

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

This section shows the catalyst characterization results of Palladium (Pd) supported on different Ce and Zr loadings.

4.1.1 BET Surface Area

The surface areas of the Pd with different Ce and Zr loading catalysts (100:0, 75:25, 50:50, 25:75, and 0:100 weight ratios of Ce to Zr) were measured by multiple BET method. The results showing effects of Ce and Zr loading and catalyst preparation method on the BET surface area of catalysts are given in Table 4.1.

Table 4.1 BET surface area of 1%Pd with different Ce and Zr support loadings calcined at 300°C for 2 hours.

Catalyst preparation method	BET surface area (m ² g ⁻¹)				
	Ce: Zr ratio				
	100:0	75:25	50:50	25:75	0:100
Co-precipitation	98.8	161.9	167.7	148.1	149.7
Impregnation on sol-gel	105.7	-	162.8	-	152

As shown in Table 4.1, it was found that BET surface area of 1%Pd/CeO₂ and 1%Pd/ZrO₂ co-precipitation catalysts were 98.8 and 149.7 m²/g, respectively. The result of the Pd supported on mixed oxide support

showed the higher surface area than 1%Pd/CeO₂ and 1%Pd/ZrO₂ alone except of 1%Pd/CeO₂-ZrO₂(25:75). For impregnation on sol-gel catalyst, the BET surface area of 1%Pd/CeO₂ and 1%Pd/ZrO₂ were 105.7 and 152 m²/g, respectively. The BET surface area of Pd supported on mixed oxide support showed the same trend as co-precipitation catalyst. It can be described that the addition of Ce on Zr increased surface area of the catalyst by stabilizing its tetragonal form (Sakulchaicharoen, 2000). Moreover, the incorporation of Ce to Zr as mixed oxides can enhance the thermal stability of CeO₂, thus causing better resistance of sintering and deactivation processes.

BET surface area of impregnation on sol-gel catalysts showed slightly higher surface area than co-precipitation catalysts. This result supported the hypothesis that the catalysts prepared by the sol-gel technique normally have a higher surface area compared to the conventional methods.

Table 4.2 shows the effect of Pd loading on the BET surface area of Pd/CeO₂ co-precipitation catalysts calcined at 300°C for 2 hours. As shown in Table 4.2, the BET surface area ranged from 91.93 to 98.8 m²/g. No trend was observed with increasing the percent of Pd loading.

Table 4.2 BET surface area of Pd/CeO₂ co-precipitation catalyst calcined at 300°C for 2 hours with different Pd loadings.

% Pd loading	BET surface area (m ² g ⁻¹)
1	98.80
3	91.93
5	95.42

The BET surface areas of 1%Pd/CeO₂ co-precipitation catalysts with different calcination temperatures are tabulated in Table 4.3. The calcination temperature had a strong effect on the surface area. The BET

surface area decreased with increasing in the calcination temperature. This result can be explained that sintering of catalyst might occur at high temperature resulting in a decreased in surface area.

Table 4.3 BET surface area of 1%Pd/CeO₂ co-precipitation catalyst with different calcination temperatures.

Calcination temperature (°C)	BET surface area (m ² g ⁻¹)
200	128.50
300	98.80
400	85.99

4.1.2 X-ray Diffraction

Figure 4.1 shows representative XRD pattern of the 1% by weight of Pd co-precipitation catalyst with different Ce and Zr support loadings calcined at 300°C for 2 hours. Jen *et al.* (1999) found that Pd (111) and PdO (110) reflections near 40° and 42° for CuK_α radiation, respectively. No evidence of Pd peaks was obtained in any of the co-precipitation catalysts, indicating small particles of PdO with mean diameter less than 5 nm and high dispersion of Pd on CeO₂ and ZrO₂ supports. The 1%Pd/CeO₂ co-precipitation catalyst showed the six main reflections typical peak of CeO₂ (at about 29°, 33°, 45°, 56°, 60°, and 70° (2θ)). For the 1%Pd/CeO₂-ZrO₂ (75:25), the XRD pattern was similar to the XRD pattern of 1%Pd/CeO₂. As the percent weight of Ce support was decreased, the intensity of CeO₂ also decreased while the intensity of ZrO₂ peak increased and gradually combined with CeO₂ to a broader peak.

The XRD pattern of sample for the impregnation on sol-gel catalysts of 1% by weight of Pd with different Ce and Zr support loadings for the sample calcined at 300°C for 2 hours is given in Figure 4.2. No evidence

of Pd peaks was obtained. The position of XRD peaks (2θ) of the 1%Pd/CeO₂ co-precipitation and impregnation on sol-gel catalysts were almost the same, but the XRD pattern of impregnation on sol-gel catalysts were sharper than co-precipitation catalysts, indicating impregnation on sol-gel catalysts had higher crystallinity than co-precipitation catalysts. The XRD pattern of 1%Pd/ZrO₂ impregnation on sol-gel catalyst showed the eight main reflection typical peaks of ZrO₂ (at about 24°, 28°, 31°, 33°, 34°, 49°, 60°, and 61° (2θ)).

The XRD pattern of Pd/CeO₂ co-precipitation catalyst with different percent loading of Pd (1%, 3%, and 5%) is shown in Figure 4.3. The XRD pattern showed only six main reflection peaks of CeO₂. Even increasing percent loading of Pd there was no evidence of Pd peaks

The XRD pattern of 1%Pd/CeO₂ co-precipitation catalyst with different calcination temperatures (200, 300, and 400°C) is illustrated in Figure 4.4. The XRD pattern showed only six main reflection peaks of CeO₂ (at about 29°, 33°, 45°, 56°, 60° and 70° (2θ)). The position of XRD peaks 2θ of the sample calcined at 200, 300, and 400°C were almost the same but the peak intensity of the sample was decreased with decreasing calcination temperature. It was observed that as the calcination temperature increased, peak of CeO₂ become sharper and thinner. This trend suggested that the catalyst has become more crystalline and had a larger crystallite size, possibly due to agglomeration at the higher temperature.

4.1.3 Atomic Absorption Spectroscopy

AAS was employed to determine the content of Pd on CeO₂, ZrO₂, and CeO₂-ZrO₂ mixed oxide support. The measured percentages loading of 1% Pd with different Ce and Zr support loading catalysts (100:0, 75:25, 50:50, 25:75, and 0:100 weight ratios of Ce to Zr) calcined at 300°C for 2 hours are shown in Table 4.4. The measured percentages loading ranged from

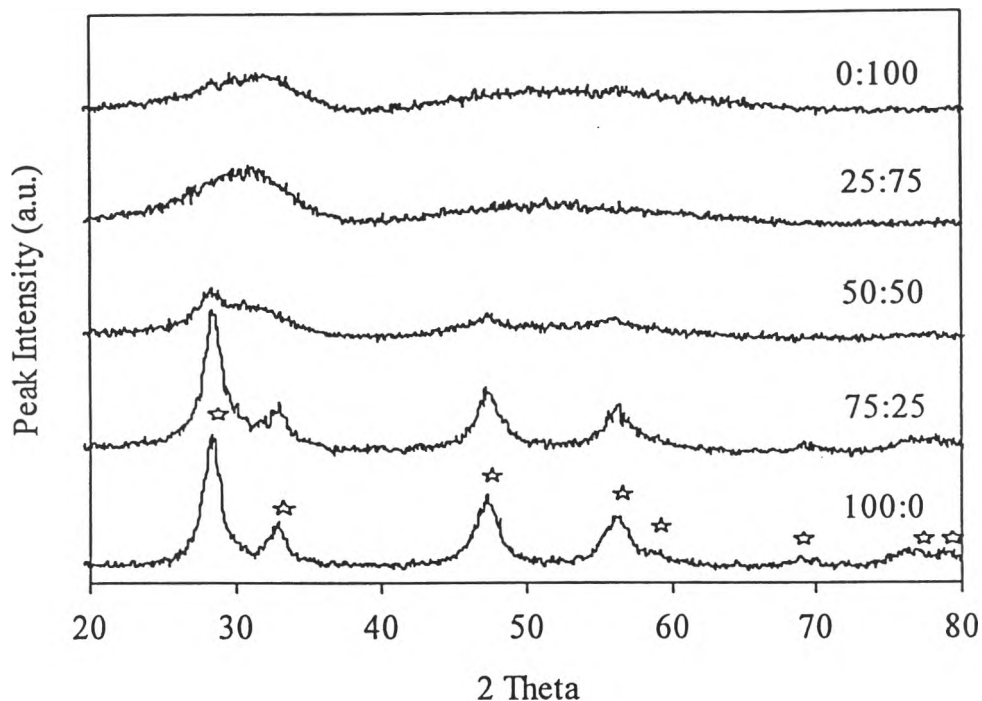


Figure 4.1 XRD pattern for 1%Pd/CeO₂-ZrO₂ (100:0, 75:25, 50:50, 25:75, and 0:100 weight ratio of Ce to Zr) co-precipitation catalysts calcined at 300°C for 2 h. (☆ = CeO₂)

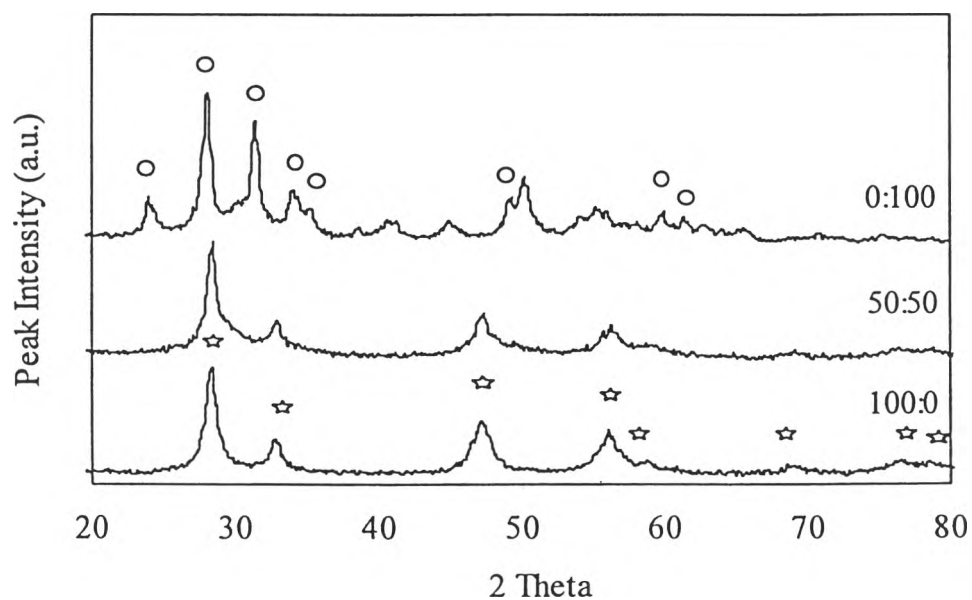


Figure 4.2 XRD pattern for 1%Pd/CeO₂-ZrO₂ (100:0, 50:50, and 0:100 weight ratio of Ce to Zr) impregnation on sol-gel catalysts calcined at 300°C for 2 h. (☆ = CeO₂, ○ = ZrO₂)

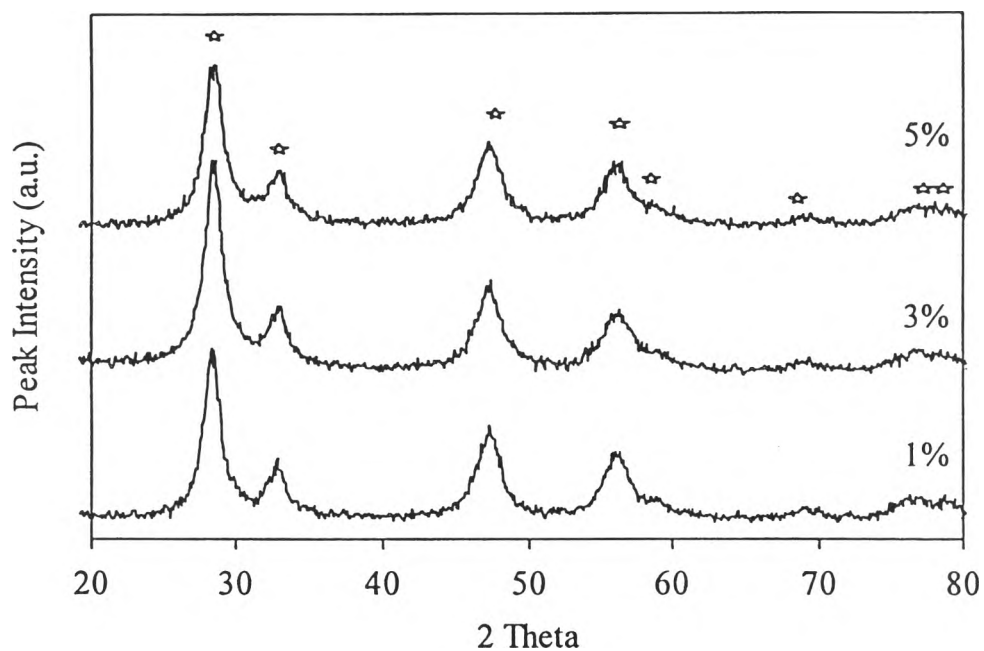


Figure 4.3 XRD pattern of Pd/CeO₂ (1%, 3%, and 5%) co-precipitation catalysts with different Pd loadings calcined at 300°C for 2 h. (☆ = CeO₂)

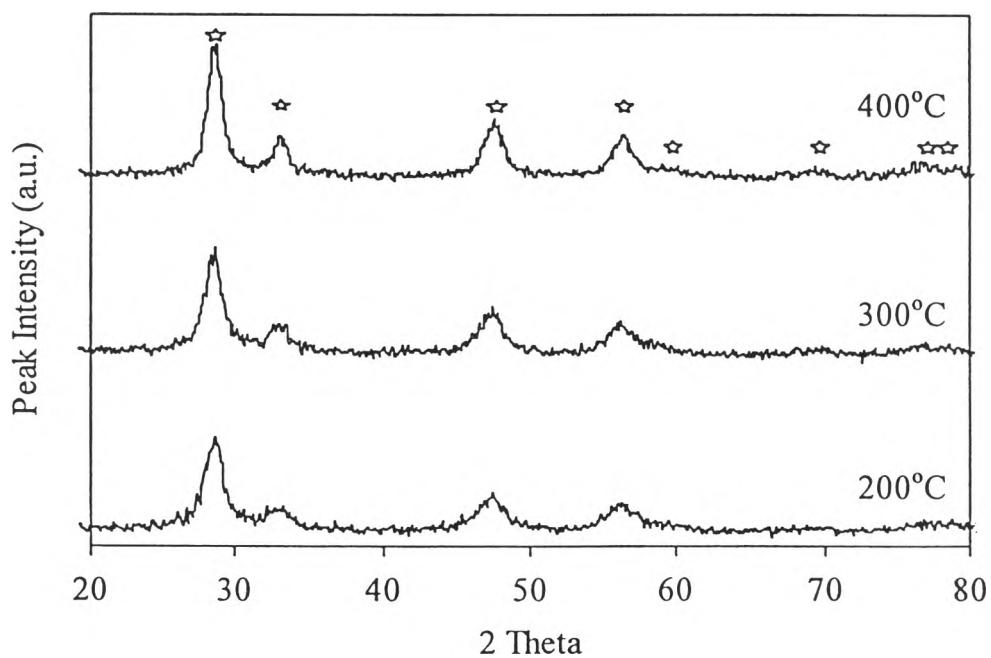


Figure 4.4 XRD pattern of 1%Pd/CeO₂ co-precipitation catalysts with different calcination temperatures (200, 300, and 400°C for 2 h.) (☆ = CeO₂)

0.666-0.755% by weight. From these results, measured percentages loading were less than one, which was the required value. The disappearance of Pd metal may be gone out with the solution in the washing step.

Table 4.4 The measured percentages loading of 1% Pd with different Ce and Zr support loadings calcined at 300°C for 2 hours.

Catalyst preparation method	% of Pd loading				
	Ce: Zr ratio				
	100:0	75:25	50:50	25:75	0:100
Co-precipitation	0.755	0.732	0.752	0.724	-
Impregnation on sol-gel	0.666	-	-	-	-

The measured percentages loading of Pd/CeO₂ co-precipitation catalyst calcined at 300°C for 2 hours with different Pd loadings are given in Table 4.5. The measured percentages loading of 1%, 3%, and 5% Pd/CeO₂ were 0.755%, 3.201%, and 5.741% by weight, respectively. The measured percentages loading were higher than the required value.

Table 4.5 The measured percentages loading of Pd/CeO₂ co-precipitation catalysts calcined at 300°C for 2 hours with different Pd loadings.

% Pd loading	% of Pd loading
1	0.755
3	3.201
5	5.741

The measured percentages loading of 1%Pd/CeO₂ co-precipitation catalyst with different calcination temperatures are shown in Table 4.6. The measured percentages loading ranged from 0.616-0.755% by weight. The measured percentages loading were less than one.

Table 4.6 The measured percentages loading of 1%Pd/CeO₂ co-precipitation catalyst with different calcination temperatures.

Calcination temperature (°C)	% of Pd loading
200	0.616
300	0.755
400	0.625

4.2 Activity Test

The selective CO oxidation reaction was carried out in the fixed bed reactor as described previously using 100 mg catalyst of 70-120 mesh size. The reactant gas containing 1%CO, 1%O₂, 2%CO₂, 2.6%H₂O, and 40%H₂ balance in helium was passed through the catalyst bed at a total flow rate of 50 ml/min (SV=30,000 ml g⁻¹h⁻¹) and at atmospheric pressure.

4.2.1 Effect of Catalyst Pretreatment

Figures 4.5(a) and (b) show the relationship between CO conversion and selectivity versus temperature of 1%Pd/CeO₂ co-precipitation catalysts calcined at 300°C for 2 hours, which were tested under different pretreatment procedures (10% H₂ pretreatment at 300°C for 3 hours, pure H₂ pretreatment at 300°C for 2 hours and pure O₂ pretreatment at 300°C for 2 hours). It was found that the pretreatment procedure had an impact on the catalyst activity. It can be observed that 10% H₂ pretreatment demonstrated the highest conversion and selectivity when compared to pure H₂ pretreatment and pure O₂ pretreatment. The conversion of all pretreatment procedures was observed to have lower activity at the beginning. After that the activity increased gradually and then dropped back again at higher temperature. The selectivity of all pretreatment procedures decreased with a rise in reaction temperature. This could be explained that H₂ oxidation became dominant at higher temperatures.

From the result, it can be concluded that 10% H₂ pretreatment demonstrated the highest conversion when compared to pure H₂ pretreatment and pure O₂ pretreatment. There have been different suggestions of the high activity for H₂ reductive pretreatment. Serre *et al.* (1993) suggested that the reduction necessary to reduce PtO and PtO₂ at the Pt-CeO₂ interface and that the metallic Pt sites close to ceria are responsible for the high activity. It can

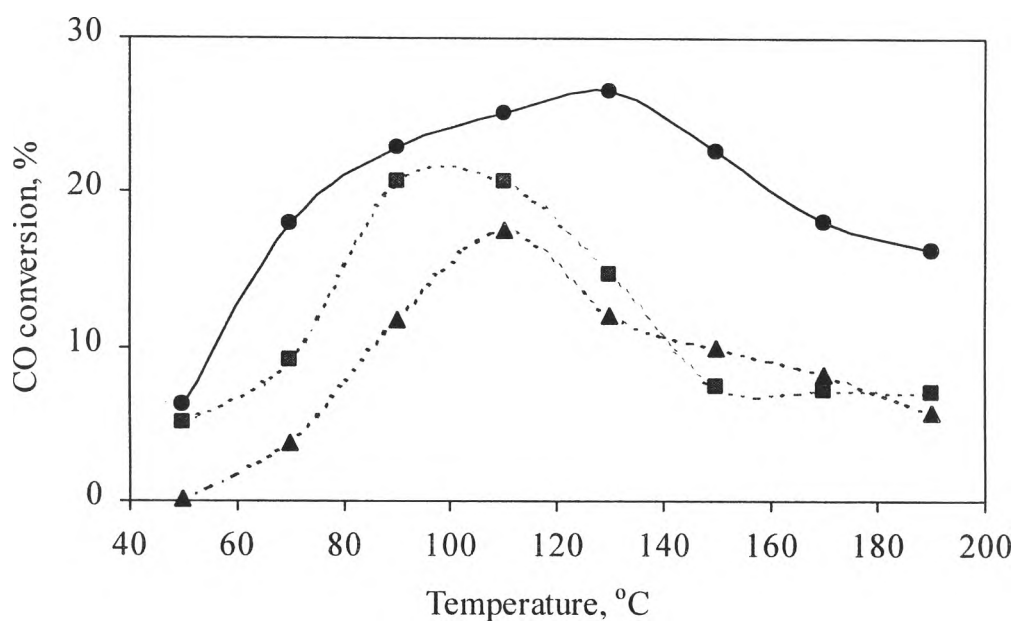


Figure 4.5(a) Effect of pretreatment method on CO conversion of 1%Pd/CeO₂ co-precipitation catalyst (●) 10% H₂ pretreatment at 300°C 3 h (■) pure H₂ pretreatment at 300°C 2 h (▲) pure O₂ pretreatment at 300°C 2 h.

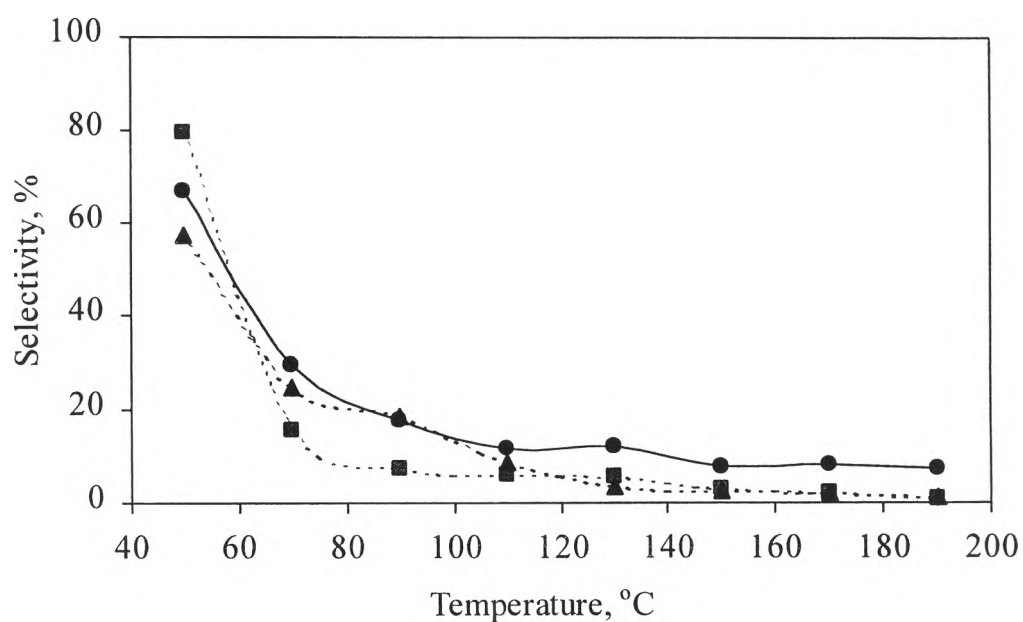


Figure 4.5(b) Effect of pretreatment method on selectivity of 1%Pd/CeO₂ co-precipitation catalyst (●) 10% H₂ pretreatment at 300°C 3 h (■) pure H₂ pretreatment at 300°C 2 h (▲) pure O₂ pretreatment at 300°C 2 h.

be described in the same way that the importance of H₂ pretreatment could come from an increased number of active Pd sites (CO may adsorb and react on Pd-CeO₂ or Pd-ZrO₂ interface instead of on CeO₂ or ZrO₂ support). Besides, the H₂ reductive pretreatment may decrease the particle size of Pd. However, low hydrogen percentages demonstrated higher activity than pure hydrogen because a lot of HCl may form and actually cause migration and sintering, when pretreated with high concentration of H₂. After this finding, 10% H₂ at 300°C for 3 hours was chosen for pretreatment method.

The result of 1%Pd/CeO₂-ZrO₂ (50:50, 75:25, and 0:100) co-precipitation catalysts shows lower CO conversion and selectivity than 1%Pd/CeO₂ catalyst. These results can be found in Figure A.1(a) and (b) to Figure A.3 (a) and (b) in Appendix A.

4.2.2 Effect of Palladium Loading

Figures 4.6(a) and (b) show the effect of Pd loading (1%, 3%, and 5%) on Pd/CeO₂ co-precipitation catalyst calcined at 300°C for 2 hours. The 1%Pd/CeO₂ catalyst had the highest catalytic activity for CO conversion and selectivity. The higher activity of selective CO oxidation was in the order of 1%, 5%, and 3%, respectively. This result can be described by the data obtained from the BET surface area measurement. Higher activities correlate with the higher surface areas.

4.2.3 Effect of Calcination Temperature

The effect of calcination temperature on the activity of 1%Pd/CeO₂ co-precipitation catalyst is illustrated in Figure 4.7(a) and (b). The higher activity was in the order of 300, 200, and 400°C, respectively. This result can be confirmed by the BET and XRD measurements. The BET surface area of these samples decreased with increasing the calcination temperature.

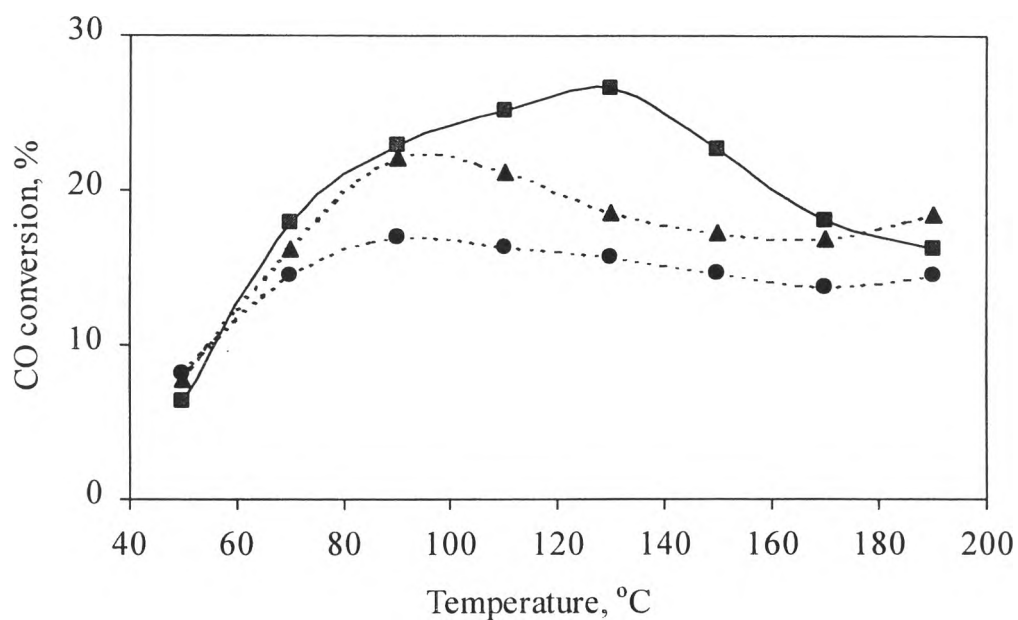


Figure 4.6(a) Effect of Pd loading on CO conversion of Pd/CeO₂ co-precipitation catalyst (■) 1%Pd loading (●) 3%Pd loading (▲) 5%Pd loading.

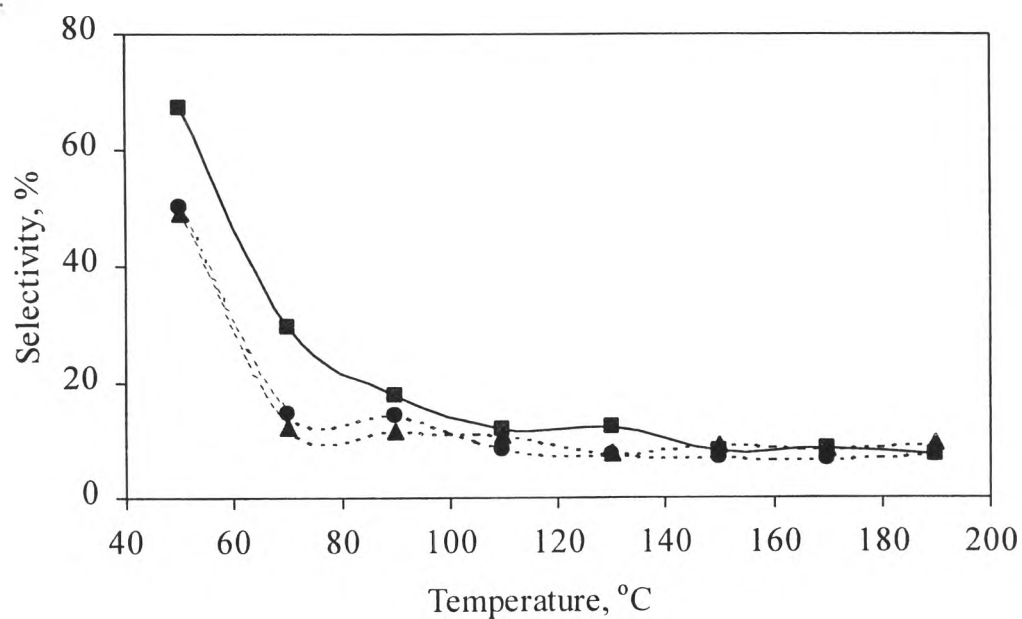


Figure 4.6(b) Effect of Pd loading on selectivity of Pd/CeO₂ co-precipitation catalyst (■) 1%Pd loading (●) 3%Pd loading (▲) 5%Pd loading.

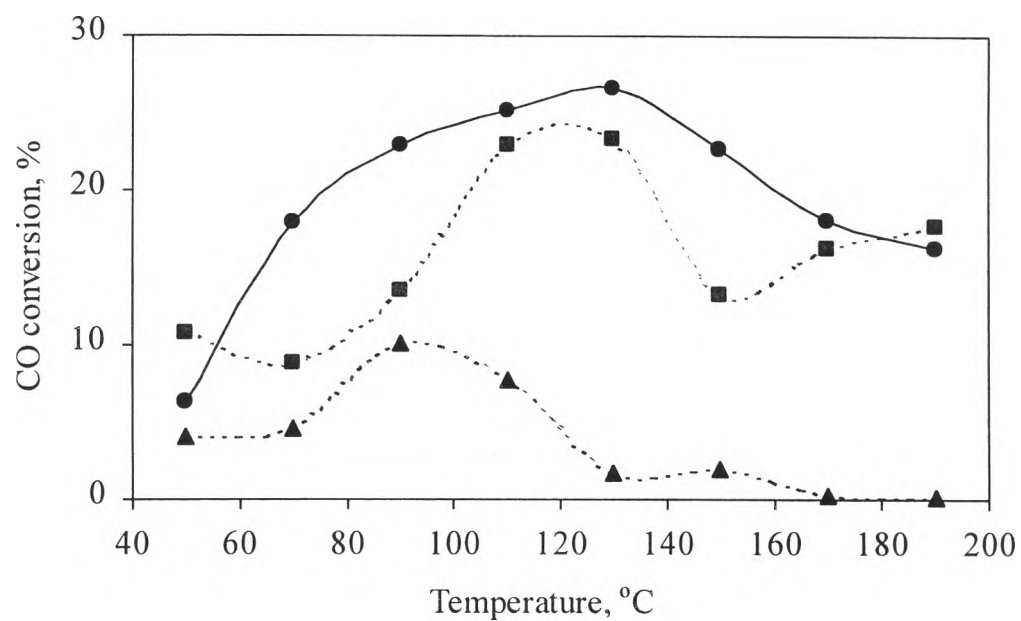


Figure 4.7(a) Effect of calcination temperature on CO conversion of 1%Pd/CeO₂ co-precipitation catalyst (■) 200°C (●) 300°C (▲) 400°C.

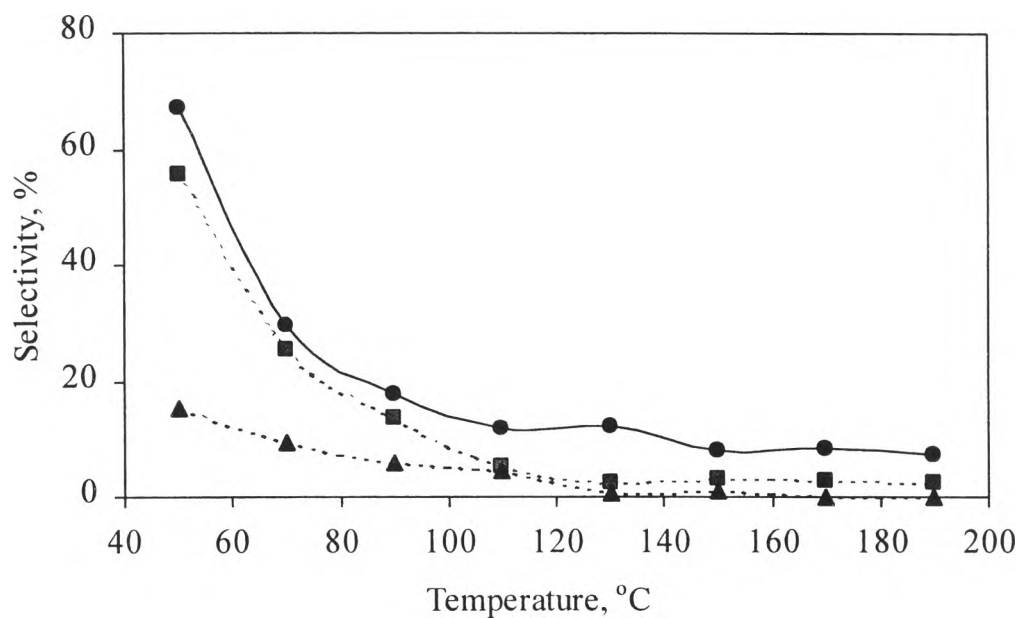


Figure 4.7(b) Effect of calcination temperature on selectivity of 1%Pd/CeO₂ co-precipitation catalyst (■) 200°C (●) 300°C (▲) 400°C.

(Table 4.5). The intensity of XRD pattern was decreased with decreasing in temperature as shown in Figure 4.4. However the activity of calcination temperature at 200°C was lower than that at 300°C possibly due to incomplete removal the excess ion at lower calcination temperature. After this part, the temperature at 300°C was selected as the optimum calcination temperature.

4.2.4 Effect of Support

Figures 4.8(a) and (b) compare the activity and selectivity between 1%Pd/CeO₂ and 1%Pd/ZrO₂ co-precipitation catalysts. The 1%Pd/CeO₂ catalyst gave higher CO conversion and slightly higher selectivity than 1%Pd/ZrO₂ catalyst. The support influenced the catalyst activity (Bekyarova *et al.*, 1998). It is believed that strong-metal support interaction occurs in CeO₂ supported metal catalyst (Cunningham *et al.*, 1990). Besides, it has been known that CeO₂ has oxidative properties and a good capacity for oxygen storage reaction (Yao *et al.*, 1997). Alessandro *et al.* (1999) found that CeO₂ influenced the selectivity and thermal stability of the automotive catalysts. Moreover, CeO₂ promoted water gas shift reaction and stabilized their dispersed state. Furthermore, the CeO₂ led to enhancement of the CO oxidation. This has been often explained with a mechanism involving a reaction between CO adsorbed on precious metal and the surface oxygen from the CeO₂. In contrast, there is no evidence that oxygen transports from zirconia support to the metal.

The results of impregnation on sol-gel catalyst showed lower CO conversion and selectivity than co-precipitation catalyst and can be found in Figure A.4 (a) and (b) in Appendix A.

4.2.5 Effect of Ratio of Ce and Zr Support

Figures 4.9(a) and (b) show the conversion and selectivity on 1%Pd/CeO₂-ZrO₂ (100:0, 75:25, and 0:100 weight ratios of Ce to Zr) co-

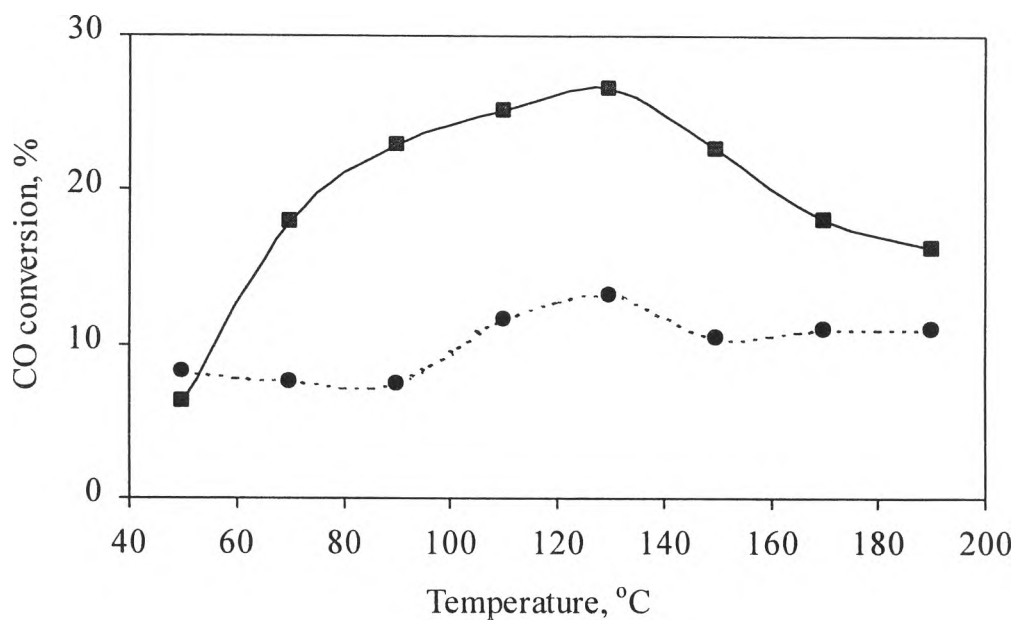


Figure 4.8(a) Effect of support on CO conversion of co-precipitation catalyst calcined at 300°C for 2 h. (■) 1%Pd/CeO₂ (●) 1%Pd/ZrO₂.

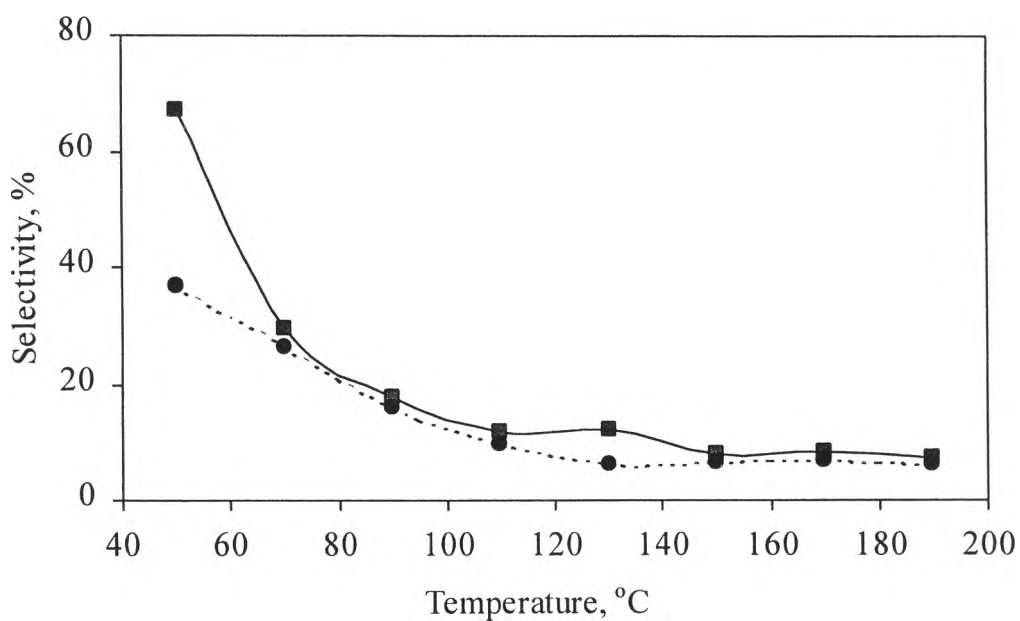


Figure 4.8(b) Effect of support on selectivity of co-precipitation catalyst calcined at 300°C for 2 h. (■) 1%Pd/CeO₂ (●) 1%Pd/ZrO₂.

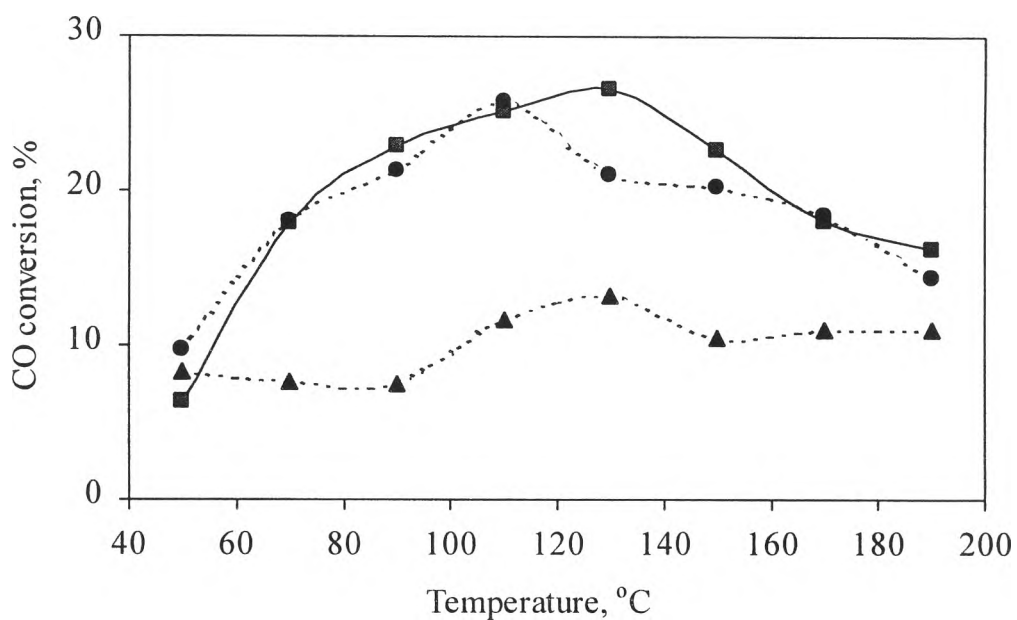


Figure 4.9(a) Effect of ratio of Ce and Zr support on CO conversion of 1%Pd/CeO₂-ZrO₂ co-precipitation catalyst (■) 100:0 (●) 75:25 (▲) 0:100.

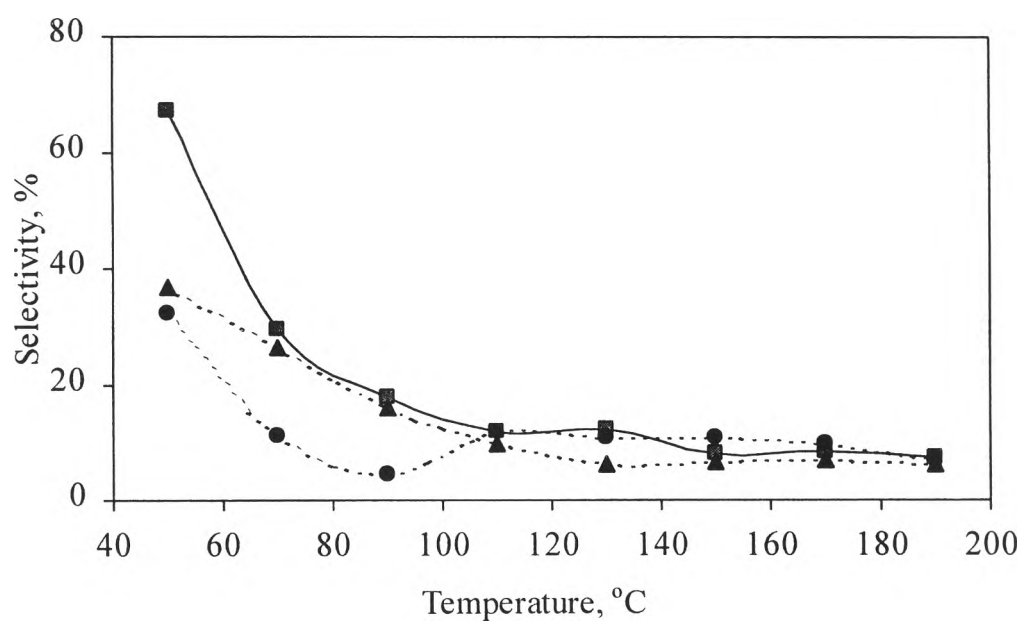


Figure 4.9(b) Effect of ratio of Ce and Zr support on selectivity of 1%Pd/CeO₂-ZrO₂ co-precipitation catalyst (■) 100:0 (●) 75:25 (▲) 0:100.

precipitation catalysts. The 1%Pd/CeO₂ and 1%Pd/CeO₂-ZrO₂ (75:25) catalyst exhibited very similar activity. This result can be explained by the XRD result in section 4.12 of these samples (Figure 4.1). It can be seen that the XRD are similar. We can interpret this as the 75-25 catalyst having the same crystal structure as the pure ceria. Both of these catalysts showed higher activity than 1%Pd/ZrO₂.

The effect of ratio of Ce to Zr on the activity of impregnation catalysts is shown in Figure A.5 (a) and (b) in Appendix A.

4.2.6 Effect of Catalyst Preparation

Figures 4.10(a) and (b) present the CO oxidation activity and selectivity on 1%Pd/CeO₂ catalyst. It is clear that co-precipitation catalyst showed higher conversion and selectivity than impregnation catalyst prepared with the sol-gel support. Gil *et al.* (1994) studied the effect of preparation method and claimed that metal support interaction strongly depends on the preparation method. Moreover, Lemonidou *et al.* (1998) concluded that the preparation technique influences on the degree of reduction. The co-precipitation or impregnation on sol-gel technique yielded catalysts with different characteristics. The difference in surface area and XRD pattern was confirmed by the BET and XRD measurements. BET surface area of impregnation on sol-gel catalyst showed higher surface area than co-precipitation catalyst. The XRD pattern of impregnation on sol-gel catalyst was sharper than co-precipitation catalyst indicating larger crystallites. This is consistent with the belief that the mobile oxygen in ceria comes from grain boundaries with defects. If the average crystallite size is larger then there are fewer grain boundaries to donate oxygen.

In fact, the co-precipitation catalyst has a well-mixed structure between support and metal because, in this method, both of them dissolve together in solution and may form chemical bonds before precipitating out.

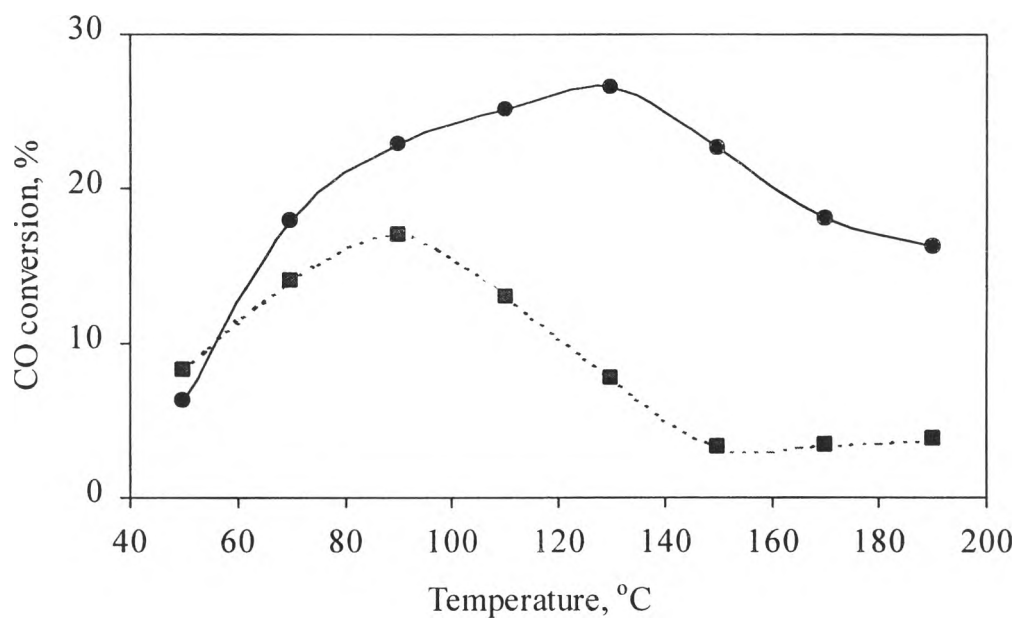


Figure 4.10(a) Effect of catalyst preparation on CO conversion of 1%Pd/CeO₂ catalyst (●) co-precipitation method (■) impregnation on sol-gel method.

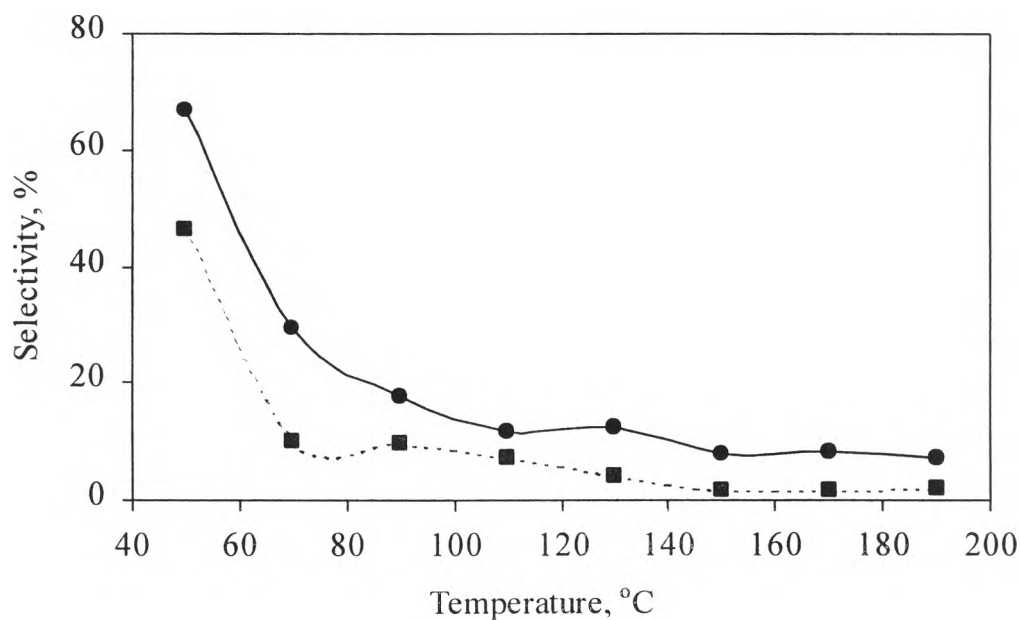


Figure 4.10(b) Effect of catalyst preparation on selectivity of 1%Pd/CeO₂ catalyst (●) co-precipitation method (■) impregnation on sol-gel method.

On the other hand, in impregnation, the metal solution is physically loaded to the pore of support, so the Pd metal may not go uniformly into the pores of the support. This can be supported by the AAS result. The impregnation on sol-gel catalyst had the lower percent Pd loading than co-precipitation catalyst.

4.2.7 Comparison of Activity with Conventional Catalyst

Figures 4.11(a) and (b) compare the activity between 1%Pd/CeO₂ co-precipitation catalyst and conventional catalyst (1%Pd/Al₂O₃ sol-gel catalyst). The 1%Pd/CeO₂ showed higher CO conversion and selectivity than 1%Pd/Al₂O₃ which has been used for fuel cell applications. 1%Pd/CeO₂ showed higher activity due to the capacity of Ce to switch between the two-oxidation states Ce³⁺ and Ce⁴⁺, which gives an oxygen-storing capacity to the oxides. This beneficial property improved the catalyst performance for the oxidation reaction because CeO₂ can act as oxygen buffer, releasing oxygen in times of oxygen deficiency and storing oxygen in times of oxygen surplus.

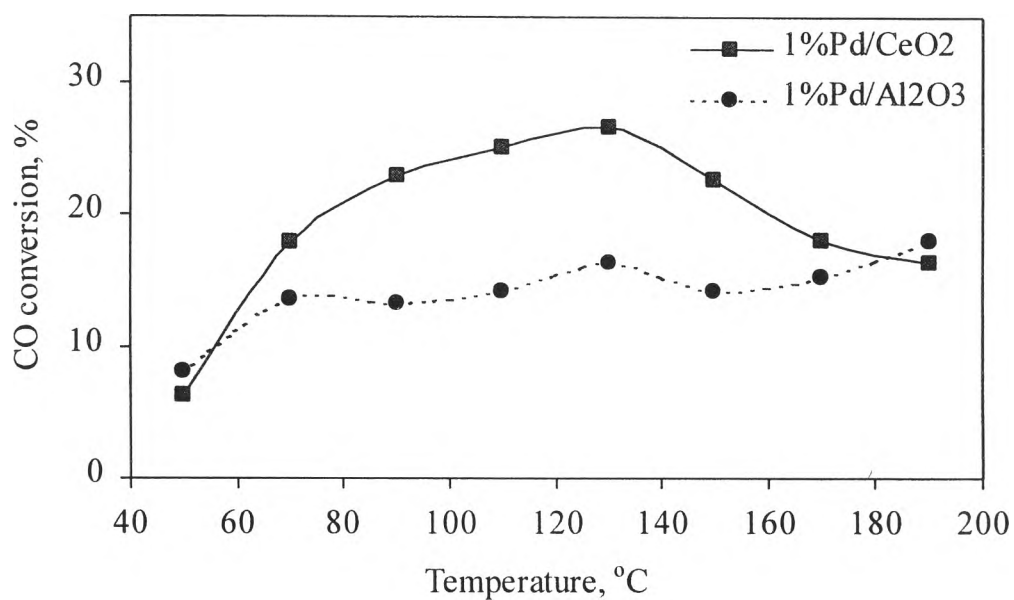


Figure 4.11(a) Comparison of CO conversion between 1%Pd/CeO₂ co-precipitation catalyst and 1%Pd/Al₂O₃ sol-gel catalyst.

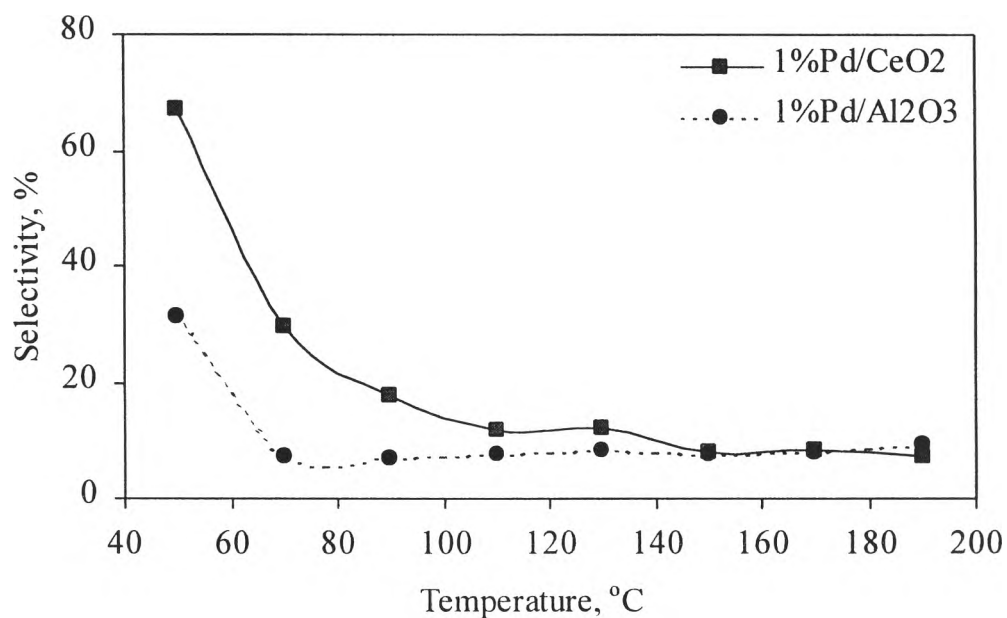


Figure 4.11(b) Comparison of selectivity between 1%Pd/CeO₂ co-precipitation catalyst and 1%Pd/Al₂O₃ sol-gel catalyst.