CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

4.1.1 Neutron Activation Analysis(NAA)

The exact amounts of the platinum and ceria analyzed by NAA are shown in Table 4.1. All calculations involving with the loading weight shown later in this chapter will be always based on these numbers instead of their nominal loadings.

4.1.2 BET Surface Area Measurement

The catalyst surface area shown in Table 4.1 significantly decreases as the ceria loading is higher. A decrease in catalyst surface area is possibly caused by ceria plugging in very small alumina pores. This observation agrees with the previous work done by Oh and Eickel (1988). They found that the BET surface area of the support decreased appreciably (from 112 to 87 m^2/g) as the Ce loading increased (from 0 to 15 wt.%) which was presumed to be due to blocking of the micropores.

Table 4.1 The catalyst characterization results

Samples	Platinum Loading (%wt)	Ceria Loading (%wt)	BET Surface Area (m^2)	Mean Ceria Particle Diameter (Å)
0.7%wt.Pt/Al2O3	0.78	0.00	112.10	-
0.7%wt.Pt/5% wt.CeO2/Al2O3	0.76	4.82	105.80	153
0.7%wt.Pt/7.5% wt.CeO2/Al2O3	0.78	7.64	99.46	159
0.7%wt.Pt/10% wt.CeO2/Al2O3	0.73	10.29	96.98	160
0.7%wt.Pt/15% wt.CeO2/Al2O3	0.80	15.02	91.54	164
0.7%wt.Pt/20% wt.CeO2/Al2O3	0.75	20.52	81.81	164
0.7%wt.Pt/23% wt.CeO2/Al2O3	0.75	22.73	80.69	162

4.1.3 X-ray Diffraction Analysis

The ceria crystallite sizes identified by XRD are shown in Table 4.1. The crystallite sizes as a function of the loading are plotted against each other as shown in Figure 4.1. From the graph, the particle size of ceria tends to increase slightly with ceria loading before becoming independent of loading, however, the variation is within the limits of uncertainty. The crystallite sizes are rather large compared to the average pore radius of around 40 Å. The growth in ceria crystallite size should be restricted by this rather small pore size of Al_2O_3. The added ceria plugs the small pores resulting in decreasing of total pore volume from 0.22 to 0.15 cm^3/g when the ceria loading increases from 5 to 23 %wt instead of forming a larger crystallite.

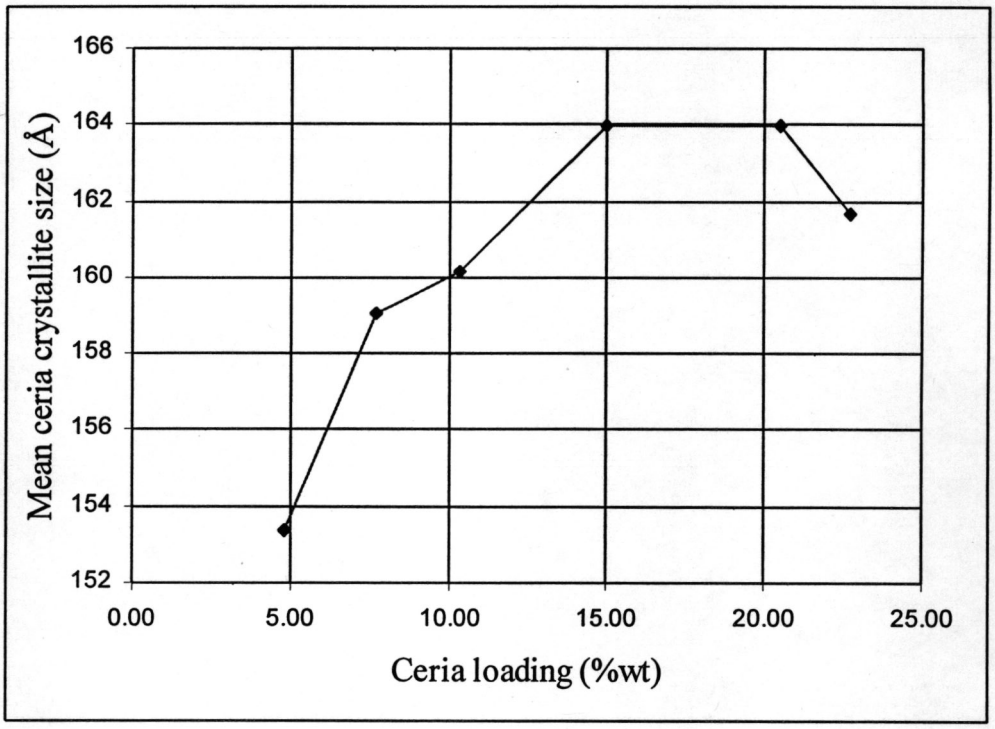

Figure 4.1 The effect of ceria loading on the mean ceria crystallite size.

4.2 The Oxygen Storage Capacity Test

4.2.1 The Oxidation Time

Table 4.2 shows that the amount of oxygen can be taken off as a function of varied oxidation time. The data were measured at some points repetitively to confirm the repeatability of the experiment. The data in Table 4.2 are plotted in Figure 4.2. The graph shows that after one hour the catalyst can not be oxidized any more. The oxidizing time of 1 hour is then used for the other experiments.

Table 4.2 The variation of oxidizing time and the corresponding oxygen released

Oxidizing time(hour)	O_2 released (mmol)
0.5	1.107
1.0	2.604
1.0	2.614
2.0	2.479
2.0	2.471
3.0	2.533
4.5	2.559

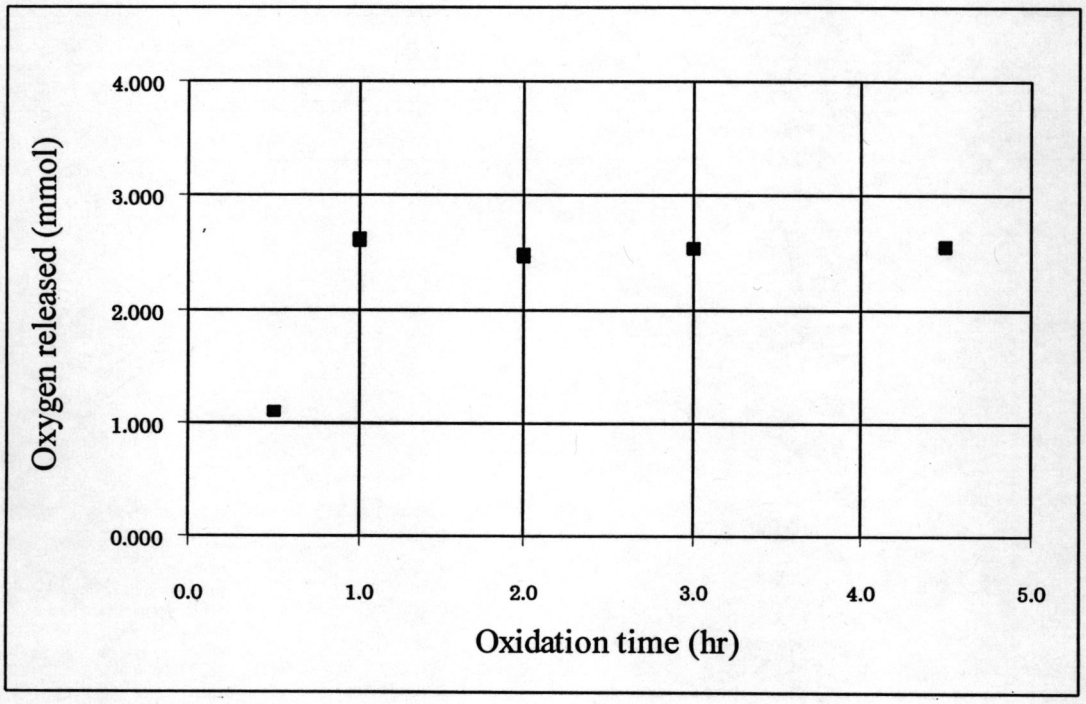

Figure 4.2 The effect of time used for catalyst oxidation on the amount of oxygen released.

4.2.2 The Dilution Ratio

Table 4.3 shows the effect of an increase in catalyst dilution ratio on the amount of the oxygen taken off per unit catalyst weight. As the catalyst dilution ratio increases, the amount of oxygen taken out per gram of catalyst increases before reaching a constant value of approximately 8 μmol/g catalyst at a dilution ratio of 300 as shown in Figure 4.3. This constant value is the maximum oxygen amount removable from the catalyst within 1 second by the carbon monoxide gas. Therefore the dilution ratio of 300 was used for all other experiments.

Table 4.3 The dilution ratio variation

Dilution Ratio	**CO Consumed (μl)**	**O_2 given out/g cat. (μmol O_2/g cat)**
50	12.933	2.38
50	12.724	
100	11.027	4.01
100	10.905	
200	8.989	6.32
200	8.723	
300	7.241	7.77
300	7.650	
300	7.451	
600	4.288	8.22
600	4.483	
600	4.519	

From Table 4.3, we can see that the data collected at high dilution ratio for the same catalyst begin to show deviation from each other compared to the data in Table 4.2 or the data at lower dilution ratios in Table 4.3 which can be repeated successfully. It is believed that this much deviation in measured values is caused by the very low catalyst amount when the dilution ratio is too high, because the fluctuation in values just appears at high dilution ratio. Therefore, the correct values were obtained by doing the experiment three times. One catalyst was tested nine times to check the repeatability of the three mean values. We found that the mean values were repeatable to 2% difference.

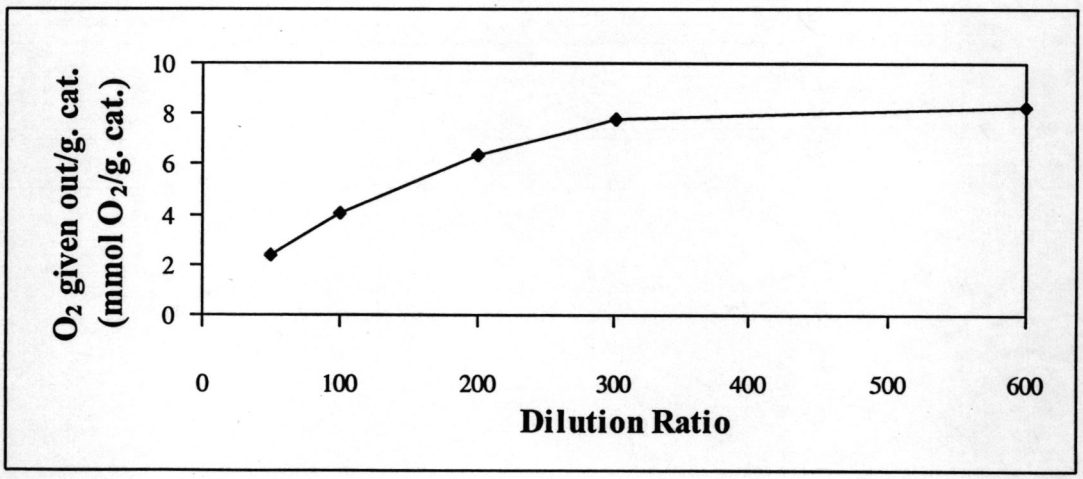

Figure 4.3 The plot of [the oxygen taken out/g cat] vs the dilution ratio.

Thus the experimental parameters were fixed at: 1 hour oxidizing time, 300 times dilution ratio and three runs for each catalyst.

4.2.3 The Catalyst Oxygen Storage Capacity

Table 4.4 contains the amount of oxygen released per BET surface area and the catalyst OSC of each catalyst. (The collected raw data for all catalysts are shown in Appendix A.)

Both of [the oxygen released/ BET surface area] and [the catalyst OSC] are plotted versus [the ceria loading] as shown in Figure 4.4 and 4.5, respectively.

Table 4.4 The catalyst oxygen storage capacity

%wt Pt	%wt CeO_2	Oxygen released/ BET Area (μmol O_2/m^2)	OSC*100 (μmol O_2/ μmol CeO_2)
0.78	0.00	0.00	0.0
0.76	4.82	2.11	47.7
0.78	7.64	4.02	54.0
0.73	10.29	6.38	62.1
0.80	15.02	6.23	39.2
0.75	20.52	6.20	25.5
0.75	22.73	6.57	24.1

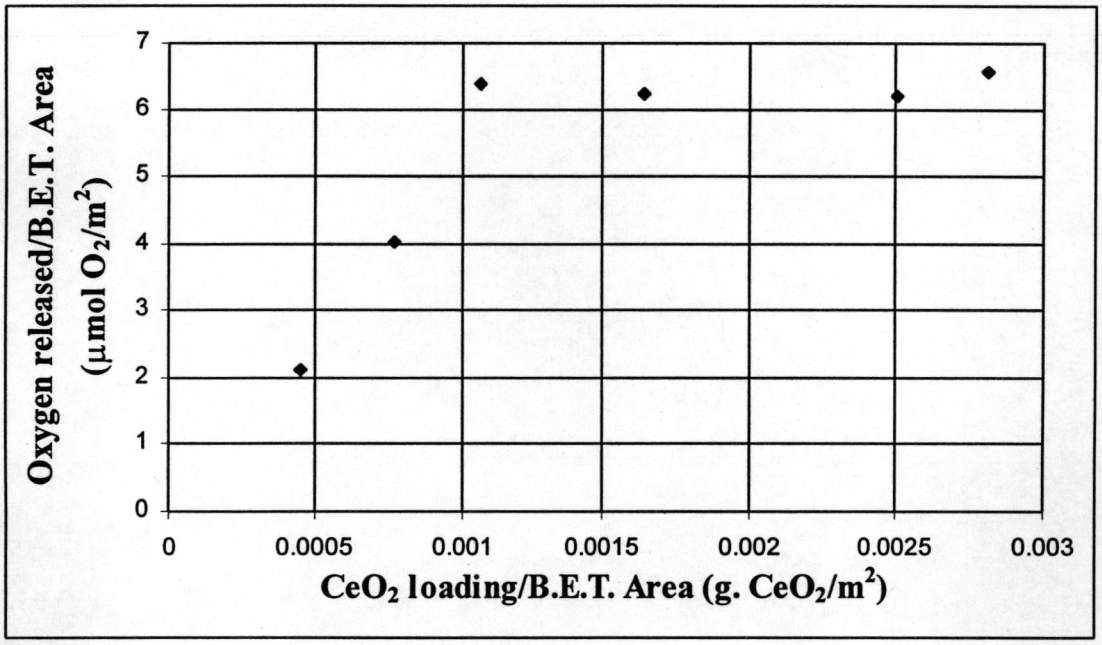

Figure 4.4 The dependence of oxygen released on ceria loading.

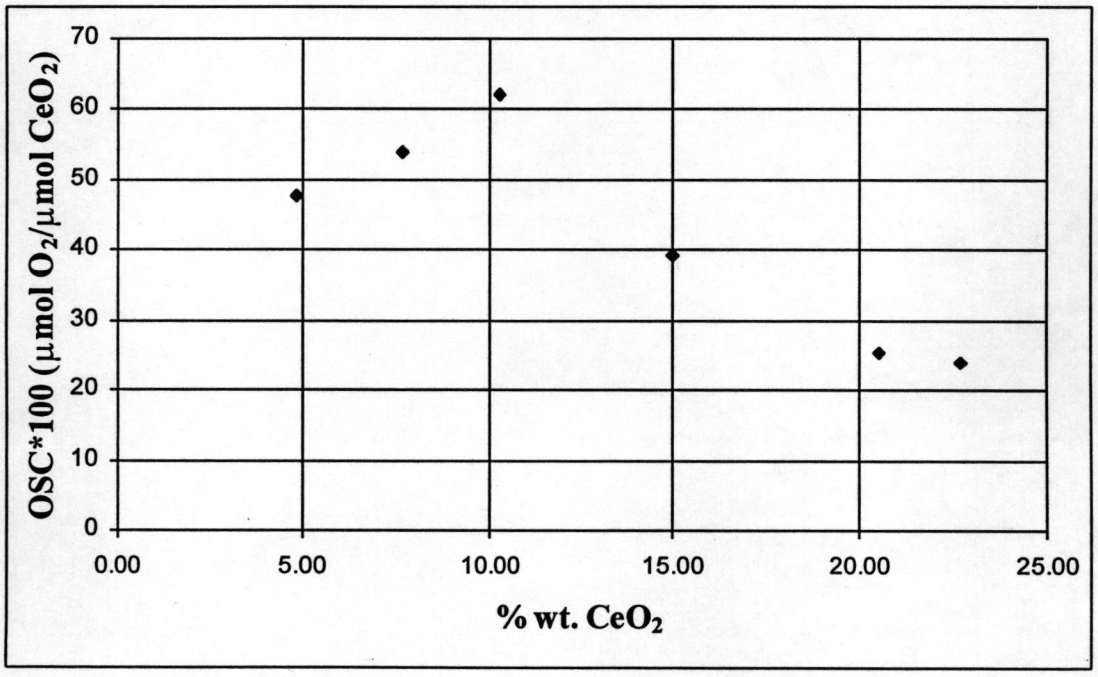

Figure 4.5 The dependence of the OSC on ceria loading.

From Figure 4.4, we can see that for ceria loadings below 10 %wt.CeO_2, the oxygen released per unit area increases sharply with the ceria loading. However, for ceria loadings over 10 % wt.CeO_2, the oxygen amount seems not vary with the ceria loading. One possible explanation is that, at lower ceria loading, an addition of ceria causes the growth of ceria crystallites resulting with both of bulk volume increasing and surface area increasing. However higher ceria loading, from XRD results, does not increase the ceria crystallite size, on the other hand, it goes to fill up small pores and becomes useless. The graph between the catalyst OSC and the ceria loading (Figure 4.5) also shows the same implication.

The OSCs of the catalysts used in this study are higher than those studied in the past. The highest value of the OSC is as high as 0.63 μmol O_2/μmol CeO_2 of 10%wt. CeO_2 sample. This OSC value is greater than that can be supplied by bulk. Therefore, the oxygen atoms or molecules which chemisorb on the ceria surface must be the primary source of these useful oxygen atoms.