# CATALYTIC STEAM AND AUTOTHERMAL REFORMING OF USED LUBRICATING OIL (ULO) OVER RH- AND NI-BASED CATALYSTS

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*Summary*

The steam reforming of used lubricating oil (ULO) over Ni- and Rh-based catalysts supported by Ce-$ZrO_2$ and $Al_2O_3$ is studied. Among all catalysts, Rh/Ce-$ZrO_2$ (10 wt% Rh) provides considerably higher reforming reactivity with excellent resistance toward carbon deposition compared to other three catalysts. Above 900°C, the main products from the steam reforming of ULO over Rh/Ce-$ZrO_2$ are mainly $H_2$, CO, and $CO_2$ with slight formation $CH_4$ observed. As for Ni/Ce-$ZrO_2$ and Ni/$Al_2O_3$, significant deactivation with time is detected; in addition, considerable amounts of $C_2H_4$ and $C_2H_6$ are also found in the product along with $H_2$, CO, $CO_2$ and $CH_4$. The effect of $O_2$ adding was further studied. This addition significantly reduces the degree of carbon deposition as well as promotes the conversion of hydrocarbons to CO and $H_2$. At the suitable amount of $O_2$, high $H_2$ yield comparable to that from the steam reforming over Rh-based catalysts can be achieved. Importantly, it must be aware that the introducing of too high $O_2$ content resulted in the lower $H_2$ production due to the combustion of $H_2$ by $O_2$ adding. Hence, the inlet $O_2$/ULO must be carefully concerned.

*Keywords*

Autothermal, Reforming, Ceria/Zirconia, Lubricating oil

## Introduction

Hydrogen-rich gas is one of the promising clean fuels in the near future. Currently, the main existing process for synthesis gas production is catalytic steam reforming and partial oxidation of various hydrocarbons e.g. natural gas, ethanol, methanol and oils. Nevertheless, the use of these hydrocarbon feedstocks for hydrogen production always faces high competitive utilization with several applications. On this basis, the production of hydrogen from wastes has the great benefit in terms of energy and environmental aspects. Used lubricating oil (ULO) is known as an important hazardous waste that currently be generated more than 35 million tons from industrial sector a year; it is one of the most serious materials for human and environment due to its toxicity and difficulty in management. In the present work, it is aimed to develop the reforming catalysts that efficiently convert ULO to hydrogen as the clean fuel, which would provide the great benefit in terms of energy and environmental aspects.

. Selection of catalyst support material is a major consideration in the present work since it has widely been reported that metal catalysts are not very active when supported on inert oxides[1]. It has been reported that a promising catalyst system for the reforming reactions appeared to be a metal on ceria-based supports[2-5]. Here, the steam and autothermal reforming of ULO was studied over Ni/Ce-$ZrO_2$, Ni/$Al_2O_3$, Rh/Ce-$ZrO_2$ and Rh/$Al_2O_3$.

## Results and Discussions

***Stability and activity toward steam reforming***

The steam reforming of ULO were studied at 900°C by introducing ULO and steam with the inlet steam to carbon ratio of 10. It was found that the reactivities of Ni/$Al_2O_3$ and Ni/Ce-$ZrO_2$ declined with time before reaching a significantly lower steady-state rate, while the activity of Rh/Ce-$ZrO_2$ declined slightly. The post-reaction temperature-programmed oxidation (TPO) experiments were carried out after a helium purge by introducing of 10% oxygen in helium in order to determine whether the observed deactivation is due to the carbon formation.

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Table 1 Product distribution and degree of carbon formation after exposure in partial oxidation of ULO at 900 °C for 48 h

| Catalyst | Product distribution (%) | | | | | | Carbon |
|---|---|---|---|---|---|---|---|
| | $S_{H2}$ | $S_{CO2}$ | $S_{CO}$ | $S_{CH4}$ | $S_{C2H4}$ | $S_{C2H6}$ | Formation |
| Rh/Ce-$ZrO_2$ | 77.1 | 48.2 | 42.2 | 7.4 | 1.8 | 0.4 | 0.8 |
| Rh/$Al_2O_3$ | 68.4 | 33.1 | 29.7 | 31.4 | 4.9 | 0.9 | 1.4 |
| Ni/Ce-$ZrO_2$ | 65.2 | 28.2 | 21.1 | 44.2 | 5.4 | 1.1 | 2.3 |
| Ni/$Al_2O_3$ | 63.0 | 23.2 | 19.9 | 49.6 | 5.5 | 1.8 | 2.6 |

TPO experiments detected significant amount of carbon species on the surface of Ni/$Al_2O_3$ and Ni/Ce-$ZrO_2$ whereas only small amount of carbon (CO and $CO_2$ from the TPO) was observed from Rh/Ce-ZrO2. Table 1 below presented the product distribution from this reaction and the detected carbon formation over several catalysts.

***Reactivity toward steam reforming with co-fed oxygen***

The dependence of oxygen on the yield of hydrogen production over Ni/Ce-$ZrO_2$ was non-monotonic. The yield of hydrogen production increased with increasing inlet $O_2$ partial pressure until the inlet $O_2$ to carbon ratio reached 0.8. Then, oxygen presented a negative effect on the hydrogen yield at higher $O_2$ to carbon molar ratio values. It was found that higher hydrogen, carbon dioxide, and carbon monoxide were observed from the oxidative steam reforming, whereas less methane, ethane, and ethylene were found at the same operating conditions. The post-reaction TPO were then carried out to determine the degree of carbon formation on catalyst surface; the quantities of carbon deposited also reduced with increasing oxygen content.

# Conclusions

Rh/Ce-$ZrO_2$ provided excellent reactivity towards the steam reforming of ULO in terms of its high $H_2$ yield and great resistance toward carbon deposition. We indicated that Ce-$ZrO_2$ support plays an important role to improve the reforming performance due to the high oxygen storage capacity (OSC) of CGO. The additions of $O_2$ along with ULO and $H_2O$ can reduce the degree of carbon deposition and promote the conversions of $CH_4$, $C_2H_4$, and $C_2H_6$ to CO and $H_2$ over Ni/Ce-$ZrO_2$. The major consideration is the suitable co-fed reactant/ULO ratio. The presence of too high $O_2$ could reduce the yield of $H_2$.

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