

Syngas Production via Combined H₂O and CO₂ reforming of Methane over Ce-promoted Ni/Al₂O₃ Catalyst: Effect of Ce addition on coke formation

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Introduction

It has been investigated to adjust the H₂/CO ratios in syngas production for application of oxo-synthesis and Fischer-tropsch process [1]. In general, the additional process are required for the control of H₂/CO ratio in conventional reforming processes such as steam reforming of methane (SRM), carbon dioxide reforming of methane (CRM) and partial oxidation of methane (POM). However, combined steam and carbon dioxide reforming of methane (CSCRM) is a feasible process for the direct control of H₂/CO ratio by adjusting the feed ratio of steam and carbon dioxide [2,3]. In this reforming process, Ni-based catalysts have been commercially used as promising catalysts because of a high activity comparable to expensive noble metal catalysts. However, the deactivation of these catalysts is mainly attributed to carbon deposition and metal sintering in severe operating conditions [4]. In this study, Ce was added into Ni/Al₂O₃ catalysts for the enhancement of coke resistance because CeO₂ has a dominant ability to supply the active oxygen species which suppresses coke formation by oxidizing surface carbon on the catalyst [5]. The Ce content over Ni/Al₂O₃ catalyst was optimized and the H₂/CO ratio of 2 which is required for F-T synthesis is achieved by controlling the feed ratio of H₂O and CO₂ in CSCRM.

Materials and Methods

The Ni-Ce/Al₂O₃ catalysts were prepared by co-impregnation method, and then the catalysts were calcined at 800°C for 6 h. The loading amount of Ni was fixed at 12 wt% and the Ce content was varied from 0 to 24 wt%. The prepared catalyst was characterized by X-ray diffraction (XRD), surface area (S_{BET}) and temperature programmed reduction (TPR). Before the reaction, the catalyst was reduced with H₂ (10%)/N₂ at 700°C for 1 h. The reforming test was carried out with CH₄: H₂O: CO₂ = 1: 0.8: 0.4 because we can get the H₂/CO ratio of 2 in this condition [6]. The space velocity was 265,000 ml/h g_{cat} and reforming temperature was varied from 750 to 650°C. The effluent was passed through a trap to condensate residual water and then analyzed by an on-line micro gas chromatography (Agilent 3000) equipped with TCD detector.

Results and Discussion

The Ce-promoted Ni/Al₂O₃ catalysts show the higher catalytic activity and coke resistance than Ni/Al₂O₃ catalyst because ceria supplies the active oxygen species by reacting with H₂O and CO₂ over catalyst surface resulting in the prevention of coke formation. As the Ce content increases, NiO crystallite size decreases while Ni dispersion and Ni surface area

increase. It can be explained that the promotion of ceria improves the Ni dispersion on the support in which highly dispersed Ni crystallites have a strong metal to support interaction (SMSI) resulting in the high coke resistance. Fig.1. shows the SEM images of used catalysts which were collected after reforming reaction at 650 °C for 15 h. It is evident that a large amount of coke was formed on the used Ni/Al₂O₃ catalyst which has the large particle due to the sintering. From the results of Ce-modified Ni/Al₂O₃ catalysts, 6 wt% Ce shows the highest catalytic activity and coke resistance in CSCRM because of the effective oxygen transfer during the reaction and SMSI.

Significance

Through the optimization of Ce content over Ni/Al₂O₃ catalyst, we can suppress effectively the coke formation which causes the catalyst deactivation in CSCRM for syngas production.

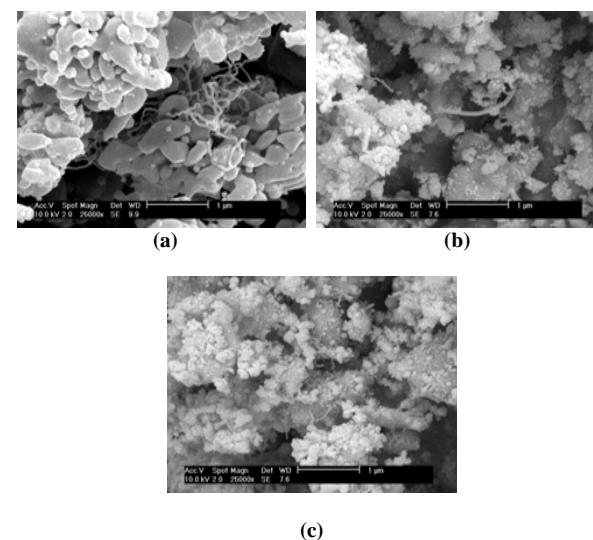


Figure 1. SEM images of used (a) Ni/Al₂O₃ catalysts and catalysts promoted with b) 6 wt% Ce and c) 12 wt% Ce

References

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