

## DEVELOPMENT OF BASE METAL OXIDE CATALYST FOR AUTOMOTIVE EMISSION CONTROL

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**Abstract** – Activity of alumina was tested for CO and hydrocarbon oxidation using the flow reactor system. The mechanism of the CO oxidation was elucidated by isotopic tracer technique using a closed circulation system. CO oxidation was found to proceed via the formation of a carbonate type of intermediate species. Water enhances the CO oxidation and CO<sub>2</sub> retards alumina activity. Carbon deposition was also investigated during CO oxidation on alumina. Carbon formed was found to act as an in-situ active site that promoted CO oxidation. Results obtained showed alumina to be promising for CO oxidation. Pb showed opposite effects on CO and hydrocarbon reactions. Hydrocarbon reactivity test conducted showed that methanol is the most reactive on alumina giving 100 % conversion at 500 °C. However, carbon deposited affected the formation of several products at this temperature. Further study on methanol oxidation using alkaline treated alumina showed better performance for auto emission control. CeO<sub>2</sub>, known to have an oxygen storage capacity, was tested as an additive to alumina for methanol oxidation and propylene oxidation. Results proved that CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> gave much higher activity for CO oxidation, methanol oxidation, and propylene oxidation than alumina.

Key words: CO Oxidation, Hydrocarbon Oxidation, Auto Emission Catalyst, Alumina, Ceria, Carbon Deposition

### INTRODUCTION

Air pollution in big cities of developing countries has worsened in recent years. A study [Gallardo, 1993] reveals that these air pollutants mainly come from mobile sources. In Metropolitan Manila, 73.4 % of these vehicles are gasoline-run and the rest are diesel-fed. Still, another study [Gallardo, 1994] shows that CO and hydrocarbon levels from gasoline-run vehicles in metro Manila are alarmingly high due to many factors such as age, maintenance, and driving mode. About 84 % of these vehicles are old and most of them are ill-maintained. At the same time, traffic congestion in the metropolis allows the cars to run in slow speed which results to lower exhaust temperature.

One of the long-term solutions recommended by experts [Engineering Science Inc, 1992] is the application of catalytic converters in cars to control emissions. This is a proven technology in advanced countries. However, a study [Gallardo and Niiyama, 1994] suggests that the situation in most developing countries does not require the use of Three-Way catalytic converters because they are easily poisoned by lead and sulfur which are still found in automobile emissions. On top of this is the fact that they are made of expensive noble metals. Thus, alternative catalysts which are more economical for CO and hydrocarbon oxidation need to be developed.

Alumina is known to be used as a support material for no-

ble metal catalyst. At the same time, it is known that hydrocarbons could reduce NO<sub>x</sub> in the presence of O<sub>2</sub> [Hamada et al., 1991]. Thus, activity of alumina as an oxidation catalyst was first investigated using a flow reactor system. A kinetic study of CO oxidation over alumina [Gallardo and Niiyama, 1997] using a differential reactor approximation reveals that the reaction is of the first order with respect to CO and of zeroth order with respect to O<sub>2</sub>. It also shows that alumina is active for CO oxidation at temperature higher than 600 °C. In addition to this, water enhances the activity of alumina at higher temperatures. It was concluded that this is due to the water-gas shift reaction. CO reacts with water to produce CO<sub>2</sub> and reactive H<sub>2</sub>. This H<sub>2</sub> further reacts with O<sub>2</sub> to yield water again. Thus, water acts like a "catalyst" which can be regenerated in the process. An isotopic tracer study [Gallardo et al., 1995] elucidated the mechanism of CO oxidation using a closed circulation system equipped with a mass spectrometer and a gas chromatography apparatus. Using <sup>18</sup>O<sub>2</sub> tracer, it was found that the reaction proceeds through a carbonate type intermediate with lattice O<sub>2</sub> participation. CO<sub>2</sub> was found to retard the rate of CO oxidation over alumina. The use of alumina as a starting material to improve CO oxidation was proven to be promising for auto emission control in developing countries [Gallardo et al., 1995].

A study on carbon deposition during CO oxidation on alumina gave very interesting results [Gallardo et al., 1996]. Carbon formed acts as an in-situ active site for CO oxidation that leads to the enhanced activity of alumina. Because carbon deposition is known to occur during hydrocarbon oxidation on

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metals and hydrocarbons are found in automobile exhaust, further studies were conducted to measure the activity of alumina for hydrocarbon oxidation. It is at this point that the surface acidity of alumina was suggested to affect the carbon deposition. This led to development of base-metal oxide as an auto emission control catalyst.

Various hydrocarbons are found in automobile exhaust such as the olefins, paraffins and the aromatics. Oxygenated hydrocarbons such as alcohols are primarily the component found in the emissions of cars run by unleaded gasoline processed by using methyl tertiary butyl ether or MTBE to increase its octane number. Thus, the study of methanol oxidation becomes significant.

Because leaded gasoline is still being used in parallel with unleaded and low-leaded gasoline in some developing countries, it is worth investigating the effect of Pb on alumina's oxidation activity. Therefore, the aim of this study was to compare the oxidation activity of alumina using different hydrocarbons and to study the effect of lead on the activity of alumina for CO and propylene oxidation. At the same time, the effect of changing the acidity of alumina is investigated to improve its overall catalytic performance for automobile exhaust treatment.

## MATERIALS AND METHODS

The study utilized the usual flow reactor system operated at atmospheric pressure. Fig. 1 shows the experimental set-up used. The liquid hydrocarbon was fed with a saturator. Gaseous feeds used were research grade purity. For safety reasons, the concentration of the feed hydrocarbon was kept below the explosion limit. The gases were analyzed by gas chromatography provided with thermal conductivity detectors.

The alumina catalyst used was BNA 069M supplied by Chi-yoda Co. of Japan. It has an average pore diameter of 30.9 nm and a surface area of 140 m<sup>2</sup>/g. Inside a quartz micro-reactor 0.5 g catalyst was set. It was pretreated at 800 °C for one hour under helium flow prior to any reaction.

Alkaline-treated alumina was prepared by a conventional impregnation method with sodium hydroxide solution to give 0.6 wt% NaOH/Al<sub>2</sub>O<sub>3</sub>. The catalyst was then dried in the oven over-

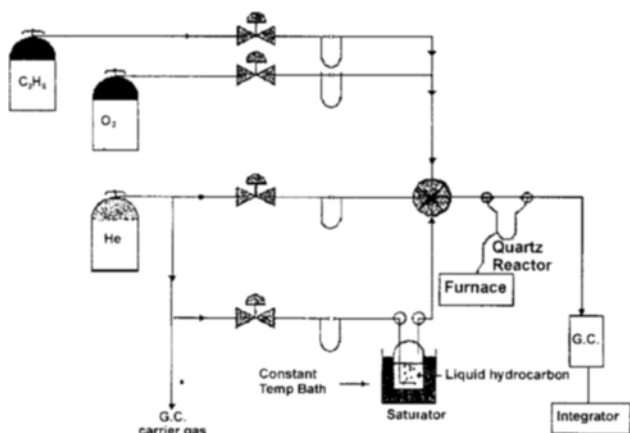


Fig. 1. Experimental set-up for hydrocarbon oxidation.

Table 1. Experimental conditions used in the experiments

CO/Hydrocarbon	CO/HC concentration (%)	Oxygen concentration (%)
CO	10.00	5.00
Toluene	0.85	7.65
n-Hexane	1.00	9.50
Methanol	5.00	7.50
Propylene	1.50	6.75

night at 110 °C. Likewise, 3 wt% CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation with cerium nitrate solution; then dried overnight at 110 °C followed by calcination in air at 700 °C. Leaded alumina was also prepared by the conventional impregnation with a solution of lead acetate to give 2 wt% Pb/Al<sub>2</sub>O<sub>3</sub>. It was dried overnight at 110 °C.

The total gas flow rate is 100 ml/minute. A stoichiometric ratio of the hydrocarbon to oxygen was used for hydrocarbon oxidation. It is the same condition used for the CO oxidation reaction. Table 1 shows these conditions. Hydrocarbons employed were toluene, n-hexane, propylene and methanol. The reaction temperature was varied from 500 °C to 750 °C. For all the tests except the time course experiment, the measurements of activity were done after 1.5 hour of the run at each temperature.

Surface areas of the used catalysts were measured with a Shimadzu Flow Sorb II 2300.

## RESULTS AND DISCUSSION

### 1. Hydrocarbon Reactivity Test

In this study, methanol represents the alcohol group, toluene represents the aromatics, hexane represents the paraffins, and propylene represents the olefins. Fig. 2 shows the effect of temperature on the activity of alumina. The activity is expressed as %hydrocarbon conversion. The temperature was varied from 500 °C to 750 °C since this is the same temperature range where CO oxidation was conducted in a previous study. Here, it is shown that methanol is very reactive on alumina giving 100 % conversion even at 500 °C. This is followed by n-hexane which is 75 % converted at 500 °C. Propylene and toluene have almost the same reactivity at 500 °C showing only 20 % and 25 % conversion, respectively. Due to the low reactivity of propylene on alumina and because 74.3 % of the

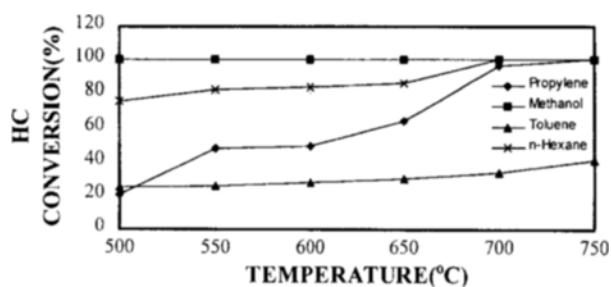


Fig. 2. Effect of temperature on hydrocarbon reactivity on alumina. Stoichiometric ratio of O<sub>2</sub> was used at a total pressure of 1 atm. Weight of catalyst is 0.5 gram and total flow rate is 100 ml/min.

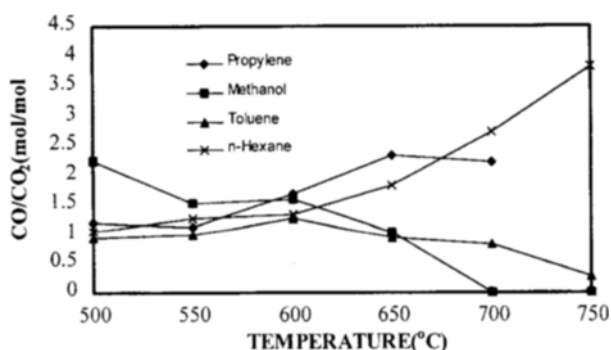


Fig. 3. Effect of temperature on the mole ratio of CO/CO<sub>2</sub> using various hydrocarbons on alumina. Stoichiometric ratio of O<sub>2</sub> was used at a total pressure of 1 atm. Weight of catalyst is 0.5 gram and total flow rate is 100 ml/min.

total hydrocarbons in automobile exhaust gases are olefins [Andersen and Boudart, 1984], further study on the oxidation of propylene over alumina is needed.

Oxidation of methanol yielded several products at different temperature. Its conversion is 100 % at all temperatures. Also, oxidation of the other hydrocarbons showed only CO as partial oxidation product. Thus, we decided to express the activity of alumina in terms of the mole ratio of the product of partial oxidation to the product of perfect oxidation (Fig. 3 shows this). From this plot, methanol gives the highest ratio with all the other hydrocarbons showing almost the same ratio at 500°C. It is clear that although methanol is reactive on alumina at 500°C, it is not selective to the formation of CO<sub>2</sub>, which is the desired product. The results when alumina surface was modified to improve its performance towards the perfect oxidation of methanol will be shown later.

In this test, a color change of the catalyst was observed after the completion of oxidation reaction from low to high temperature. Alumina turned off-white after the oxidation of n-hexane; it turned light brown after methanol oxidation; it turned grey after the oxidation of propylene and it was black after toluene oxidation. This is an indication that carbon deposition occurred in all of the hydrocarbon oxidation reactions.

## 2. Propylene Oxidation

In order to verify the effect of carbon on activity of alumina during propylene oxidation, the reaction temperature was varied by using two consecutive steps in one run. The first step is heating from 500°C to 750°C. The second step is cooling from 750°C to 500°C passing the same temperatures used in the first step. Fig. 4 shows the result. Looking at the %C<sub>3</sub>H<sub>6</sub> conversion, we see that an appreciable temperature hysteresis is formed at the lower temperature range of 500°C to 650°C. However, from 700-750°C, the hysteresis is negligibly small. Also, from 500°C to 650°C, lower activity of alumina is observed during the cooling step than in the heating step. Then, for 700°C to 750°C, the opposite trend is obtained. Thus, the heating line and cooling line intersect at about 680°C. It is evident that the hysteresis is caused by the carbon soot deposited during the reaction. It is, therefore, suggested that two parallel reaction mechanisms occur on the surface of alumina during propylene reaction with oxygen. One is the di-

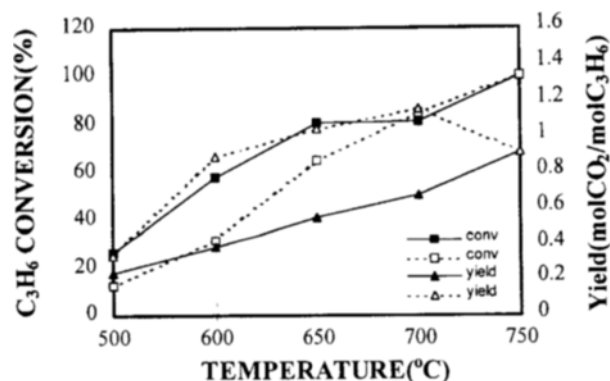


Fig. 4. Effect of temperature on C<sub>3</sub>H<sub>6</sub> conversion using alumina. Solid line is for heating and broken line is for cooling.

merization of propylene to form the carbon soot and the other is the oxidation of propylene to CO<sub>2</sub> and CO. It is known that dimerization of hydrocarbons easily occurs on acidic surfaces. In this study, the alumina surface turned gray, which is an indication of the formation of carbonaceous substance. Alumina is known to have acidic properties. At temperature lower than 680°C, it is presumed that the rate of oxidation is lower than that of dimerization. When the catalysts is heated above 680°C, the carbon is burned exposing new alumina surface because the rate of oxidation is faster than the rate of dimerization.

Fig. 4 shows the effect of carbon deposited on the yield of CO<sub>2</sub>. A large hysteresis is also formed when alumina is subjected to a heating and cooling cycle during the propylene oxidation. It shows the positive effect of carbon on the formation of CO<sub>2</sub> since the yield of CO<sub>2</sub> is always higher during the cooling step than in the heating step. It is found from the previous experiment on CO oxidation over alumina [Gallardo et al., 1996] that carbon accelerates the CO oxidation. However, in excess amount, it retards the same reaction.

Another experiment that shows interesting results and verifies the findings above was the time course activity test at different temperatures. Results of two runs at 600°C and at 700°C are shown in Fig. 5. At 600°C, the activity of alumina decreases with time until a steady state value is attained. Contrary to what is expected, the alumina activity increases with time until steady condition is reached at 700°C. However, for both temperatures, the yield of CO<sub>2</sub> decreases to a

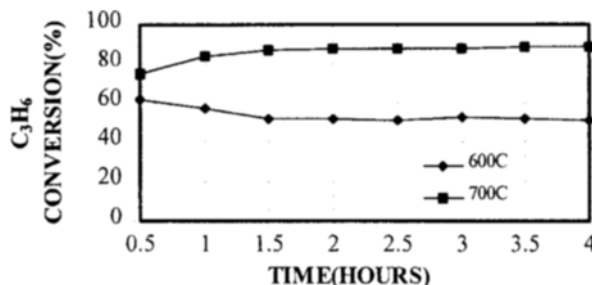


Fig. 5. Effect of time on C<sub>3</sub>H<sub>6</sub> conversion using alumina at 600°C and 700°C. Stoichiometric ratio of C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> was used.

constant value. This indicates that carbon plays a role in changing the acidity of the alumina surface. These results point out that surface acidity is the key to the development of a good catalyst for automotive emission control.

In order to reduce the acidity of alumina, 0.6 wt% NaOH on alumina was employed. This was subjected to the same activity test of varying the reaction temperature in two consecutive steps. Fig. 6 shows that the activity of the alkaline treated alumina is always higher during the heating step than in the cooling step at all temperatures except at 650 °C when the conversion is almost the same. This indicates that carbon formation is reduced as indicated by the color observed after the reaction. The catalyst only turned into light brown at the upper bed of the catalyst. It is also shown that there is a negligible hysteresis for the yield of CO<sub>2</sub>.

When alumina is compared with alkaline treated alumina, the addition of an alkali does not seem to improve the propylene conversion. The conversion is almost the same for both catalysts. However, the addition of an alkali affected the yield of CO<sub>2</sub>. Alumina gives higher CO<sub>2</sub> yield during the cooling step for all temperatures used than the alkaline treated alumina. However, during the heating step, alkalined alumina shows higher CO<sub>2</sub> yield at 700 °C and 750 °C than alumina. They have the same yield from 500 °C to 650 °C.

It is well known that CeO<sub>2</sub> not only has a redox property but also an oxygen storage capacity. In addition to this, it is also a basic metal oxide. Base metal promoters, such as cerium, are incorporated into the three-way catalyst formulations to give significant NO<sub>x</sub> and CO reductions near the stoichiometric A/F ratio [Williamson et al., 1992]. Fig. 7 shows the result of propylene oxidation over 3 wt% CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> at different temperatures following the same heating and cooling cycle described before. Ceria-alumina proves to be better than alumina since the conversion of propylene is 100 % at 600 °C and the catalyst is moderately active at lower temperature of 450 °C showing 50 % conversion of propylene. It also shows that a very small temperature hysteresis was formed showing negligible carbon deposit. We also observed that the catalyst was not discolored except at the topmost layer of the bed. The yellowish color of ceria-alumina turned to dirty white

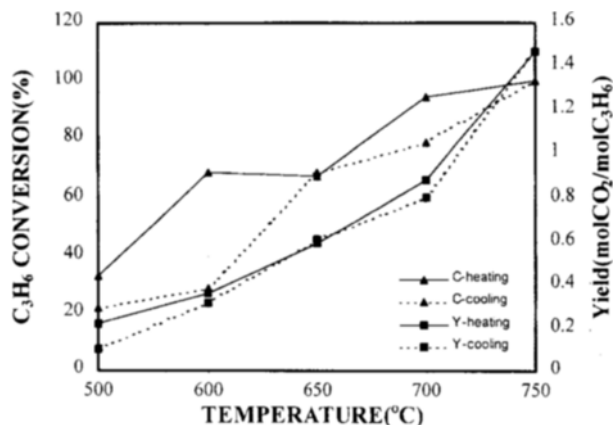


Fig. 6. Effect of temperature on C<sub>3</sub>H<sub>6</sub> conversion using alkaline treated alumina. Solid line is for heating and broken line is for cooling.

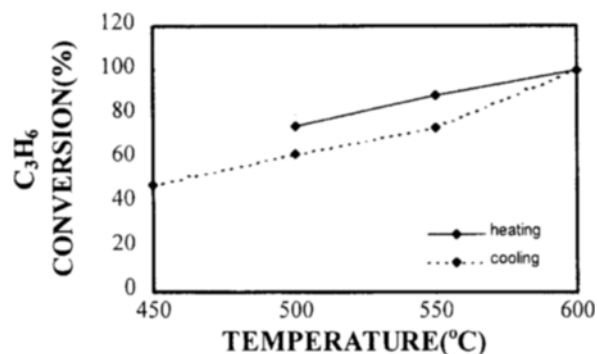


Fig. 7. Effect of temperature on C<sub>3</sub>H<sub>6</sub> conversion using CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

after the entire run. Thus, the addition of ceria decreases the acidity of alumina leading to the suppression of soot formation and increases the rate of oxidation.

### 3. Methanol Oxidation

A parallel study was also done to further verify the effect of carbon on alumina activity during methanol oxidation. Unlike propylene oxidation where only CO and CO<sub>2</sub> are primarily formed together with carbon soot and water, methanol oxidation yielded several products such as methane, dimethyl ether, CO<sub>2</sub>, CO, carbon deposits, and water. In a report [Gallardo et al., 1997], it is shown that alumina shows different selectivity to these products at different temperatures. Selectivity to CO<sub>2</sub> over alumina was improved by the addition of an alkali. Further, a 3 wt% CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst shows excellent performance to yield perfect oxidation at 700 °C. This is shown in Fig. 8. Again, the addition of ceria increases the basicity of alumina, which makes the catalyst more selective to the formation of carbon dioxide and suppresses the formation of other partial oxidation products except carbon monoxide.

### 4. Carbon Monoxide Oxidation on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and on Al<sub>2</sub>O<sub>3</sub>

The improved performance of CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> led to further investigation of its activity during CO oxidation. It is compared to the activity of alumina in Fig. 9. Ceria-alumina shows moderate activity at low temperature of 450 °C while alumina becomes active only at 600 °C. This increase in activity of alumina after the addition of ceria may be attributed to the decrease of acidity of the catalyst surface. The role of CeO<sub>2</sub> in CO oxidation is not yet fully understood. However, ceria-alumina proves to have better activity than alumina for both hydrocarbon and CO oxidation reactions.

### 5. Effect of Pb on Alumina

Results of the activity tests at different temperatures dur-

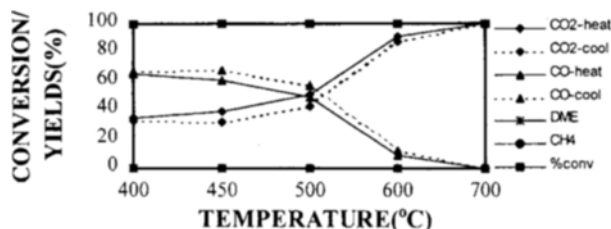


Fig. 8. Effect of temperature on methanol conversion and conversion into products using CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

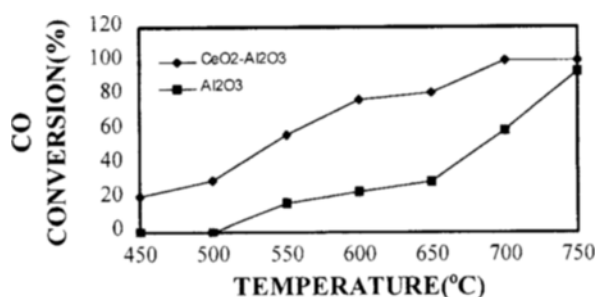


Fig. 9. Effect of temperature on CO conversion using CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Stoichiometric ratio of CO/O<sub>2</sub> was used.

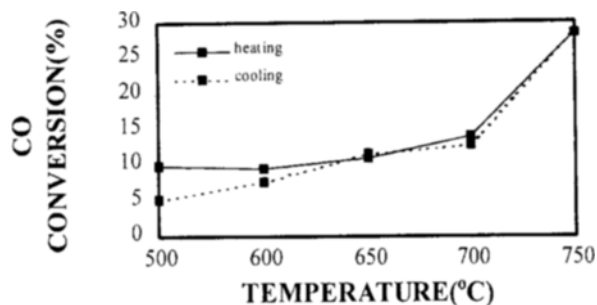


Fig. 10. Effect of temperature on CO conversion using leaded alumina.

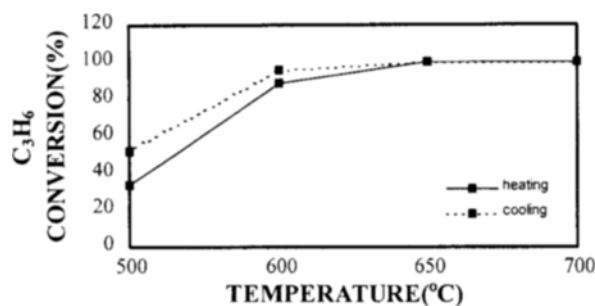


Fig. 11. Effect of temperature on C<sub>3</sub>H<sub>6</sub> conversion using leaded alumina.

ing CO oxidation and during propylene oxidation over 2 wt% Pb/Al<sub>2</sub>O<sub>3</sub> are shown in Figs. 10 and 11, respectively. It is shown that lead decreases alumina activity for carbon monoxide oxidation while it increases alumina activity for propylene oxidation. The unused and used catalysts were subjected to surface area measurements. Results are shown in Table 2. The unused leaded-alumina has a bigger surface area than the unused alumina. However, the used leaded alumina catalysts for CO oxidation and for propylene oxidation have smaller area. It can be explained by the surface area measurement why the leaded alumina exhibits higher activity for propylene oxidation. At the same time, PbO may be formed on alumina, which has a basic property. As discussed, the basicity of alumina facilitates the partial oxidation of hydrocarbons on alumina. PbO blocks the pores of alumina by forming a glassy structure, which leads to a decreased surface area. It is also worth noting that carbon deposition occurred during propylene oxidation, as evidenced by the brown discoloration at the

Table 2. Surface area measurements

Catalyst	Bet surface area (m <sup>2</sup> /g)
Unused alumina	140
Unused leaded alumina	177
Used leaded alumina for CO oxidation	151
Used leaded alumina for C <sub>3</sub> H <sub>6</sub> oxidation	135

top layer of the catalyst bed. This also led to a decrease of the catalyst surface area, and this is also why the decrease of surface area in CO oxidation is smaller than in C<sub>3</sub>H<sub>6</sub> oxidation.

## FUTURE PLANS

The development of base metal oxide catalysts is still going on with parallel studies done in Japan and in the Philippines. The salient points to consider now, based on the foregoing discussions, are summarized here.

Since carbon deposits enhance the CO oxidation and propylene oxidation to some extent, there is a need to confirm what acid sites in alumina are active towards carbon formation. There is also a need to study and confirm the formation of carbonate type of intermediate species during CO oxidation on alumina. Presently, studies using FTIR and TPD are being done to confirm this and also to measure the acid strength of alumina. It is important to correlate these to the results of the activity tests reported here.

The effect of sulfur is also important to consider in the development of auto emission control catalysts. Laboratory tests are being conducted to confirm this effect.

Ceria-alumina has been proven to be a very promising auto emission control catalyst to work partially in developing countries where emission standards are not too stringent. It is therefore important to study the effect of Pb and sulfur in the laboratory as well as to compare its acidity and basicity to alumina. All these works are being done presently. Lastly, the actual test of any catalyst of proven performance in the laboratory should be subjected to actual activity test in the field. Parallel to our laboratory work, an experimental car is now fitted with ceria-alumina catalytic converter and run in Metro Manila. The results of this field testing and laboratory studies are to be reported in another paper.

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