CHAPTER IV SELECTIVE CO OXIDATION ACTIVITY OF Pt/CeO₂ AND Pt/CeO₂.Al₂O₃ CATALYSTS

In this chapter, a comparative study of the catalytic performance of the Pt/CeO_2 and $Pt/CeO_2.Al_2O_3$ catalysts will be presented as a function of catalyst preparation technique and reaction condition. The main focus of this chapter was on the investigation of low temperature catalysts for the selective CO oxidation activity.

4.1 Pt/CeO₂ Catalysts

As mentioned in Chapter III, three catalyst preparation methods gave significantly different catalysts. Therefore, the impregnation method was used with high and low surface area CeO_2 to produce different catalysts. Likewise, the sol-gel technique catalysts were prepared by using different procedures as described below.

There are five methods of catalyst preparation in this chapter; impregnation methods A and B, co-precipitation, and the sol-gel methods A and B, were conducted to prepare Pt/CeO_2 catalysts.

Impregnation method A The catalyst was obtained by impregnation of the low surface area CeO₂ support with an aqueous solution of $H_2PtCl_6.6H_2O$ containing appropriate amount of Pt.

Impregnation method B The catalyst was prepared by the same procedure as method A except high surface area CeO_2 support was used. The low and high surface area of CeO_2 have surface areas of 10 and 119 m²/g, respectively.

Co-precipitation method An aqueous solution of Na_2CO_3 was added to an aqueous mixture of $H_2PtCl_6.6H_2O$ and $Ce(NO_3)_3.6H_2O$ and the mixture was kept at room temperature and at constant pH of 8.0. The precipitate formed was aged for an hour and then was washed several times with distilled water until the solution conductivity did not change.

Sol-gel method A The catalyst was prepared by hydrolyzing a solution of Ce acetate and $H_2PtCl_{6.6}H_2O$ with NH₄OH. 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 catalyst was dried overnight at 110°C and calcined at 500°C for 5 h.

Sol-gel method B The catalyst was prepared by following procedure:

a) The solutions used for this method were salts of platinum, cerium and urea. They were prepared by dissolving in deionized water.

b) The sample was made by mixing equal volumes of stock solutions of CeO_2 and urea together.

c) The mixture was measured into the Glass Schott bottle; the bottle was sealed and put in the oven at 100°C for 50 h.

d) After the desired reaction time was passed, the sample was taken outside the oven, and allowed to cool down.

e) The sample was separated by centrifuging at 2,000 rpm for five minutes. The washing procedure was repeated several times until the conductivity change of supernatant was insignificant.

f) The sample was washed in the same way with ethanol to prevent the hydroxides from forming agglomerates after the sample had dried. The sample was dried at 110°C overnight and calcined in air at temperature of 500°C for 5 h.

4.1.1 Catalyst Characterization

The catalysts were characterized by BET and XRD, to determine approximate surface area and phases present. In summary, the catalysts can be ranked from the one having the highest to the lowest physical properties as shown in Table 4.1.

Surface area: impregnation method B > co-precipitation > sol-gel method B > sol-gel method A > impregnation method A

Pore volume : impregnation method B > co-precipitation >impregnation method A > sol-gel method B > sol-gel method A

Pore volume of the catalysts follows the same trend as the surface area.

Method of preparation	Surface area (m ² /g)	Pore volume (cc/g)
Sol-gel method A	55.00	7.03×10^{-3}
Sol-gel method B	68.54	6.27×10^{-3}
Impregnation method A	8.50	3.55×10^{-3}
Impregnation method B	116.10	4.64×10^{-2}
Co-precipitation method	114.00	5.29 x 10 ⁻²

Table 4.1 Physical properties of 1%Pt/CeO₂ catalysts.

4.1.2 Effect of Catalyst Preparation Method on Pt/CeO₂ Catalysts

All experiments reported in the following sections were conducted with catalysts in the temperature range of 50-190°C. The feed contained 1% CO, 1% O_2 , 2.6% H_2O , 2% CO_2 , 40 % H_2 and helium.

The effect of preparation method on CO conversion activity as a function of reaction temperature is shown in Figure 4.1. The catalyst prepared by the sol-gel method A has the higher activity of CO conversion than sol-gel method B the impregnation method B gives higher activity than impregnation method A and the co-precipitation method which showed very low activity. Therefore, the overall order activity is: sol-gel method A, sol-gel method B, impregnation method B, impregnation method A and then co-precipitation.

The sol-gel method A catalyst reaches a maximum conversion of 85% at a temperature of 110°C. The sol-gel method B catalyst reaches a maximum activity of 60% conversion at 110°C. Not unexpectedly the higher surface area ceria impregnation catalyst is more active than the low surface area ceria impregnation catalyst and reaches a conversion of 55% at 110°C. The low surface area impregnation catalyst also has respectable activity and gives a conversion of 50% at 130°C.

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Figure 4.1 The activity of 1% Pt/CeO₂ catalysts prepared by different methods versus temperature. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (\bullet) sol-gel A; (\blacksquare) sol gel B; (\diamond) impregnation A; (\blacktriangle) impregnation B; (O) co-precipitation.

4.1.3 <u>Response of the Pt/CeO₂ Impregnation Method B Catalyst to</u> <u>Presence of Water Vapor</u>

Because the impregnation method catalyst B has the highest surface area and pore volume and as a result we tested this catalyst further as discussed below.

Effect of Water Addition

In this section, the roles of surface area of the catalysts are investigated by considering the catalytic performance in dry and wet gas stream as a function of temperature.

The experiments were performed over the temperature range from 50-190°C. The reactant streams were humidified by bubbling through a temperature controlled water bubbler, yielding 2.6% water vapor in the reactant gas. The activity and selectivity of Pt/CeO₂ impregnation method B is illustrated in Figures 4.2 and 4.3. Figure 4.2 compares the CO conversion of impregnation method B catalysts in the presence of 2.6% water vapor and without water. It is clear that for this catalyst, water vapor has a little negative effect over the wide range of temperature window. The maximum conversion of impregnation catalysts decreases to about 60% from 65%. It was found that the addition of water have no effect on the temperature at maximum CO conversion. Figure 4.3 shows the effect of water on the selectivity of impregnation method B catalysts. It was found that water has a little effect on selectivity of this catalyst.



Figure 4.2 Effect of water vapor on CO conversion of the 1% Pt/CeO₂ impregnation catalyst. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (•) w/o water; (•) water.



Figure 4.3 Effect of water vapor on selectivity of the 1%Pt/CeO₂ impregnation catalyst. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (•) w/o water; (•) water.

4.1.4 <u>Response of the Pt/CeO₂ Sol-gel Method B Catalyst to</u> <u>Various Pretreatments and Oxygen Concentration</u> *Effect of Pretreatment*

The effect of pretreatment was tested over the temperature range of 50 to 190°C. The reactant stream consisted of 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium. Figure 4.4 shows the effect of pretreatment on CO conversion of sol-gel method B catalysts. The maximum conversion of H₂ pretreatment sol-gel method B catalyst O₂ pretreatment are the same. However, the reductive pretreatment of Pt/CeO₂ catalyst gave a broader activity peak and reached maximum activity at a temperature ~20°C lower (90°C versus 110°C). This result can be understood through activation of Pt by partial reduction of CeO₂ close to Pt, which induces a high oxygen transport to platinum (Holmgren *et al.*, 1999).



Figure 4.4 Effect of pretreatment method on performance of 1% Pt/CeO₂ sol-gel method B catalyst. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (\bullet) H₂ pretreatment; (\blacksquare) O₂ pretreatment.

Effect of Oxygen Concentration

The effects of O_2 concentration on CO conversion and selectivity over Pt/CeO₂ sol-gel catalyst are shown in Figures 4.5 and 4.6, respectively. The O_2 concentration in the feed was varied from 0.5 to 2%. With 0.5, 1 and 2% O_2 the maxima in CO conversion are ~ 56, 58 and 99% at 110°C, respectively, while selectivities at the point of maximum conversion for the three O_2 concentrations are 79, 78 and 56% at 70°C, respectively. The CO conversion increases with increasing O_2 concentration while selectivity decreases with increasing O_2 concentration.



Figure 4.5 Effect of O₂ concentration on CO conversion of 1% Pt/CeO₂ sol-gel method B catalyst. Reactant composition: 1% CO, 0.5-2% O₂, 2% O₂, 2.6% H₂O, 40% H₂ and helium; (\bullet) 0.5% O₂; (\blacksquare) 1% O₂; (\blacklozenge) 2% O₂.



Figure 4.6 Effect of O₂ concentration on selectivity of 1% Pt/CeO₂ sol-gel method B catalyst. Reactant composition: 1% CO, 0.5-2% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (\blacklozenge) 0.5% O₂; (\blacklozenge) 1% O₂; (\blacksquare) 2% O₂.

4.2 Pt/CeO₂.Al₂O₃ Catalysts

Over the past several years, CeO₂ and CeO₂ containing materials have come under intense scrutiny as catalysts and as structural and electronic promoters of heterogeneous catalytic reaction (Martinez-Arias *et al.*, 1998). CeO₂ is considered one of the essential ingredients of modern automotive exhaust catalysts where it functions synergetically with precious metal components such as Pt, Pd, and Rh. It has been also reported that the addition of CeO₂ generally improves the behavior of alumina-based catalysts used for automotive emission control. Pt/CeO₂.Al₂O₃ catalysts have been found to show high activity in CO oxidation as reported by Summers and Ausen (1979). A review of the literature reveals only the influence of CeO₂ on the activity of Pt in automotive exhaust catalysis. Therefore, a comprehensive investigation on the role of CeO₂ as a promoter in selective CO oxidation is needed. The effects of CeO₂ addition, pretreatment and Pt loading to Pt/Al₂O₃ catalysts were studied to optimally design an effective catalyst for this reaction.

4.2.1 Catalyst Preparation

The catalysts were prepared by impregnation of sol-gel Al_2O_3 support with aqueous solutions of Ce(NO₃)₃ for CeO₂ and H₂PtCl₆ for Pt. Samples with 5 and 10 wt% of promoter were studied. The Pt/CeO₂.Al₂O₃ catalysts were obtained by successive impregnations, of CeO₂ first, followed by the impregnation of platinum. After each impregnation, samples were dried overnight at 110°C and subsequently calcined at 400°C for 2 h in air before storage in a dessicator.

4.2.2 Catalyst Characterization

The catalysts were characterized by BET and XRD as shown in Table 4.2 and Figures 4.7 and 4.8.

BET measurements were done to determine the surface areas and pore sizes of the catalysts Table 4.2 shows the BET areas corresponding to the fresh catalysts with different Pt and CeO₂ loadings. The 1%Pt/10%CeO₂.Al₂O₃ catalyst has the lowest surface area and pore size. The surface areas of all catalysts were less than that measured for the Al_2O_3 support material itself. Summers and Ausen (1979) showed that the effect of Ce addition to Al_2O_3 was to plug some of the pores of the Al_2O_3 support and thereby cause a decrease in pore volume with a concomitant loss of surface area. The 2%Pt/5%CeO₂.Al₂O₃ catalyst has the highest surface area and pore size. It is interesting to note that the activities closely parallel the surface area. The 2%Pt/5%CeO₂.Al₂O₃ is the best catalyst among the three catalysts and has highest surface area and pore size.

Method of preparation	Surface area (m ² /g)	Pore radius (Å)
1%Pt/5%CeO ₂ .Al ₂ O ₃	276.7	72.54
1%Pt/10%CeO ₂ .Al ₂ O ₃	271.2	69.36
$2\% Pt/5\% CeO_2.Al_2O_3$	296.3	78.02
3%Pt/5%CeO ₂ .Al ₂ O ₃	290.1	81.16

Table 4.2 Physical properties of Pt/CeO2.Al2O3 catalysts.

The X-ray diffraction peaks from the CeO_2 were analyzed to determine integrated intensities and width widths. The average crystallite size determined from the broadening of the diffracted peaks was approximately 100 Å.



Figure 4.7 XRD patterns of $1\%Pt/5\%CeO_2.Al_2O_3$ and $1\%Pt/10\%CeO_2.Al_2O_3$ catalysts; (\$\$) CeO_2.



Figure 4.8 XRD patterns of $1\%Pt/5\%CeO_2.Al_2O_3$, $2\%Pt/5\%CeO_2.Al_2O_3$ and $3\%Pt/5\%CeO_2.Al_2O_3$ catalysts; (\$\$) CeO_2.

4.2.3 Effect of Cerium Loading

The increased levels of CeO₂ present in three way catalysts have focused some attention on CeO₂ physical properties and thermal stability. In this work we studied the activity of CeO₂ promoted on Pt catalysts in this system. Two Ce loadings were used 5 and 10% Ce (by weight percent of the metal Ce). The performance of these catalysts in the simulated reformer stream clearly demonstrated CeO₂-promotion of activity for CO conversion. From Figure 4.9, it is seen that the introduction of 10% Ce on alumina resulted in changing the activity curve (compared to pure ceria support) the maximum activity remained essentially constant but the higher temperature side activity decreased significantly. However, the catalyst with 5% Ce had only a maximum conversion of \sim 40% but its activity did not decrease from 100°C to 200° C. This result shown in Figure 4.9 agree with Summers and Ausen (1979) who found that at higher Ce:Pt ratios, CO conversion over the catalyst seriously deteriorated. It has been reported that high amounts of promoters generally decrease catalytic activity due to the coverage of active sites. For the fresh 1%Pt/CeO₂.Al₂O₃ catalysts, the apparent Pt dispersion decreases with increasing Ce content.

Improvements in the CO oxidation activity have been investigated by several researchers to the donation of lattice oxygen from CeO₂ for participation in the oxidation of adsorbed CO to CO₂ (Jin *et al.*, 1987 and Serre *et al.*, 1993). The enhancement of CO oxidation occurs at lower Ce loadings. This phenomenon must be due to Pt-Ce interactions (Serre *et al.*, 1993) since CeO₂.Al₂O₃ by itself does not significantly oxidize CO under the conditions that activity measurements were carried out. They believed that a slight increase in Pt oxidation state may reflect charge transfer from metal to ceria, indicating that Ce is slightly reduced which was supported by TPR measurements (Tiernan and Finlayson 1998).



Figure 4.9 Effect of Ce addition over 1% Pt/CeO₂.Al₂O₃ catalysts. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (•) 10% Ce; (•) 5% Ce; (•) 0% Ce.

4.2.4 Effect of Reductive and Oxidative Pretreatments on Activity and Selectivity

We tested the effect of reductive and oxidative pretreatments with the $1\%Pt/5\%Ce.Al_2O_3$ impregnation catalyst. Figure 4.10 shows the relationship between CO conversion versus temperature for the $1\%Pt/5\%Ce.Al_2O_3$ impregnation catalysts, which were tested after either a pure H₂ pretreatment and pure O₂ pretreatment at 300°C for 2 h. It can be observed that pure H₂ pretreatment gives higher conversions when compared to pure O₂ pretreatment over the temperatures below 180°C. Obviously, the pretreatment atmosphere affects considerably the activity of the Pt/Ce.Al₂O₃. Diwell *et al.* (1991) found that the pre-reduction of a 0.9% Pt/CeO₂ catalyst resulted in enhanced conversion of CO, NO, H₂ and C₃H₆. It was proposed that an induced Pt-CeO₂ interaction occurred during reduction which greatly affected the nature and activity of the catalytic sites. The high low temperature activity of the pre-reduced Pt/CeO₂ and Pt/CeO₂ sites localized at the Pt-CeO₂ interface. The key point of the low temperature activity would be the oxidation of CO adsorbed on Pt by migration of atomic oxygen from CeO₂ (Serre *et al.*, 1993).



Figure 4.10 Effect of pretreatment over $1\%Pt/5\%Ce.Al_2O_3$ catalyst. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (•) O₂ pretreatment; (•) H₂ pretreatment; (• conversion, --- selectivity).

4.2.5 Effect of Pt Loading on Activity and Selectivity

The percentage loading of Pt was varied from 1, 2 and 3% and the percentage loading of cerium was kept at 5% by weight. The Al₂O₃ support was prepared by the sol-gel method and had a surface area of approximately 300 m²/g. All experiments were conducted in the range of 50-190°C. The feed consisted of 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium. As we see from Figure 4.11 the activity does not parallel the loading. 2% Pt has the highest and 1% Pt has the lowest activity. All of the conversion curves are S shaped and do not exhibit a decrease in activity at high temperatures. The 2%Pt/5%CeO₂.Al₂O₃ gave the highest CO conversion of 75% at 190°C. Figure 4.12 shows that 2%Pt/5%CeO₂.Al₂O₃ has the highest selectivity at temperatures above 110°C. However, the selectivities are all relatively poor for all three catalysts.



Figure 4.11 Effect of Pt loading on CO conversion over Pt/CeO_2 .Al₂O₃ impregnation catalysts. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (•) 1% Pt; (•) 2% Pt; (•) 3% Pt.



Figure 4.12 Effect of Pt loading on selectivity over $Pt/CeO_2.Al_2O_3$ impregnation catalysts. Reactant composition: 1% CO, 1% O₂, 2% CO₂, 2.6% H₂O, 40% H₂ and helium; (\bullet) 1% Pt; (\blacksquare) 2% Pt; (\blacklozenge) 3% Pt.

In order to clearly discern the promotional effect of CeO₂, we compared the performance of 1%Pt/5%Ce.Al₂O₃ and 1%Pt/Al₂O₃ catalysts under identical conditions. As shown in Figure 4.11, 1%Pt/5%Ce.Al₂O₃ gives significantly higher than $1\%Pt/Al_2O_3$ and ceria promotion increases activity by about 20-30% which confirms the outstanding role of ceria in this reaction. The loading of Ce introduced has been shown to improve the CO oxidation activity. These activity changes were attributed to Pt-Ce interactions because Ce-Al₂O₃ did not appreciably catalyse CO oxidation under conditions used in these experiments. Several previous studies have reported that the presence of CeO₂ can improve the CO total oxidation activity of pre-reduced noble metal catalysts (Holmgren et al., 1997 and Martinez-Arias et al., 1998). The promoting effect of ceria on the low-temperature activity was also observed by Törncorna et al. (1997). The light-off temperatures for CO and propene over the Pt/Ce.Al₂O₃ catalyst is about 100°C lower than over Pt/Al₂O₃. This result was also supported by Korotkikh and Farrauto (2000). They reported that the activity of Pt/Al₂O₃ catalyst was increased from 13.2 to 68% at 90°C for a Fe₂O₃ promoted catalyst. They believe that the promoter metal oxide provides sufficient dissociated O_2 to enhance the oxidation rate. Furthermore, Törncorna et al. (1997) found that the amount of adsorbed CO on Pt/CeO2.Al2O3 is six times more than that adsorbed on the Pt/Al₂O₃ catalyst, which would correspond to an increase of the Pt dispersion from 6 to 34%.



Figure 4.13 Comparison of promoted Pt catalyst with conventional Pt/Al_2O_3 catalyst. Reactant composition: 1% CO, 1% O_2 , 2% CO₂, 2.6% H_2O , 40% H_2 and helium; (•) 1% Pt/Al_2O_3 ; (•) 1% Pt/5%Ce.Al₂O₃.

4.3 Conclusions

In this chapter, it was found that the catalytic activity and selectivity of the 1% Pt/CeO₂ catalyst had a strong correlation with the catalyst preparation method. Among the three catalyst preparation methods, 1% Pt/CeO₂ sol-gel catalyst exhibited the highest activities. Furthermore, this present work showed that Ce and Pt loadings have a significant effect on the activity of Pt/Al₂O₃ catalyst. It was found that the surface interactions were formed between all components. To summarize, the effects of the base-metal oxide on catalyst activity depended on the loading of CeO₂ and Pt and the pretreatment method to which the catalysts were exposed resulting in CO oxidation activity.