

# HIGHLY EFFICIENT CONVERSION OF GASOLINE ON NOVEL Ni-Re ALLOY CATALYSTS FOR PRODUCING HYDROGEN: ENHANCEMENT OF CATALYST STABILITY BY MODIFICATION WITH Ce

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## Abstract

The catalytic performance of Ni-Re/Al<sub>2</sub>O<sub>3</sub> is remarkably improved by addition of ceria to the catalyst for oxidative steam reforming of gasoline to produce hydrogen. Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits the better activity maintenance than Ni-Re/Al<sub>2</sub>O<sub>3</sub> for oxidative steam reforming of sulfur-containing gasoline fuel. The optimum ratios of Ni/Re/Ce for the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts is about 10/2/2-4.

## Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered as the most appropriate power sources for future generation vehicles because of their higher energy efficiency and lower emissions. Higher energy efficiency itself will lead to a reduction in carbon dioxide emissions. The atmospheric pollutants such as CO, NOx will not be formed in the fuel cells powered vehicles. Hydrogen is the ideal fuel for PEMFCs. Hydrogen is generally generated from fossil fuels or from bio-fuels by steam reforming or oxidative steam reforming. The reformats is generally composed of hydrogen, CO, CO<sub>2</sub> and CH<sub>4</sub>. CO can be removed by water-gas shift reaction and preferential oxidation reaction. Methane is an component of the greenhouse gases and formation of methane may lead to decrease in production of hydrogen. Therefore it is of significance that to inhibit formation of methane in the reforming process for efficiently utilizing gasoline and enhancing production of hydrogen. Recently some progresses on developing sulfur-tolerant and coke-resistant catalysts for steam reforming of gasoline have been reported by us [1-2]. More recently, about 700 h of test for gasoline reforming on the bimetallic Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst with the gasoline conversion of 100% and a very low methane concentration of near 0 in product has been completed by us [3]. In the present study, a green process for highly efficient conversion of gasoline to hydrogen for applications in PEMFCs on Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is reported. The promotional effect of Ce on the Ni-Re/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogen generation from gasoline and the mechanism for the role of Ce in Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is investigated.

## Experimental

Re/Al<sub>2</sub>O<sub>3</sub> was prepared by impregnating activated Al<sub>2</sub>O<sub>3</sub> with NH<sub>4</sub>ReO<sub>4</sub> aqueous solutions, followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. Ni-Re/Al<sub>2</sub>O<sub>3</sub> was prepared by co-impregnating Re/Al<sub>2</sub>O<sub>3</sub> with Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O aqueous solutions, then followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> was prepared by co-impregnating Re/Al<sub>2</sub>O<sub>3</sub> with Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O aqueous solutions, then followed by drying at 383 K for 6 h and calcination at 773 K for 6 h. The specific surface area

of the activated Al<sub>2</sub>O<sub>3</sub> is about 120 m<sup>2</sup>/g and the particle size of the alumina is about 75 μm (about 200 mesh). The Ni loading is about 10% and Re loading is about 2% in weight. The loading of Ce is from 1 to 6% in weight. Catalytic tests were carried out with about 0.4g of catalyst placed in a fixed bed continuous-flow quartz reactor. Before the steam reforming reaction, the catalysts were first pre-treated by flowing air at 873K for 0.5h and then reduced by H<sub>2</sub>/N<sub>2</sub> at 773K for 2h. Flow rates of gasoline and water (H<sub>2</sub>O) were controlled by liquid pumps and preheated in an evaporator before passing through the catalyst bed in the reactor. The flow rate of N<sub>2</sub> was controlled by a mass flow rate-controller. The premium gasoline fuel containing about 3.8ppm sulfur and the regular gasoline fuel containing about 40ppm sulfur were used for the catalytic tests. The reforming products were withdrawn periodically from the outlet of reactor and analyzed by a two on-line gas chromatographs, Shimadzu GC-14B and GC-8A, equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) respectively. Hydrocarbon products were separated on a 4 mm × 1 m Porapak P column and CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> were analyzed on a 4 mm×1m active carbon column. Conversion, selectivity and formation rates of products were calculated by an internal standard analysing method. The method is presented briefly as follows. Even if the total flow rate changed at the outlet from that at the inlet of reactor ( $F_{\text{Total}}^{\text{inlet}}$ ,  $F_{\text{Total}}^{\text{outlet}}$ ), the flow rate of non-reactive internal standard gas ( $F_{\text{st}}$ ) is kept constant.

$$F_{\text{st}} = F_{\text{Total}}^{\text{outlet}} \times X_{\text{st}}^{\text{outlet}} = F_{\text{Total}}^{\text{inlet}} \times X_{\text{st}}^{\text{inlet}}$$

Here  $X_{\text{st}}$  refers to concentration of the internal standard gas. Formation rate of  $i$  product ( $F_i$ ) can be calculated as:

$$F_i = F_{\text{Total}}^{\text{outlet}} \times X_i^{\text{outlet}} = F_{\text{st}} \times X_i^{\text{outlet}} / X_{\text{st}}^{\text{outlet}}$$

Conversion of liquid hydrocarbon ( $C_{\text{HC}}$ ) was calculated on the basis of carbon balance. It was calculated by dividing the sum of carbon in gaseous products by the carbon in feed as Eq. 1.

$$C_{\text{gasoline}} = (F_{\text{CO}}^{\text{outlet}} + F_{\text{CO}_2}^{\text{outlet}} + F_{\text{CH}_4}^{\text{outlet}}) / F_{\text{gasoline}}^{\text{inlet}} \quad (1)$$

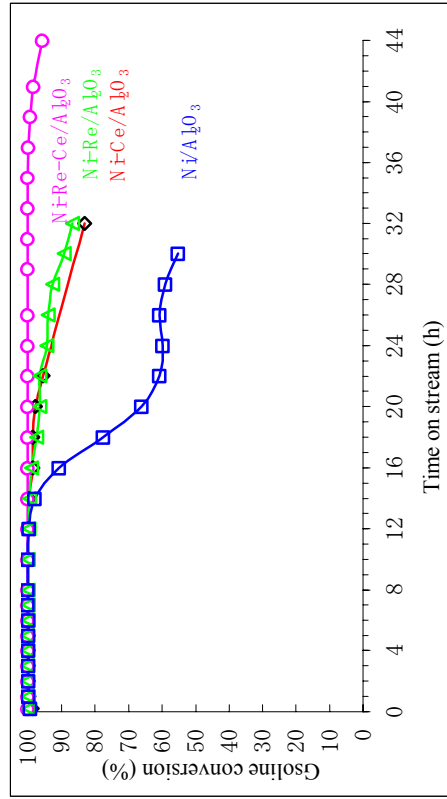
$F_{\text{gasolineinlet}}$  is the flow rate of gasoline feed and controlled by a liquid pump. In the same way,  $H_2O$  conversion ( $C_{\text{H}_2\text{O}}$ ) is calculated on the basis of oxygen balance and calculated by dividing the sum of oxygen in gaseous products by the oxygen in feed as Eq. 2.

$$C_{\text{H}_2\text{O}} = (F_{\text{CO}}^{\text{outlet}} + 2F_{\text{CO}_2}^{\text{outlet}} - 2F_{\text{O}_2}^{\text{inlet}}) / F_{\text{H}_2\text{O}}^{\text{inlet}} \quad (2)$$

$F_{\text{H}_2\text{O}}^{\text{inlet}}$  is the flow rate of water and controlled by another liquid pump.

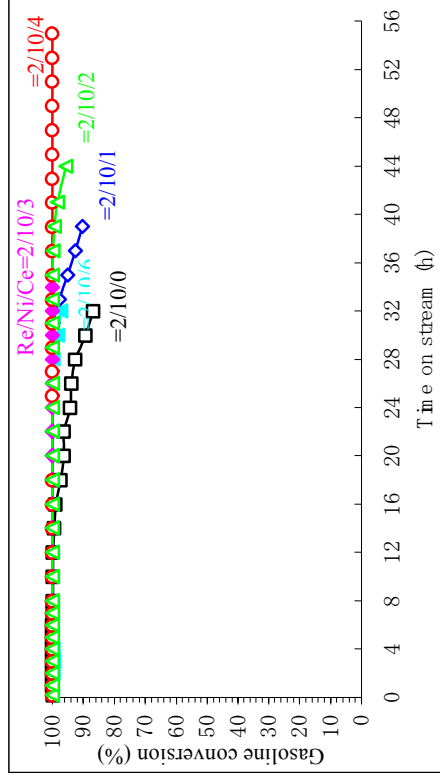
## Results and discussion

Figure 1 shows the time on stream results for oxidative steam reforming of the premium gasoline fuel containing about 3.8ppm sulfur on Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub>, Ni-Re/Al<sub>2</sub>O<sub>3</sub>, Ni-Ce/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 953K and a gasoline WSV of 3h<sup>-1</sup>.



**Figure 1.** The time on stream results for oxidative steam reforming of the premium gasoline fuel containing about 3.8ppm sulfur on Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub>, Ni-Re/Al<sub>2</sub>O<sub>3</sub>, Ni-Ce/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 953K and a gasoline WSV of 3h<sup>-1</sup>

A high gasoline conversion of 100% is obtained for the oxidative steam reforming of the premium gasoline fuel on all the catalyst of Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub>, Ni-Re/Al<sub>2</sub>O<sub>3</sub>, Ni-Ce/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 953K and the gasoline WSV of 3h<sup>-1</sup> in the initial stage of the reaction. However, the activity maintenance of the different catalyst is quite different. The activity of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst starts to decline after about 12h of time on stream. The activity maintenance of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is evidently improved by addition of Re or Ce as a promoter because the activity of Ni-Re/Al<sub>2</sub>O<sub>3</sub> or Ni-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts is maintained much better than Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits the best activity maintenance with time on stream. The high gasoline conversion of 100% is maintained well with time on stream for oxidative steam reforming of gasoline on Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst even after 40h of time on stream as shown in Figure 1. This indicates that the activity maintenance of Ni-Re/Al<sub>2</sub>O<sub>3</sub> is effectively enhanced by modification with ceria. Effect of the Ni/Re/Ce ratios of Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> on the activity maintenance of the catalyst is also investigated. The activity maintenance of the catalyst is remarkably enhanced with increase of Ce loading from 0 to 2 as shown in Figure 2. The optimum ratio of Ni/Re/Ce for Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is about 10/2/2-4. The gasoline conversion of 100% is maintained well for over 55h of time on stream over the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst with the Ni/Re/Ce ratio of 10/2/4. However, the activity of Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst with the Ni/Re/Ce ratio of 10/2/6 starts to decline after 28h of time on stream as shown in Figure 2. Effect of sulfur content in gasoline fuels on the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with the different Ni/Re/Ce ratios is also investigated. It has been found that the role of Ce in the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is to improve the sulfur-tolerance and coking-resistance of the catalyst for oxidative steam reforming of sulfur-containing gasoline fuels.



**Figure 2.** Effect of Re/Ni/Ce ratio on the activity maintenance of Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts for oxidative steam reforming of gasoline at 953K and the WSV of 3h<sup>-1</sup>

Effect of sulfur content in gasoline fuels on the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with the different Ni/Re/Ce ratios is also investigated. It has been found that the role of Ce in the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is to improve the sulfur-tolerance and coking-resistance of the catalyst for oxidative steam reforming of sulfur-containing gasoline fuels.

### Conclusion

The catalytic performance of Ni-Re/Al<sub>2</sub>O<sub>3</sub> is remarkably improved by addition of ceria to the catalyst for oxidative steam reforming of gasoline to produce hydrogen. Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits the better activity maintenance than Ni-Re/Al<sub>2</sub>O<sub>3</sub> for oxidative steam reforming of sulfur-containing gasoline fuel. The optimum ratio of Ni/Re/Ce for the Ni-Re-Ce/Al<sub>2</sub>O<sub>3</sub> catalysts is about 10/2/2-4.

### References

- (1) L. Wang, K. Murata, M. Inaba, Industrial & Engineering Chemistry Research, 43 (2004) 3228
- (2) L. Wang, K. Murata, M. Inaba, Journal of Power Sources, 145 (2005) 707
- (3) L. Wang, K. Murata, M. Inaba, Y. Matsumura, to be published in Energy & Fuels, 2006