CHAPTER V

ACTVITY OF Pt/CeO_2 AND Au/CeO_2 CATALYSTS

In previous comparative studies, it was shown that the activity of the Pt catalyst depends on the support material and catalyst preparation. In this chapter, the results on the activity of Pt/CeO_2 and Au/CeO_2 catalysts are presented as a function of reaction temperature. The effects of preparation method, O_2, water vapor and CO_2 concentration in feed stream on the selective CO oxidation over Pt/CeO_2 and Au/CeO_2 catalysts were investigated in the temperature range of 50-190°C. Catalytic stability test was also performed.

5.1 Experimental Details

5.1.1 Catalyst Preparation

Three methods of the catalyst preparation; impregnation, co-precipitation and sol-gel were used in this work.

Impregnation method The Pt catalysts were obtained by impregnation of the commercial CeO_2 support with an aqueous solution of $H_2PtCl_6.6H_2O$ containing the appropriate amount of Pt. The catalysts were dried overnight at 110°C and calcined at 500°C for 5 h.

Co-precipitation method An aqueous solution of Na_2CO_3 (1M) was added into an aqueous mixture of $H_2PtCl_6.6H_2O$ (Alfa AESAR) and $Ce(NO_3)_3.6H_2O$ (Fluka) and kept at room temperature and constant pH of 8.0. The precipitate was aged for an hour and then was washed several times with distilled water until there was no excess anions. After washing with deionized water, the catalysts were dried overnight at 110°C and calcined at 500°C for 5 h.

Sol-gel method The single step sol-gel catalysts were prepared by hydrolyzing a solution of Ce acetate (Alfa AESAR) and $H_2PtCl_6.6H_2O$ with NH_4OH. The reaction mixture was kept at 80°C while the pH was maintained between 9.0-9.5. Then, HNO_3 was added until gelation, the catalysts were dried overnight at 110°C and calcined at 500°C for 5 h.

For the Au/CeO_2 catalyst, $HAuCl_4.xH_2O$ (Alfa AESAR) was used as a precursor.

5.1.2 Catalyst Characterization

Powder X-ray diffraction (XRD) was used to obtain information about the structure and composition of crystalline materials. A Rigaku X-ray diffractometer system equipped with a graphite monochromator and a Cu tube for generating a CuK radiation was used to obtain the XRD patterns.

The Brunauer-Emmett-Teller (BET) method was used to determine the surface area and pore size of the catalysts by N_2 adsorption/desorption at -196°C. Specific surface area was determined by using an Autosorb-1 surface area analyzer.

The particle morphology of the catalysts was observed by Scanning Electron Microscope (SEM) using JEOL JSM -5410 LV scanning microscope operated at 15 kV. The Transmission Electron Microscopy (TEM) images were attained using a JEM 2010 operating at 200 kV in bright and dark field modes. Crystallinity and crystal structure of the samples were evaluated from the selected area electron diffraction patterns.

5.1.3 Activity Measurement

Catalytic activity studies were conducted in the reactant gas typically consisted of 1% CO, 0.5-2% O_2, 2-20% CO_2, 0-10% H_2O, 40% H_2 and helium. The space velocity was 30,000 ml/g.h. The reactant and product gases were analyzed both qualitatively and quantitatively by an on-line gas chromatography (Hewlett Packard 5890 Series II equipped with thermal conductivity detector). The column utilized in the chromatography was a Carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column.

The CO conversion was calculated based on the carbon dioxide formation. The selectivity of CO oxidation was defined as the oxygen consumption for CO oxidation divided by the total oxygen consumption. There was no methane formation observed under reaction conditions performed in this study.

5.2 Results and Discussion

5.2.1 Catalyst Characterization

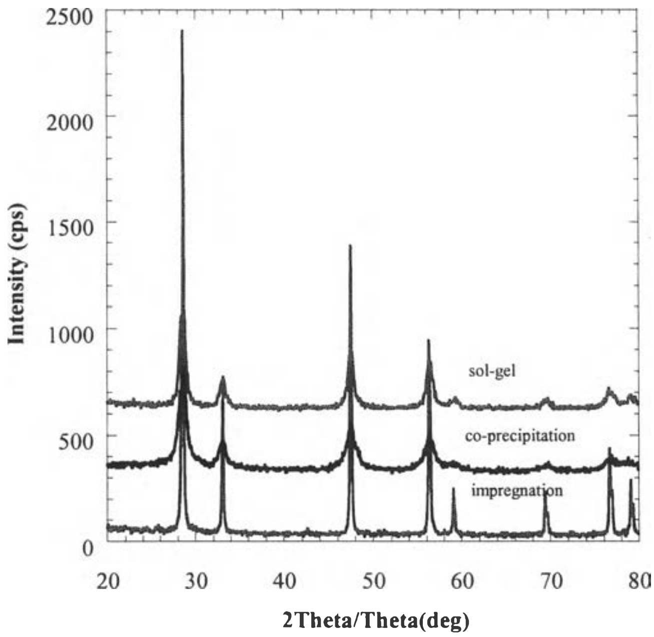
Table 5.1 lists the BET surface areas and CeO_2 crystallite sizes of the Pt/CeO_2 and Au/CeO_2 catalysts studied. The surface area varies significantly with the catalyst preparation method. The Pt/CeO_2 catalysts had BET surface areas of 116, 114 and 55 m^2/g for impregnation, co-precipitation and sol-gel methods, respectively. In comparison the Au/CeO_2 catalysts, had surface areas of 124.1, 66.7 and 104.2 m^2/g, for the co-precipitation, sol-gel, and impregnation methods, respectively. The BET surface area of the commercial CeO_2 support for impregnation catalyst was 118.8 m^2/g.

The typical XRD patterns of the CeO_2 in the samples prepared by three different methods are shown in Figure 5.1. It is apparent that the patterns consist of eight main reflections, typical of a cubic, fluorite structure of CeO_2 corresponding to (111), (200), (220), (311), (222), and (400) planes. Almost XRD patterns of Pt/CeO_2 and Au/CeO_2 catalysts showed no metal peaks indicating that the metallic particle size of the catalysts might be smaller than 5 nm. The CeO_2 crystallite sizes of the catalysts were determined from X-ray line-broadening using the Debye Scherrer equation. The CeO_2 crystallite size of Pt/CeO_2 prepared by impregnation, co-precipitation, and sol-gel methods are 12.6, 15.8, and 34.8 nm, respectively. For three catalyst preparation methods of Au/CeO_2 catalysts, the CeO_2 crystallite sizes are 17.4, 14.5, and 38.6 nm, respectively. The sol-gel method gave the largest crystallite size of CeO_2 while co-precipitation method gave the smallest crystallite size of CeO_2 on both Pt and Au catalysts. The sizes of CeO_2 crystallites are inversely correlated with the surface areas of the catalysts. Au/CeO_2 co-precipitation catalyst showed no metal peaks indicating that the metallic particle size of the catalyst might be smaller than 5 nm. This observation was also confirmed by TEM investigations. The evidence of Au in metallic form on impregnation and sol-gel catalysts was observed at $2\theta = 38.2^{o}$ and the average Au crystallite sizes were 29 and 30 nm, respectively.

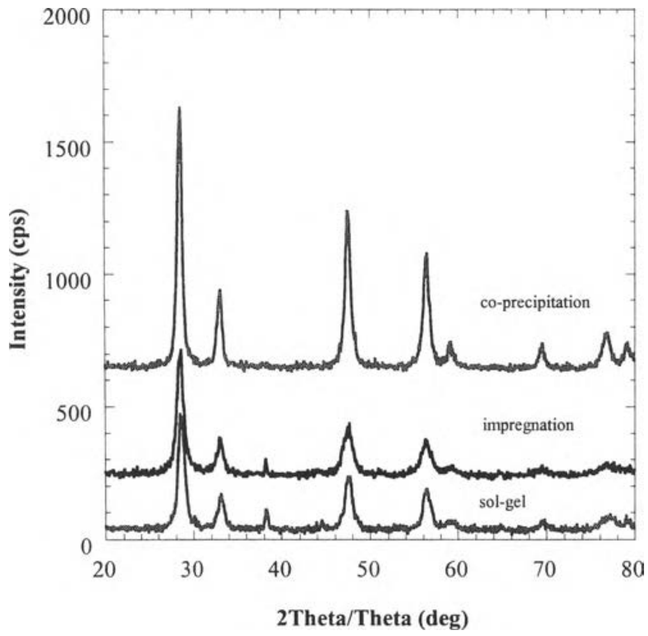
The SEM and TEM results of Pt/CeO_2 and Au/CeO_2 catalysts are given in Figures 5.2-5.5. The TEM picture of 1%Au/CeO_2 co-precipitation catalyst shown in the Figure 5.3 (b) reveals the presence of the gold particles as dark spots in the catalyst. The existence of Au particles on CeO_2 support was verified by using EDS focusing on the regions containing highly contrast spots under TEM. For 1%Au/CeO_2 co-precipitation catalyst, the Au particles were seen as highly contrast spots both on and inside the support and the average particle size of Au is about 4.5 nm.

Table 5.1 Catalyst surface area and crystallite size of 1% Pt/CeO_2 and 1% Au/CeO_2.

Catalyst	**Preparation method**	**BET surface area (m^2/g)**	**Ceria crystallite size (Å)**
1% Pt/CeO_2	Impregnation	116.0	126
1% Pt/CeO_2	Co-precipitation	114.0	158
1% Pt/CeO_2	Sol-gel	55.0	348
1% Au/CeO_2	Impregnation	104.2	174
1% Au/CeO_2	Co-precipitation	124.1	145
1% Au/CeO_2	Sol-gel	66.7	386

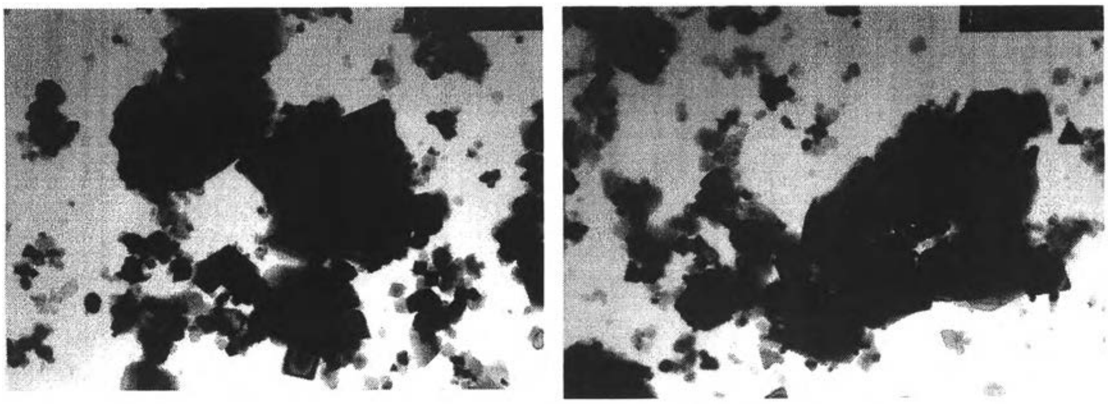


(a) Pt/CeO$_2$

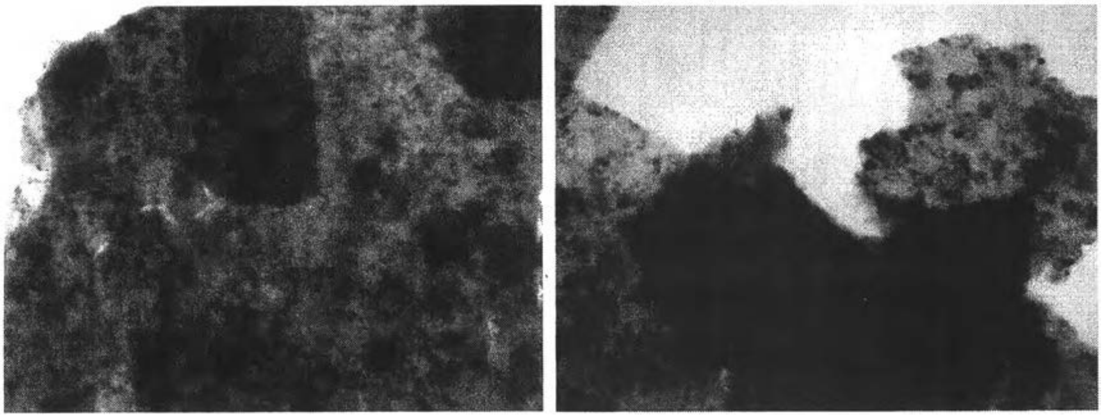


(b) Au/CeO$_2$

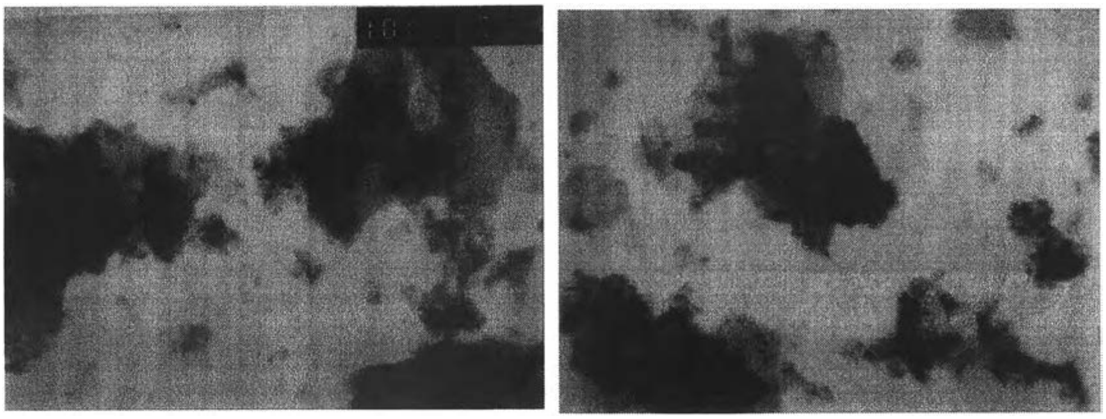
Figure 5.1 XRD patterns of Pt/CeO$_2$ and Au/CeO$_2$ catalysts.



a) Pt/CeO$_2$ impregnation catalyst

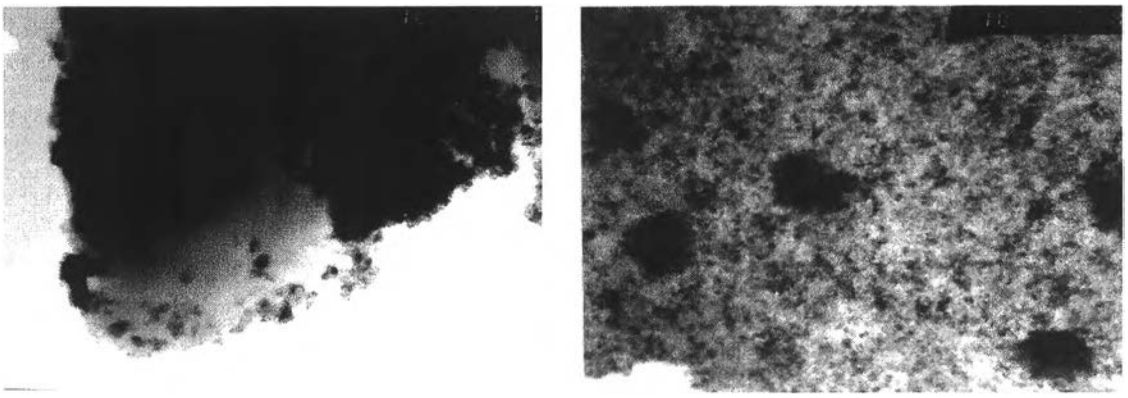


b) Pt/CeO$_2$ co-precipitation catalyst

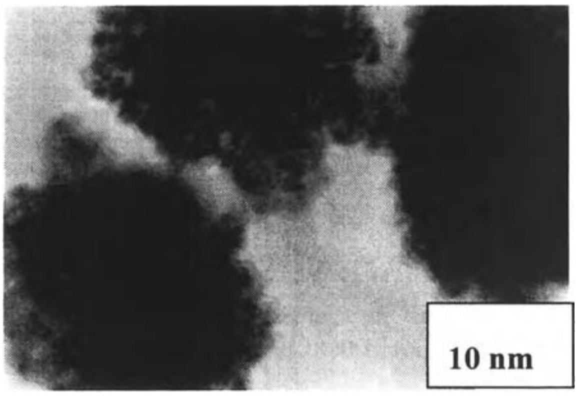


c) Pt/CeO$_2$ sol-gel catalyst

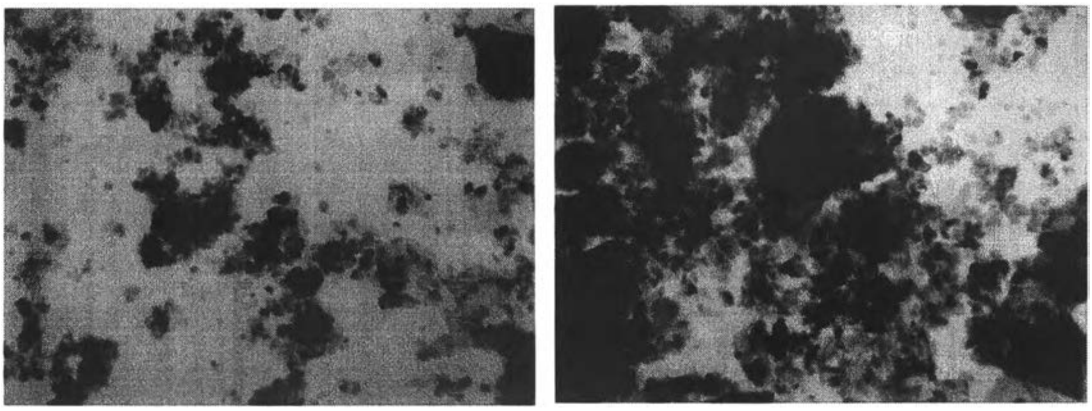
Figure 5.2 TEM pictures of Pt/CeO$_2$ catalysts.



a) Au/CeO_2 impregnation catalyst



b) Au/CeO_2 co-precipitation catalyst



c) Au/CeO_2 sol-gel catalyst

Figure 5.3 TEM pictures of Au/CeO_2 catalysts.

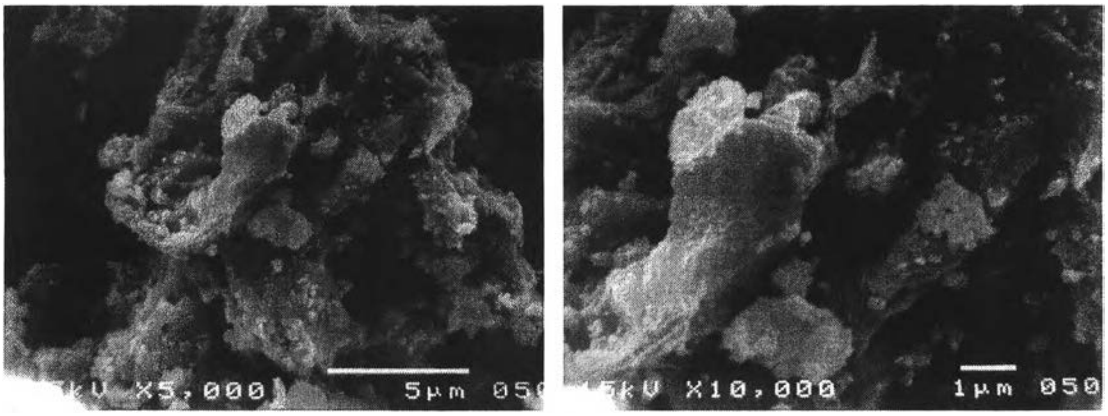
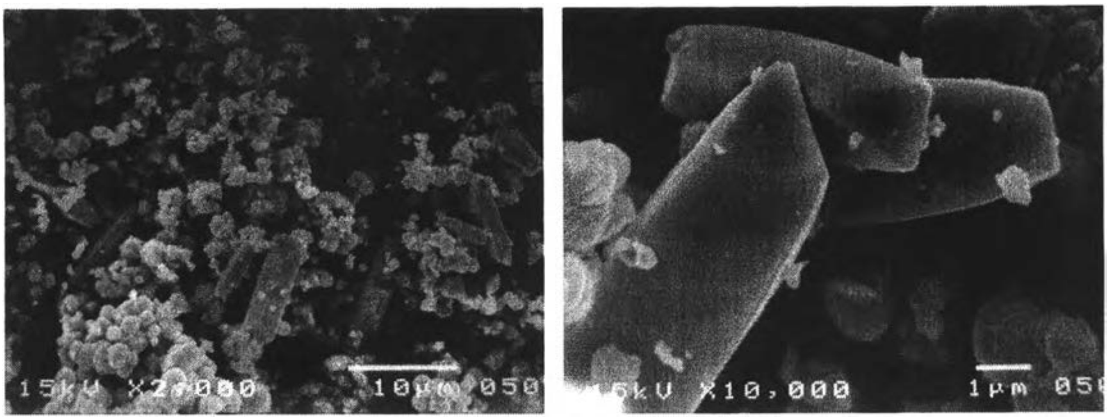
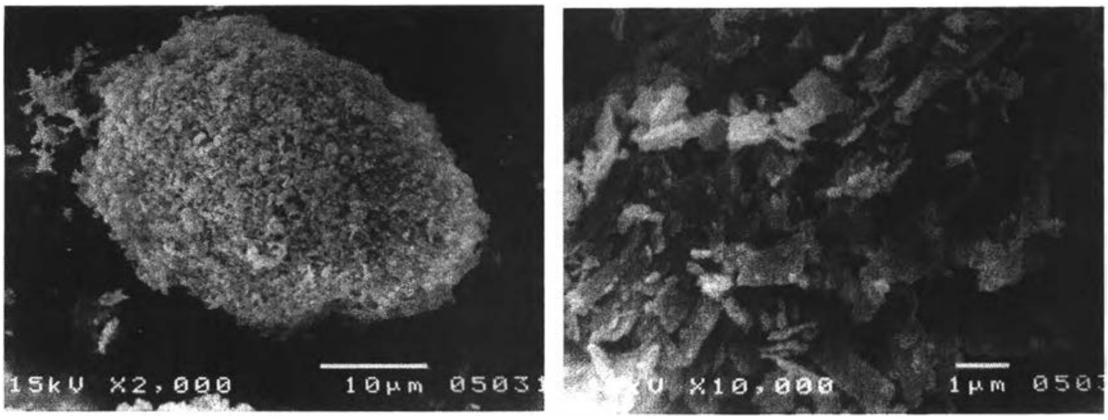


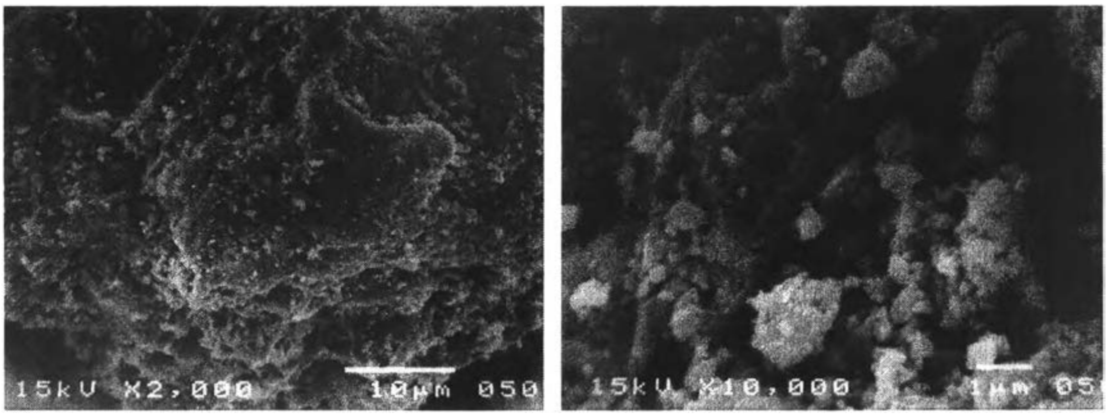
Figure 5.4 SEM pictures of Pt/CeO_2 sol-gel catalyst.



a) Au/CeO_2 impregnation catalyst



b) Au/CeO_2 co-precipitation catalyst



c) Au/CeO_2 sol-gel catalyst

Figure 5.5 SEM pictures of Au/CeO_2 catalysts.

5.2.2 Effect of Preparation Method

The CO oxidation activity of the 1%Pt/CeO_2 catalysts as a function of reaction temperature with a feed of 1% CO, 1% O_2, 2% CO_2, 2.6% H_2O and 40% H_2 in helium is shown in Figure 5.6. As can be seen, the catalyst activity greatly depended on the catalyst preparation method. Catalyst activity was found to increase over the temperature range investigated and showed a peak on the impregnation and sol-gel catalysts. In contrast, the co-precipitation catalyst was found to be inactive for CO oxidation activity under the reaction conditions. The sol-gel catalyst is the most active one reaching a maximum conversion of about 85% at 110°C. The reaction at 110°C is the most suitable temperature for the fuel cell operating temperature level (80-120°C) (Gottesfeld *et al.*, 1988).

Figure 5.7 shows the conversion and selectivity as a function of operating temperature for the Pt/CeO_2 sol-gel catalyst. Interestingly, unlike the observations of Watanabe *et al.*, 1995 who found that the high selectivity is observed at low temperature for the Pt/zeolite catalysts. In this work, the selectivity of Pt/CeO_2 sol-gel catalyst increases with temperature in parallel to conversion. A maximum of about 50% selectivity is reached between 90°C and 110°C coinciding with the maximum in conversion temperature.

The variation of catalytic activity and selectivity as a function of operating temperature may be explained in terms of adsorption and desorption of CO. At low temperature, CO adsorbs and covers the catalyst surface. High coverage of CO inhibits the disscociative chemisorption of O_2. Therefore, CO conversion and selectivity are low at low temperature. When the rate of desorption increases with an increase in temperature, CO conversion is increased. However, with increasing temperatures the rate of H_2 oxidation increases even faster resulting in decreased selectivity towards CO oxidation. The low temperature behavior of the selectivity is in agreement with the studies of Igarashi *et al.*, 1997 and Kahlich *et al.*, 1997.

It is believed that a synergistic effect in CeO_2 supported Pt catalysts could lead to very active catalyst since CeO_2 itself does not oxidize CO under the same condition. Temperature-programmed reduction (TPR) measurements (Nunan *et al.*, 1992 and Diwell *et al.*, 1991) showed that Ce not only promotes reduction of the

Pt but also undergoes a synergistic reduction with the Pt. Hence, the observed high activity of Pt/CeO_2 could be attributed to a unique synergistic effect which is brought up by single step sol-gel. Hardacre *et al.* (1994) reported that CO oxidation is strongly promoted on Pt partially covered by CeO_2. Their XPS results indicate that the chemical state of the oxide form corresponds essentially to CeO_2.

The performances of our catalysts could not be compared directly with the other worker's results due to difference in operating conditions. From our results, the maximum conversion of 85% by Pt/CeO_2 sol-gel catalyst is lower than Pt/Al_2O_3 catalysts (Oh *et al.*, 1993) which showed almost 100% conversion and the selectivity of 40% under mild condition (0.85%H_2, 900 ppm CO and 800 ppm O_2). However, the temperature at maximum conversion of the Pt/CeO_2 sol-gel catalyst is ~105°C which is lower than the temperature of 200°C in the studies by Oh *et al.* (1993) and Kahlich *et al.* (1997). Besides, the above studies were done under the condition without H_2O and CO_2 which is less realistic condition.

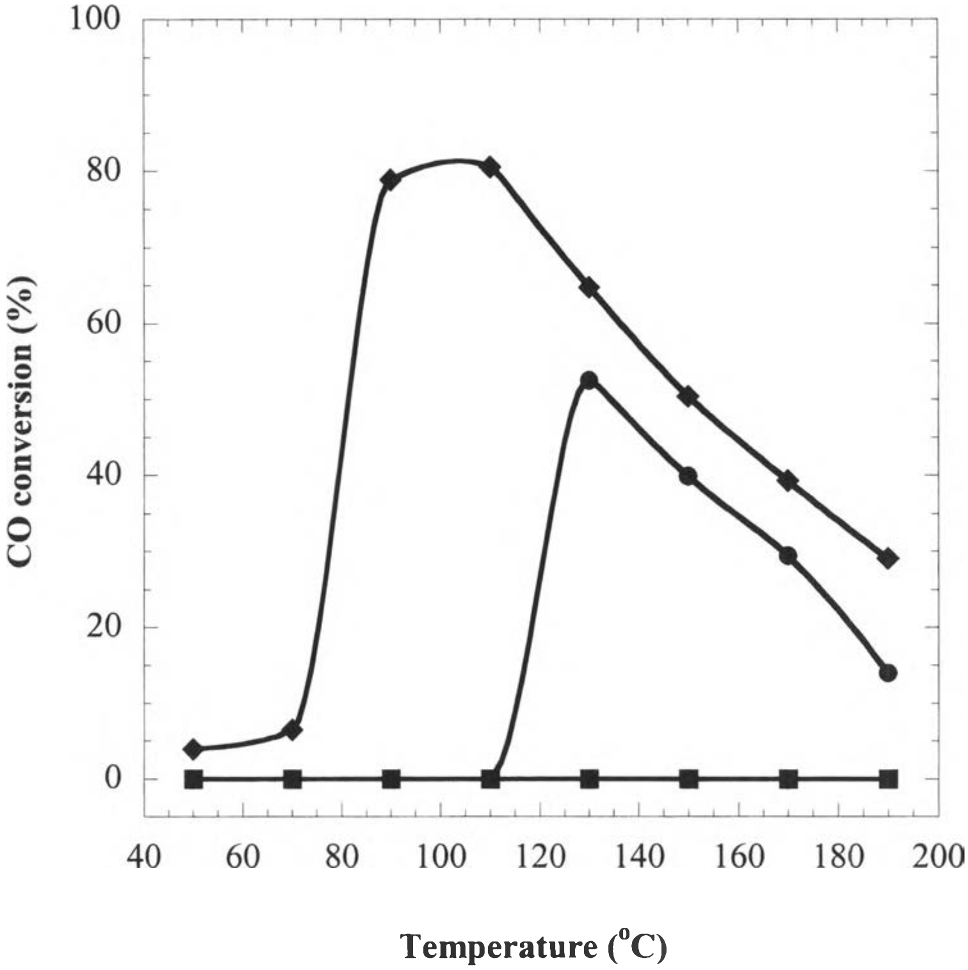


Figure 5.6 Temperature dependence of CO conversion of 1% Pt/CeO_2 catalysts. Reactant composition: 1% CO, 1% O_2, 2.6% H_2O, 2% CO_2, 40% H_2 and helium: (■) co-precipitation; (●) impregnation; (◆) sol-gel.

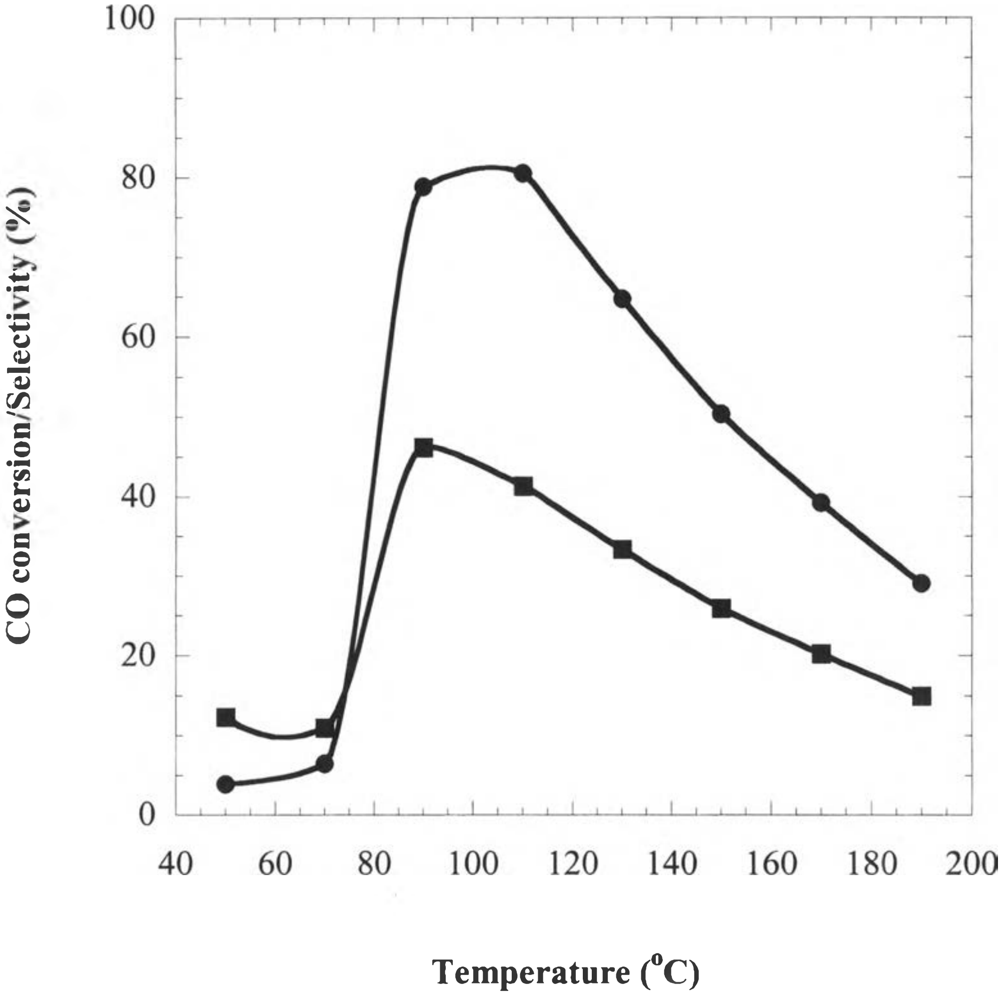


Figure 5.7 Temperature dependence of CO conversion and selectivity of 1% Pt/CeO_2 sol-gel catalyst. Reactant composition: 1% CO, 1% O_2, 2.6% H_2O, 2% CO_2, 40% H_2 and helium: (●) conversion; (■) selectivity.

Figure 5.8 illustrates the effect of catalyst preparation method on the activity of 1%Au/CeO_2. The Au/CeO_2 co-precipitation catalyst has the best performance among the three types of catalyst preparation. The CO conversion showed a peak on all catalysts. The CO conversion and selectivity of the Au/CeO_2 co-precipitation catalyst is shown in Figure 5.9. It shows that the CO oxidation and selectivity activities of the Au/CeO_2 co-precipitation catalyst are higher than that of the Pt/CeO_2 sol-gel catalysts at temperature of 110°C. This may be caused by the more weakly adsorbed CO on the Au surface in comparison to the strong chemisorption of CO on Pt surface at low temperatures (Haruta, 1997). It is known that only gold in a finely divided state exhibits high activity for CO oxidation.

The temperature at which the activity of the Au/CeO_2 co-precipitation catalyst was maximum was 110°C. The reaction at 110°C is the most suitable temperature for the fuel cell operating temperature level (80 –120°C). At higher temperature, there is a continuous decrease in selectivity, indicating higher activation energy for the H_2 oxidation than for the CO oxidation. The low temperature behavior of the selectivity is in agreement with the result of Pt/CeO_2 catalyst.

The morphologies of Au/CeO_2 co-precipitation catalyst by SEM and XRD are very different from those of impregnation and sol-gel catalysts. It was found that the co-precipitation catalyst has a crystallite size of about 4.5 nm which is much smaller than those prepared by impregnation and sol-gel methods which have Au crystallite sizes of 29 and 30 nm, respectively. The results obtained with the Au/CeO_2 catalyst prepared by co-precipitation method were similar to those observed with the co-precipitation catalyst reported by Haruta *et al.* (1993) and Scirè *et al.* (2003). Besides, from SEM pictures, we observed only crystalline ceria on Au/CeO_2 co-precipitation catalyst which is also confirmed by the XRD results. It is then concluded that the Au/CeO_2 co-precipitation catalyst exhibits much higher activity than other two catalysts due to the aforementioned characteristic. It has been reported that the high activity of Au/CeO_2 catalyst might be related to the capacity of Au nanoparticles to weaken the Ce-O bond. Thus, the mobility/reactivity of the surface lattice oxygen is increased (Scirè *et al.,* 2003).

The performance of Au catalysts in this work can be compared with Au/MnO_x and Au/Fe_2O_3 catalysts available in the literature. Kahlich *et al.* (1999) and

Torres Sanchez *et al.* (1997) reported that the high activity and selectivity at the considerably lower temperature of 120 and 80 °C were observed over Au/MnO_x and Au/Fe_2O_3 catalysts, respectively. However, their reactant gas mixture used containing CO, O_2 and H_2 was not a typical simulated reformed gas. In addition, Au/CeO_2 co-precipitation catalyst is the most active at 110 °C which is suitable for the system connected directly to PEM fuel cells. This catalyst shows much higher activity and selectivity when compared to the Ag-based composite oxide catalysts reported by Güldür *et al.* (2002). However, recent work by Avgouropoulos *et al.* (2002) at similar reaction conditions shows that CuO-CeO_2 sol-gel catalyst exhibited very high activity with selectivity close to 90%.

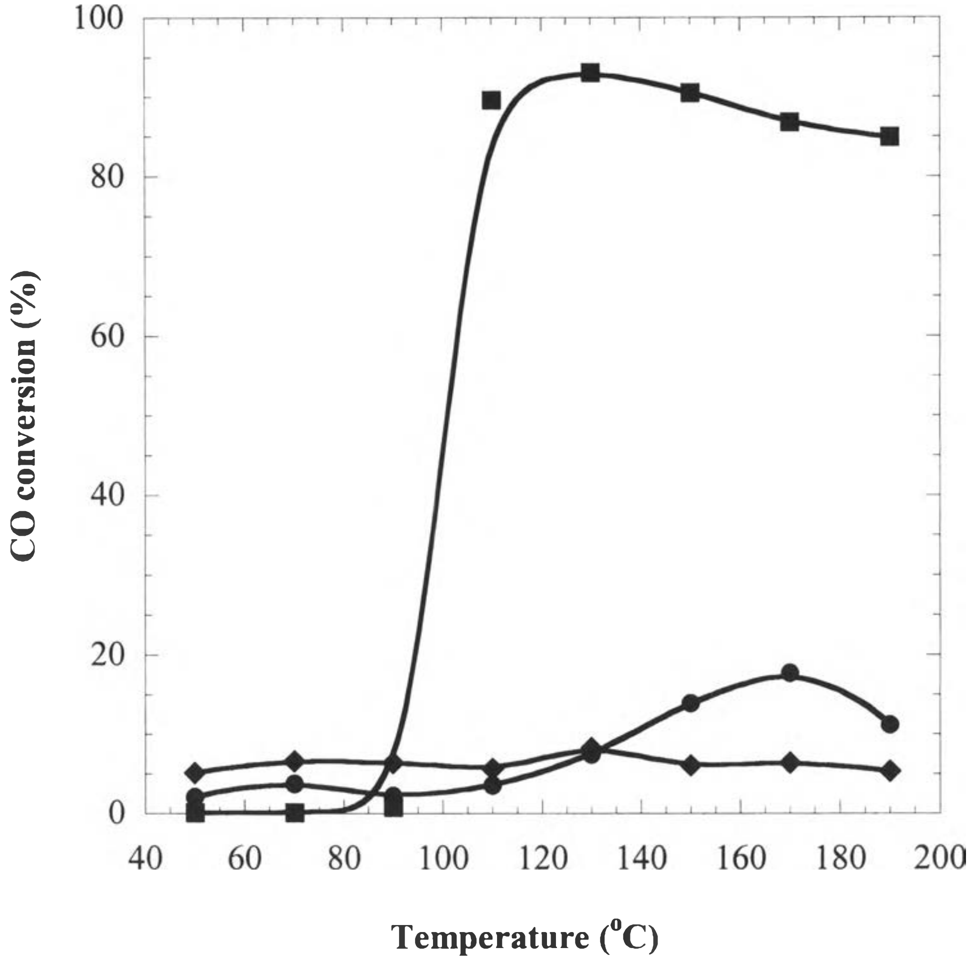


Figure 5.8 Temperature dependence of CO conversion of 1%Au/CeO_2 catalysts. Reactant composition: 1% CO, 1% O_2, 2.6% H_2O, 2% CO_2, 40% H_2 and helium: (■) co-precipitation; (●) impregnation; (◆) sol-gel.

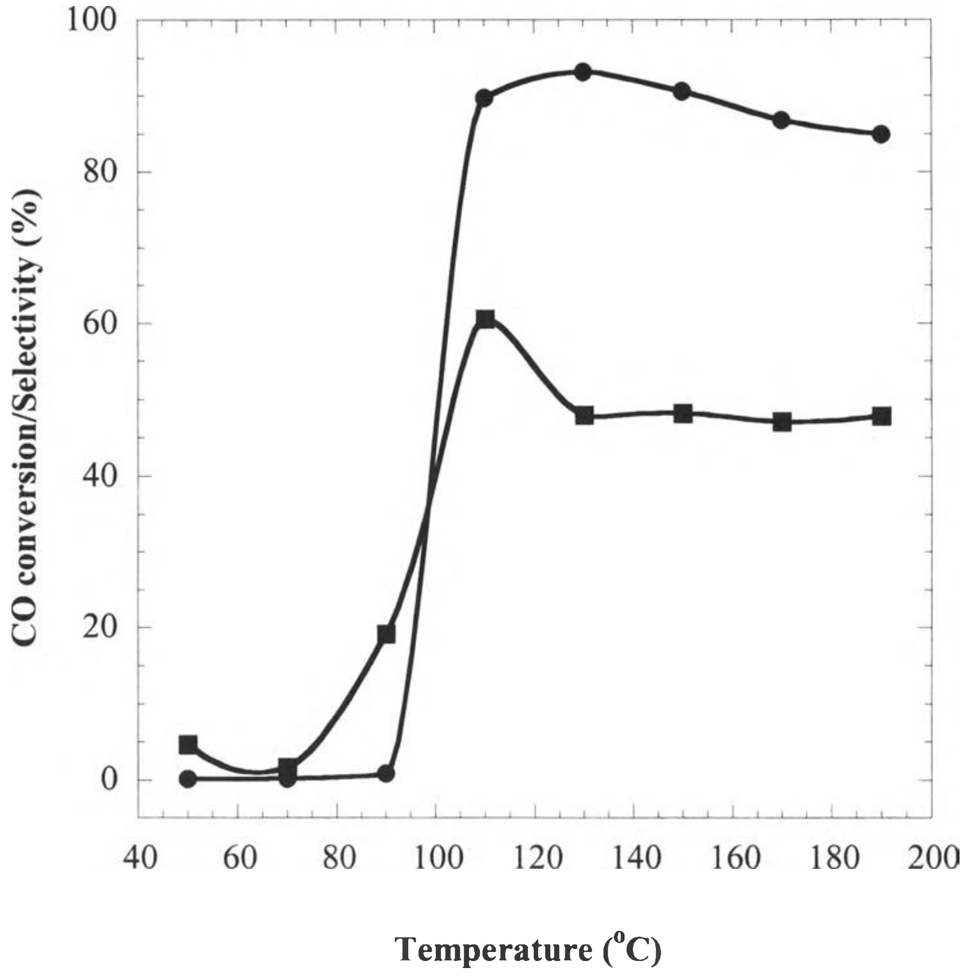


Figure 5.9 Temperature dependence of CO conversion and selectivity of 1% Au/CeO_2 co-precipitation catalyst. Reactant composition: 1% CO, 1% O_2, 2.6% H_2O, 2% CO_2, 40% H_2 and helium: (●) conversion; (■) selectivity.

5.2.3 Effect of Oxygen Concentration

The CO conversion and selectivity as a function of O_2 concentration in the feed for the Pt/CeO_2 sol-gel is shown in Figure 5.10. As expected, the CO conversion increases with increasing O_2 concentration while selectivity decreases with increasing O_2 concentration. With 0.5% O_2 (the stoichiometric amount) the maximum in CO conversion is about 55% at 110°C, with 1% O_2 the maximum conversion increases to about 80% and the temperature of maximum conversion moves down to about 100°C, with 2% O_2 100% conversion is reached between 80-110°C. The selectivities at the point of maximum conversion for 0.5, 1.0 and 2.0% O_2 concentration are 50, 45 and 25%, respectively. It is clear that an enhanced selectivity is obtained on Pt/CeO_2 catalyst with decreasing O_2 content. The effects of O_2 concentration on CO conversion and selectivity over Au/CeO_2 co-precipitation catalyst are shown in Figure 5.11. With 0.5%, 1% and 2% O_2 the maxima in CO conversion are ~ 70%, 92% and 98% at 110°C, respectively. The selectivities at the point of maximum conversion for the three O_2 concentrations are 64, 62 and 48%, respectively. The optimal O_2 concentration needed for oxidizing 1%CO in the feed is 1% with high selectivity and minimal loss of hydrogen.

It should be pointed out that the highest selectivities are obtained at the peak conversion temperature. For a PEM vehicle technology, both a high CO conversion and a high selectivity are crucial. Within these restrictions, the optimal O_2 concentration needed for oxidizing 1%CO in the feed is 1% with high selectivity and minimal loss of hydrogen.

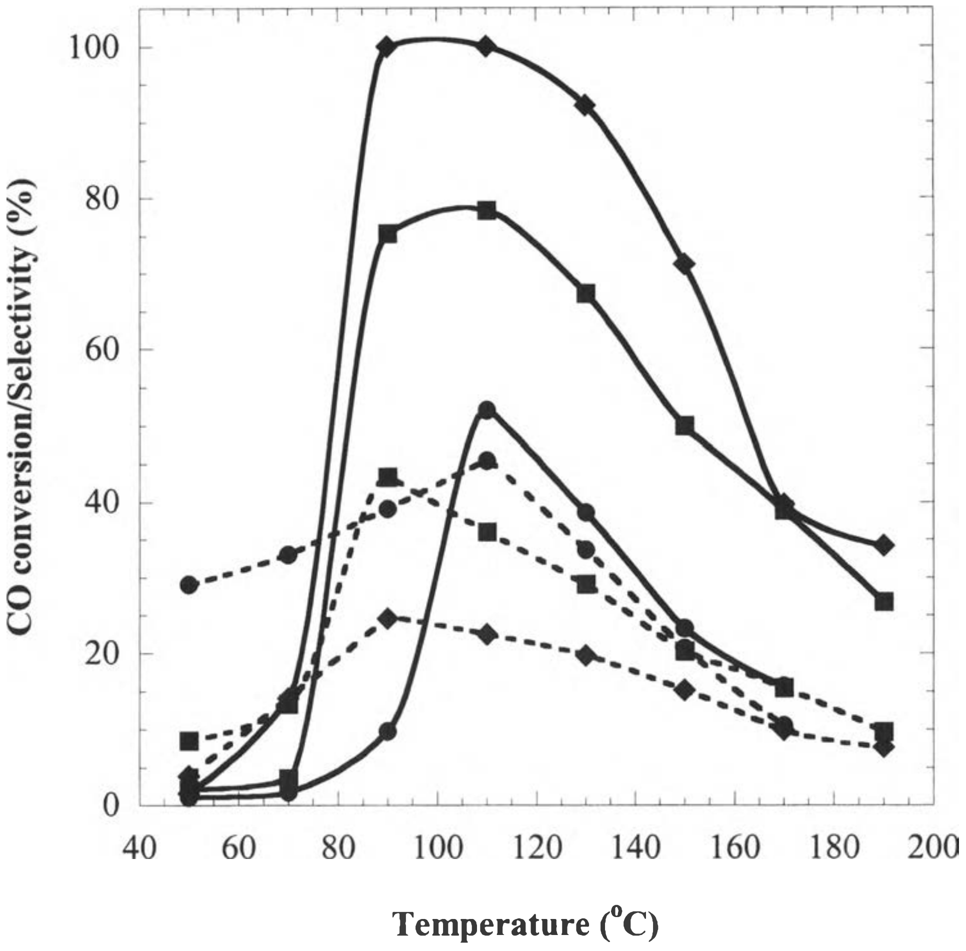


Figure 5.10 Effect of O_2 concentration in reactant gas over 1% Pt/CeO_2 sol-gel catalyst. Reactant composition: 1% CO, 0.5-2% O_2, 2.6% H_2O, 2% CO_2, 40% H_2 and helium: (●) 0.5% O_2; (■) 1% O_2; (◆) 2% O_2; (—) CO conversion; (---) selectivity.

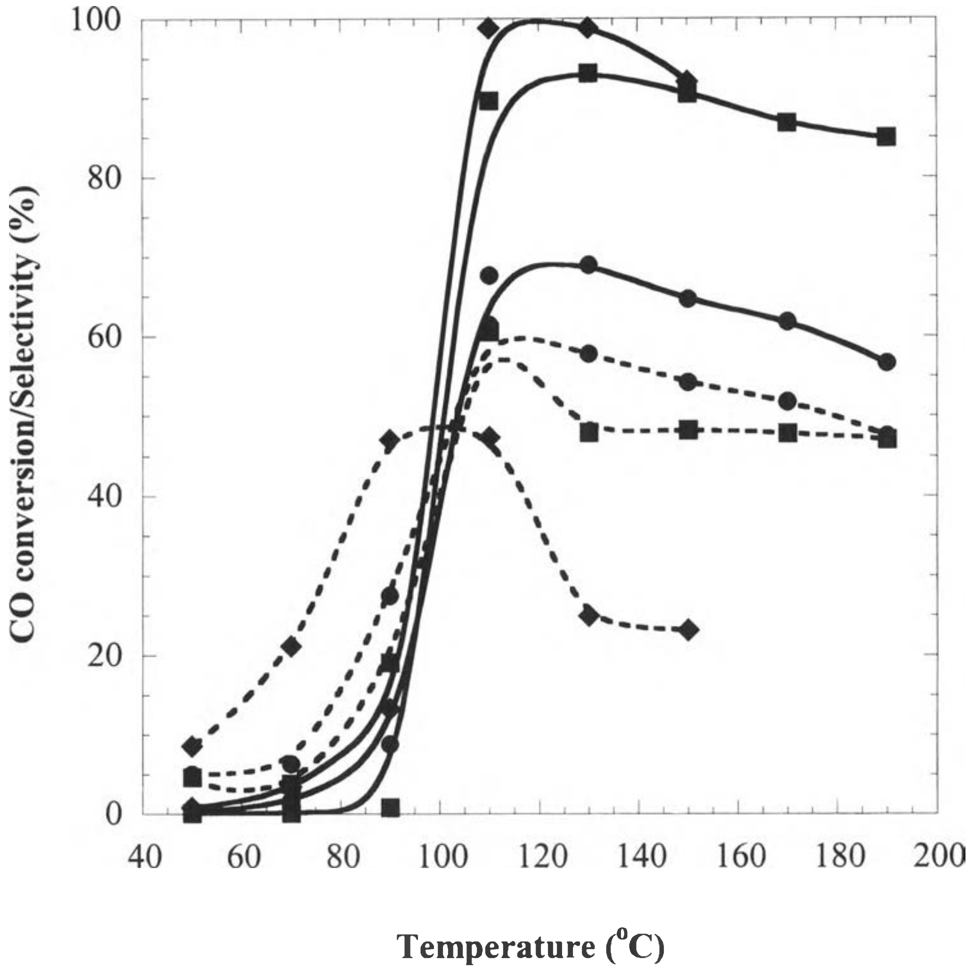


Figure 5.11 Effect of O_2 concentration in reactant gas over 1% Au/CeO_2 catalyst. Reactant composition: 1% CO, 0.5-2% O_2, 2.6% H_2O, 2% CO_2, 40% H_2 and helium: (●) 0.5% O_2; (■) 1% O_2; (◆) 2% O_2; (—) CO conversion; (---) selectivity.

5.2.4 Effect of Water Vapor

In general, it is believed that the catalytic activity of the catalyst is liable to be suppressed in the presence of water vapor. The effect of water vapor in the feedstream on the CO oxidation activity of Pt/CeO_2 sol-gel and Au/CeO_2 co-precipitation catalysts are shown in Figures 5.12 and 5.13. The feed gas mixture was humidified by bubbling through temperature controlled water, yielding 2.6% and 10% water vapor in the reactant gas. When humidified, the maximum activity of the Pt/CeO_2 catalyst became significantly higher when compared to the dry conditions. The presence of water vapor in the feed increased the maximum conversion from 55% to ~75%. Two mechanisms have been proposed for this effect on Pt : (i) Pt can dissociate H_2O to OH which is a strong oxidant as oxygen. (ii) Bunluesin *et al.*, (1998) have invoked a redox process to explain the reaction as CO adsorbs on transition metal sites and reacts with O_2 from ceria, which in turn is oxidized by H_2O. Evidence for this mechanism came mainly from kinetic and Temperature-programmed desorption (TPD) studies. However, with 10% water vapor the maximum in conversion also shifted from ~90°C to ~130°C. It is believed that this shift is simply due to the strong adsorption of water on the active site (Daté *et al.*, 2002). Comparing to the Pt/γ-Al_2O_3 catalyst reported by Avgouropoulos *et al.* (2002), the presence of water vapor also provokes a significant increase on the activity of the Pt catalyst. This observation is contrary to the findings of Korotkikh *et al.* (2000) who found that 3% water vapor decreases CO conversion from 75% to about 68% on the catalysts which contains 5% Pt promoted by a base metal oxide impregnated onto γ-alumina.

On the other hand, the results of water addition to the feed stream had no significant effect on conversion of the Au/CeO_2 catalyst as shown in Figure 5.13. Under the humidified condition, water lowered CO conversion in the region of temperature lower than 100°C compared to the unhumidified condition. However, at high temperatures water seemed to be slightly favorable to the catalyst activity since it provided a hydroxyl group which is necessary for reaction to take place (Haruta *et al.*, 1993, Haruta, 1997 and Wang *et al.*, 2002). The selectivity of the catalyst was slightly affected by the presence of water vapor which is similar to CuO-CeO_2 catalyst (Avgouropoulos *et al.*, 2002). Kang and Wan (1995) have concluded that stability also depends on the gold species present on the catalyst. On gold hydroxide the water molecules were found less strongly adsorbed and therefore catalysts containing this gold species are more stable if trace amounts of water are present in the feed.

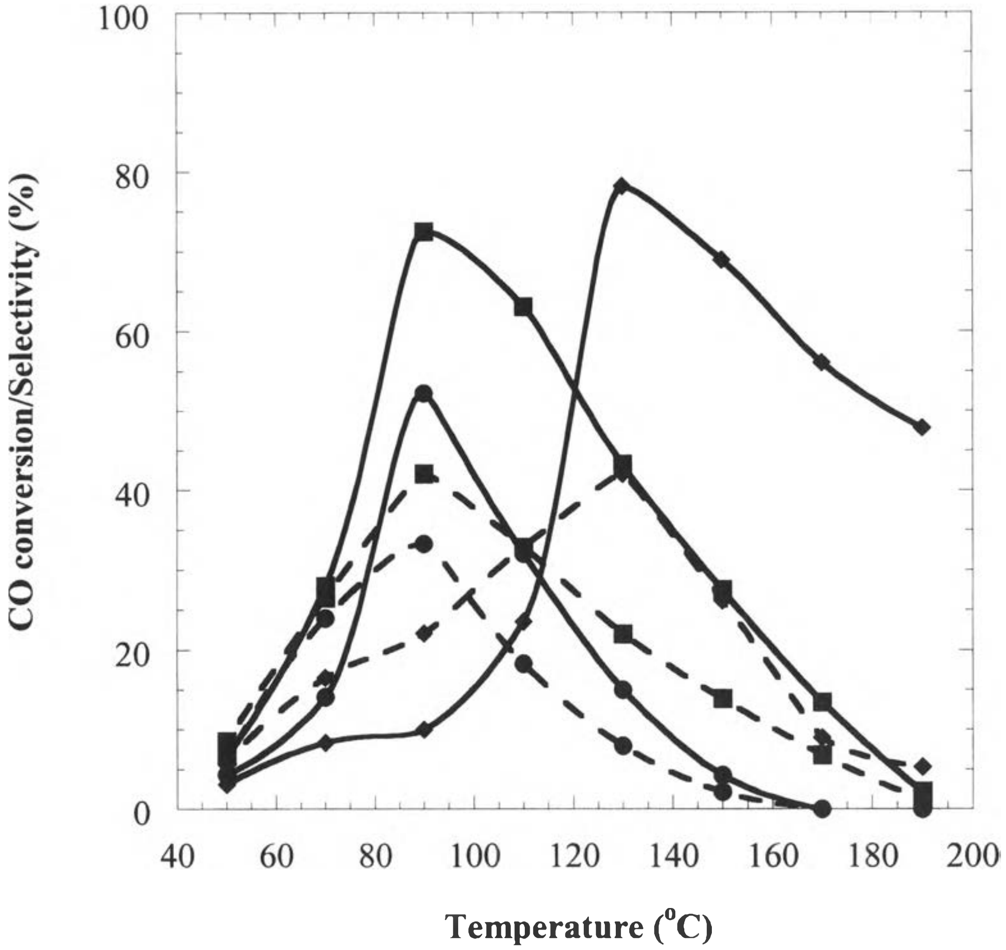


Figure 5.12 Effect of water addition in reactant gas over 1% Pt/CeO_2 sol-gel catalyst. Reactant composition: 1% CO, 1% O_2, 0-10% H_2O, 2% CO_2, 40% H_2 and helium: (●) w/o water; (■) 2.6% water; (◆) 10% water; (—) CO conversion; (---) selectivity.

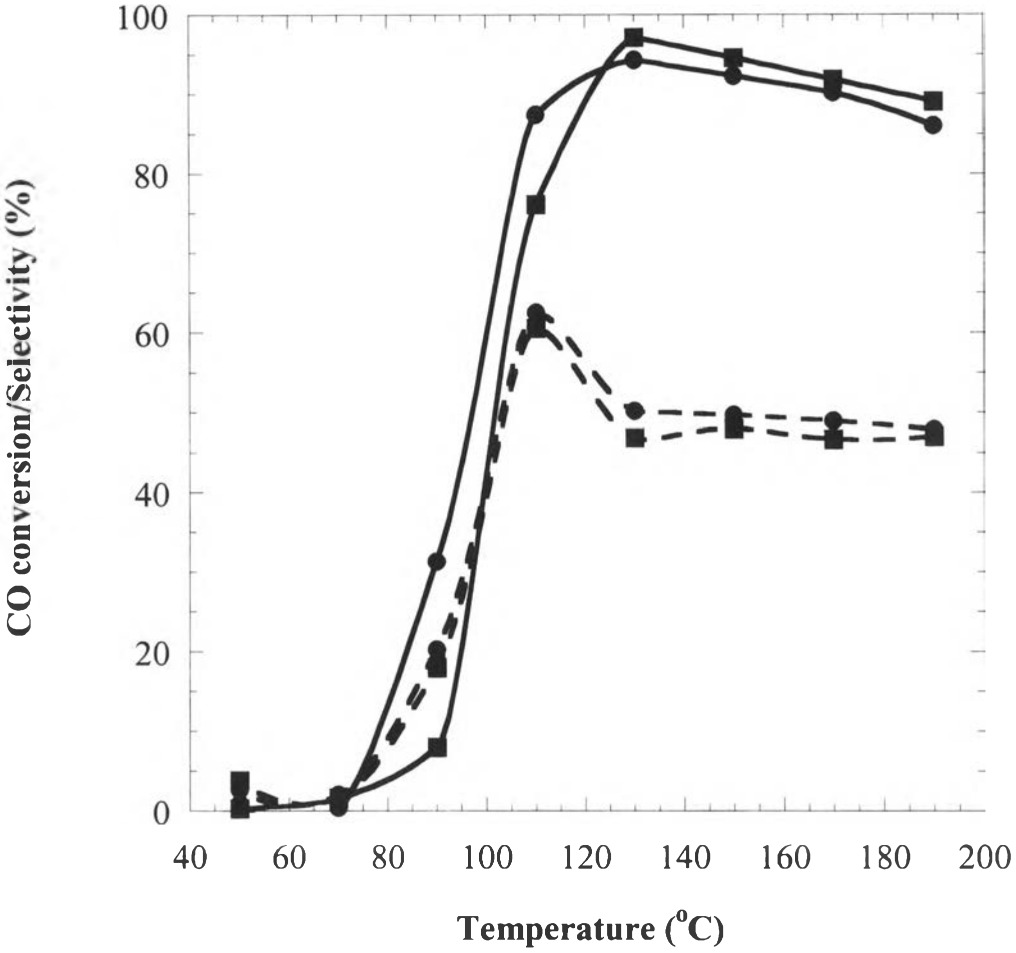


Figure 5.13 Effect of water addition in reactant gas over 1% Au/CeO_2 co-precipitation catalyst. Reactant composition: 1% CO, 1% O_2, 0-10% H_2O, 2% CO_2, 40% H_2 and helium: (●) w/o water; (◆) 10% water; (—) CO conversion; (---) selectivity.

5.2.5 Effect of Carbon Dioxide

Figures 5.14 and 5.15 show the effect of CO_2 addition to the feed stream on the activities of both catalysts. Increasing the CO_2 concentration from 2% to 20% significantly reduced the activity of the Pt/CeO_2 catalyst. The maximum in conversion dropped from ~75% to ~ 45% with a shift of ~20 °C higher temperature. We believe this negative effect is due to the reverse water gas shift reaction which is consistent with the thermodynamics for this reaction at temperature above 90^oC. However, the catalytic performance over the $Pt/\gamma\text{-}Al_2O_3$ catalyst reported by Avgouropoulos *et al.* (2002) is unaffected by the presence of CO_2. A less dramatic but similar effect is seen with the Au/CeO_2 catalyst. The maximum in conversion drops from ~92% to ~85 with a shift of ~30 °C to higher temperatures. The selectivities of the catalysts were not significantly impacted by the presence of water vapor or CO_2 in the feed.

Our findings with the Au/CeO_2 catalyst partially agrees with Torres Sanchez *et al.* (1997) who reported that gold catalyst was resistive to both CO_2 and water contained in the feed stream with a wide range of concentrations.

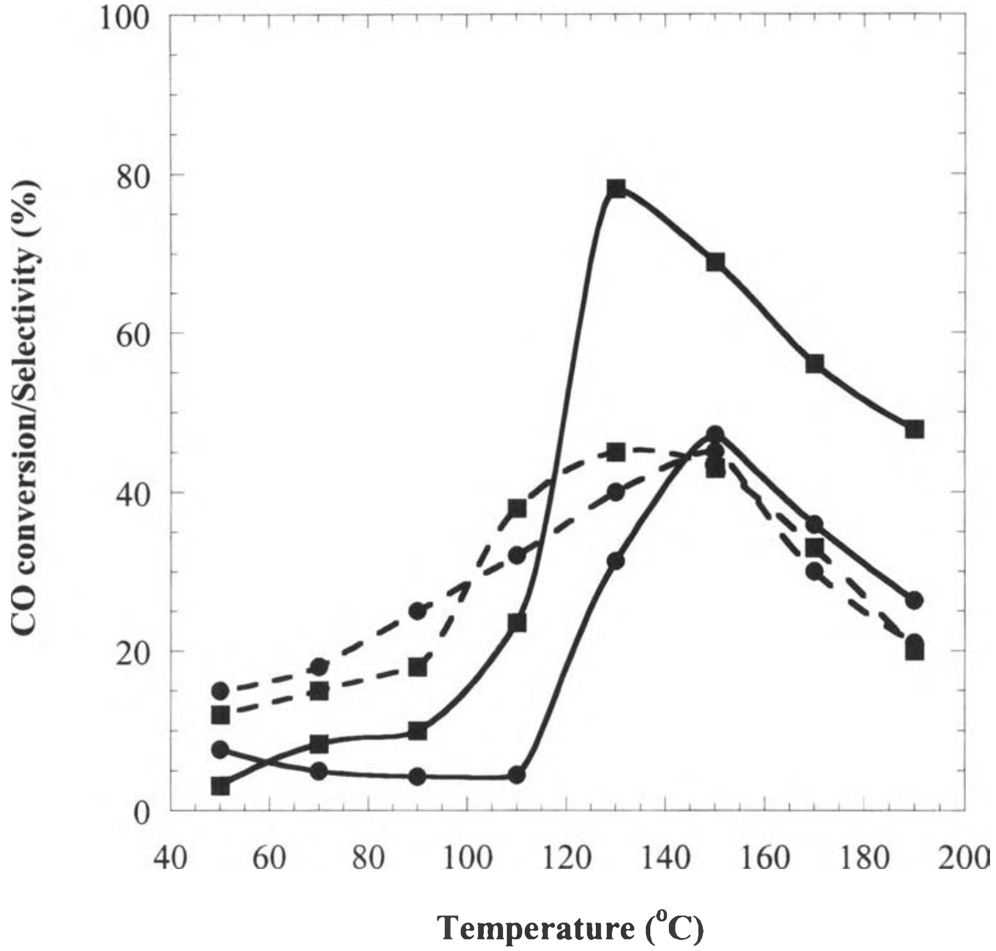


Figure 5.14 Effect of CO_2 concentration in reactant gas over 1% Pt/CeO_2 sol-gel catalyst. Reactant composition: 1% CO, 1% O_2, 10% H_2O, 2-20% CO_2, 40% H_2 and helium: (■) 2%CO_2; (●) 20% CO_2; (—) CO conversion; (---) selectivity.

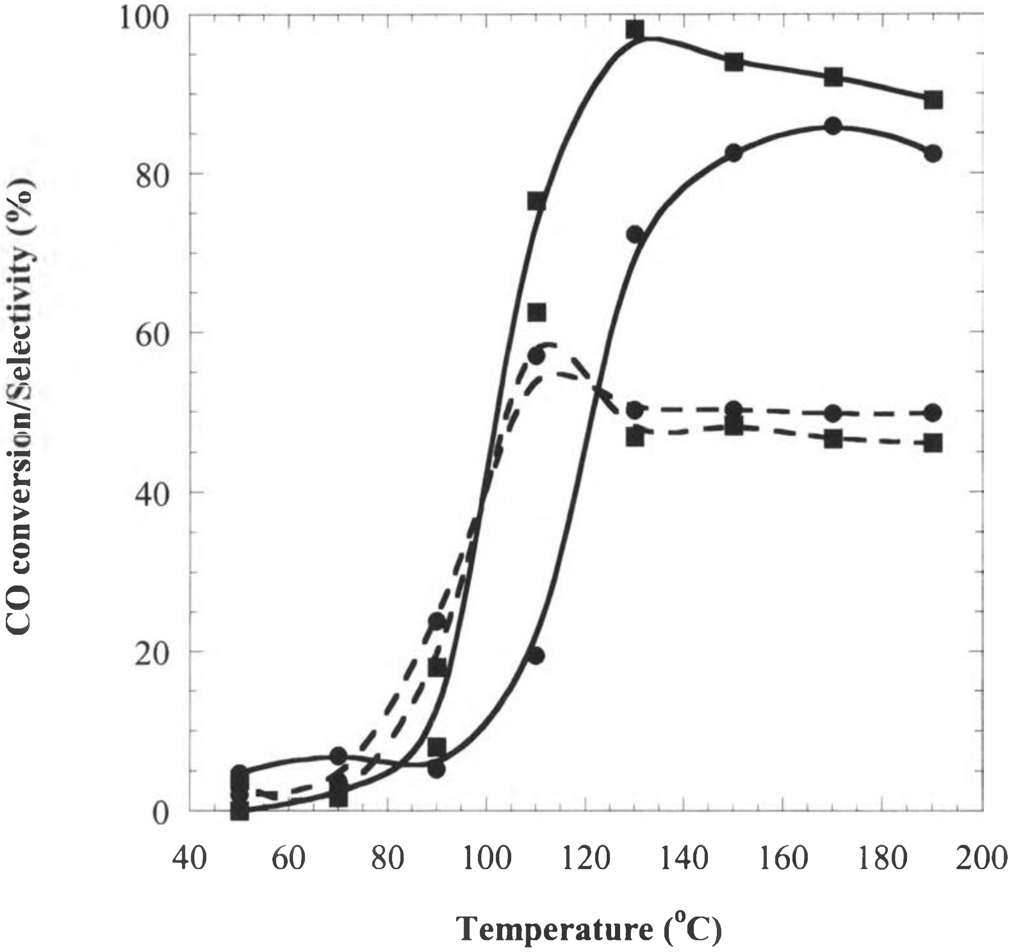
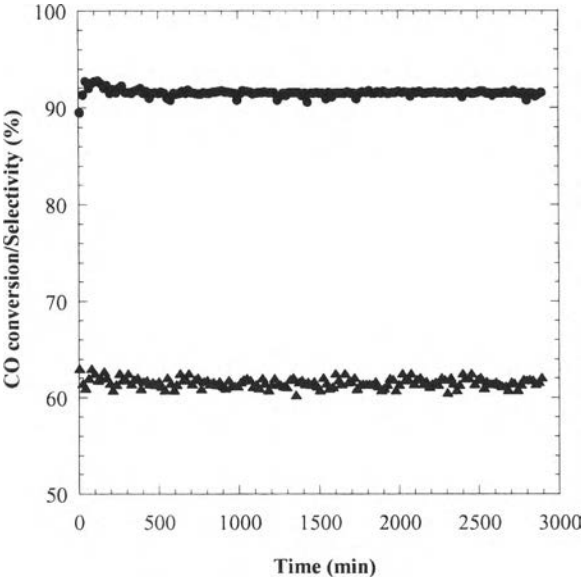


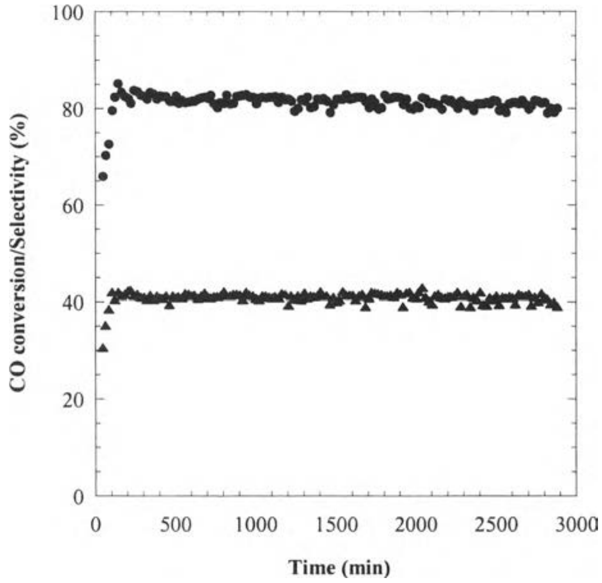
Figure 5.15 Effect of CO_2 concentration in reactant gas over 1% Au/CeO_2 co-precipitation catalyst. Reactant composition: 1% CO, 1% O_2, 10% H_2O, 2-20% CO_2, 40% H_2 and helium: (■) 2%CO_2; (●) 20% CO_2; (—) CO conversion; (---) selectivity.

5.2.6 Deactivation Test

Catalytic stability of Pt/CeO_2 sol-gel and Au/CeO_2 co-precipitation catalysts, which showed the high conversion with high selectivity to CO oxidation, was tested at the temperature of 110°C. As can be seen from Figure 5.16, the CO conversion at 110°C was maintained for 2 days with very slight loss of activity. The result shows good stability of the catalyst as compared with Pt/zeolite catalyst reported by Igarashi *et al.*, 1997 and Au/Fe_2O_3, CuO-CeO_2 and Au/TiO_2 catalysts reported by Kahlich *et al.* (1999), Avgouropoulos *et al.* (2002) and Lin *et al.* (1993), respectively.



(a) Au/CeO_2



(b) Pt/CeO_2

Figure 5.16 Deactivation test over 1% Pt/CeO_2 sol-gel and 1% Au/CeO_2 co-precipitation catalysts in a feedstream containing 1 % CO, 1% O_2, 2% CO_2, 2.6% H_2O, 40% H_2, and helium: (●) CO conversion; (▲) Selectivity.

5.3 Conclusions

In this study, the activity of Pt/CeO_2 and Au/CeO_2 catalysts was found to be dependent on the catalyst preparation method. The Pt/CeO_2 sol-gel and Au/CeO_2 co-precipitation catalysts are the most active catalysts for selective CO oxidation in a large amount of H_2, exhibiting high activity and good selectivity at 110°C. The optimal amount of O_2 required for oxidizing 1%CO in the feed is 1%. The presence of water vapor in the feed stream increased the catalytic activity of the catalyst while the addition of CO_2 in the feed stream caused a decrease in catalytic performance of Pt catalyst. For Au catalyst, the presence of water vapor in the feed stream lowered the CO conversion only in the lower temperature region. Increasing CO_2 concentration in the feed stream significantly reduced the CO conversion. However, both water vapor and CO_2 showed no significant effect on the CO selectivity. Both catalysts were found to be quite stable in the deactivation test. In comparison to the Pt/A-zeolite (Watanabe *et al.*, 1995), Pt/mordenite (Igarashi *et al.*, 1997) and Pt/γ-Al_2O_3 (Kahlich *et al.*, 1997) catalysts which are active at temperatures above 200°C. Both catalysts are able to operate at temperatures below 120°C which is suitable for fuel cell operation.