

The performance of CeO₂-modified Ni/Al₂O₃ catalyst in the autothermal reforming of iso-octane

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Introduction

Autothermal reforming (ATR) is considered as one of promising processes to produce hydrogen. Even though Ni/Al₂O₃, which is generally used as a commercial catalyst for steam reforming of CH₄, shows a high activity in gasoline ATR, the catalyst is easily deactivated by coking [1]. Therefore, in order to extend the catalyst lifetime, it is necessary that the amounts of coke deposited on the catalyst surface are minimized. In this study, two types of CeO₂-modified Ni/Al₂O₃ catalysts were prepared by an impregnation method with different sequences of Ni and CeO₂ addition, i.e. Ni-CeO₂/Al₂O₃ (Ni-CeX) and Ni/CeO₂-Al₂O₃ (Ni/CeX), and their performance in iso-octane ATR was investigated. Coke was characterized by elemental (EA) and thermogravimetric analyses (TGA).

Materials and Methods

5 wt% Ni/Al₂O₃ was prepared as a reference catalyst by an incipient wetness impregnation method using gamma alumina support (CONDEA, surface area = 206.6 m²/g, pore volume = 0.48 cm³/g) and Ni(NO₃)₂·6H₂O as a Ni precursor. CeO₂-modified Ni/Al₂O₃ catalysts were prepared by impregnating γ -Al₂O₃ with an aqueous solution containing Ni(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O by changing the impregnation sequence, followed by calcination at 500 °C for 5 h. That is, Ni/CeX and Ni-CeX, with 'X' denoting the amounts of added CeO₂ in 1 wt% units, were obtained by adding Ni to CeO₂-containing alumina and CeO₂ to Ni-containing alumina, respectively.

Iso-octane ATR was performed in a quartz micro-reactor at an atmospheric pressure using iso-octane (Aldrich, 99.8%) as a feed at 600 °C. H₂O/C/O ratios in the reactant stream were maintained at 3/3/0.25 and the total flow rate was 68.8 ml/min. Reaction products were analyzed with an on-line G.C. (Agilent, model 6890 series with TCD) using a packed column.

Results and Discussion

Figure 1 shows the deactivation behavior of the catalysts, presented by changes in the H₂ production normalized to the initial value of each catalyst, as a function of reaction time. In the case of Ni/Al₂O₃, the H₂ production was decreased by 25% of the initial value in 24 h and then rapidly decreased to 11% of the initial value afterwards. Ni-CeX showed the same trend in deactivation behavior as obtained with Ni/Al₂O₃, that is, Ni-Ce04 and Ni-Ce06 were slowly deactivated until 24 h and significantly decreased by 67% of the initial value after 48 h. On the other hand, the deactivation behavior of Ni/CeX differs from that of Ni/Al₂O₃, i.e. Ni/Ce06 and Ni/Ce10 maintained 70% and 64% of the initial H₂ production after the reaction

time of 48 h. This result indicates that added CeO₂ suppresses the deactivation of catalysts, particularly when CeO₂ is added to Al₂O₃ prior to Ni impregnation.

EA results indicated that the amounts of coke deposited on Ni/Al₂O₃, Ni-Ce04 and Ni/Ce06 were 46.4%, 37.2% and 34.8%, respectively. Figure 2 shows the results of DTGA, obtained from the TGA curve, which show two kinds of peaks: Peak I at temperatures below 500 °C, representing reversible coke, and Peak II at temperatures higher than 500 °C, representing graphitic coke [2]. Reversible coke decreased in the order Ni-Ce04 > Ni/Ce06 > Ni/Al₂O₃ and was eliminated at lower temperatures from Ni/Ce06 than in the case of Ni-Ce04. On the other hand, graphitic coke decreased in the order Ni/Al₂O₃ > Ni-Ce04 \approx Ni/Ce06. EA and DTGA indicated that Ni/Ce06, which showed a longer lifetime than Ni-CeX, produced less amounts and different types of coke on the catalyst surface compared with the case of Ni-CeX.

Significance

Among two kinds of CeO₂-modified Ni/Al₂O₃ examined in this study, Ni/CeX showed higher hydrogen production and was deactivated more slowly than Ni-CeX and Ni-only catalysts. In particular, Ni/Ce06 showed the best catalytic performance among tested catalysts.

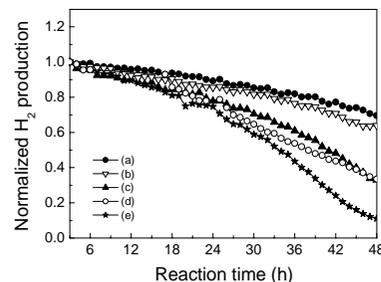


Figure 1. Deactivation of sample catalysts vs. reaction time (H₂O/C/O = 3/3/0.25, reaction temperature = 600 °C, total flow rate = 68.8 ml/min): (a) Ni/Ce06; (b) Ni/Ce10; (c) Ni-Ce04; (d) Ni-Ce06; (e) Ni/Al₂O₃.

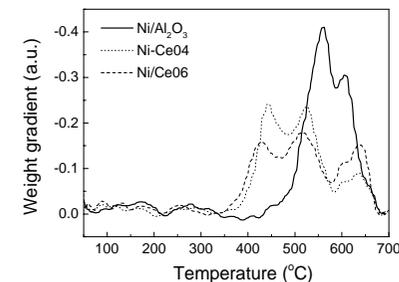


Figure 2. DTGA profiles of deactivated Ni/Al₂O₃, Ni-Ce04 and Ni/Ce06. (Deactivated catalysts were obtained after reaction test at 600 °C for 48 h.)

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References

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