COMPARISON OF THE ACTIVITY OF Pt/Al_2O_3 AND OF $Pt/CeO_2/Al_2O_3$ TO CO OXIDATION REACTION

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ABSTRACT

The activity of platinum promoted with ceria over alumina to CO oxidation reaction was investigated over the temperature range of 100°C to 200°C. The results indicated that the presence of ceria doped in alumina as a support dramatically enhanced the activity of platinum over pure alumina. This can be observed from $T_{1/2}$ of each catalyst. From the experiments, $T_{1/2}$ of the $5\%Pt/Al_2O_3$ was 170°C while$T_{1/2}$ of the $5\%Pt/15\%CeO_2/Al_2O_3$ was 145°C. This behavior can be explained from the FTIR results. Under the condition that 1%CO in He was purged over the $5\%Pt/15CeO_2/Al_2O_3$, CO_2 was observed. This implied that the formation of CO_2 occurred from reaction between CO molecules and O atoms from ceria lattice. These catalysts were tested under different oxygen concentrations. The results showed that the CO conversion for the $5\%Pt/15\%CeO_2/Al_2O_3$ at a range of 100°C to 150°C was not different under $1\%O_2$ and $2\%O_2$, respectively. On the other hand, for the $5\%Pt/Al_2O_3$, CO conversion at the studied temperatures incredibly increased with the increasing of O_2 concentration from $1\%O_2$ to $2\%O_2$. Therefore, the improvement of the performance of platinum over alumina to CO oxidation at temperatures less than 160°C can be done by doping with a little amount of ceria.

KEYWORDS: CO oxidation, Platinum over alumina, sol gel method, ceria, oxygen storage properties

1. INTRODUCTION

The catalytic CO oxidation has been intensively investigated. Many catalysts have been used for this reaction such as noble catalysts [1-3]: Pt/Al_2O_3, Pt/SiO_2, Ru/Al_2O_3, Rh/Al_2O_3, Pd/Al_2O_3, Au/Al_2O_3, Au/Fe_2O_3, Au/MnO_2 or transition catalysts [4,5]: silver cobalt composite oxide, Co_2O_3, Fe_2O_3, CuO/Al_2O_3. Each catalyst works under different conditions. However, platinum over other supports is a well known one due to their activity and stability at high temperatures (>160°C). The mechanism of CO oxidation reaction over platinum catalysts is well developed as known to be a Langmuir-Heinshelwood model. In this model, CO molecules strongly adsorb on Pt site and so do oxygen molecules. Oxygen molecules will dissociate to oxygen atoms and then react with CO molecules adsorbed at the adjacent site. From this mechanism, the rate of reaction depends on the available sites of Pt, and rate of adsorption of both species. Ideally, the rate of reaction will increase if abundant of active site are available for each molecule to be adsorbed. This might be implied that the enhancement of catalyst to CO oxidation could be done by: i) increase the number of active sites. One way to do this is to obtain high specific surface area supports by preparing via sol gel method. ii) dope this catalyst with the other component which is either an electron donor such as K or having an oxygen storage property [6,7]such as ceria or iron oxide.

These bring about the objectives of this work. First is to compare the results of the performances of a $5\%Pt/Al_2O_3$ and of a $5\%Pt/15\%CeO_2/Al_2O_3$ to CO oxidation reaction. In order to obtain high specific surface area of supports, a $15\%CeO_2/Al_2O_3$ was prepared by sol gel method. Second is to study the effect of O_2 concentration in the feed stream to a conversion of CO via CO oxidation reaction. This result could be used to clearly explain the role of ceria.

2. MATERIALS AND METHODS

A. Catalyst preparation

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Platinum over alumina was prepared by incipient wetness impregnation. Alumina support was obtained from Aldrich Company. Hydrogen Hexachloroplatinate(IV)hydrate was used as a precursor. By this method, the known amount of platinum precursor was dissolved in deionized water.

The amount of deionized water must be enough to wet alumina support. Then this solution was well mixed with a known amount of alumina. The obtained solid was dried in a conventional oven overnight and calcined at an appropriate temperature. Before testing this catalyst to CO oxidation, it was reduced under H_2 conditions at 400 °C for 4 hrs.

Platinum over ceria alumina was prepared by sol gel [8] and incipient wetness impregnation. Cerium (IV) nitrate hexahydrate and alumina isopropoxide were use as precursors for support preparation. The support was prepared as the following procedure: the known amount of alumina isopropoxide precursor was added into hot deionized water. The solution was kept stirring for 30 min. Then, a suitable amount of nitric acid was added in the solution. After the solution became clear, the desired amount of cerium precursor was added. The final solution was stirred for 30 min. to obtain a uniform solution. Next, the obtained solution was aged overnight at a room temperature. This solution now is called "Sol". After aging, the sol was heated until it became gel. The obtained gel was again aged overnight. The final gel was dried under conventional oven and then calcined at the desired temperature. The obtained solid oxide was ground and sieved to 80-100 mesh. This oxide is used as a support for this catalyst. Pt precursor was impregnated into this support by incipient wetness impregnation (explained above).

B. Activity test

The catalysts were tested in an integral flow reaction consisting of a flow control manifold and temperature controller with the average space velocity of 48,000 cc/g/h. K-type thermocouple was placed on the top of catalyst bed to measure the reaction temperatures. The reaction temperatures were in a range of 100°C to 200°C. The composition of gas feed was 1%CO, 0.5-2%O_2, and the rest of He. The gas feed stream and product stream were analyzed with a gas chromatograph and occasionally with FTIR to determine the limiting concentration of CO.

3. RESULTS AND DISCUSSION

A. Catalyst characterization

Surface area measurement is one parameter needed to know for explaining the dispersion of metal over support. The specific surface area of each support was measured by an Autosorb-1 Gas sorption system (Quantachrome Corporation) and reported in table 1.

Table 1. Specific surface area of supports

Supports	Specific surface area (m^2/g)
Commercial alumina	155
Sol-gel alumina	228
15%CeO_2/Al_2O_3(Sol-gel)	217

As can be seen from table 1, supports prepared via sol gel method gave a higher specific surface area than the other approximately 35%. Also the addition of cerium oxide on alumina led to the lower of specific surface area of the mixed oxide.

B. Activity of catalysts to CO oxidation

All three supports were tested their activity to CO oxidation under 1%CO, 1%O_2 and the rest of He with the temperature range of 100°C to 200°C. They all were not active to this reaction as shown in figure 1. This means that these supports were inert to the reaction at the studied temperatures. Then 5%Pt over commercial alumina support, sol gel alumina support and ceria doped alumina sol gel support were tested their activities to CO oxidation. The results were shown in Figure 1. Both commercial alumina and sol gel alumina gave very close results even though their specific surface areas were dramatically different. This could be explained that platinum was well dispersed in both supports. In addition, the dispersion of metals was measured by CO chemisorption technique. The dispersions of Pt of these catalysts were approximately 70% for both catalysts. The catalysts also were measured their metal crystalline size by X-ray diffraction technique. However, no Pt peak was

observed and this means metal crystalline size was less than 3 nm. From these results, we could confirm that the effect of specific surface area of supports was negligible for this particular case. Furthermore, we observed that the addition of 15% CeO_2 in the support increased the activity of catalyst to have a high CO conversion at lower range of temperatures as can be seen in figure 2. Indeed, it could be observed from $T_{1/2}$ defined as the temperature which 50% of reactants reacts and produces products. $T_{1/2}$ of the 5%Pt/Al_2O_3 was 170°C while $T_{1/2}$ of the 5%Pt/15%CeO_2/Al_2O_3 was 145°C. Interestingly, at temperatures above 170 °C, all catalysts performed the same activity to CO oxidation. This incident occurred because of the desorption process of CO from Pt surface sites at temperature greater than 160 °C.

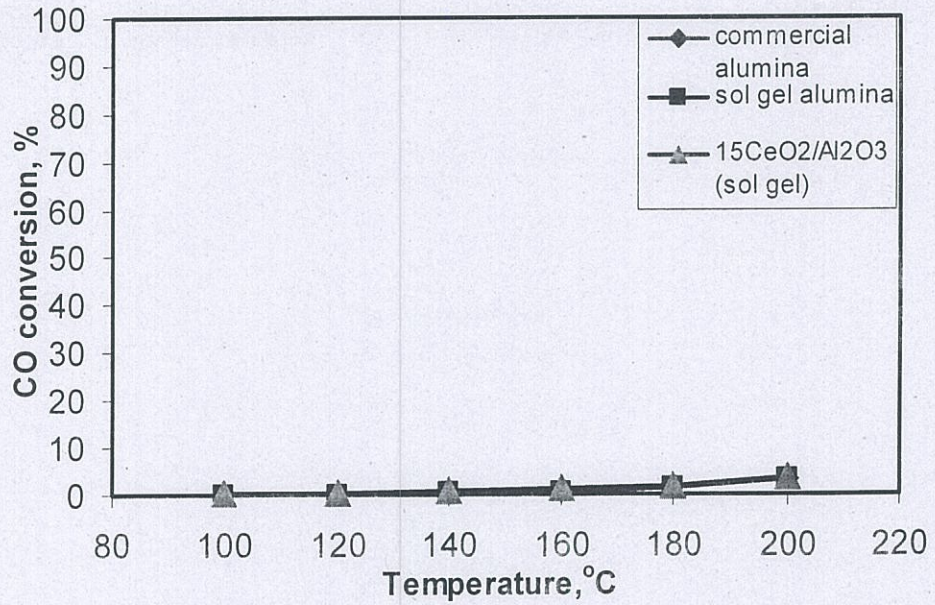

Figure 1. CO oxidation of pure supports. Gas compositions: 1%CO, 1%O_2 and balance with He. SV = 48,000 cc/g/h.

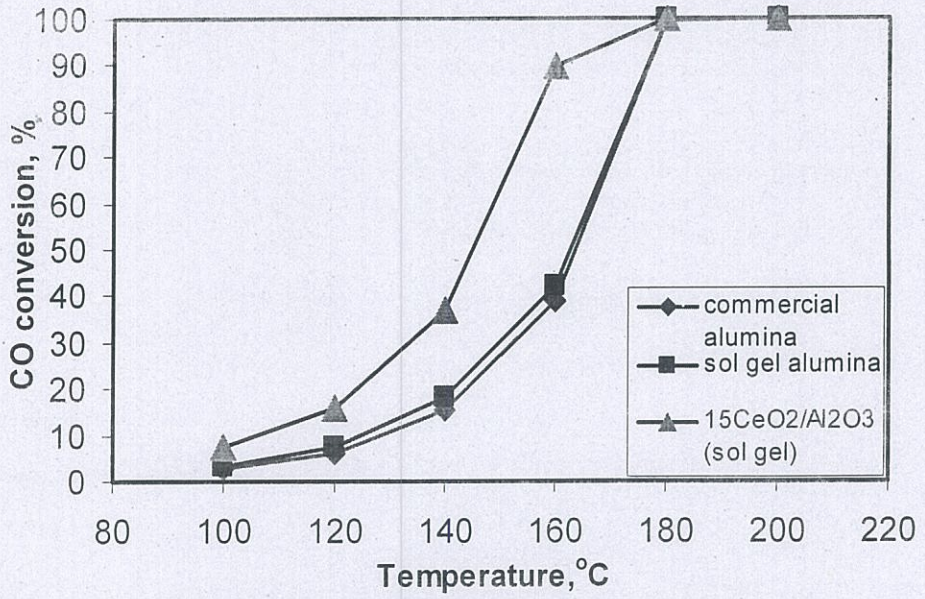

Figure 2 CO oxidation of different supports with 5%Pt loading. Gas composition: 1%CO, 1%O_2 and balance with He. SV=48,000 cc/g/h.

C. Effect of O_2

The effect of O_2 to activity of catalyst to CO oxidation was studied. The results were shown in Figure 3 and Figure 4.

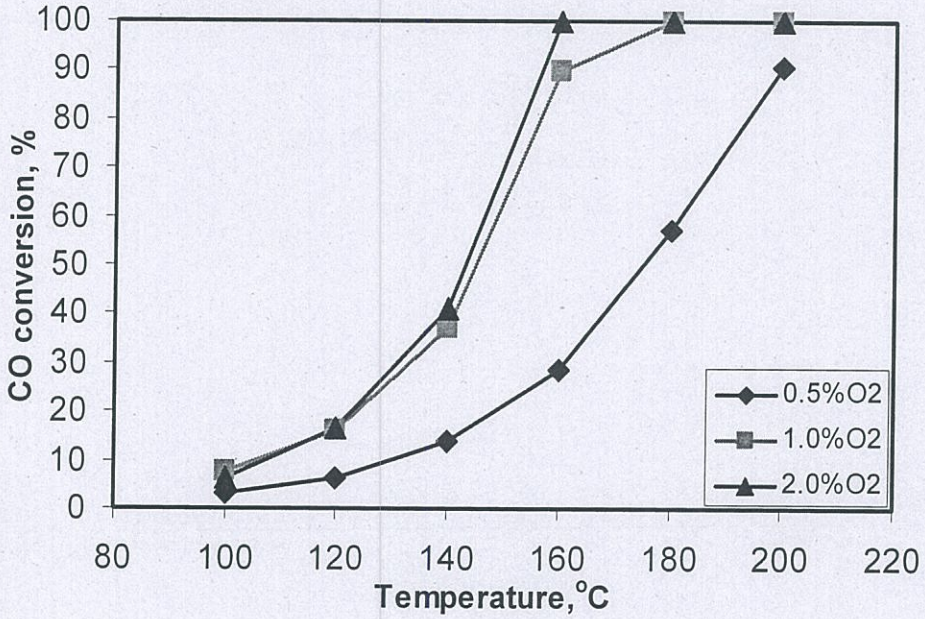

Figure 3 Effect of O_2 to CO oxidation for a 5%Pt/15%CeO_2/Al_2O_3. Gas Composition: 1%CO, 0.5, 1.0 and 2.0%O_2 and balance with He. SV = 48,000 cc/g/h.

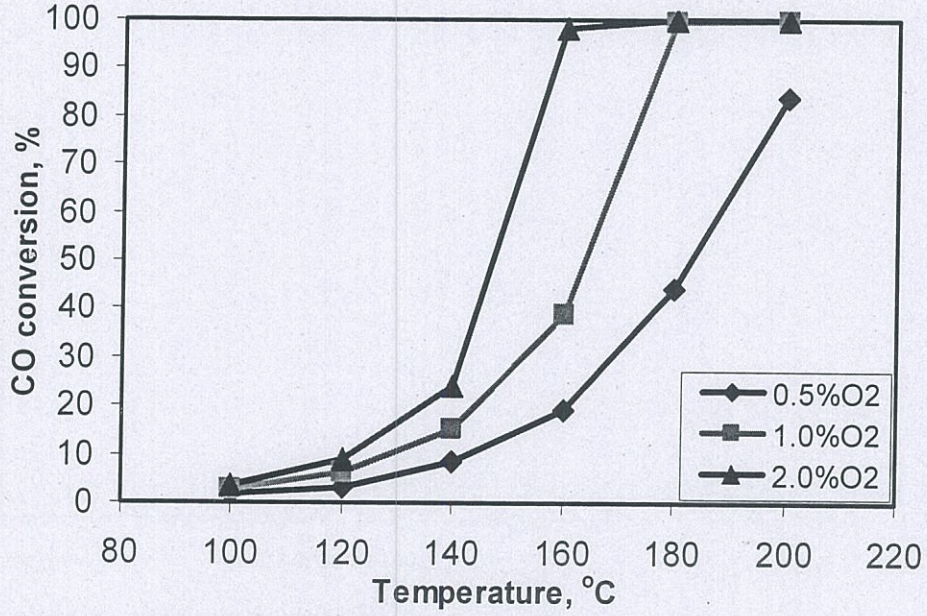

Figure 4 Effect of O_2 to CO oxidation for a 5%Pt/Al_2O_3. Gas Composition: 1%CO, 0.5, 1.0 and 2.0%O_2 and balance with He. SV = 48,000 cc/g/h.

As can be seen from the figures, an increasing of oxygen concentration in the feed stream increased CO conversion for both catalysts. However, the variation of O_2 concentration showed a

stronger effect to the 5%Pt/Al_2O_3 than the 5%Pt/15%CeO_2/Al_2O_3. This could be explained by the transferring of lattice O atom at interface between Pt and CeO_2 and led to the changing of oxidation state of Ce from Ce^{+4} to Ce^{+3} at low temperature ranges. At high temperatures, CO started desorbing from Pt sites. This results to available Pt sites for O_2 molecules. This mechanism led to the enhancement of the activity of Pt over alumina catalyst after doping with ceria.

4. CONCLUSIONS

The addition of CeO_2 into alumina support by sol gel technique incredibly enhanced the activity of a 5%Pt/Al_2O_3 to CO oxidation at the low range of temperatures (<160°). This is due to the interaction between Pt and CeO_2 at their interface. Furthermore, the effect of O_2 concentration in the gas feed was investigated. I found that the variation of oxygen concentration did not show a strong effect to CO oxidation for the 5%Pt/15%CeO_2/Al_2O_3 but did to the 5%Pt/Al_2O_3. This result could be explained via the transferring of oxygen atom in the lattice of CeO_2 at low temperature range and in turn the excess of oxygen even at low temperatures.

5. ACKNOWLEDGEMENTS

I would like to thank Prof. Levi Thompson from Chemical Engineering Department, the University of Michigan, Ann Arbor, for allowing me to use a surface area measurement instrument and also CO chemisorption instrument. Also special thanks would go to Prof. Erdogan Gulari from Chemical Engineering Department, the University of Michigan, Ann Arbor, he did not only let me use a setup in his laboratory but also gave some valuable suggestions. This research has been granted by NRCT (2004) and TRF (Grant # MRG 4680140)

REFERENCES

[1] Bourane, A., Derrouiche, S., and Bianchi, D. **2004** Impact of Pt Dispersion on the Elementary Steps of CO Oxidation by O_2 Over Pt/Al_2O_3, *Journal of Catalysis*, 2, 288-297.

[2] Costello, C.K., Kung, M.C., Oh, H-S., Wang, Y., and Kung, H.H. **2002**, Nature of the Active Site for CO Oxidation on Highly Active Au/γ-Al_2O_3, *Applied Catalysis A: General*, 2(232), 159-168.

[3] Ruth, K., Hayes, M., Burch, R., Tsubota, S., and Haruta, M. **2000** The Effect of SO_2 on the Oxidation of CO and Propane on Supported Pt and Au Catalysts, *Applied Catalysis B: Environmental*, 24, L133-L138.

[4] Gulari, E., Guldur, C., Srivannavit, S., and Osuwan, S.**1999** CO Oxidation by Silver Cobalt Composite Oxide, *Applied Catalysis A: General*, 182, 147-163.

[5] Kobayashi, M., and Takegami, H. **1984** Heterogeneity of a Silver Surface Used in the Oxidation of Carbon Monoxide, J. Chem. Soc., Faraday Trans. 1, 80, 1221-1231.

[6] Holmgren, A., Duprez., D., and Andersson, B. **1999** A Model of Oxygen Transport in Pt/Ceria Catalysts from Isotope Exchange, Journal of Catalysis, 182, 441-448.

[7] Rogemond, E., Frety, R., Perrichon, V., Primet, M., Salasc, S., Chevrier, C., Gauthier, C., and Mathis, F. **1997** Preparation of Alumina-Supported Ceria II. Measurement of Ceria Surface Area after Impregnation with Platinum and Rhodium, Journal of Catalysis, 169, 120-131.

[8] Yoldas, G.E.**1975** Preparation of Solid Oxide via Alkoxide by Sol-Gel Method, Ceramic Bulletin, 54, 298-301.