CARBON MONOXIDE OXIDATION OVER Pt/γ-ALUMINA CATALYST

by

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ABSTRACT

Oxidation of CO has been studied on Pt/γ-alumina catalyst. The catalyst was produced by impregnating γ-alumina with hexachloroplatinic acid solution, calcined, oxidized and reduced at the optimum condition. Catalyst was characterized by nitrogen sorption measurement and scanning electron microscope (SEM). By optimization of calcination, oxidation and reduction on the catalyst preparation, a residual surface area of $129.14\ m^2$*/gram was obtained. The resulting catalyst has a high activity for the conversion of CO to* CO_2*.*

I. INTRODUCTION

Carbon monoxide is particularly dangerous because it is both colorless and odorless. One way that carbon monoxide can be formed is by burning hydrocarbon in a limited supply of oxygen; this is exactly the condition that exists in gasoline engines, and produces some carbon monoxide. Carbon monoxide is very toxic; it binds to hemoglobin in the blood, thereby preventing it from carrying oxygen. That is why it is dangerous to be in an enclosed space with a running automobile engine.

In the 1994, the Indonesian government decided to limit the pollutant carbon monoxide (CO), hydrocarbon (HC) and nitrogen monoxide (NO) in the automotive exhaust gas. Typically, the HC and CO emissions of 2-stroke small engines are very high: HC approx. 1% and CO 6-8% of total emissions (Tarvainem, 1994). Exhaust gas of a 2-stroke engine typically contains relatively higher residual oxygen than that of a 4-stroke engine. It is possible to oxidize most of HC, but not enough to oxidize CO. By using catalytic converter, after leaving the engine, residual CO will soon be oxidized by catalyst. The temperature of the catalyst should be more than 300 °C (Abthof, 1990).

The catalytic oxidation of CO by platinum supported on γ-alumina has been intensively studied in this research. This reaction is very interesting from two points of view. In the first place, from the scientific point of view, the participating molecules contain only two atoms each, so that the surface species formed during the reaction are expected to be relatively simple (Barshad, 1985). It is hoped that the mechanism can be understood easily. Secondly, the reaction is practically important in view of the requirement to control the composition of exhaust gases (Theodore, 1988).

Platinum, despite of the cost, has so far been found to be the cheapest sufficiently durable catalyst with the high activity for oxidation as well as reduction or hydrogenation (Gasser, 1985). The plan of this research will be to consider the activity interpretation of catalytic experiments.

For catalyst to be able to function, chemisorption and diffusion of the reactant (HC and CO in case of exhaust gas) must take place on the surface of the catalyst. After reaction the products are desorbed from the surface of the catalyst to the exhaust gas. The catalytically active material may be so expensive that bulk of this material alone is economically unacceptable. In such a case (e.g. platinum) the catalytically active material is finely dispersed on the surface of the pore of pellets of porous support material such as silica, alumina or zeolite.

In this experiment, platinum that hastens the reaction, i.e. the catalyst, is supported on alumina. To synthesize catalyst, alumina is immersed in a platinum complex solution. Platinum is dispersed on the catalyst as a result of calcination, oxidation and followed by reduction. The platinum does not itself take part in the chemical reaction; it simply speeds up the process and makes the reaction take place at lower temperature.

The target of this research is to synthesize the catalyst for CO to CO_2 reaction to protect people against harmful pollutants surrounding them, especially in big cities where the traffic is very crowded.

II. EXPERIMENTAL

A. *Catalyst Preparation*

Gamma-alumina (surface area = 130.78 m^2/gram, pore volume = 0.195 cm^3/gram) calcined at 450°C was impregnated with H_2PtCl_6 aqueous solution by the following manner: 40 gram of alumina were soaked with 500 mL of solution during 24 hours, then dried at 120°C. Calcination was conducted in nitrogen stream for 2 hours at 500°C.

The Pt/γ-alumina catalyst contains 1% platinum on γ-alumina and has a surface area of 129.14 m^2/gram and pore volume of 0.224 cm^3/gram. Hydrogen chemisorption, measured by a flow technique, was 4 micromol of H_2/gram catalyst. On the other hand, Pt-Ce/γ-alumina catalyst contains 1% platinum and 0,5% cerium, has surface area of 112 m^2/gram and pore volume of 117 cm^3/gram. Hydrogen chemisorption of this catalyst was 4.8 micromol/gram.

Before using in the reaction, the catalyst was evacuated for one hour at room temperature followed by sweeping in oxygen for one hour. Under oxygen flow (10 mL/s) the temperature was raised at a rate of 3°C/min, to 350°C. Oxygen flow was continued for 2 hours at 350 °C.

B. *Characterization of Catalyst*

Specific surface area of the sample was determined with the gravimetric BET apparatus using N_2 at liquid nitrogen temperature.

The electron microscope was operated at magnification of 2400 and further magnification to 15000 was obtained by enlargement, so that a distance of one millimeter on the final print corresponded about 66 nm. The platinum containing particles was imaged on the micrograph as bright rectangular spots. Hydrogen adsorption was performed to measure platinum dispersion on the surface of γ-alumina.

C. *Catalyst Activity*

The catalytic conversions reported in this investigation were carried out in a microflow reactor with catalyst loading of 1 gram. Mixture of carbon monoxide and air (1:2) flow rates were 30, 60 and 90 mL/min. This condition provided differential or near-differential conversions, thus permitting direct calculation of conversion from the observed conversions. All of the non-condensable gas was analyzed by non-dispersive infrared spectroscopy.

III. RESULT AND DISCUSSION

A. *Electron Microscopy*

Platinum particle on the γ-alumina exhibited essentially small particles. The diameter of the particles is in the range of 1-3 mm, mostly cube-like Pt crystallites at the outer surface of the zeolite grains (Figure 2). Small metal particle is very important to have high metal particles on the surface needed for the reaction to proceed.

B. *Nitrogen Sorption*

1. Surface area

The determination of surface areas from the BET theory is a straightforward application of equation:

$$\frac{1}{W\,[(Po/P)-1]} = \frac{1}{Wm.C} + \frac{(C-1)}{Wm.C}\,(Po/P)$$

W = weight of nitrogen adsorbed
Po = saturated nitrogen vapor pressure
P = nitrogen pressure applied
Wm = Weight of nitrogen adsorbed in a completed monolayer
C = BET constant

A plot of $1/[W/(Po/P)\text{-}1]$ versus P/Po will yield a straight line in the range $0{,}05 < P/Po < 0{,}35$. Wm can be calculated from the slope and intercept of the straight line.

$$\text{Specific surface area, } \frac{Wm.N.\delta}{M.g}$$

N = Avogadro's number
δ = Nitrogen molecule cross sectional area
M = Molecular mass of nitrogen
G = Weight of catalyst

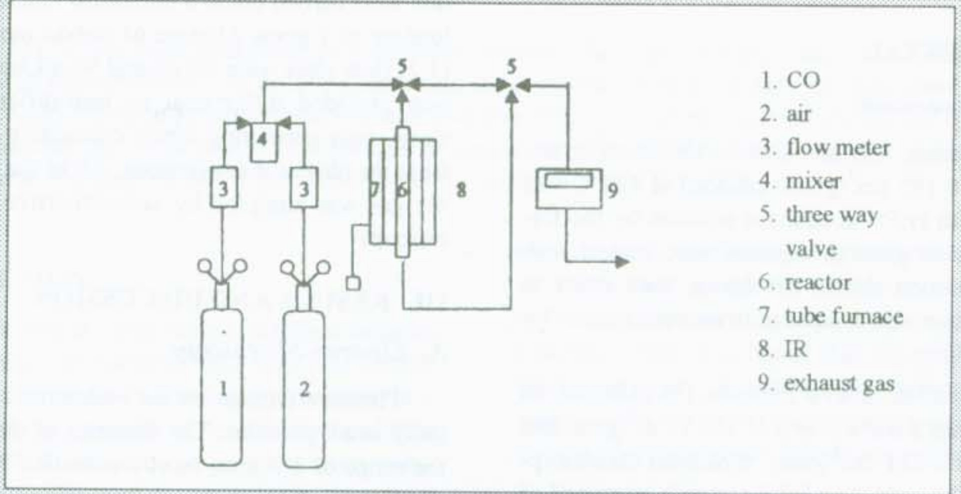

Figure 1
Experimental set-up for oxidation process

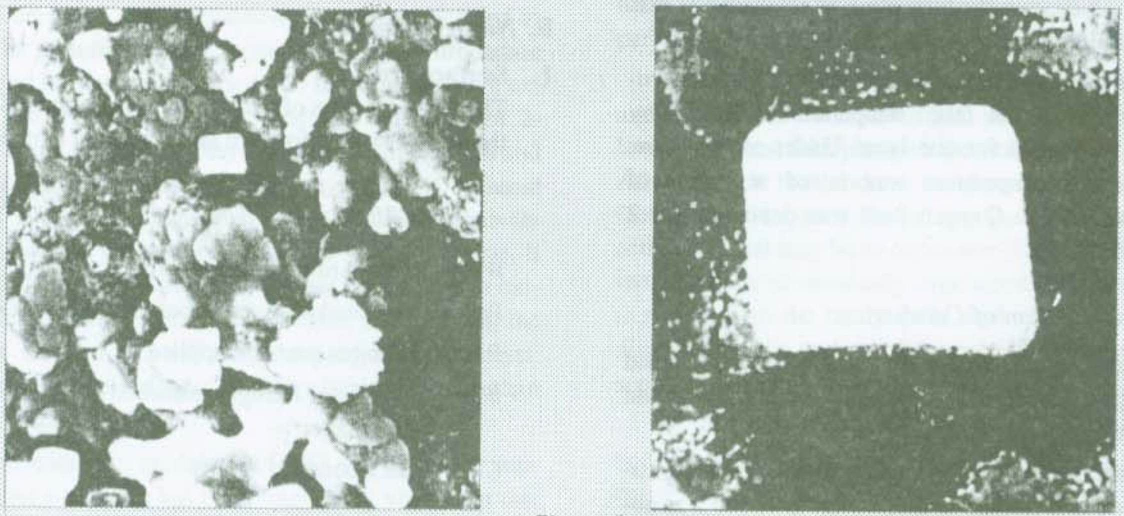

Figure 2
Micrograph of catalyst taken using SEM

2. **Pore volume**

   If Wa grams of nitrogen are adsorbed at P/Po = 0,99 then the corresponding

   Volume of pores Vp is given by

   $$Vp = \frac{Wa}{liquid\ nitrogen\ density}$$

3. **Pore size**

   Using assumption that of cylindrical geometry of pores, the average pore radius r can be calculated from the ratio of the total pore volume and the BET surface area from the following equation

   $$r = \frac{2.Vp}{S}$$

   Based on the measurement of nitrogen adsorption, values of surface area, pore volume and average pore size are summarized in Table 1.

In the preliminary experiments, the reaction rate per unit area of catalytically bulk platinum is small. Thus, it becomes necessary to produce high surface area of platinum per unit weight of the material. Very small particle sizes are thus inducted, but consideration of pressure drop rules out the use of beds of such particles. Thus pellets of material which are porous are generally used. The pellets are large enough (cylindrical, diameter and length both 5 mm) to flow through a bed of them to be possible at acceptable pressure drop. They are porous and have large surface area and pore volume. Surface area of catalyst was 129,14 m^2/gram and 112,75 m^2/gram for Pt/γ-alumina and for Pt-Ce/γ-alumina, respectively.

A pellet catalyst is strong enough, the pellets were not either collapsing or the physical strength weakened by the leaching effect of the fluid.

C. *Metal dispersion/hydrogen chemisorption*

The metallic Pt surface and the apparent Pt dispersion were calculated from hydrogen titration. The extent of hydrogen adsorbed, as determined from adsorption isotherms obtained using conventional volumetric apparatus, is a measurement commonly used to obtain a value for the degree of the active metallic constituent of a supported metal catalyst.

From the measurement of hydrogen adsorption, 1 gram of Pt/γ-alumina catalyst which contains 0,01 gram platinum or about 3.10^{19} atom platinum, adsorbs 4,1 x 10^{-6} mol hydrogen (STP) or about 2,5 x 10^{18} hydrogen atom. With the assumption that one hydrogen atom is adsorbed on one atom platinum, the dispersion of platinum on the support is 8,3%. The low apparent dispersion of the Pt reduced sample is in accordance with the big crystal of Pt detected by SEM. On the other hand 1 gram of Pt/γ-alumina catalyst contains of 0,011 gram platinum or about 3.10^{19} atom platinum and 2 gram cerium adsorbs $4{,}8.10^{-6}$ mol hydrogen (STP) or about 3.10^{18} hydrogen atom. Based on the above assumption the dispersion of platinum on the support is 10%. From the measurement of both catalysts, it may be concluded that addition of cerium increases metal dispersion.

One of the important roles of the promoters is definitely to create as well as to maintain high metal dispersion (Augustine, 1994). It really happened in this

Table 1
The characteristic of the catalyst

Catalyst	Pt (%)	Surface area (m^2)/γ	Pore volume (10^{-3}cc/γ)	Pore size (Angstrom)
γ-Alumina	-	130.87	195.23	29.78
Pt/γ-Alumina	1	129.41	124.42	24.72
Pt-Ce/γ-Alumina*	1	112.75	117.1	31.55

* *Concentration of Ce is 0,5% (b/w) of the catalyst*

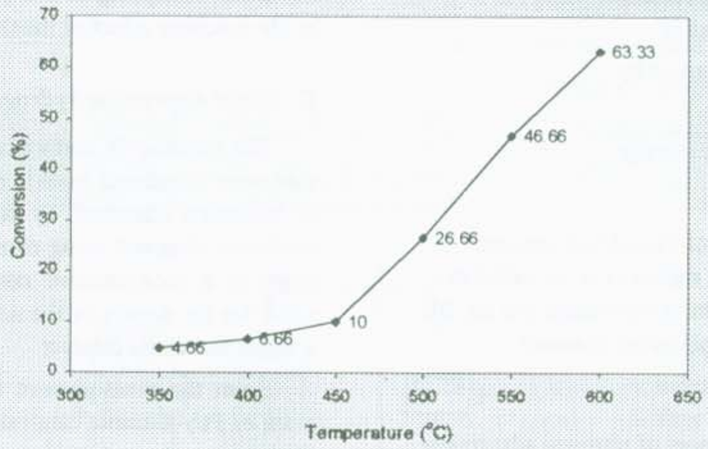

Figure 3
Catalytic activity of Pt/γ-alumina as a function of reaction temperature. Mixture of CO and air flow

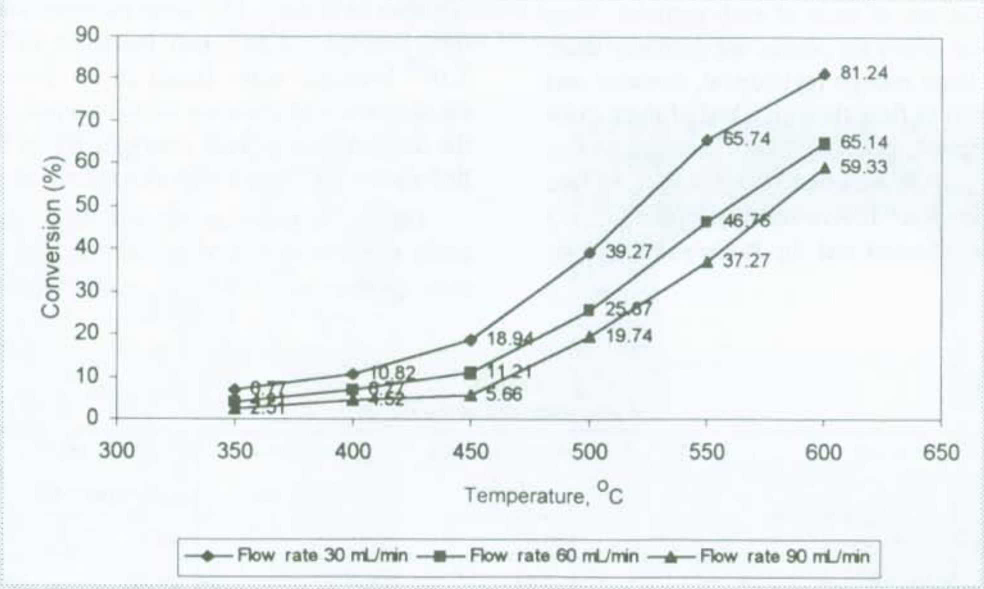

Figure 4
Catalytic activity of Pt-Ce/γ- alumina as a function of reaction temperature and feed

experiment. Such a function of the promoter is realized by its fine distribution in the catalyst. Although the overall concentration of cerium is rather small, the cerium concentration in the surface of the reduced catalyst is much higher than in the bulk. It can be estimated, but has not proved yet in this experiment.

D. *Catalytic activity*

1. Temperature dependence of oxidation rate

Figures 3 and 4 show the catalytic activity of Pt/γ-alumina and of Pt-Ce/γ-alumina as a function of reaction temperature.

There is a rise almost linearly of the conversion from a low level at 350 °C to 450 °C but more sharply above 450° up to 600 °C. In designing the experiment we have to take account of the considerations that the saturation uptake of CO and oxygen decline on the platinum surface as the temperature raised, and have become very low at high temperature. From this experiment at the higher temperature, therefore, the oxidation rate or conversion for the reaction on the surface increases almost in the normal way. It may be due to strong enough bonding of CO and oxygen to the catalyst up to 600°C.

Again, there is a rise of the conversion from 6,25% at 350 °C to 81.24% at 600 °C, the same behavior occurs as on Pt/γ-alumina catalyst. The higher conversion of Pt-Ce/γ-alumina revealed that cerium has a promoting effect to Pt/γ-alumina. According to the measurement of metal dispersion that cerium increases the metal atom on the surface, it is expected that the higher activity of Pt-Ce/γ-alumina is due to the higher platinum atom on the surface. In addition of cerium to Pt/γ-alumina the catalytic activity increases despite the decrease in the catalyst surface area. It seems that the higher platinum dispersion is responsible for strengthening of the catalytic activity.

Eventhough the conversion is still increasing linearly, temperature above 600 °C is not performed in this experiment. There are two reasons. Firstly, the experiment of Shigeshi (1987) showed that CO described from Pt(111) at about 620°C, when CO described (as a gas phase) is unable to react to form carbon dioxide, The second reason is in the practical utility of the catalyst for the removal of carbon monoxide presents in auto exhaust gases, temperature never reached 600 °C.

The experimental data obtained in this work also shows that at higher flow rate of the mixture of reactant causes the conversion decreases. It is understandable that the higher the flow rates the shorter the contact time between reactants and catalyst and causes lower conversion.

In the catalyst used in this experiment, γ-alumina is the support material and cerium is the promoter. These are substances which, while not catalytically active themselves, enhance the activity of platinum. Gamma-alumina enhances the activity by serving its high surface area for dispersing platinum, while that of cerium by producing higher dispersions of platinum. It is proved in this experiment that by using γ-alumina and cerium themselves at temperature up to 600°C, no conversion occurred.

Finally, this experiment is especially interesting because the idea will not stop here; more stringent environmental regulations require the catalytic control of not only carbon monoxide but also of hydrocarbons and nitrogen oxides. Afterwards, demands on the catalytic converter require continued improvement in conversion performance, durability, cost and some other parameters of the catalyst for conversion of toxic compound in exhaust gas in order to meet mounting public demand for strict emission standards.

III. CONCLUSIONS

The catalyst developed in the laboratory can be used for oxidation of carbon monoxide (the most potential component of waste gases) up to 81.25% conversion. If this type of catalyst is used in the industries or automobile converter, the air pollution can be reduced.

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