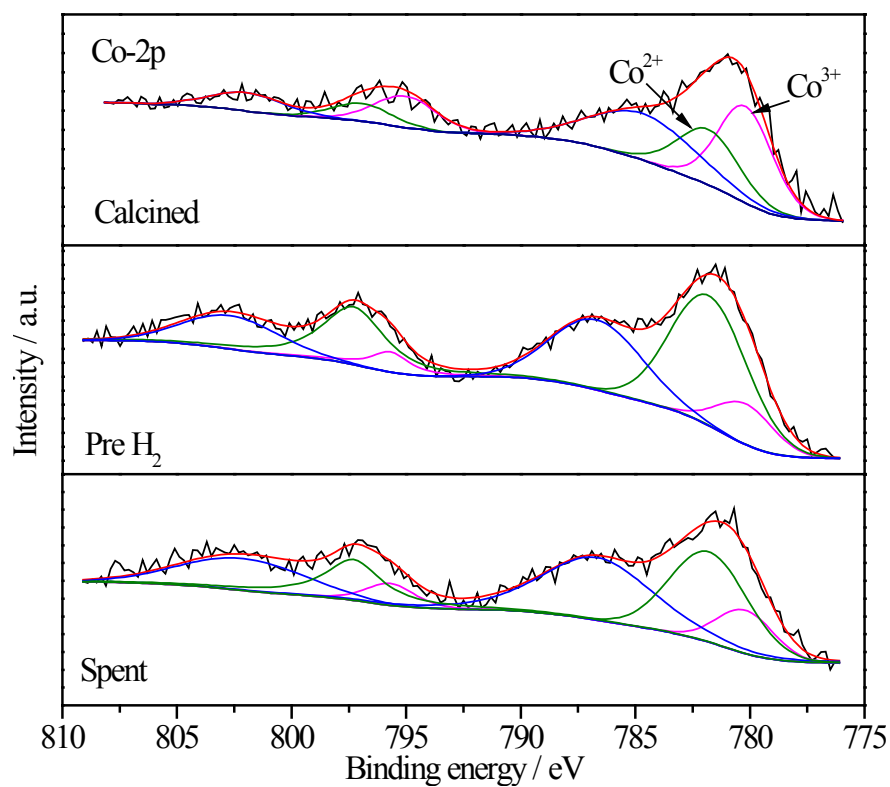


Figure 16. Co-2p XPS spectra of the calcined, reduced, and spent Pt/CoO_x/TiO₂.

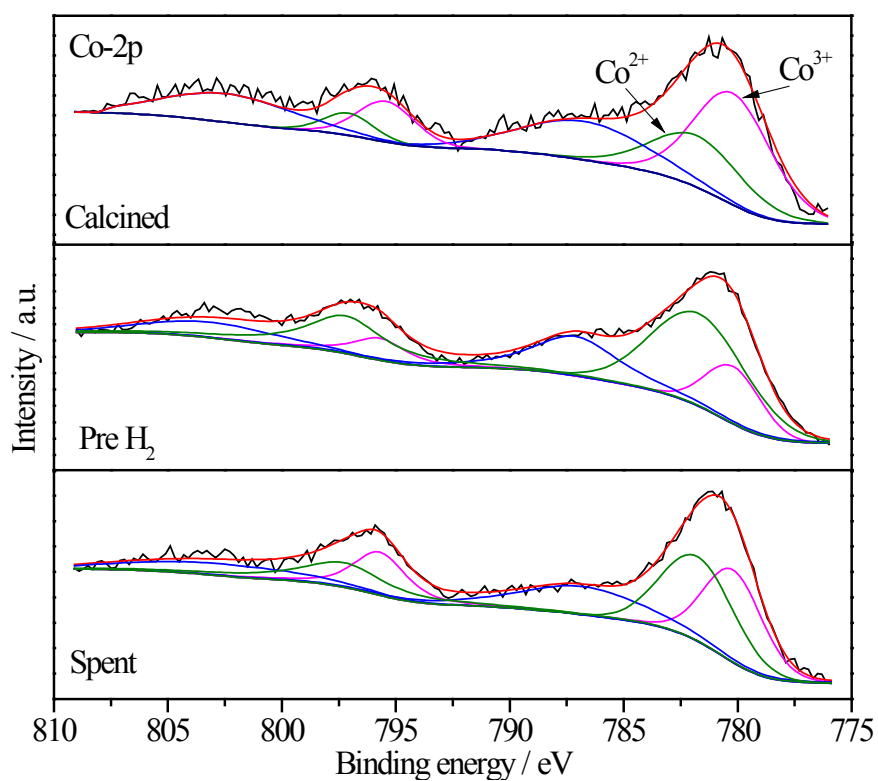


Figure 17. Co-2p XPS spectra of the calcined, reduced, and spent Pt/CoO_x/Al₂O₃.

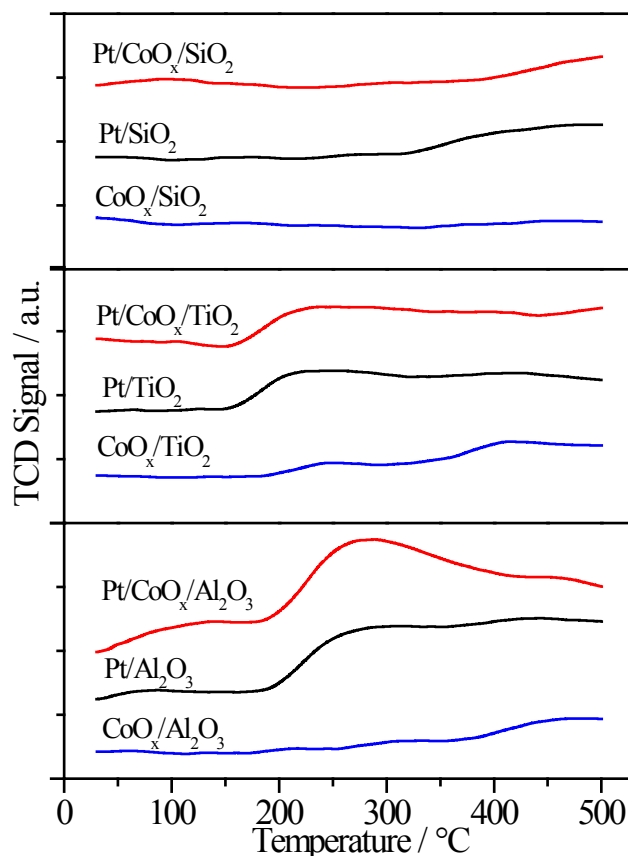


Figure 18. CO-TPD profiles of SiO₂, TiO₂, and Al₂O₃-based samples.

As shown in Figure 18, a common feature of the data is that there is virtually no desorption of CO from CoO_x/SiO₂, CoO_x/TiO₂, and CoO_x/Al₂O₃ supports, indicating that the adsorption of CO on these supports at room temperature is very limited. The CO-TPD profiles of Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃ are similar to those of Pt/SiO₂, Pt/TiO₂, and Pt/Al₂O₃, respectively, but quite different from those of CoO_x/SiO₂, CoO_x/TiO₂, and CoO_x/Al₂O₃, indicating that CO adsorbs mainly on Pt.

2.6.6. O₂-TPD

Figure 19 shows the O₂-TPD profiles of Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, Pt/CoO_x/Al₂O₃ and some reference samples. There is no clear desorption of O₂ from Pt/SiO₂, Pt/TiO₂, and Pt/Al₂O₃ catalysts, indicating that the adsorption of O₂ at 50 °C on these samples is limited. The desorption of O₂ from CoO_x/SiO₂, CoO_x/TiO₂, and CoO_x/Al₂O₃ is also limited. On the other hand, there is enhanced desorption of O₂ from Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃, indicating that O₂ can adsorb more on these catalysts at 50 °C. In particular, the effect is the most obvious for Pt/CoO_x/Al₂O₃, consistent with that fact that Pt/CoO_x/Al₂O₃ shows the highest activity at room temperature.

2.6.7. CO₂-TPD

It is known that enhanced basicity of support can enhance the activity of supported Pt catalysts for CO oxidation [48–50]. CO₂ is a weak acid, and the temperature-programmed desorption of CO₂ can indicate the basicity of catalysts. As shown in Figure S6, there is virtually no desorption of CO₂ from Pt/SiO₂,

Pt/TiO₂, Pt/Al₂O₃, and their CoO_x-modified counterparts, indicating that the promotion of activity by CoO_x additives is not due to the creation of more basic sites.

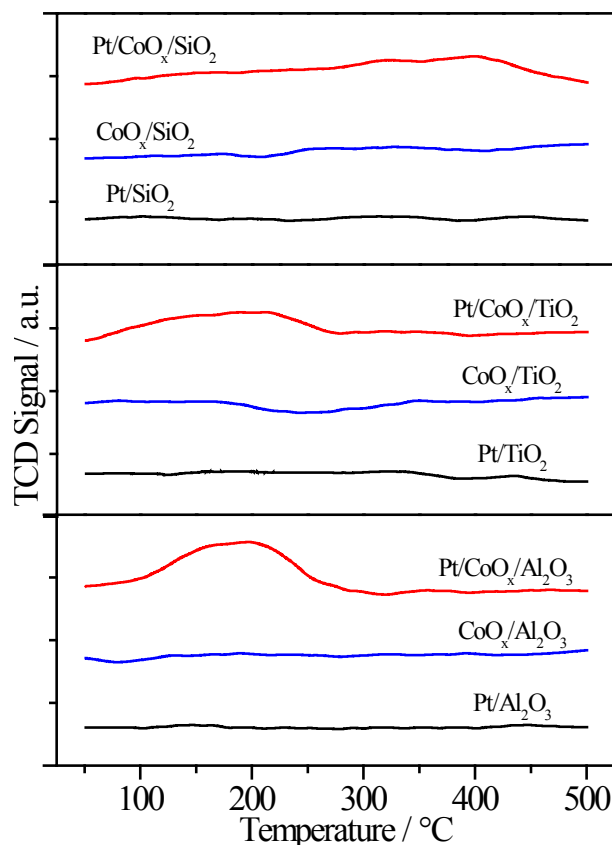


Figure 19. O₂-TPD profiles of SiO₂, TiO₂, and Al₂O₃-based samples.

2.6.8. Catalyst Stability

Figure S7 shows CO conversions on six Pt catalysts (pretreated in 4% H₂ at 300 °C) as a function of reaction time on stream. Normally 0.25 g catalyst was loaded in a U-type tube in each test, and the reaction temperature was chosen to be no higher than T₁₀₀. The only exception is that only 0.1 g Pt/CoO_x/Al₂O₃ was used because of its super high activity at room temperature. As shown in Figure S7, Pt/SiO₂ and Pt/Al₂O₃ are stable on stream, whereas Pt/TiO₂ shows quick deactivation at the initial stage of reaction. The deactivation of Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃ is more obvious, especially during the initial stage of reaction. Nevertheless, the catalytic activities seem to be stabilized during the later stage of reaction, which means that in practical applications, 100% CO conversion can still be maintained if more catalyst is used or the reaction temperature is higher. The deactivation of catalysts here may be due to the accumulation of carbonate species or the partial oxidation of Pt⁰, Pt²⁺ and/or Co²⁺ during the reaction. More work is needed in the future to understand this process.

2.7. Discussion

A supported metal catalyst is usually composed of an active metal and a solid support. The active metal, dispersed on support surfaces, plays a main role in catalyzing chemical reactions, whereas the solid support can not only disperse metal nanoparticles and assure their thermal stability, but also influence the catalytic

performance in different ways. A series of papers concerning modified platinum catalysts have been published [13–23]. The addition of new components may sometimes stabilize Pt particles and produce new interfaces beneficial to the catalytic performance.

Here we have found that the activity of supported Pt catalysts can be tuned by the presence of different MO_x additives. Some MO_x additives can facilitate the dispersion of Pt nanoparticles (Figures 2, 4, and 6), keeping the Pt particles in a small size. The MO_x additives can increase the interaction between Pt and support, minimizing the sintering of Pt.

The most interesting result in this study is that among three series of catalysts ($\text{Pt}/\text{MO}_x/\text{SiO}_2$, $\text{Pt}/\text{MO}_x/\text{TiO}_2$, and $\text{Pt}/\text{MO}_x/\text{Al}_2\text{O}_3$), CoO_x -promoted Pt catalysts are the most active. In particular, $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ shows complete CO conversion at room temperature. These CoO_x -promoted Pt catalysts are more active than the corresponding CoO_x -promoted supports and Pt/CoO_x prepared for reference, indicating that the “Pt- CoO_x -support” three-component system is important for enhancing the catalytic activity in CO oxidation.

The addition of CoO_x reduces the mean size of Pt nanoparticles from 13 nm for Pt/SiO_2 to 2.4 nm for $\text{Pt}/\text{CoO}_x/\text{SiO}_2$ (Figure 8). It is recognized that small Pt particles are necessary for achieving high activity in CO oxidation, although the Pt particle size is not the only factor that determines the activity.

CoO_x additives also affect the chemical features of supported Pt catalysts. For calcined catalysts, Pt^{2+} and Pt^{4+} are the main Pt species, but in the catalysts pretreated by 4% H_2 at 300 °C, Pt^0 and Pt^{2+} become the main Pt species. Prerduced samples show better catalytic activity in CO oxidation, implying that Pt^0 and Pt^{2+} are the main working species for CO oxidation. Pt^0 and Pt^{2+} have better CO adsorption ability than Pt^{4+} [51–54].

The proportion of Co^{3+} and Co^{2+} is almost 2:1 on the surface of calcined catalysts, indicating that the CoO_x is Co_3O_4 . The relative proportions of Co^{2+} among Co species increase to 59.5%, 81.2%, and 73.6% for prerduced $\text{Pt}/\text{CoO}_x/\text{SiO}_2$, $\text{Pt}/\text{CoO}_x/\text{TiO}_2$, and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ catalysts. Co^{2+} ions can dissociate the O_2 to O atom [21,55]. CoO_x serves as an O-supplier for the reaction. The presence of more active oxygen species on CoO_x -promoted Pt catalysts may account for the higher activities of these catalysts in CO oxidation.

From our CO-TPD data (Figure 18), it is clear that CO does not adsorb on $\text{CoO}_x/\text{SiO}_2$, $\text{CoO}_x/\text{TiO}_2$, and $\text{CoO}_x/\text{Al}_2\text{O}_3$. A comparison of “Pt/support” and “Pt/ CoO_x /support” shows the presence of CoO_x does not have an obvious effect on the adsorption of CO. CO tends to adsorb on Pt.

In this paper, the presence of CoO_x on supported Pt catalysts can enhance the adsorption of O_2 , whereas the presence of only CoO_x on SiO_2 , TiO_2 , and Al_2O_3 supports (without Pt) does not lead to enhanced O_2 adsorption (Figure 19), indicating the interface between Pt and CoO_x is important for O_2 adsorption in this reaction.

In conclusion, the oxidation of CO over Pt/CoO_x /support may follow this process: CO is adsorbed on Pt. O_2 is adsorbed on the Pt- CoO_x interface and dissociated by CoO_x . CO_a on Pt will react with O_a on cobalt to form CO_2 which is then desorbed into the gas phase. This reaction may take place at the interface between Pt and CoO_x . It is also possible that O_a migrates from the CoO_x to the Pt, in which case the reaction proceeds on the Pt surface.

After discussing the common promotional effect of CoO_x additives in this study, we then turn to the question of why $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ is the most active. In Table 4, H_2 -pretreated $\text{Pt}/\text{CoO}_x/\text{TiO}_2$ has a higher relative proportion of Pt^0 (46.2%) than $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ (16.6%). As for oxidation of CO, Co^{2+} is preferred

over Co^{3+} for CO oxidation. The relative proportions of Co^{2+} of H_2 -pretreated $\text{Pt}/\text{CoO}_x/\text{TiO}_2$ and $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ are 74.0% and 73.6%, respectively. However, $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ is still the most active. That is because the activity of catalysts is not solely determined by the proportion of Pt^0 and Co^{2+} . As we can see, $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ has smaller Pt particle size (Figure 10) and the $\text{CoO}_x/\text{Al}_2\text{O}_3$ is inherently more active than $\text{CoO}_x/\text{TiO}_2$ and $\text{CoO}_x/\text{SiO}_2$ (Figure 7), so the loading of small Pt nanoparticles onto $\text{CoO}_x/\text{Al}_2\text{O}_3$ can make the final catalyst more active. In addition, more CO and O_2 can adsorb on $\text{Pt}/\text{CoO}_x/\text{Al}_2\text{O}_3$ (Figures 18 and 19), which is beneficial for CO oxidation.

The objective of this work is to identify the MO_x modifiers that can promote supported Pt catalysts. It should be mentioned that current synthesis adopts impregnation of a soluble Pt salt, which is conventionally adopted in the laboratories and in industry. As we can see from our reported results, in particular the XRD results (Figures 2, 4, and 6), the Pt particle sizes on different modified and unmodified supports are quite different, which makes the comparison less straightforward, *i.e.*, there exist many complex/interrelated factors that can influence the activity of a final catalyst. Although here the sizes of Pt particles are not the same using the conventional impregnation, we believe that after the catalyst screening is done, further research can be carried out by using catalysts prepared by depositing Pt colloids with controlled sizes onto supports.

3. Experimental Section

3.1. Synthesis of Modified Supports

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent, AR, Shanghai, China), SiO_2 (Aladdin, 99.99%, Shanghai, China), TiO_2 (ACROS, 98%+, Fair Lawn, NJ, USA), Al_2O_3 (Aladdin, 99.99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sinopharm Chemical Reagent, AR), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACROS, 99%+), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ACROS, 98%+), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (ACROS, 99%+), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent, AR), $\text{Ba}(\text{NO}_3)_2$ (Sinopharm Chemical Reagent, AR), and $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aladdin, 99.9%,) were used as received.

Metal oxide-modified SiO_2 , TiO_2 , Al_2O_3 supports were prepared via incipient wetness impregnation. A calculated amount of metal nitrate was dissolved in deionized water (typically 10 mL water per gram of support) in a 250 mL beaker, and a support (SiO_2 , TiO_2 , or Al_2O_3) was subsequently added. The intended loading was 0.05 g MO_x per g support. Here MO_x refers to a metal oxide additive with the highest oxidation state of M. The actual M contents were determined by ICP analysis. The slurry was stirred using a glass rod, kept static at room temperature overnight, and then dried at 80 °C for 12 h. The solid product deposited at the bottom of the beaker was collected and ground into fine powders, and further calcined in air at 500 °C for 3 h.

3.2. Synthesis of Catalysis

Pt was loaded onto commercial and modified supports by incipient wetness impregnation. In a typical synthesis, 3.92 g support was immersed into 21 mL H_2PtCl_6 solution (0.01 g/mL) in a 250 mL beaker. The Pt loading was intended to be 2 wt.%, and the actual value was determined by ICP analysis. The slurry was stirred using a glass rod, kept static at room temperature overnight, and dried at 80 °C for 12 h. The

obtained solid was ground into fine powders, and further calcined in a muffle oven under static air at 500 °C for 3 h.

3.3. Characterization

ICP analyses of catalysts were conducted using an Optima 8000 spectrometer (PerkinElmer, Waltham, MA, USA) after dissolution of the sample in aqua and appropriate dilution.

BET surface areas were measured by N₂ adsorption at 77 K using a Micrometrics ASAP 2020 M+C surface area and porosity analyzer (Micromeritics, Norcross, GA, USA). Before the measurement, a sample (0.1–0.2 g) was degassed at 200 °C for 6 h, the weight of the sample was measured again, and the sample was then subjected to N₂ adsorption-desorption.

XRD experiments were conducted on a PW3040/60X'Pert PRO (PANalytical, Almelo, Netherlands) X-ray diffractometer with Cu K α radiation. The scanning was conducted at $2\theta = 20^\circ$ – 90° and the scanning rate was 6°/min.

TEM experiments were conducted on a JOEL JEM2100F field-emission transmission electron microscope (JOEL Ltd., Tokyo, Japan) with an acceleration voltage of 200 kV. Prior to recording TEM images, a small portion of sample was dispersed in ethanol, and a few drops were dropped onto a Cu grid-supported carbon films and dried under an infrared lamp.

XPS spectra were recorded on a PerkinElmer PHI 5000C ESCA (Perkin Elmer, Waltham, MA, USA) system operating at a voltage of 14 kV and a current of 20 mA, with MgK α radiation source. The obtained binding energies were corrected by using the binding energy of C1s as a reference, and the XPS data were processed using XPS PEAK41 software. The Co-2p spectra in Figure 15 were obtained using Kratos Axis Ultra-DLD (Kratos, Beijing, China) system.

H₂-TPR experiments were performed in a FINESORB-3010 instrument (FINETEC, Hangzhou, China). A sample (0.12 g, 40–60 mesh) was loaded into a U-shaped quartz tube. A reducing gas (10% H₂/Ar) was introduced at a flow rate of 30 mL/min. The temperature was held on 30 °C for 2 h and then increased to 800 °C at a rate of 10 °C/min. The H₂ consumption was detected by a TCD (thermal conductivity detector) and recorded as a function of temperature.

CO-TPD, O₂-TPD, and CO₂-TPD experiments were performed in a FINESORB-3010 instrument (FINETEC, Hangzhou, China). A sample (0.25 g, 40–60 mesh) was loaded into a U-shaped quartz tube, 4% H₂ (balance He, total flow rate 50 mL/min) was then used to sweep the sample, and the temperature was ramped from room temperature to 300 °C (at a rate of 10 °C/min) in the presence of 4% H₂, and kept at 300 °C for 2 h. Then the sample was cooled down to 30 °C (CO-TPD, O₂-TPD) or 50 °C (CO₂-TPD), and exposed to 2% CO/He (CO-TPD) or pure O₂ (O₂-TPD) or 5% CO₂/He (CO₂-TPD) for 1 h to allow for adsorption. The flowing gas was then switched to He and swept by the flow for 3 h. The temperature was then ramped to 500 °C (CO-TPD, O₂-TPD) or 600 °C (CO₂-TPD) at a rate of 10 °C/min, while the desorbed gases were monitored using a TCD detector.

3.4. Catalytic Testing

Catalytic CO oxidation was conducted in a fixed bed reactor (FINESORB-3010 temperature-programmed chemisorber, FINETEC, Hangzhou, China). The experimental conditions and procedures were reported previously [50]. Briefly, A catalyst (0.25 g) loaded into the reactor was pretreated

in flowing 4% H₂ (balance He) at 300 °C for 2 h, cooled down to room temperature, and the gas stream was switched to 1% CO (balance air, flow rate: 50 mL/min). The catalyst was maintained at room temperature for 1 h, and then heated to 200 °C at a rate of 0.5 °C/min. The exiting stream was analyzed by GC (Agilent 7890A) every 10 min to record CO and CO₂ peaks. The CO conversion was calculated as

$$([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/[\text{CO}]_{\text{in}} \times 100\%$$

4. Conclusions

Three series of metal oxide-modified Pt catalysts (*i.e.*, Pt/MO_x/SiO₂, Pt/MO_x/TiO₂, and Pt/MO_x/Al₂O₃, where M = Al, Fe, Co, Cu, Zn, Ba, La) were prepared and tested for CO oxidation. Among them, Pt/CoO_x/SiO₂, Pt/CoO_x/TiO₂, and Pt/CoO_x/Al₂O₃ exhibited the highest catalytic activities. The presence of the “Pt-CoO_x-support” three-component system is important because the catalytic activity of any two-component system was found to be significantly lower. The higher activity of CoO_x-promoted Pt catalysts is ascribed to the greater supply of active oxygen. Although here we chose CO oxidation as a probe reaction, we believe that the Pt/MO_x/support catalysts may find applications in other reactions, considering the functionality furnished by both Pt and MO_x-modified supports.

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Author Contributions

Hongmei Qin and Xiaoshuang Qian conducted all of the synthesis and the catalytic testing. Tao Meng and Yi Lin carried out the XRD characterization. Hongmei Qin conducted the TPR/TPD experiments. Tao Meng helped to maintain the catalytic testing apparatus. Zhen Ma guided the TEM characterization. Hongmei Qin and Zhen Ma interpreted the results and wrote the manuscript. All contributed to the discussions.

Conflicts of Interest

The authors declare no conflict of interest.

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