

## EFFECT OF IMPREGNATION PROCEDURE OF Pt/ $\gamma$ -AL<sub>2</sub>O<sub>3</sub> CATALYSTS UPON CATALYTIC OXIDATION OF CO

Triyono

Chemistry Department, Faculty of Mathematics and Natural Sciences  
Gadjah Mada University, Yogyakarta

### ABSTRACT

The oxidation of carbon monoxide by oxygen using two catalysts prepared by two different methods has been investigated. In the first method, catalyst prepared by immersing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into the hexachloroplatinic acid solution at 80°C for 4 h, resulted Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst having platinum highly dispersed on the support. While that of immersing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the hexachloroplatinic acid solution at room temperature for 12 h, produced Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst where platinum dispersion was much lower. Catalytic activity test showed that platinum well dispersed on the support enhanced the activity for oxidation of carbon monoxide. The platinum impregnated at room temperature resulted in the poor activity.

Keywords: platinum catalyst, alumina, supported material, oxidation

### INTRODUCTION

Improvement, or at least limitation of damage, to the environment will be the focus of greater public awareness, political debate and increasingly more stringent legislation [1]. Users of fuel oil may need, or choose, to invest in post-combustion clean up of emissions or innovative conversion and combustion processes, such as conversion of CO to CO<sub>2</sub> in exhausted emissions.

Carbon monoxide (CO) is one of the most dangerous pollutant gases in the atmosphere. This colorless gas which usually produce from the combustion system has damaging effect toward human and animal life [2]. Environmental Protection Agency has determined that the environmental quality standard is limited to about 9 ppm for CO in the atmosphere. One of the alternative efforts to manage and treat the pollutant gases produced by transportation activities is conversion of those gases [3], especially for CO gas, it can be converted to CO<sub>2</sub> by catalytic process [4]

Development of catalysts for automotive emission control is a great challenge because of the extreme operating condition variation encountered. While the most industrial catalytic operations involves continuous and steady-state conditions, automobile operations are intermittent and transient, with wide fluctuations of flow rate and temperature that depend on driving conditions and cold or warm engine starts. Exhaust gas-flow rate can vary from 20 to more than 200 SCF/min, and exhaust temperatures from 250 to 1100°C [5].

Only precious metal catalysts have thus far been used commercially to meet the many difficult

specifications. In most cases, the metal is dispersed as small crystallites on thermally stable, chemically inactive supports such as alumina.

The rate per unit area of catalytically-active material may be small. Thus it becomes necessary to produce high surface areas of catalyst per unit weight of the material. Very small particle sizes are thus indicated. In such a case the catalyst may be finely dispersed on the surface of the pores of a support material such as alumina.

### EXPERIMENTAL

Catalysts used here were 0.5 wt% Pt supported on alumina, prepared by two different impregnation methods according to the procedures given below. First method was the conventional impregnation; immersing alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) powder in aqueous solution of platinum chloride at room temperature while stirring for 12 h. Second method was dipping-impregnation methods, that is immersing alumina powder in aqueous solution of platinum chloride at 80°C while stirring for 4 h.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used as support material has surface area 198 m<sup>2</sup>/gram, average pore radius 26.2 Angstrom and pore volume 0.46 cc/gram.

The characterization of the catalysts consist of several testings such as platinum content, surface area, pore volume, average pore size and platinum dispersion. Platinum content was determined using AAS, surface area, pore volume and average pore size were measured by nitrogen adsorption at liquid nitrogen temperature, while platinum dispersion was measured by oxygen chemisorptions at room temperature.

All the catalysts were dried and calcined at 500°C or 800°C for 3 h before submitting to the oxidation reaction. These four kinds of the catalysts were submitted to the oxidation reaction using gases consisting 1000 ppm CO, 500 ppm oxygen with W/F being 0.2 g.s.cm<sup>-3</sup>, in order to see which was the more effective factor, physical parameters or dispersion states. The reaction temperature was 500°C, and the conversion of CO was measured by using non-dispersive infrared spectroscopy.

## RESULT AND DISCUSSION

### Physical properties of the catalysts.

In Table 1 are given the physical parameters of four catalysts prepared in the laboratory, indicating that those of the room temperature impregnated catalysts were similar to those of the 80°C impregnated catalysts.

Table shows that the difference of surface area, average pore radius and pore volume are more prominently due to catalyst calcination temperatures compared with that of by impregnation temperatures. However, the physical properties of the support are significantly different with those for metal-support catalysts produced. The difference in physical properties of those catalysts can be explained as follows: Interaction between metal and support occurs when the solute to be deposited establishes a bond with the surface of the support at the time of wetting. Such interaction results in a near-atomic dispersion of the precursors active species. The interaction between alumina and chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) is an exchange of the anion PtCl<sub>6</sub><sup>-</sup> in the solution for two OH<sup>-</sup> ions of alumina. This anion exchange is a veritable neutralization of a weak base (alumina) by a strong acids (H<sub>2</sub>PtCl<sub>6</sub>); and for this reason it proceeds to a complete exchange of all the surface hydroxyl ions and proceeds very rapid. In this case the rate of diffusion becomes limiting for the overall processes, therefore, during impregnation the colloidal system

must be stirred. Considered kinetically, the rate of the exchange reaction was in this case much greater than the rate of diffusion of solute in the pores, as shown by the preferential deposition of the PtCl<sub>6</sub><sup>-</sup> ion in the periphery of the granules. Considering this standpoint, reducing surface area and pore volume together with increasing average pore diameter resulted by impregnation of precursor solution onto the support material are reasonable and accepted. Data also shows decreasing surface area while pore volume and average pore increase. Those changes were caused by disappearance of small pore due to pore collapse and attrition of small pores to be wider.

### Dispersed state of the active agent

It is well understood, although the catalyst compositions are the same, the catalytic activity happen to depend upon the catalyst preparation routes. This may be ascribed to the difference in the dispersion state of active species or in the physical properties of the support used [6]. In this paper, the dispersion state figured as percent dispersion of active species was measured in order to explain the difference the catalytic activities of the catalysts prepared in difference routes.

Platinum dispersion in these catalysts were measured by oxygen adsorption at room temperature. Dispersion was calculated based on the oxygen adsorption capacity by assuming that oxygen is adsorbed dissociatively and one platinum atom on the catalyst surface is able to bind one oxygen atom. The number of platinum surface atom Pt<sub>s</sub>, can be derive from the following equations:

$$Pt_s = (V/V_M) \cdot N_A \cdot n$$

Where V = volume of gas chemisorbed,

V<sub>M</sub> = molar volume of oxygen,

n = stoichiometry of chemisorption reaction,

N<sub>A</sub> = Avogadro number.

Based on the calculation, the dispersion of platinum an the catalyst are summarized in table 2.

**Table 1** Physical properties of the catalysts

Catalyst		Calcination temp (°C)	Surface area (m <sup>2</sup> /g)	Av.pore radius (Angst)	Pore volume (cc/g)
Impregnation at room T for 12 h.	1	500	152	28	0.22
	2	800	137	32	0.27
Impregnation at 80°C T for 4h.	3	500	148	29	0.21
	4	800	129	34	0.22

Note: Alumina; Surface area 200 m<sup>2</sup>/g, av. Pore radius 26.2 Angs, Pore vol 0.46 cc/g.

**Table 2** Metal content, hydrogen adsorption and dispersion of catalysts\*.

Catalyst	Calcination temp (°C)	oxygen uptake (10 <sup>20</sup> molecule)	Dispersion (% metal atom on the surface)
Impregnation at room T for 12 h.	500	2.13	29
	800	1.91	26
Impregnation at 80°C for 4h.	500	4.40	60
	800	3.74	51

\*) The platinum atom content in all catalyst are identical., i.e.  $1.45 \cdot 10^{21}$  atom/g.cat.

**Table 3** CO oxidation activity and dispersion of catalysts.

Catalyst	Calcination temp (°C)	Metal content (atom)/g.cat.	Dispersion (% metal atom on the surface)	CO oxidation activity at 500°C
Impregnation at room T for 12 h.	500	0.47	29	34
	800	0.47	26	31
Impregnation at 80°C for 4h.	500	0.47	60	48
	800	0.48	51	52

Those data indicating that the platinum is highly dispersed on alumina supports of catalyst prepared by dipping impregnation. Calcination at 800°C producing lower dispersion than at 500°C. The metal sites on a catalysts are found on its surface, however heating catalysts results in agglomeration of the small particulates into larger, less efficient, entities. Heat promotes the coalescence into increasingly larger entities and a corresponding loss of platinum atoms on the surface. The extent of agglomeration is a function of the particular catalyst, the temperature and the time the catalyst is exposed to the heat. For most catalytically active metal particles, agglomeration or sintering may be observed at temperatures above 450°C. For Platinum supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> does not usually sinter at temperature under 500°C [7]. In this investigation, sintering was occurred at 800°C as shown by decreasing metal dispersion.

As shown in table 1, the physical parameters of the impregnated catalyst calcined at 500°C were similar to those of the dipping-impregnated catalyst calcined at 500°C. However, table 2 suggests that the dispersion state of platinum in the impregnated catalyst were different from those in the dipping-impregnated catalyst calcined at 500°C. Considering the results given for activity, it can be concluded that, for the oxidation reaction on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the dispersion states of platinum is more effective factor than the physical parameters of the catalyst.

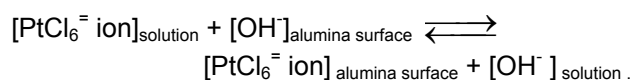
When the active species are supported, there is no longer a direct relation between the total specific surface area and the observed catalytic performance, particularly the activity; and it is necessary to determine the available active

surface, i.e., the number of molecules or atoms of active agents accessible to the reactants.

### Catalytic activity

In order to show the usefulness of oxygen chemisorption, the relation between the rates of various reactions of CO oxidation at several temperature is presented in table 3.

Table 3 shows that all catalysts prepared contain the same amount of platinum. Therefore, impregnation at 80°C for 4 hours was enough to dispersed almost all of the platinum content in the solution. Moreover calcination at two different temperature was not have any effect of the metal content in the catalysts. However, the activity of the catalysts were different significantly. In contrast effect calcination temperature was shown by Okazaki [8], by calcining cobalt or nickel-loaded alumina at high temperature suppressed the oxidation of ethene by oxygen. On the other hand, catalyst prepared by impregnation at 80°C showed higher activity. The different in activity may be addressed to the different state of platinum dispersed on the catalyst. Depending on the impregnation temperature, the exchange reaction between PtCl<sub>6</sub><sup>=</sup> ion and OH<sup>-</sup> ion belong to the equilibrium equation of ionic exchanges:



At room temperature, reaction were observed to be almost complete and to give an uneven deposit to the accessible surface sites producing platinum particles accumulated on the outer surfaces. While

the impregnation at 80°C achieve equilibrium and lead to better distribution of the platinum on the whole surface, because, at higher temperature the platinum were easier to migrate toward the internal pore and resulted better dispersion and smaller platinum particles.

When the platinum species are dispersed on the support, there is no longer a direct relation between the total platinum content and the observed catalytic performance, particularly the activity; it depends on the available active sites or the number of molecules or atoms of active agents accessible to the reactants. Facilitated by smaller platinum particle, at the same platinum content, there are more active platinum accessible to the reactant results higher activity.

### CONCLUSION

1. The physical parameters of the impregnated catalysts calcined at 500°C or at 800°C were similar to those of the dipping-impregnated catalysts calcined at 500°C or at 800°C.
2. The activity of the impregnated catalysts were lower than those of the dipping-impregnated catalysts.
3. The dispersion state of platinum in the impregnated catalysts were lower than those in the dipping-impregnated catalysts.
4. For oxidation of carbon monoxide on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the dispersion states of platinum is more effective factor than the physical parameters of the catalyst.

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