

## A Multi Layer Catalyst and Fuel Reforming Performance

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A multi-layer catalyst comprising of a core of oxides alumina- based silicate covering the core, and an outer layer was developed and was evaluated as to the economy. The test results showed that the catalyst, higher molecular hydrocarbons especially such a less molecular weight components, resulting in better combustion efficiency.

Key words: Multi Layer Catalyst, Fuel Reform

### 1. INTRODUCTION

Fuels for internal combustion engines have been improved to be more combustible and less pollutant in order to meet tighter exhaust emission regulations. But people's increasing concern on the effects of exhaust emissions from internal combustion engines to their health initiated more stringent regulations which require further reduction of specific species of hydrocarbons such as benzene. In Japan, a revision of the standard to lower the contents of benzene in gasoline from 5 % to below 1 % is underway, but it is still very useful to reform fuels supplied from gas stations to more combustible substances by an onboard device if it can be done. At oil refineries, such a reforming is processed by adding hydrogen and it seems almost impossible to have this kind of onboard device in vehicles, but the recent progress of material technology for warm temperature superconductivity gave a derivative of ceramic catalysts made of oxides of transition metals which can perform this reaction in the fuel tank.

### 2. HEATING VALUE OF HYDROCARBONS

The heating value of a hydrocarbon depends largely on the bonding structure of carbons in the molecule. There are 3 bonding structures of carbon to carbon in hydrocarbons and the energy required to dissociate these bondings are listed in Table I along with the bonding energy of C-H (carbon-hydrogen).

Table I Dissociation energy of carbon bonding

Bonding structure	Dissociation Energy (KJ/mol)
C - H	413.24
C - C	348.34
C = C	677.92
C ≡ C	829.41

of transition metals, an intermediate layer of an layer of a noble metal alloy covering the intermediate reforming performance and its effects on fuel with help of water contained in gasoline, can crack combustible substance like aromatics to a lower combustion efficiency.

The combustion process of hydrocarbon includes thousands of decomposition processes, but most of them are endothermic. It is well known that aromatic hydrocarbons are less combustible in comparison with paraffin primarily because its benzene ring is stable and has 3 double carbon to carbon bondings which require more dissociation energy. Hydrogen has a bigger heating value than carbon in specific weight and in the case of paraffin, the smaller the carbon number, the more the heating value per weight. This explains the typical specific heating value/weight of gasoline, diesel oil and benzene as shown in Table

Table II Heating value of fuels

Fuels	Heating value (MJ/kg)
Gasoline	47
Diesel oil	43
Benzene	40.2

It is also well known that the double bonding of carbon (C=C) is a cause of soot in diesel engines. These facts lead to a motivation to reform higher molecular weight hydrocarbons and aromatics to lower molecular weight ones, preferably smaller carbon number paraffin, aiming at the following improvements.

1. more combustible substances
2. faster combustion speed
3. more specific heating value per weight

To make these possible, it is required to add hydrogen to hydrocarbon like it is commonly done in the petroleum refinery complex, but if it is tried in low temperature, it is thought very powerful catalyst is needed.

### 3. STRUCTURE OF CATALYST

Fig 1 shows the cross-sectional view schematically illustrating the structure of the catalyst developed (1).

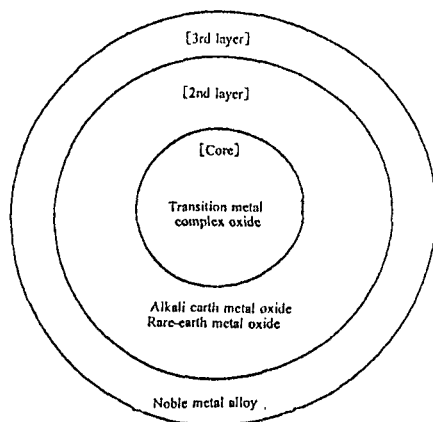


FIG. 1 Cross-sectional view of multi layer catalyst

It has a three-layer structure comprising a core of a complex oxide ceramic of transition metals namely,  $MnO_2$ ,  $NiO$ ,  $CoO$  and  $CuO$ , an intermediate layer of a silicate ceramic consisting essentially of alumina covering the core and the outer layer of ceramic containing a noble metal alloy covering the intermediate layer. The outer and intermediate layer are of porous materials having pores that allow the passage of fuels to and from the outside. The core is also porous, but the porosity is greater than that of the intermediate and outer layer. The boundaries between the individual layers are of a slanted structure in which the composition changes gradually. This allows electrons to move smoothly at the boundaries. The core has a perovskite-type crystal structure and can keep free electrons. It has also performance of an oxidation-reduction catalytic action and the electron acquired by oxidation can be transmitted to the intermediate or outer layer where the electrons reduce contamination such as sulfur, lead and other inorganic substances, resulting in regenerating catalytic performance of the intermediate and outer layer.

#### Embodiments of Catalyst

##### Core Catalyst

To a mixture consisting of 54 g of  $MnO_2$ , 15 g of  $NiO$ , 15 g of  $CoO$  and 16 g of  $CuO$ , all in powder form, was added 58 ml of a 7 percent by weight aqueous solution of polyvinyl alcohol. The mixture thus obtained was fired at  $950^\circ C$ . and the fired product was pulverized. A paste prepared by adding 30 ml of a 7 percent by weight aqueous solution of polyvinyl alcohol to the pre-fired powder was formed into balls of

approximately 2 mm in diameter. The core catalyst was obtained by sintering the balls at  $1200^\circ C$ .

##### Intermediate Layer Catalyst

To a mixture of 100 g consisting of 85 g of alumina, 5 g of kaoline and 10 g of carbon-bearing quartz was added 40 ml of a 7 percent by weight aqueous solution of polyvinyl alcohol. The mixture thus obtained was fired at  $1150^\circ C$ . and the fired product was pulverized. A paste was prepared by adding 30 ml of a 7 percent by weight aqueous solution of polyvinyl alcohol and 10 ml of a 12 percent by weight aqueous solution of calcium carbonate to the pre-fired powder. The paste thus obtained was coated over the ball-shaped core catalyst to a thickness of approximately 1 mm. By sintering the coated ball at  $900^\circ C$ , a catalyst consisting of the core coated with the intermediate layer was obtained.

##### Outer Layer Catalyst

A mixture consisting of equal amounts of a Pt—Pd—Rh alloy, which consists of Pt, Pd and Rh in a ratio of 3:1:1, and  $Al_2O_3$  was fired at approximately  $900^\circ C$ . Then, equal amounts of the fired mixture of the Pt—Pd—Rh alloy and  $Al_2O_3$ , a Mo— $Al_2O_3$  catalyst (consisting of Mo and  $Al_2O_3$  (consisting of  $Al_2O_3$  and vanadium oxide in a ratio of 9:1), an Ag— $Al_2O_3$  catalyst (consisting of Ag and  $Al_2O_3$  in a ratio of 1:9) and a  $La_{0.5}$ — $Sr_{0.5}CoO_3$  catalyst were mixed (weighing 100 g in total). A paste of the mixture was prepared by adding 30 ml of a 7 percent by weight aqueous solution of polyvinyl alcohol and 10 ml of a 12 percent by weight aqueous solution of calcium carbonate. The obtained paste was coated over the fired catalyst ball consisting of the core and intermediate layer to a thickness of approximately 1 mm. A three-layer ceramic catalyst was obtained by firing the coated ball at  $670^\circ C$ . in a carbon monoxide atmosphere.

#### Reforming Performance

In 1 liter of light oil was immersed 130 mg of the catalyst balls prepared as described above. The light oil was allowed to stand for one hour at room temperature and gas-chromatographed. By using a Hewlett-Packard's 5290 series II chromatograph and an aluminum powder column, chromatography was carried out at  $350^\circ C$ . FIGS. 2 and 3 show

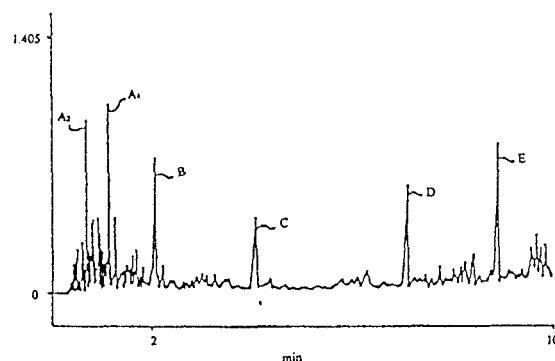


FIG. 2 BEFORE CATALYST IMMERSION

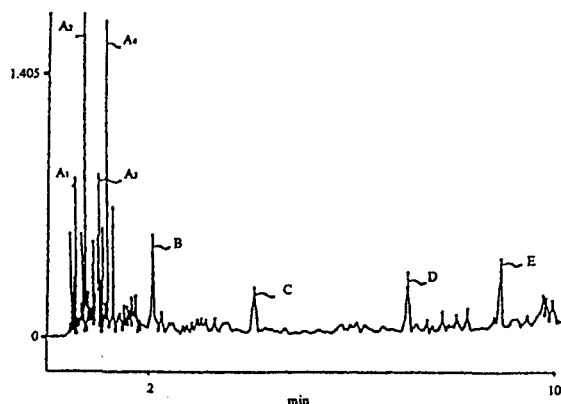


FIG. 3 AFTER CATALYST IMMERSION

chromatograms obtained before and after the immersion of the catalyst balls. In FIGS. 2 and 3, A<sub>1</sub> and A<sub>2</sub> denote methane-based combustible substances, A<sub>3</sub> ethane-, ethylene- and acetylene-based combustible substances, A<sub>4</sub> propane- and propylene-based combustible substances, B pentane, C butane, D methylpentene, and E benzene. As is obvious from the chromatograms, incombustible substances, such as methylpentene and benzene, decrease and combustible substances increase after immersion of the catalyst according to this invention.

Activation of Oxygen Dissolved in Fuel

In 1 liter of gasoline was immersed 130 mg of the catalyst balls prepared as described above. Production of oxygen radicals in the gasoline that was allowed to stand at room temperature for one hour was confirmed by electron spin resonance (ESR) spectrum (FIG. 4). a<sub>1</sub> to a<sub>8</sub> designate oxygen radicals.

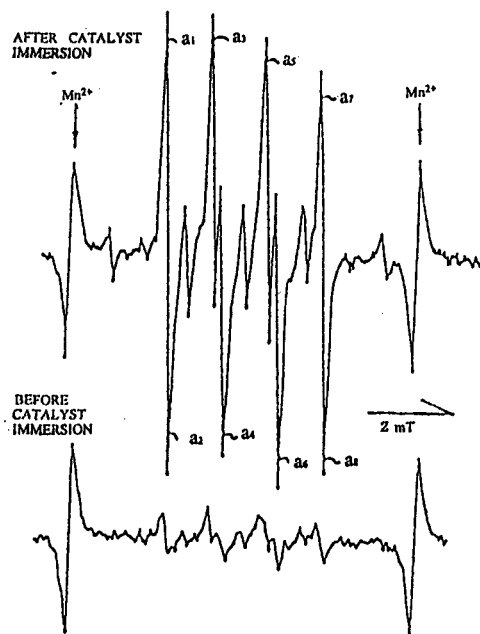


FIG. 4 ESR of Oxygen Radicals in Reformed

**Decrease of Aldehyde Concentration in Exhaust Gas**  
By immersing approximately 8 g of the catalyst prepared as described above in the fuel tank (having a capacity of 60

liters) of automobiles equipped with a 1200 cc gasoline engine, the relationship between the rotating speed of the engine and the total aldehyde concentration in the exhaust gas was determined. The concentration was determined by measuring the absorption spectrum obtained by spectrum analysis (by using an infrared-ray spectroscope FTIR-2 manufactured by Shimadzu Corp.). FIG. 5 shows the results obtained with and without the immersion of the catalyst (averaged over six automobiles). As can be seen in FIG. 5, immersion of the catalyst significantly decreased the total aldehyde concentration irrespective of the engine speed.

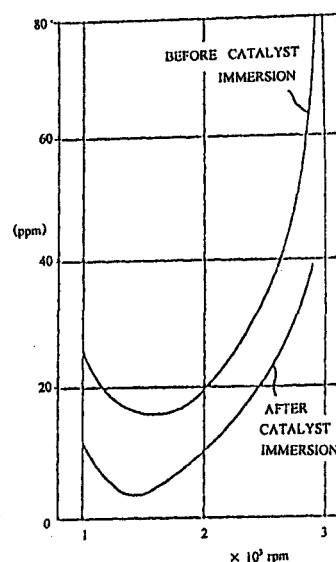


FIG. 5 Aldehyde Concentration in Exhaust Gas

Decrease of NOx Concentration in Exhaust Gas

By immersing approximately 8 g of the catalyst prepared as described above in the fuel tank (having a capacity of 60 liters) of automobiles equipped with a 1200 cc gasoline engine, the relationship between the running speed of the automobile and the NOx concentration in the exhaust gas

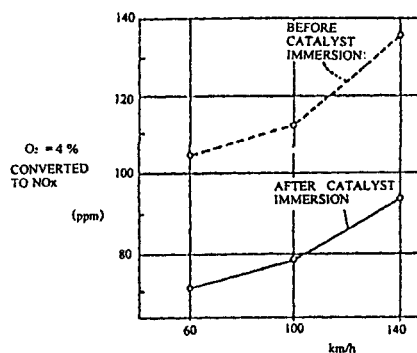


FIG. 6 NOx Concentration in Exhaust Gas

was determined. The concentration was determined by gas chromatography. FIG. 6 shows the results obtained with and without the immersion of the catalyst. As can be seen in FIG.

6. immersion of the catalyst significantly (by approximately 29 to 33 percent) decreased the NO<sub>x</sub> concentration in the exhaust gas irrespective of the running speed. The thermal decomposition temperature (ignition point) measured by differential thermal analysis dropped by approximately 7° C. from 278° C. before the immersion of the catalyst to 271° C. after the immersion. This temperature drop is considered to suppress the evolution of NO<sub>x</sub>.

**Composition of Combustion Gases in the Cylinders** By immersing approximately 8 g of the catalyst prepared as described above in the fuel tank (having a capacity of 60 liters) of automobiles equipped with a 1200 cc gasoline engine, the composition of combustion gases in the engine cylinders was determined by gas chromatography. Five milliliters of gases discharged when the pistons returned to the original position after ignition and explosion in the

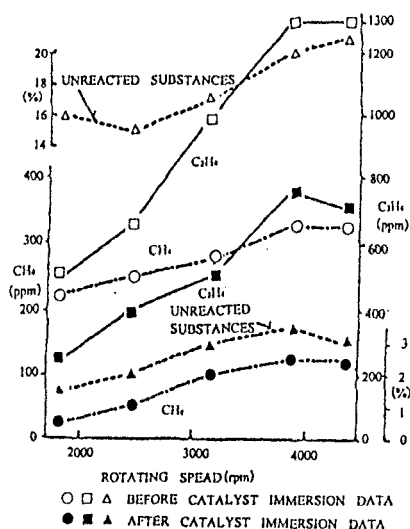


FIG. 7 Composition of Combustion Gases

cylinders were sampled as specimens. As can be seen in FIG. 7 that shows the obtained results, the unreacted substances significantly decreased from approximately 15 to 21 percent before the immersion of the catalyst to approximately 1.5 to 3.5 percent after the immersion. The concentrations of methane and ethylene also decreased greatly after the immersion of the catalyst.

#### Relationship between Catalyst and Octane Number

Changes in octane number were determined by immersing different quantities of the catalyst prepared as described earlier in regular gasoline whose initial octane number was approximately 86 before the immersion. As shown in FIG. 8, the immersion of the catalyst significantly increased octane number. Octane number increased substantially linearly with an increase in the quantity of the catalyst immersed (mg per liter).

#### Relationship with Combustion Efficiency

Combustion efficiencies of gasoline engines before and after immersing the catalyst in regular gasoline at a rate of 130 mg per liter were determined. FIG. 9 shows the combustion efficiencies before and after the immersion of the catalyst in regular gasoline. The measurements were taken under the conditions where constant fuel consumption was

maintained. As can be seen in FIG. 9, the catalyst immersion increased combustion efficiency by approximately 30 percent when the air-fuel ratio was 16.7.

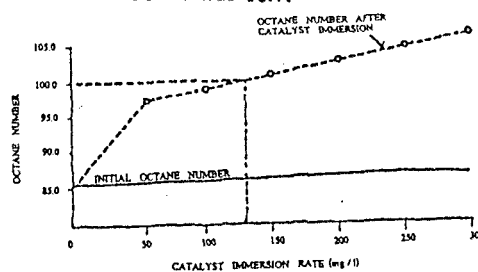


FIG. 8 Relationship between Catalyst and Octane Number

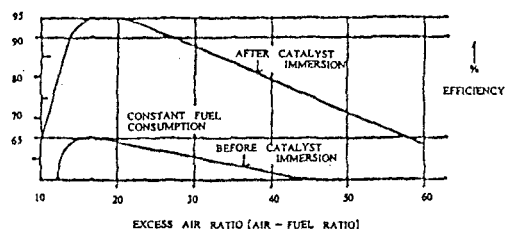


FIG. 9 Relatio with Combustion Efficiency

## 4. SUMMARY

A fuel reforming performance of a multi-layer catalyst comprising of a core of oxides of transition metals, an intermediate layer of an alumina-based silicate covering the core, and an outer layer of a noble metal alloy covering the intermediate layer was confirmed qualitatively by gas chromatographic analysis and the fuel treated with this catalyst exhibit an improvement of fuel economy and reduction of pollutant exhaust emissions at low load and low engine rpm. The future trend of combustion technology is moving toward the active radical combustion in which specific hydrocarbon species with fast combustibility are preferred and aromatics which have higher a octane number but less combustibility will not be preferred. This ceramic catalyst can provide engineers a powerful tool to reform such aromatics to better combustible hydrocarbons so that they can improve internal combustion engines which are being challenged by fuel cells with respects to the fuel economy and pollutant emissions.

## REFERENCE

- (1) Ichimura S.: Fluid fuel reforming ceramic catalyst and their manufacturing methods. Japanese patent pending:H9-103680