



## Effect of Cerium Oxide and Zirconium Oxide to Activity of Catalysts

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### ABSTRACT

In this work, the activities of platinum over alumina promoted with cerium oxide and zirconium oxide were investigated. Each support contained various weight percents of cerium oxide and zirconium oxide to alumina was prepared by sol gel method. The weight percent of cerium oxide to zirconium oxide was kept constant at 60 to 40. Specific surface areas of each support were measured. It was found that the addition of 20%CeO<sub>2</sub>-ZrO<sub>2</sub> in alumina support offered the highest specific surface area of 215 m<sup>2</sup>/g. Furthermore, crystalline phase and size of mixed oxide were determined by XRD. XRD results also showed that Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> was formed in the support. The amount of cerium oxide, zirconium oxide and alumina had a strong effect to their crystalline size in the final form. Then, each support was impregnated with 1%Pt loading and tested its activity to CO oxidation reaction. The results showed that T<sub>1/2</sub> of each catalyst was 210°C, 139°C, 145°C, 150°C and 261°C for a 1%Pt/Al<sub>2</sub>O<sub>3</sub>, a 1%Pt/20%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, a 1%Pt/40%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, a 1%Pt/60%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and a 1%Pt/CeO<sub>2</sub>-ZrO<sub>2</sub>, respectively. The enhancement of activity of platinum over alumina catalyst resulted from an oxygen storage property of cerium oxide together with zirconium oxide. Finally, the 1%Pt/40%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> has showed the best activity to CO oxidation.

**Keywords:** CO oxidation, promoter, cerium oxide, zirconium oxide, oxygen storage.

### 1. INTRODUCTION

CO oxidation is the reaction used for removing or eliminating CO by burning it with oxygen or air. In general, this reaction rarely occurs unless there is some suitable catalyst present. Several metals together with supports such as Au/Al<sub>2</sub>O<sub>3</sub>, Au/CeO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub> or Pt over zeolite have been widely investigated for this reaction. However, platinum over alumina seems to be the well known catalyst extensively studied the activity and the mechanism to CO oxidation over four

decades. This is due to the stability and activity of platinum [1]. Unfortunately, this catalyst is active to this reaction at temperatures greater than 160°C. This causes by the chemisorptions of CO over platinum active sites at low temperatures and the competition between CO molecules and oxygen molecules to adsorb on platinum. To develop this catalyst to be active at lower range of temperatures, it could be done by either adding other compounds such as cerium oxide, iron oxide

and so on [2,3] or using suitable preparation method [4]. As known from many works on three way catalysts, cerium oxide is used in order to provide extra oxygen from their lattice in the condition of deficiency of oxygen [5-7]. This is so called an oxygen storage property. Moreover, zirconium oxide is well known as temperature resistant compound. The use of it combining together with cerium oxide offers the better the oxygen storage property [8,9]. However, the suitable amount of cerium oxide and zirconium oxide in alumina support for the improvement of platinum catalyst is still unrevealed.

In this work, catalysts cooperated together with different amounts of cerium oxide, zirconium oxide and aluminium oxide prepared by sol gel method and impregnated with 1%Pt were investigated their activities to CO oxidation. From this study, the effect of addition of cerium oxide and zirconium oxide into the support,  $\text{CeO}_2\text{-ZrO}_2/\text{Al}_2\text{O}_3$ , was studied.

## 2. MATERIALS AND METHODS

### 2.1 Catalyst preparation

Aluminium isopropoxide, cerium (III) nitrate and zirconium nitrate obtained from Sigma-Aldrich Company were used in this preparation. Mixed oxide of ceria, zirconia and alumina was prepared by sol gel method. Aluminium isopropoxide was weighted and then added into hot deionized water. The solution was kept stirring to obtain uniformity. Next, nitric acid was added into the solution until this solution became clear. After stirring 30 min., cerium (III) nitrate and zirconium nitrate were added into the obtained solution, respectively. The solution was aged overnight and is called "sol". Next, the sol was heated to obtain gel. The gel was aged overnight. After aging, the gel was dried at 110°C for 10 hr. followed by calcined at 500°C for 8 hr. The final oxide was ground and sieved to 100

mesh. All supports containing mixed oxide were impregnated with 1% platinum loading by incipient wetness impregnation.

For catalyst characterization, specific surface areas of each support were measured by Autosorption-1 (Quantachrome Corporation). Phase and crystalline size of each mixed oxide was analyzed by X-ray diffractometer from Bruker AXS Model D8 Discover.

### 2.2 Activity test

All supports and catalysts were tested their activities to CO oxidation in the micro-reactor. Reaction temperature was controlled by temperature controller with K-type thermocouple placed on the top of the catalyst bed. The range of reaction temperatures was 100-300°C. The amount of catalysts used was 80 mg. Gas composition contained 1%CO, 1%O<sub>2</sub> and 98%He. The total gas flow rate was adjusted to achieve 100 cc/min. The mixed gas was delivered by a mass flow controller (Porter Company). The accuracy of flow was within 1%. A Varian CP 3800 gas chromatograph (GC) equipped with carbosphere 80/100 and a thermal conductivity detector was used to determine the inlet and outlet gas compositions. Before, each catalyst was tested its activity to CO oxidation, it was purged under H<sub>2</sub> gas at 400°C for 4hr.

## 3. RESULTS AND DISCUSSION

### 3.1 Catalyst characterization

In this work, supports contained various amount of cerium oxide, zirconium oxide and aluminium oxide was prepared by sol gel method. The weight percent between cerium oxide and zirconium oxide was kept constant at 60 to 40. The weight percents between both mentioned oxides and aluminium oxide were varied to the ratio of 100 to 0, 60 to 40, 40 to 60, 20 to 80 and 0 to 100. For example, the first sample contained only cerium oxide

and zirconium oxide with the weight percent of 60 to 40. The second sample contained 60% of cerium oxide and zirconium oxide and 40% of aluminium oxide. This means the second sample containing 36% cerium oxide and 24% zirconium oxide (weight ratio of 60 to 40). The last sample contained only aluminium oxide. Then, all supports were

measured their specific surface areas by Autosorption-1(Quantachrom). The results from this study could be used to explain the effect of the addition of cerium oxide and zirconium oxide to the physical properties of the final supports. The results were showed in Table 1.

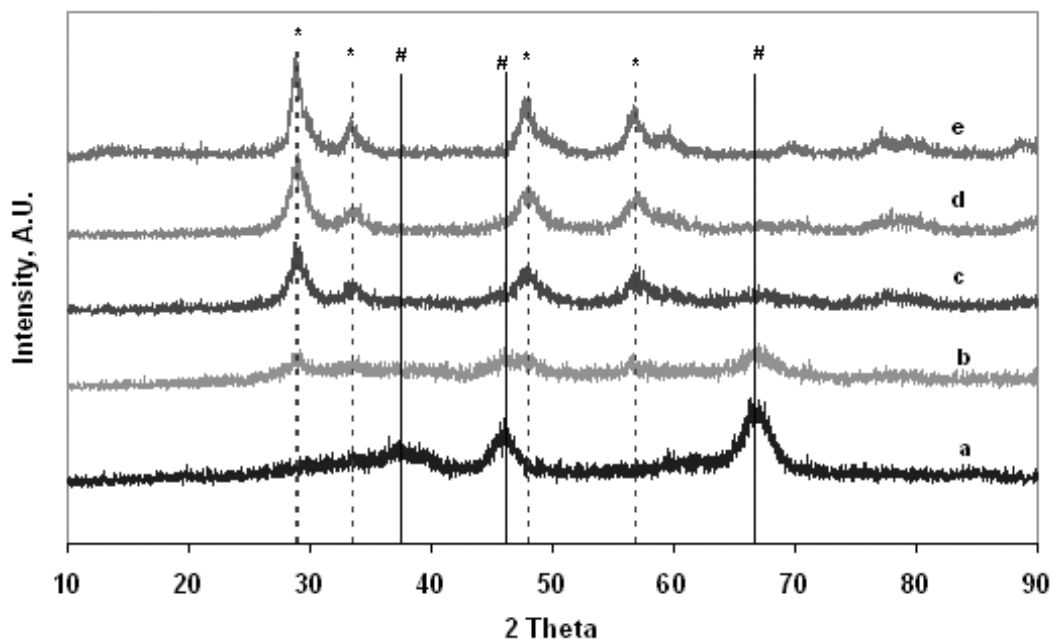
**Table 1.** Specific surface area of supports with different amount of cerium oxide and zirconium oxide to aluminium oxide (weight ratio of cerium oxide and zirconium oxide was kept constant at 60:40).

Sample No.	Supports	Specific surface area, m <sup>2</sup> /g
1	Al <sub>2</sub> O <sub>3</sub> (Aldrich company)	155
2	Al <sub>2</sub> O <sub>3</sub> (sol gel)	190
3	20%wt CeO <sub>2</sub> -ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	215
4	40%wt CeO <sub>2</sub> -ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	194
5	60%wt CeO <sub>2</sub> -ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	147
6	100%wt CeO <sub>2</sub> -ZrO <sub>2</sub>	47

As can be seen from Table 1, sample 1 was pure alumina obtained from Aldrich company. Its specific area was 155 m<sup>2</sup>/g while specific surface area of sample 2, pure alumina prepared by sol gel method, was 190 m<sup>2</sup>/g. From this result, it seemed that sol gel method offers high specific surface areas for the final oxides. This causes from solvent trapped inside the solid structure (gel). When gel is dry, solvent evaporates from the solid network and in turn leave empty pores inside the solid. Therefore, the final oxide prepared by this method has high specific surface area. Sample 3 was a mixed oxide of cerium oxide, zirconium oxide and alumina. Interestingly, the specific surface area of sample 3 was 13% greater than that of sample 2. This result was in agreement with works done by Matina T. et.al. [10]. They prepared different ratio of

mixed oxides of cerium oxide and zirconium oxide. They found that an increase in weight percent of zirconium oxide increased specific surface area of the final oxides. This result implied that the presence of cerium oxide and zirconium oxide improved thermal resistance for the final oxide. However, further increasing amount of cerium oxide and zirconium oxide led to decreasing of specific surface area as observed from samples no. 4-6. This may cause from the growth of crystalline size of cerium oxide and zirconium oxide. From these results, it can be concluded that amount of cerium oxide and zirconium oxide in the mixed oxides has strong effect to the specific surface area of the final oxides. Indeed, the 20% doping mixed oxides of cerium and zirconium offered the highest specific surface area.

Furthermore, these supports were analyzed phase and crystalline size by X-ray diffraction. The results were shown in Figure 1.



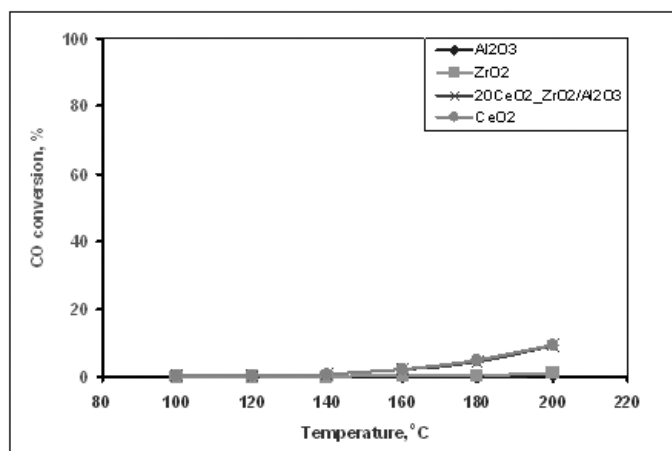
**Figure 1.** XRD patterns of each support: (a) pure alumina, (b) 20%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, (c) 40%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, (d) 60%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and (e) 100%CeO<sub>2</sub>-ZrO<sub>2</sub>; \*refers to reference peaks of Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and # refers to reference peaks of Al<sub>2</sub>O<sub>3</sub>.

As can be seen in Figure 1, no XRD patterns of CeO<sub>2</sub> and ZrO<sub>2</sub> were observed. XRD patterns of supports matched with XRD patterns of Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Al<sub>2</sub>O<sub>3</sub>. This may be explained as following: During condensation reaction in sol gel process, hydroxyl groups from hydrolysis reaction can combine together and form Ce-O-Zr bonds. Therefore, vertical dash lines in the samples at 2 theta of 29°, 33.5°, 48° and 57° were observed. These angles are corresponding to reference peaks for Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>. In Figure 1 a, a sample contained pure alumina only. The XRD pattern of this sample was in agreement with the reference peak pattern of pure alumina. The addition of 20% cerium oxide and zirconium oxide (Figure 1 b) reduced the intensity of

aluminium oxide patterns and in turn observed the other peaks in the same positions as a reference pattern of Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>. As amount of cerium oxide and zirconium oxide inside samples increased, the intensities of XRD patterns at these positions increased as shown in Figure 1 c, d and e. This meant crystalline size of Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> was getting larger. The growth of metal crystalline size may cause the reduction of the specific surface area of mixed oxides.

### 3.2 Activity of pure supports

Pure supports were tested their activities to CO oxidation before they were impregnated with 1%Pt. The results were shown in Figure 2.



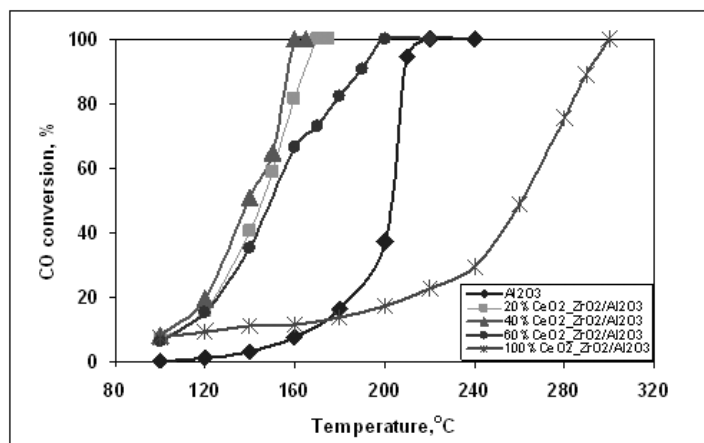
**Figure 2.** Activities of pure supports to CO oxidation. Gas composition: 1%CO, 1%O<sub>2</sub> and He as balance. SV=75,000cc/g/h.

In Figure 2, x-axis represents reaction temperature (°C), and y-axis represents CO conversion (%). The studied temperatures were in the range of 100°C to 200°C. As reaction temperatures increased from 100°C to 140 °C, CO conversions were nearly zero for all pure supports. When reaction temperatures were greater than 150°C, CO conversion slightly increased for 2 supports: 20%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. However, CO conversion was less than 10% even at reaction temperature of 200 °C. These results

implied that pure supports were not active to the reaction.

### 3.3 Effect of amount of cerium oxide and cerium oxide in support

Each support with various weight percents of cerium oxide, zirconium oxide and alumina was impregnated with 1%Pt loading. Then, they were tested their activities to CO oxidation reaction. The results were showed in Figure 3.



**Figure 3.** Activities of catalysts to CO oxidation reaction. Each catalyst contained various amounts of cerium oxide and zirconium oxide and aluminium oxide loading with 1%Pt. Gas composition: 1%CO, 1%O<sub>2</sub> and He as balance. SV=75,000cc/g/h.

In Figure 3, CO conversion increased with increasing of reaction temperatures for all catalysts. However, the activities of these catalysts were different. For a 1%Pt/Al<sub>2</sub>O<sub>3</sub>, CO conversion slowly increased with an increase of reaction temperatures until reaction temperatures were greater than 160°C. Above this temperature, CO conversions dramatically increased and reached 100% at 220°C. This could be explained in terms of T<sub>1/2</sub> defined as temperature at which half of CO concentration was consumed by the reaction. T<sub>1/2</sub> of this catalyst was approximately 201°C. The addition of 20% CeO<sub>2</sub>-ZrO<sub>2</sub> into aluminium oxide support incredibly enhanced the activity of platinum based catalysts. The active temperatures lowered down by 56°C and T<sub>1/2</sub> of this catalyst was 145°C. This may cause by the presence of CeO<sub>2</sub> together with ZrO<sub>2</sub>. This result was confirmed by the work done by Mattos, L.V., and Noronha, F.B.[11]. They studied the oxygen transfer capacity and oxygen storage property of CeO<sub>2</sub>-ZrO<sub>2</sub> used as a support for platinum in partial oxidation reaction of ethanol. They found that in the absence of cerium oxide, the catalyst can store oxygen about 9 mmol/g of catalyst while the catalyst contained CeO<sub>2</sub> without zirconium oxide could store oxygen about 194mmol/g of catalyst and the catalyst combining both cerium and zirconium oxides with the molar ratio of 50 to 50 (Pt/Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub>) could store oxygen up to 696mmol/g of catalyst. Therefore, the presence of cerium oxide and zirconium oxide in the platinum over alumina catalysts improved the activity of the catalyst to CO oxidation. Lattice oxygen from cerium oxide could transfer and react with CO adsorbed over Pt active sites at the interface between Pt and cerium oxide [12]. Further investigation was conducted on varying the weight percent of cerium and zirconium oxides in aluminium oxide support.

As can be seen from Figure 3, a 1%Pt/40%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> performed the best activity to CO oxidation. T<sub>1/2</sub> of this catalyst was 139°C while T<sub>1/2</sub> of others were 145°C, 150°C and 261°C for a 1%Pt/20% CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, a 1%Pt/60%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and a 1%Pt/CeO<sub>2</sub>-ZrO<sub>2</sub>, respectively. The differences in T<sub>1/2</sub> for each catalyst may cause from the specific surface area and crystalline size of cerium zirconium oxide. As known from Table 1, an increase of the amount of cerium oxide and zirconium oxide led to decreasing of specific surface area of the sample and in turn increasing the peak intensity from XRD pattern. This meant a growth of crystalline size of mixed oxide. These results may cause the difference in Pt dispersion of each catalyst. As been known that the activity of Pt based catalyst to CO oxidation depends on crystalline size of Pt. The highly dispersion Pt or small crystalline size Pt led to the better the activity to CO oxidation [13]. According to the specific surface area results, they implied that an increase in weight percent of cerium oxide and zirconium oxide in alumina lowered the degree of dispersion of Pt in the sample. Therefore, the last sample, no alumina in the support, was the worst activity to CO oxidation. However, for 20%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 40%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, both has similar specific surface area. Their activities to CO oxidation were close within error. In this case, the oxygen storage properties caused from the presence of cerium oxide and zirconium oxide was a dominant evidence to enhance the reaction.

#### 4. CONCLUSION

The activity to CO oxidation of platinum over alumina catalysts can be improved by adding some compounds into the alumina support. In this work, the results showed that the addition of 40%CeO<sub>2</sub>-ZrO<sub>2</sub> into alumina

support followed by platinum to obtain a 1%Pt/40%CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> dramatically enhanced the activity of Pt based catalyst to CO oxidation and showed the best performance to CO oxidation. T<sub>1/2</sub> of the 1%Pt/Al<sub>2</sub>O<sub>3</sub> was 201°C and T<sub>1/2</sub> of the 1%Pt/40%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was 139°C. This was due to an oxygen storage capacity of cerium oxide together with zirconium oxide. However, further increasing the amount of cerium oxide and zirconium oxide into the alumina support lowered the activity of the catalyst to this reaction. This may cause from the lower of the specific surface area of the mixed oxide supports and thus in turn lead to less dispersion of Pt.

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