Journal of Science, Technology, and Humanities : July - December 2005, Vol. 3, No. 2, pp. 87-93

THE EFFECT OF PREPARATION METHODS FOR PROMOTED PLATINUM OVER ALUMINA TO CO OXIDATION REACTION

Akkarat Wongkaew[a]*, and Piyasan Praserthdum[b]

[a] *Department of Chemical Engineering, Faculty of Engineering, Burapha University, Chonburi 20131, Thailand.*
[b] *Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand.*

Received September 2005; accepted May 2006.

ABSTRACT

The activity of platinum promoted with ceria over alumina was investigated. The presence of ceria doped in alumina by sol gel method dramatically increased the activity of platinum over alumina at a low range of temperatures. $T_{1/2}$ of the 5%Pt/5%CeO_2/Al_2O_3 was 145°C, while $T_{1/2}$ of the 5%Pt over commercial alumina was 170°C. This may result from the oxygen storage properties of ceria. Furthermore, sol gel method offered the uniformity to the final metal oxide and in turns led to a better activity to CO oxidation comparing to that of the other catalyst preparation technique.

Finally, iron oxide was used as an oxygen storage compound. However, the result was not as good as the result from ceria. The activity of platinum over alumina catalyst containing 5%Fe_2O_3 increased about 12% comparing with that of platinum over commercial alumina. Interestingly, CO was completely converted to CO_2 at temperature of 180°C for all catalysts.

Keywords: CO oxidation, promoted platinum over alumina catalyst, oxygen storage, sol gel method, impregnation.

INTRODUCTION

The catalytic CO oxidation has been extensively studied around the world due to a variety of applications for this reaction, such as CO sensors (Chen et al., 2005; Neri et al., 2003), CO detector in households (Fan and Zhang 2001), and CO_2 lasers (Meixer et al., 1995; Gersum and Roth, 1996). Many types of metals, both transition and noble metals, have been investigated for CO oxidation reaction. Noble metals, such as Pt, Pd, and Au are expensive but they are very stable for the reaction. Indeed, Pt is the well-known metal used in this reaction (Kapoor et al., 2005; Manasilp and Gulari, 2002; Oran and Uner, 2004; Zhang et al., 2005). The high dispersion of Pt over various

* Corresponding author. E-mail address: akkarat@buu.ac.th

RESULTS AND DISCUSSION

Catalyst characterization

A specific surface area of each support was measured and the results are shown in Table 3.1. This Table showed that a specific surface area of a commercial alumina was the least, comparing to others. A specific surface area of supports prepared by sol gel method was around 37% greater than that of a commercial alumina. This was due to the nature of sol gel method itself. Indeed, the presence of a modifier (such as -diol compounds) always increased the specific surface area of those solid oxides. From the Table, the specific surface area of a $5\%CeO_2/Al_2O_3$ with a modifier was 45% greater than that of a $5\%CeO_2/Al_2O_3$ without a modifier. The presence of different doping compounds led to different specific surface area of the final solid oxides. The results also showed that with the same preparation technique (sol-gel), a specific surface area of a $5\%FeO_2/Al_2O_3$ was 4% less than that of the $5\%CeO_2/Al_2O_3$ without a modifier. This might be caused by the atomic size of Ce and Fe.

Table 3.1. Specific surface areas of supports.

Supports	Specific surface area (m^2/g)
Commercial Al_2O_3	157.0
Sol-gel Al_2O_3	228.0
$5\%CeO_2/Al_2O_3$ (SG)	217.0
$5\%CeO_2/Al_2O_3$ with modifier (SG)	314.0
$5\%Fe_2O_3/Al_2O_3$ (SG)	209.0
$15\%Fe_2O_3/Al_2O_3$ (SG)	206.0

Note: SG = sol gel method

All supports were impregnated with 5%Pt loading via incipient wetness impregnation technique. Platinum crystalline size of each sample was measured by XRD. However, there was no peak of platinum observed. This means that Pt crystalline size of each sample was less than five nm. In other word, Pt was well dispersed in all supports.

Activity of catalysts to CO oxidation

1. Activity of supports to CO oxidation

The supports such as commercial alumina, $5\%CeO_2/Al_2O_3$ (SG) and $5\%Fe_2O_3/Al_2O_3$, were tested their activity under 1%CO, $1\%O_2$ balance with He. The results are shown in Figure 3.1. It was found that over the studied temperatures (100-220°C), CO conversion was nearly zero. This means that no supports are active to CO oxidation reaction.

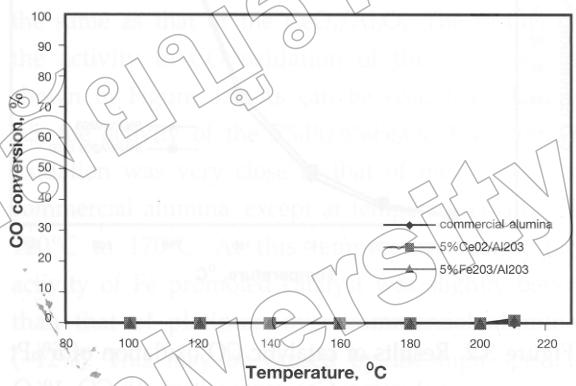

Figure 3.1. Activity of supports to CO oxidation. Gas composition: 1%CO, $1\%O_2$ and He as balance. SV = 48,000 cc/g/h.

2. Activity of platinum over alumina catalysts

The platinum was impregnated into the supports in order to study the effect of metal over supports to the activity of catalyst to CO oxidation. A commercial alumina was obtained from Sigma-Aldrich Company meanwhile the other was prepared via sol gel method. The specific surface areas of these two supports were 157.0 m^2/g and 228.0 m^2/g, respectively. It was found that at temperatures around 130°C to 160°C, a 5%Pt over sol gel alumina showed slightly better activity to CO oxidation than that of a 5%Pt over commercial alumina (approximately 3%), as shown in Figure 3.2, Furthermore, both catalysts showed that CO was completely converted to CO_2 at 180°C. This was caused by desorption process of CO over Pt

sites at high temperatures. Although the sol gel alumina has a higher specific surface area than the commercial alumina, the activities of these two catalysts impregnated with the same Pt loading to CO oxidation reaction are very close. Therefore, the specific surface area might not be a dominant parameter to increase the activity of these catalysts to CO oxidation.

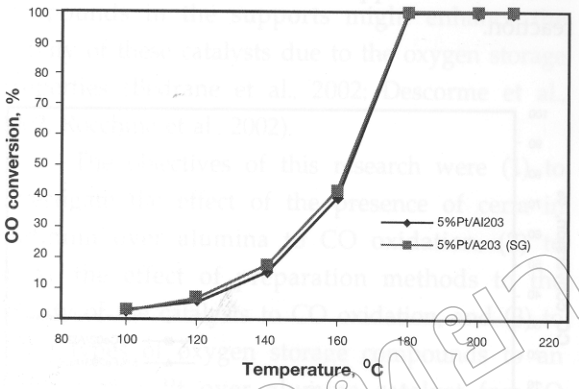

Figure 3.2. Results of catalytic CO oxidation of 5%Pt over alumina. Gas composition: 1%CO, 1%O_2 and He as balance. SV = 48,000 cc/g/h.

3. Effect of ceria to CO oxidation

The effect of the addition of oxygen storage compounds into platinum over alumina catalysts was studied. The 5%CeO_2/Al_2O_3 support was prepared via sol gel method. Its specific surface area was 217.0 m^2/g. The activity of the support to CO oxidation was subsequently determined. The result is shown in Figure 3.3. The 5%CeO_2/Al_2O_3 was not active to CO oxidation at all. However, when the 5 %wt Pt or 5%Pt was impregnated and loaded into this support, the activity of the platinum over alumina with the addition of 5%CeO_2 dramatically increased the rate of CO oxidation reaction. It was found that CO conversion increased from 0% CO conversion for pure support and 13%CO conversion for 5%Pt/commercial alumina to 40% CO conversion for 5%Pt/5%CeO_2/Al_2O_3 at the temperature of 140°C. The $T_{1/2}$ of the promoted catalyst was compared with that of the platinum over alumina. $T_{1/2}$ is defined as the temperature at which 50% of CO at the initial concentration was converted to CO_2. It was found that $T_{1/2}$ of a 5%Pt/Al_2O_3 was 170°C and $T_{1/2}$ of a 5%Pt/5%CeO_2/Al_2O_3 was 145°C. This means that the addition of 5% ceria oxide in the alumina support has a positive effect to the activity of the catalyst to CO oxidation reaction. Another interesting point is that both catalysts with and without ceria oxides can completely convert CO to CO_2 at the same temperatures (~180°C). In fact, the presence of ceria increased the performance of platinum over alumina only at low temperature ranges. This phenomenon could be explained as follows: Ceria is an oxygen storage compound. Its

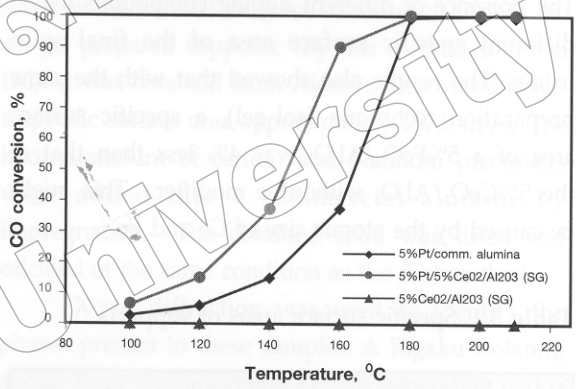

Figure 3.3. Effect of ceria containing in platinum alumina catalyst to CO oxidation. Gas composition: 1%CO, 1%O_2 and He as balance. SV = 48,000 cc/g/h.

oxidation state can be +3 or +4. At low temperature, the support contained cerium oxide itself can release oxygen atom in the lattice. This leads to the changing of oxidation state of ceria from +4 to +3. When an oxygen molecule in the gas mixture is adsorbed on the same site, the oxygen molecule will dissociate and fill back to the position losing an oxygen atom. This results in the changing of oxidation state of Ce atom from +3 to +4. This phenomenon increases the possibility of CO adsorbed and O adsorbed to be reacted and formed CO_2 as a product. However, this phenomenon does not dominate at high temperatures (>170°C)

because of the adsorption-desorption mechanism. Therefore, CO conversion at high temperatures was the same for both catalysts.

4. Effect of preparation method

Further study was conducted with a commercial alumina. The ceria precursor and platinum precursor were impregnated into a commercial alumina by incipient wetness impregnation method. The obtained catalyst was a 5%Pt/5%CeO_2/Al_2O_3. The performance of this catalyst to CO oxidation was tested under 1%CO, 1%O_2 and He as balance. The result is shown in Figure 3.4. This result was compared with those obtained from a 5%Pt/commercial alumina and a 5%Pt/5%CeO_2/Al_2O_3 (SG). It was found that the activity of a 5%Pt/5%CeO_2/Al_2O_3 prepared from the impregnation of cerium and platinum precursor into a commercial alumina was quite the same as the activity of the 5%Pt over commercial alumina. These results obviously indicated that the preparation method had a strong effect to the performance of the catalyst to CO oxidation. One major reason might be from the uniformity of CeO_2/Al_2O_3 oxide prepared by sol gel method. Both ceria and alumina were well mixed together in the sol and then they were bonding together during the condensation reactions to obtain gel. On the other hand, ceria in the impregnation catalyst was physically deposited on alumina. The uniformity of ceria over alumina depends on the way to introduce ceria precursor into alumina. These may lead to the different structures of ceria oxide in alumina and may cause the differences in the activities of both catalysts to CO oxidation.

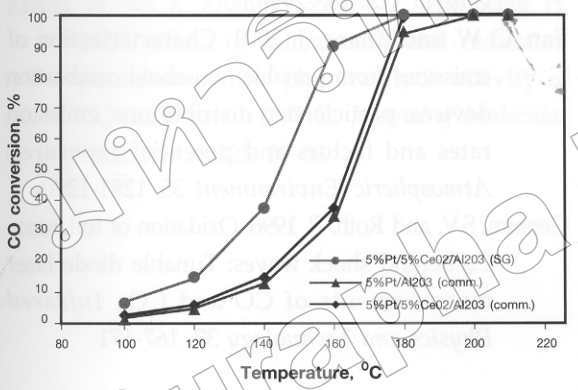

Figure 3.4. Effect of catalyst preparation method to CO oxidation. Gas composition: 1%CO, 1%O_2 and He as balance. SV = 48,000 cc/g/h.

The set of experiment on a type of oxygen storage was further carried on. The 5%Pt/5%Fe_2O_3/Al_2O_3 and 5%Pt/15%Fe_2O_3/Al_2O_3 catalysts were prepared by sol gel method. A ferrous nitrate was used as a precursor. The preparation procedure was the same as that of the CeO_2/Al_2O_3. The results of the activity to CO oxidation of this catalyst are shown in Figure 3.5. As can be seen from Figure 3.5, the activity of the 5%Pt/5%Fe_2O_3/Al_2O_3 to CO oxidation was very close to that of the 5%Pt over commercial alumina, except at temperatures around 120°C to 170°C. At this temperature range, the activity of Fe promoted catalyst was slightly better than that of platinum over commercial alumina (~12%). This may be caused by the high specific surface area of this support (209 m^2/g). However, once the result of a 5%Pt was compared with that of sol gel alumina (specific surface area of 228 m^2/g), it was expected that a better performance to CO oxidation was not only from a higher specific surface area of supports but also from the presence

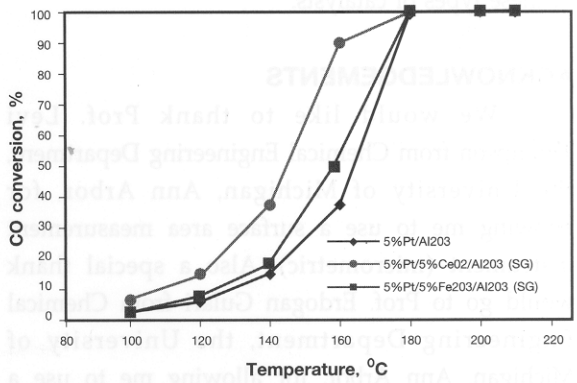

Figure 3.5. Results of CO oxidation of promoted platinum over alumina. Gas composition: 1% CO, 1%O_2 and He as balance. SV = 8,000 cc/g/h.

supports has a positive effect to the activity of this catalyst to CO oxidation (Bourane et al., 2004). Moreover, this catalyst is very stable (no deactivation observed). This results in intensive development of platinum over different supports. One possible way to improve the activity of platinum over alumina catalysts to a CO oxidation reaction is the addition of some compounds, such as cerium oxide or iron oxide. The presence of these compounds in the supports might enhance the activity of these catalysts due to the oxygen storage properties (Bedrane et al., 2002; Descorme et al., 2002; Rocchine et al., 2002).

The objectives of this research were (1) to investigate the effect of the presence of ceria in platinum over alumina to CO oxidation, (2) to study the effect of preparation methods to the activity of the catalysts to CO oxidation, and (3) to study types of oxygen storage compounds to an activity of a Pt over alumina catalyst for CO oxidation reaction. In this study, the catalyst supports were prepared by sol gel method and tested the activity of these catalysts to CO oxidation reaction. The obtained results were compared with the activity of the catalysts over supports obtained from commercials.

EXPERIMENTAL DETAILS

Catalyst preparation

Promoted aluminium oxides were prepared by sol gel and impregnation methods. Cerium (IV) nitrate hexahydrate [$Ce(NO_3)_4.6H_2O$], aluminium isopropoxide [$Al(OC_2H_5)_3$, 97.5%], and ferrous nitrate [$Fe(NO_3)_3$] were obtained from Aldrich. They were used as a precursor in the preparation of supports by sol-gel method (Brinker and Scherer, 1990; Jones, 1989). Various supports were prepared as the following procedure: Alumina isopropoxide was used as a starting precursor. The known amount of this precursor was added into hot water. The solution was stirred for 30 min until the solution was uniform. Then, a suitable amount of nitric acid was added in order to peptize the sol. After the sol became clear, a known amount of cerium (IV) nitrate or of ferrous nitrate was added into the solution, and this solution was stirred for 30 min. The obtained solution was subsequently aged overnight at a room temperature. After aging, the sol was heated until it became gel. The obtained gel was aging overnight. The final gel was dried under conventional oven and then calcined at an appropriate temperature. The obtained solid oxide used as a support was ground and sieved to 80-100 meshes. The obtained supports were impregnated with a known amount of Pt precursor by incipient wetness impregnation method. The obtained catalysts were purged under H_2 conditions before testing their activity to CO oxidation.

The other method used for the preparation of doped alumina was an impregnation, which was the same as the method used for introducing Pt into the sol-gel prepared supports. By this method, alumina (Al_2O_3) was obtained from Aldrich. This alumina has a specific surface area approximately 157.0 m^2/g. The known amount of cerium and platinum precursors were added into a commercial alumina by impregnation. The obtained solid was dried and calcined at the same condition as the first method.

X-ray diffraction was used to identify the phases present in these samples. A Rigaku Rotating anode X-ray diffractometer system generating CuKα radiation was used to obtain the XRD patterns. Furthermore, the BET surface area and average pore radius of catalysts were measured by an Autosorb-1 Gas Sorption System (Quantachrome Corporation).

Activity measurement

The activity of these catalysts was tested in a micro reactor. The amount of catalysts used was 100 mg. The total gas flow rate was 80 cc/min. The inlet gas composition contained 1%CO, 1%O_2 and balance with He. The reaction temperature was controlled by a temperature controller with a K-type thermocouple placed on the top of the catalyst bed. The accuracy of the temperature measurement was ±1°C. The range of studied temperatures was from 100°C to 220°C. All gases were trapped to remove moisture before they passed through GC. The gas composition at the entrance and at the exit of the reactor was analyzed by GC with TCD detector.

of an oxygen storage compound such as Fe_2O_3. This results from the changing for oxidation state of Fe from +3 to +2 causing Fe as an oxygen storage element (similar to Ce). However, its performance was weaker than that of Ce. Therefore, the better activity of catalyst to CO oxidation was observed when there was a presence of cerium oxide in the catalyst. Again, all catalysts completely converted CO to CO_2 at a temperature of 180°C.

CONCLUSIONS

This investigation may be concluded as follows:

1. The addition of an oxygen storage compound, such as cerium oxide and iron oxide, into platinum over alumina catalyst has a positive effect on its performance to CO oxidation.

2. The preparation method is a dominant factor to obtain a high activity of promoted platinum catalyst to CO oxidation.

3. $T_{1/2}$ of a 5%Pt/5%CeO_2/Al_2O_3 (SG) was 145°C and $T_{1/2}$ of a 5%Pt over commercial alumina was 170°C. This result may be caused by the presence of ceria as an oxygen storage compound.

4. Specific surface area was not a strong parameter to obtain a high activity to CO oxidation of these types of catalysts.

ACKNOWLEDGEMENTS

We 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 (micrometric). Also a special thank would go to Prof. Erdogan Gulari from Chemical Engineering Department, the University of Michigan, Ann Arbor, for allowing me to use a setup in his laboratory and for giving some valuable suggestions. This research was supported by grants from NRCT (2004) and TRF (Grant# MRG4680140).

REFERENCES

Bedrane, S., Descorme, C., and Duprez, D. 2002. Investigation of the oxygen storage process on ceria- and ceria-zirconia supported catalysts. *Catalysis Today* 75: 401-405.

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.

Brinker, C. J. and Scherer, G.W. 1990. *Sol-gel science.* Academic Press, New York.

Chen, C., He, J., Xu, D., Zhou, X., and Wang, Z. 2005. Study of nano-Au-assembled amperometric CO gas sensors. *Sensors and Actuators B* 107: 866-871.

Descorme, C., Taha, R., Mouaddib-Moral, N., and Duprez, D. 2002. Oxygen storage capacity measurements of three way catalysts under transient conditions. *Applied catalysis A: general* 123: 287-299.

Fan, C. W. and Zhang, J. 2001. Characterization of emissions from portable household combustion devices: particle size distributions, emission rates and factors and potential exposures. *Atmospheric Environment* 35: 1281-1290.

Gersum, S.V. and Roth, P. 1996. Oxidation of fullerence C_{60} behind shock waves: Tunable diode laser measurements of CO and CO_2. *Infrared Physics and Technology* 37: 167-171.

technology. Brookfield, VT: Institute of Metals.

Kapoor, S., Belapurkar, A.D., Mittal, J.P., and Mukherjee, T. 2005. Catalytic oxidation of carbon monoxide over radiolytically prepared Pt nanoparticles supported on glass. *Materials Research Bulletin* 40: 1654-1661.

Manasilp, A. and Gulari, E. 2002. Selective CO oxidation over Pt/Alumina catalysts for fuel cell application. *Applied catalysis* B: *environmental* 37: 17-25.

Meixer, H., Gerblinger, J., Lampe, U., and Fleischer, M. 1995. Thin film gas sensors based on semi-conducting metal oxides. *Sensors and Actuators B* 23: 119-125.

Neri, G., Vonarita, A., Milone, C., and Galvagno, S. 2003. Role of the Au oxidation state in the CO sensing mechanism of Au/iron oxide-based gas sensor. *Sensors and Actuators B* 93: 402-408.

Oran, U. and Uner, D. 2004. Mechanism of CO oxidation reaction and effect of chlorine ions on the CO oxidation reaction over Pt/CeO_2 and $Pt/CeO_2/\gamma\text{-}Al_2O_3$. *Applied catalysis B: environmental* 54: 183-191.

Rocchini, E., Vicario, M., Liorca, J., Leitenburg, C., Dolcetti, G., and Trovarelli, A. 2002. Reduction and oxygen storage behavior of noble metals supported on silica doped ceria. *Journal of Catalysis* 211: 407-421.

Zhang, M., Jin, Z., Zhang, J., Zhang, Z., and Dang, H. 2005. Effect of calcinations and reduction treatment on the photocatalytic activity of CO oxidation on Pt/TiO_2. *Journal of Molecular Catalysis A* 225: 59-63.