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# Investigation of Alumina-Supported Ni and Ni-Pd Catalysts by Partial Oxidation and Steam Reforming of n-Octane

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**Abstract**−A series of nickel and nickel-palladium supported upon alumina catalysts were prepared in order to obtain a suitable catalyst that could be used in the process of producing hydrogen by partial oxidation and steam reforming of n-octane. Hydrogen production by partial oxidation and steam reforming (POSR) of n-octane was investigated over alumina-supported Ni and Ni-Pd catalysts. The process occurred by a combination of exothermic partial oxidation and endothermic steam reforming of n-octane. It was found that $Ni/Al_2O_3$ catalyst activity was high at high temperatures and increased with the Ni loadings. Its activity, however, was not obviously increased when Ni loadings were over 5.0 wt%. Compared with nickel catalyst, the bimetallic catalyst of $Ni\text{-}Pd/Al_2O_3$ showed markedly increased activity and hydrogen selectivity at experimental conditions. The catalytic performance also became more stable when the palladium was added, which indicated that palladium plays an essential role in the catalytic action. The used catalysts of $Ni\text{-}Pd/Al_2O_3$ were regenerated three times by using air at space velocity of 2,000 $h^{-1}$ to obtain a long duration catalyst. Also, the typical catalyst was characterized by using SEM, BET, TG and ICP methods in detail.

Key words: Fuel Cells, Partial Oxidation, Steam Reforming, Regeneration, Hydrocarbons

## INTRODUCTION

Hydrogen is a clean burning and highly reactive fuel that offers high thermal efficiencies of 35-45% in comparison with 25-30% typical of normal petroleum-fueled engines [Wang, 2000; Tang and Yang, 1995; Chi et al., 1990]. Hydrogen-powered vehicles using fuel cells (e.g., polymer electrolyte fuel cell (PEFC)) are, therefore, under development in an effort to reduce $CO_2$ emissions that accelerate global warming.

During the 1970s, the Jet Propulsion Laboratory proposed the concept of injecting hydrogen into an internal combustion engine [Keith, 1994] as a way of improving efficiency and lowering $NO_x$ emissions. In the following decade, Volkswagen tested a similar concept for methanol-combustion engines [Jiang, 1993], again using some of the primary fuel to produce hydrogen in situ. It now seems highly probable that internal-combustion powered vehicles will be superseded by electric vehicles in the future. The incentives for this change come from the stringent legislation for controlling local pollution. In the design of vehicles, the conflicting demands of both high performance and environmental protection can be overcome by using a fuel cell to generate on-board electric power. The paramount issue facing fuel cells right now is how to get the hydrogen to the vehicles. One solution to this problem is the on-board hydrogen generation from a suitable high energy density liquid fuel. In recent years, many researchers have worked on the technologies of producing hydrogen from methanol, ethanol and hydrocarbons [Jiang, 1993; Ronny and Michal, 1997; Lee and Park, 1998], such as catalytic partial oxidation of methane [Aparicio, 1997; Dybkijar, 1995; Lee and Yoon, 2001; Yoon et al., 1999; Kong et al., 1999], steam reforming of methanol and ethanol [Qi, 1999], direct methanol decomposition [Lee et al., 1998], and steam reforming of heavy oil [Wang, 2000]. Compared with the above fuels, gasoline has the advantages of higher heat value, large amounts of storage hydrogen and steady supply as countless power stations can be found all over the world. The method of producing hydrogen from gasoline through partial oxidation and steam reforming enjoys the merit of low energy requirement, due to the opposite contribution of the exothermic hydrocarbon oxidation and endothermic steam reforming. The process, however, needs a suitable and active catalyst, which is not well developed at present time.

The objective of the present investigation is to develop an effective catalytic system for the selective production of hydrogen for fuel cell applications by POSR of hydrocarbons. A series of nickel and nickel-palladium supported upon alumina catalysts were prepared in order to obtain a suitable catalyst that could be used in the process of producing hydrogen from n-octane by POSR method. Also, the used catalysts of $Ni/\gamma\text{-}Al_2O_3$ and $Ni\text{-}Pd/\gamma\text{-}Al_2O_3$ were regenerated three times by using air at 600°C and space velocity of 2,000 $h^{-1}$ to obtain a long duration catalyst. Finally, the typical catalyst was characterized by using SEM, BET, TG and ICP methods in detail.

## EXPERIMENTAL

### 1. Experimental Setup

Catalytic experiments were performed in a fixed-bed reactor at atmospheric pressure. A scheme of the experimental system is depicted in Fig. 1. The reactor was constructed with a stainless steel pipe of 10 mm inner diameter and 500 mm length. At the bottom a

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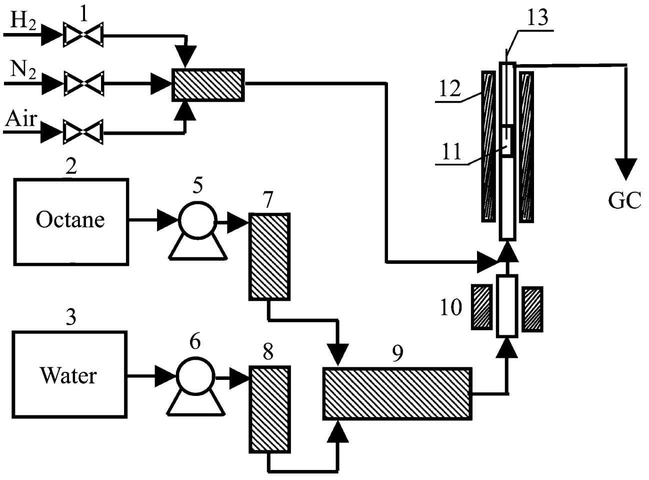


**Fig. 1. Schematic view of the experimental set-up for reaction and regeneration.**

1. Adjusting valve
2. Octane vessel
3. Water vessel
4. Gas mixing vessel
5. Oil metering pump
6. Water metering pump

7, 8. Vaporizer
9. Reactant mixing vessel
10. Preheater
11. Catalyst bed
12. Temperature controller
13. Thermocouple

perforated gas distributor was equipped. The reactor was placed inside an electric furnace equipped with an electric heater driven by a proportional-integral-derivative (PID) electronic temperature controller. About 1 ml catalyst was sandwiched between quartz wool. The temperature of the catalytic bed was monitored with a thermocouple sliding inside a stainless steel pipe that was well inserted in the catalyst bed. Because of the high exothermic hydrocarbon oxidation and endothermic steam reforming, the catalyst bed temperature was varied at the beginning of the reaction. All the data were collected when the temperature equilibrium was established.

## 2. Catalyst Preparation

The catalysts used in the experiment were obtained by the impregnation of $Al_2O_3$ support with the solution containing the desired ionic metals, followed by drying in an oven at 80 °C overnight under vacuum condition and calcining in a muffle furnace at 800 °C for 6 h. The solution temperature during impregnation was kept constant at 35 °C by using a thermostatic bath. The reduced catalyst was obtained through reducing catalyst in the fixed-bed reactor at 450 °C with a mixture of hydrogen and dilute nitrogen that were fed to the reactor via the mass controller. All the prepared catalysts were kept in a drying utensil and used as catalysts for the POSR reaction.

## 3. Experimental Method

n-Octane (99.99% purity), which was used as experimental reactant instead of gasoline for the simplicity of the experimental procedure, was tested as feedstock through POSR for the production of hydrogen. Distilled water was fed through a metering pump and got vaporized in the preheating section prior to injection into the reactor; n-octane was likewise sent through a metering pump into the reactor. n-Octane was vaporized in the preheating zone before being fed into the reactor. Product gas from the reactor was analyzed by two sets of gas chromatographs. $H_2$, CO, $CO_2$, $CH_4$, $N_2$ were measured by a thermal conductivity detector (TCD) with a column consisting of Molecular sieve 5A and 13X with argon as a carrier gas at 120 °C. Whereas $C_2$, $C_3$ and other organic compounds were analyzed by an OV-1 capillary column connected to flame ionization detector (FID) at 30 °C. C, H and O balance always closed within ±5%. The catalyst activities and selectivity were evaluated based on its conversion of n-octane and hydrogen production at the conditions of determined molar ratios of $H_2O$/lC and $O_2$/n-$C_8H_{18}$, respectively. All the experiments were conducted with a gas hourly space velocity (GHSV) of 1,000 $h^{-1}$. During the activity tests (over Ni and Ni-Pd/$Al_2O_3$ catalysts), temperature was varied in the range of 500-750 °C. The used catalyst was also regenerated in this set-up through combustion method with air at 600 °C temperature and 2,000 $h^{-1}$. After that, the catalyst again was reduced with mixture of hydrogen and dilute with nitrogen before the process occurred for producing hydrogen by POSR of n-octane.

## 4. Characterization of Typical Catalysts

To elucidate the catalyst activity deterioration, fresh catalyst and typical used catalysts were characterized. Surface area was measured by a Micromeritics ASAP2010 BET apparatus using $N_2$ adsorption. Surface characterization of the catalysts was done by the scanning electron microscope (SEM), and its composition was measured by inductively coupled plasma (ICP). TG characterization results were obtained by using the apparatus of PCT-1A.

# RESULTS AND DISCUSSION

## 1. Performance of Ni/$Al_2O_3$ Catalysts

The $O_2/C_8H_{18}$ and $H_2O/C$ gas mixtures with a molar ratio of 1.0 and 3.0, respectively, were used as the feed gas and the partial oxidation, and steam reforming of n-octane was conducted at atmospheric pressure, 500 °C and 750 °C over $Al_2O_3$-supported Ni catalysts. As shown in Fig. 2, n-octane conversion and hydrogen selectivity rose when the Ni loading was increased from 1.0 to 5.0 wt% at the same reaction temperature; they remained, however, almost unchanged when Ni loadings≥5.0 wt%. It can be noted that the supported Ni catalyst activities rose notably when the temperature was increased from 500 to 750 °C at the same Ni loadings. The 5.0 wt% Ni/$Al_2O_3$ catalyst provided about 90% n-octane conversion, 92% hydrogen selectivity at 750 °C temperature.

## 2. Performance of Ni-Pd/$Al_2O_3$ Catalysts

Pd is the less expensive among the noble metals, and it is more

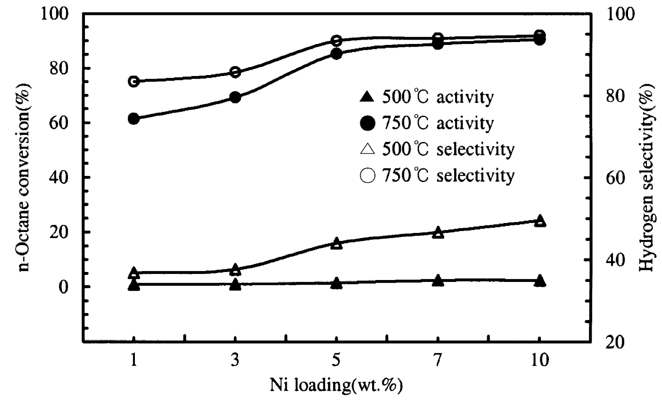


**Fig. 2. Effect of Ni loadings on the catalytic activity and selectivity at reaction temperature of 500 °C and 750 °C, respectively (mol$O_2$/mol$C_8H_{18}$=1.0, mol$H_2O$/molC=3.0).**

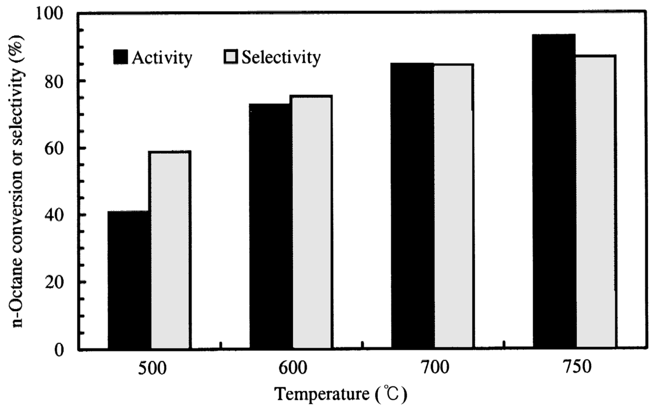


**Fig. 3. Effect of adding little Pd on Ni-Pd/$Al_2O_3$ catalyst activity and selectivity at different temperature (reaction conditions are same as in Fig. 2).**

stable than Ni because it does not form carbonyls with high vapor pressure at the reaction conditions [Jiang, 1993]. Fig. 3 shows the n-octane conversion and hydrogen selectivity over Ni-Pd/$Al_2O_3$ catalyst as a function of the furnace temperature at molar ratio of $O_2/C_8H_{18}=1.0$, $H_2O/C=3.0$, respectively. It shows that addition of 0.8 wt% Pd into Ni/$Al_2O_3$ catalyst notably improved its activity and hydrogen selectivity at same molar ratios of $O_2/C_8H_{18}$ and $H_2O/C$, which indicates that palladium plays an essential role in POSR reaction. Compared with the Ni/$Al_2O_3$ catalyst, the Ni-Pd/$Al_2O_3$ catalyst remarkably improved its activity and hydrogen selectivity at lower reaction temperature, as shown in Fig. 2 and Fig. 3.

## 3. Stability of Ni/$Al_2O_3$ Catalyst

The effect of time on stream, up to 50 h, is presented in Fig. 4 for the 5.0 wt% fresh and multi regenerated Ni/$Al_2O_3$ catalyst. As shown in Fig. 4, the n-octane conversion for the fresh catalyst remained almost unchanged during the 30 h time. After that, the conversion decreasing with time provided evidence for certain instability onstream in the POSR process. It also shows that the decreasing tendency is evident with the multi regeneration cycles for the used catalyst. To know some reasons why Ni/γ-$Al_2O_3$ catalyst easily lost its activity during the POSR process, some characterization results were obtained by using basic methods. Those results are listed in Table 1. Characterization results show that Ni/γ-$Al_2O_3$ catalyst surface area was obviously decreased with regeneration cycles. Compared with fresh catalyst, the surface area of third regeneration catalyst was decreased about 30%. It also provided the fact that the amount of carbon deposition on Ni/γ-$Al_2O_3$ was increased with regeneration cycles. However, the content of Ni on Ni/γ-$Al_2O_3$ catalyst was invariable. It should be concluded that the instability reasons of Ni/γ-$Al_2O_3$ catalyst during the POSR process were mainly probably caused by sintering phenomena and carbon deposition. Further study to investigate Ni/γ-$Al_2O_3$ catalyst instability during POSR process should be carried out.

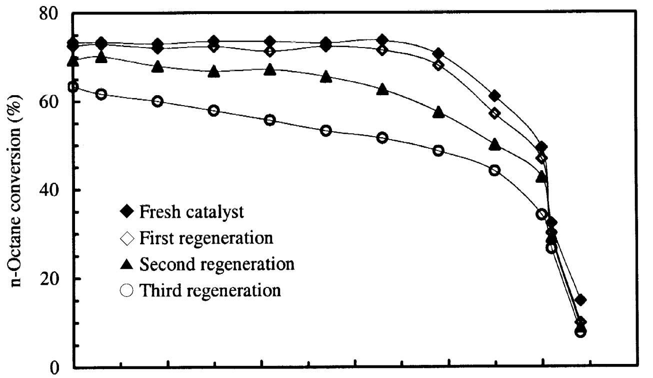


**Fig. 4. Effect of time on stream on the catalytic activity of Ni/$Al_2O_3$ ($molO_2/molC_8H_{18}=1.0$, $molH_2O/molC=5.0$, T=750).**

**Table 1. Characterization results of 5.0 wt% Ni/γ-$Al_2O_3$ catalyst**

| Cycles | Surface area ($m^2$/g-cat) | Carbon deposition (mg/g-cat) | Content of Ni (wt%) |
|---|---|---|---|
| Fresh catalyst | 152 | 5.4 | 5.0 |
| Third regeneration | 106 | 5.8 | 5.0 |

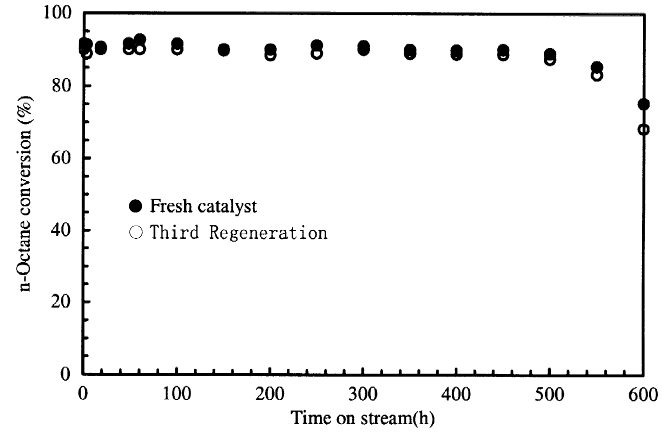


**Fig. 5. Effect of time on stream on the catalytic activity of Ni-Pd/$Al_2O_3$ ($molO_2/molC_8H_{18}=1.0$, $molH_2O/molC=3.0$, T=750).**

## 4. Stability of Ni-Pd/$Al_2O_3$ Catalyst

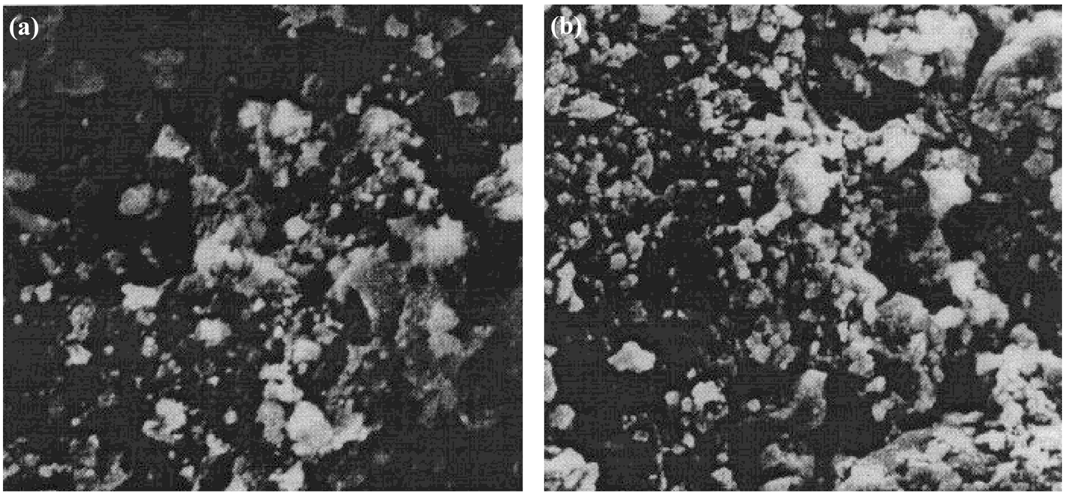
The effect of time on stream, up to 600 h, is presented in Fig. 5 for Ni-Pd/$Al_2O_3$ catalyst. As shown in Fig. 5, the n-octane conversion for fresh and multi cycles regenerated catalyst remained almost unchanged during the 500 h time, which indicated that bimetallic catalyst of Ni-Pd/$Al_2O_3$ could be a promising catalyst for the production of hydrogen from hydrocarbons. Some characterization results of Ni-Pd/γ-$Al_2O_3$ catalyst were also obtained as listed in Table 2. Those results show that Ni-Pd/γ-$Al_2O_3$ catalyst surface area, amounts of carbon deposition on catalyst and content of catalytic components of Ni and Pd were almost invariable with regeneration cycles during the POSR process. Especially, the amount of carbon deposition on Ni-Pd/γ-$Al_2O_3$ catalyst was decreased about 70% compared with that of carbon deposition on Ni/γ-$Al_2O_3$ catalyst, which shows that Pd plays an essential role in the catalytic action.

## 5. SEM Characterization of the Catalysts

The catalysts surface property for the fresh and third regenerated catalysts was characterized by the scanning electron microscope (SEM). The Ni/$Al_2O_3$ catalyst SEM is in Fig. 6. It shows that the surface property for the fresh and third regenerated Ni/$Al_2O_3$ catalyst had become different. The third regenerated catalyst evidently had sintering phenomena, which partially indicated the reason why

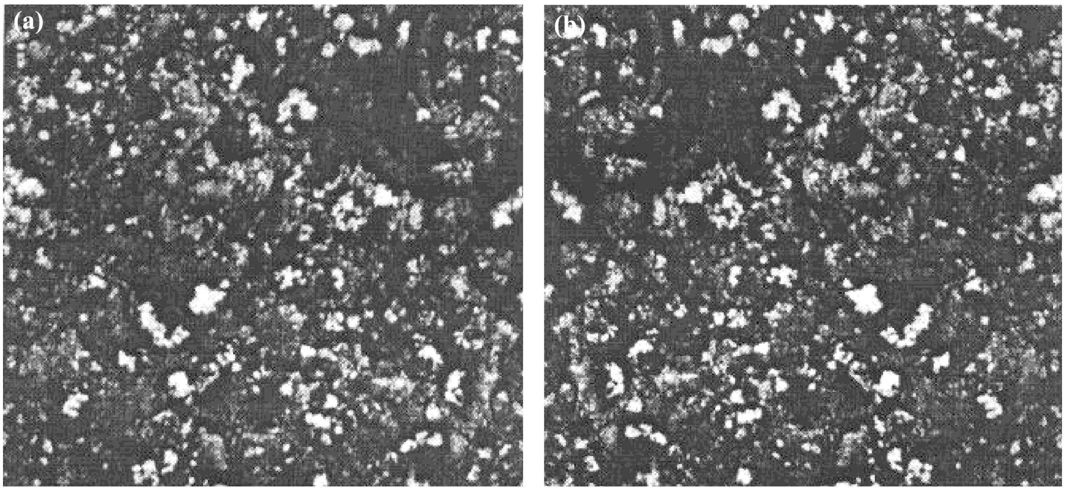
**Table 2. Characterization results of Ni-Pd/$\gamma$-$Al_2O_3$ catalyst**

| Cycles | Surface area ($m^2$/g-cat) | Carbon deposition (mg/g-cat) | Content of Ni (wt%) | Content of Pd (wt%) |
|---|---|---|---|---|
| Fresh catalyst | 148 | 1.6 | 5.0 | 0.8 |
| Third regeneration | 145 | 1.9 | 4.9 | 0.8 |



(a) Fresh catalyst (b) Third regeneration

**Fig. 6. SEM results of the fresh and third regenerated Ni/$Al_2O_3$ catalyst.**



(a) Fresh catalyst (b) Third regeneration

**Fig. 7. SEM results of the fresh and third regenerated Ni-Pd/$Al_2O_3$ catalyst.**

the deterioration tendency of catalyst activity became more serious with the increasing regeneration cycles.

The Ni-Pd/$Al_2O_3$ catalyst SEM is in Fig. 7. It shows that the surface property for the fresh and third regenerated Ni-Pd/$Al_2O_3$ catalyst had become almost same, which possibly indicates the reason why the Ni-Pd/$Al_2O_3$ catalyst had better duration for the process of production hydrogen by POSR of n-octane at the experimental conditions.

## CONCLUSIONS

A series of nickel and nickel-palladium supported upon alumina catalysts were prepared in order to obtain a suitable catalyst that could be used in the process of producing hydrogen by POSR of n-octane. The following conclusion could be obtained according to the experimental results:

1. For $Al_2O_3$-supported Ni catalysts, its activity and selectivity were increased when Ni loading was increased from 1.0 to 5.0 wt%; they remained almost unchanged for Ni loadings≥5.0 wt%.
2. The Ni/$Al_2O_3$ catalyst showed unstable properties during our experiment up to 50 h. Its deterioration became evident with the increasing multi regeneration cycles.
3. The instability of Ni/$\gamma$-$Al_2O_3$ catalyst during the POSR pro-

cess was mainly probably caused by sintering phenomena and carbon deposition.

4. When small amount of Pd was added into Ni/$Al_2O_3$ catalyst, its activity and selectivity were improved notably, which indicates that palladium plays an essential role in the catalytic action.

5. The fresh and multi regeneration Ni-Pd/$Al_2O_3$ catalyst remained stable during the POSR process that could last for 500 h, which indicates that bimetallic catalyst of Ni-Pd/$Al_2O_3$ could be a promising catalyst for the production of hydrogen from hydrocarbons.

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