

Hydrogen production by steam reforming of LNG over Ni/Al₂O₃-ZrO₂ catalysts: Effect of ZrO₂ and preparation method of Al₂O₃-ZrO₂

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Abstract—An Al₂O₃-ZrO₂ support was prepared by grafting a zirconium precursor onto the surface of commercial γ -Al₂O₃. A physical mixture of Al₂O₃-ZrO₂ was also prepared for the purpose of comparison. Ni/Al₂O₃-ZrO₂ catalysts were then prepared by an impregnation method, and were applied to the hydrogen production by steam reforming of liquefied natural gas (LNG). The effect of ZrO₂ and preparation method of Al₂O₃-ZrO₂ on the performance of supported nickel catalysts in the steam reforming of LNG was investigated. The Al₂O₃-ZrO₂ prepared by a grafting method was more efficient as a support for nickel catalyst than the physical mixture of Al₂O₃-ZrO₂ in the hydrogen production by steam reforming of LNG. The well-developed tetragonal phase of ZrO₂ and the high dispersion of ZrO₂ on the surface of γ -Al₂O₃ were responsible for the enhanced catalytic performance of Ni/Al₂O₃-ZrO₂ prepared by way of a grafting method.

Key words: Hydrogen, Liquefied Natural Gas (LNG), Steam Reforming, Al₂O₃-ZrO₂, Supported Nickel Catalyst

INTRODUCTION

Hydrogen has attracted considerable attention as a promising energy due to its potential applicability in fuel cell systems [1-5]. Therefore, reforming technologies for the production of hydrogen have been extensively studied [6-12]. Among these, steam reforming has been recognized as a feasible method to produce hydrogen from liquefied natural gas (LNG). The extensive piping system for LNG in modern cities makes LNG well suited as a hydrogen source for residential reformers.

Nickel-based catalysts have been widely studied in the steam reforming of LNG although nickel-based catalysts require a high reaction temperature and an excess amount of steam to prevent coke deposition on the catalyst surface [13-15]. However, it has been reported that ZrO₂ support enhances the adsorption of steam onto its surface and activates the gasification of hydrocarbons adsorbed on the catalyst surface in the steam reforming reactions, resulting in an enhancement in hydrogen production and coke resistance [16,17]. Therefore, the addition of ZrO₂ into the conventional nickel-based catalysts can be a promising choice to improve the performance of the nickel-based catalysts.

In this work, an Al₂O₃-ZrO₂ support was prepared by grafting a zirconium precursor onto the surface of γ -Al₂O₃. For the purpose of comparison, a physical mixture of Al₂O₃-ZrO₂ was also prepared. Ni/Al₂O₃-ZrO₂ and Ni/ γ -Al₂O₃ catalysts were then prepared by an impregnation method for use in hydrogen production by steam reforming of LNG. The effect of ZrO₂ and preparation method of Al₂O₃-ZrO₂ on the performance of supported nickel catalysts in the steam reforming of LNG was investigated.

EXPERIMENTAL

An Al₂O₃-ZrO₂ support was prepared by grafting an appropriate amount of zirconium precursor onto the surface of γ -Al₂O₃ [17-19]. A known amount of alumina (γ -Al₂O₃, Degussa) was added to 100 ml of anhydrous toluene (Aldrich) for uniform dispersion, and an excess amount of triethylamine (TEA, Fluka) was then added to the alumina slurry to activate the hydroxyl groups on the alumina surface. An appropriate amount of zirconium precursor (Zr(OBu)₄, Aldrich) was slowly added to the slurry with constant stirring for 1 h, and the resulting slurry was stirred at room temperature for 6 h to achieve the complete reaction of the activated surface hydroxyl groups of alumina with the butoxide groups of zirconium precursor. After removing the unreacted zirconium precursor and butanol (by-product) by centrifugation, the slurry was washed several times with anhydrous toluene. Upon the addition of an excess amount of deionized water to the washed slurry, a white gel was formed. After maintaining the white gel in deionized water for 6 h, a solid product was obtained by filtration. The solid product was dried overnight at 120 °C, and then calcined at 700 °C for 5 h to yield the Al₂O₃-ZrO₂ support (denoted as AZ-graft). A physical mixture of Al₂O₃-ZrO₂ was also prepared by a direct hydrolysis of zirconium precursor (Zr(OBu)₄, Aldrich) onto the surface of γ -Al₂O₃ (Degussa) for the purpose of comparison (denoted as AZ-mix). The supported nickel catalysts were then prepared by impregnating known amounts of a nickel precursor (Ni(NO₃)₂·6H₂O, Aldrich) onto the supports. The prepared catalysts were denoted as Ni/ γ -Al₂O₃, Ni/AZ-graft, and Ni/AZ-mix. The nickel loading was fixed at 20 wt% in all cases.

In order to investigate reducibility of the supported nickel catalysts, temperature-programmed reduction (TPR) measurements were carried out in a conventional flow system with a moisture trap connected to a thermal conductivity detector (TCD) at temperatures ranging from room temperature to 1,000 °C with a ramping rate of 5 °C/min. For the TPR measurements, a mixed stream of H₂ (2 ml/min) and N₂ (20 ml/min) was used for 0.1 g of catalyst sample.

Steam reforming of LNG was carried out in a continuous flow

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Table 1. Chemical compositions of supports determined by ICP-AES analyses

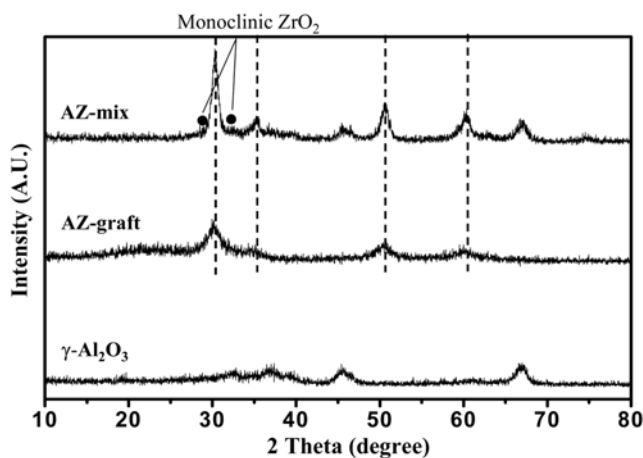
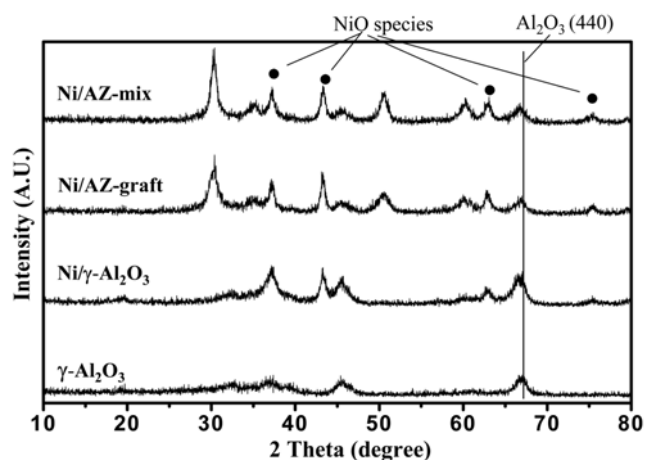
Support	Zr loading (wt%)	Zr/Al atomic ratio
γ -Al ₂ O ₃	0	0
AZ-graft	21.9	0.17
AZ-mix	20.7	0.16

fixed-bed reactor. Each catalyst was pretreated with a mixed stream of H₂ (10 ml/min) and N₂ (30 ml/min) at 800 °C for 3 h. Water was sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor together with LNG (92 vol% CH₄ and 8.0 vol% C₂H₆) and N₂ carrier (30 ml/min). The steam reforming of LNG was conducted at 600 °C. The steam/carbon ratio was fixed at 2.0, and the total feed flow rate was maintained at 27,000 ml·h⁻¹/g-catalyst. The reaction products were periodically sampled and analyzed using an on-line gas chromatograph (Younglin, ACME 6000) equipped with a TCD.

RESULTS AND DISCUSSION

Table 1 shows the chemical compositions of AZ-graft and AZ-mix supports determined by ICP-AES analyses. The Zr/Al atomic ratio of AZ-graft was found to be 0.17, indicating that Al₂O₃-ZrO₂ support was successfully prepared by a grafting method. For the purpose of comparison, the Zr/Al atomic ratio of AZ-mix was intentionally adjusted to have a similar value to that of AZ-graft.

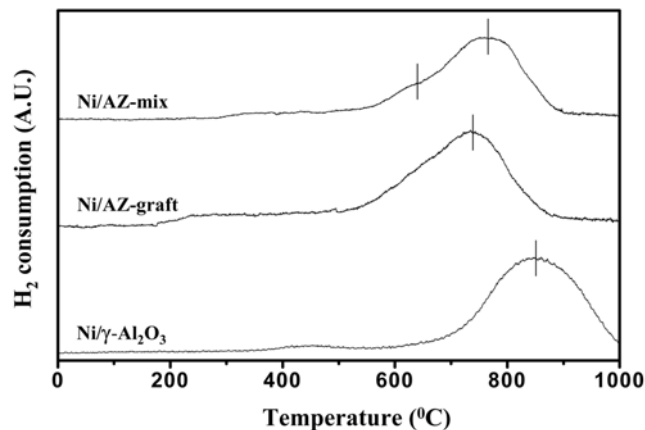
Fig. 1 shows the XRD patterns of supports. Dashed lines in Fig. 1 represent the tetragonal phase of zirconia. It was found that AZ-graft retained pure tetragonal phase of zirconia, while AZ-mix had both monoclinic phase and tetragonal phase of zirconia. Furthermore, AZ-graft showed relatively broader diffraction peaks of zirconia than AZ-mix. This indicates that zirconia was highly dispersed in the AZ-graft by the reaction between activated hydroxyl groups of alumina and zirconium precursor, resulting in the formation of an Al₂O₃-ZrO₂ composite structure. It is believed that the metastable tetragonal phase of zirconia was stabilized by its incorporation into the lattice of alumina in the AZ-graft support. In the AZ-mix support, on the other hand, zirconium precursor was easily

**Fig. 1. XRD patterns of γ -Al₂O₃, AZ-graft, and AZ-mix supports.****Fig. 2. XRD patterns of Ni/ γ -Al₂O₃, Ni/AZ-graft, and Ni/AZ-mix catalysts.**

aggregated during the hydrolysis and condensation steps. This means that the particle size of zirconia in the AZ-mix exceeded the critical size for causing a phase transformation of zirconia from the tetragonal phase to the monoclinic phase.

Fig. 2 shows the XRD patterns of supported nickel catalysts. All the supported nickel catalysts showed the diffraction peaks corresponding to NiO species. A noticeable point is that the (440) diffraction peak of alumina in the Ni/ γ -Al₂O₃ and Ni/AZ-mix catalysts slightly shifted to a lower angle. This indicates that Ni²⁺ was incorporated into the lattice of γ -Al₂O₃, resulting in the increment of lattice parameter of alumina in the Ni/ γ -Al₂O₃ and Ni/AZ-mix catalysts [20-22]. In the Ni/AZ-graft catalyst, however, the shift of (440) diffraction peak of alumina was not observed. It is believed that the highly dispersed ZrO₂ inhibited the incorporation of Ni²⁺ into the lattice of alumina in the Ni/AZ-graft catalyst.

Fig. 3 shows the TPR profiles of supported nickel catalysts. Ni/ γ -Al₂O₃ catalyst showed a reduction band at around 850 °C, which was attributed to the reduction of nickel aluminate. On the other hand, Ni/AZ-graft catalyst showed a reduction band at around 730 °C, which was believed to be due to the reduction of NiO species strongly interacted with support. These results indicate that the grafted ZrO₂

**Fig. 3. TPR profiles of Ni/ γ -Al₂O₃, Ni/AZ-graft, and Ni/AZ-mix catalysts.**

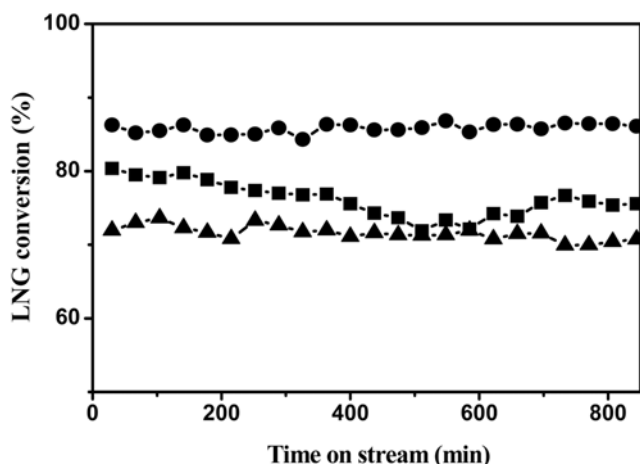


Fig. 4. LNG conversions with time on stream at 600 °C (▲=Ni/γ-Al₂O₃, ■=Ni/AZ-mix, ●=Ni/AZ-graft).

inhibited the formation of nickel aluminate species through the formation of a favorable Al₂O₃-ZrO₂ composite structure. Ni/AZ-mix catalyst showed a shoulder at around 620 °C along with a main reduction band at around 760 °C. This means that nickel species were supported not only on the surface of γ-Al₂O₃ but also on the surface of ZrO₂ in the Ni/AZ-mix catalyst. Among the catalysts tested, the Ni/AZ-graft showed the highest reducibility.

Fig. 4 shows the LNG conversions with time on stream in the steam reforming of LNG at 600 °C. The LNG conversions were decreased in the order of Ni/AZ-graft>Ni/AZ-mix>Ni/γ-Al₂O₃, in good agreement with the trend of reducibility. Both Ni/AZ-graft and Ni/AZ-mix catalysts showed a higher LNG conversion than Ni/γ-Al₂O₃. This may be explained by the steam adsorption capability of ZrO₂. It is well known that methane is adsorbed on the surface of metallic nickel, while steam is adsorbed not only on the metallic nickel but also on the support [16]. The adsorbed steam, therefore, should migrate to the nickel surface for the steam reforming reaction. Steam adsorption capability of support is very important, because nickel-based catalysts catalyze not only steam reforming reaction but also carbon deposition. The above results strongly support that the Ni/AZ-graft and Ni/AZ-mix catalysts retained a higher steam adsorption capability than the Ni/γ-Al₂O₃ catalyst. The Ni/AZ-graft catalyst showed a higher LNG conversion than the Ni/AZ-mix catalyst, because ZrO₂ was highly dispersed on the surface of γ-Al₂O₃ in the Ni/AZ-graft catalyst. The hydrogen compositions (dry gas basis) over the supported nickel catalysts after the 800 min-reaction decreased in the order of Ni/AZ-graft (69.2%)>Ni/AZ-mix (67.8%)>Ni/γ-Al₂O₃ (65.8%). The CO compositions (dry gas basis) decreased in the order of Ni/AZ-graft (11.5%)>Ni/AZ-mix (11.2%)>Ni/γ-Al₂O₃ (10.2%), and the CO₂ compositions (dry gas basis) also decreased in the order of Ni/AZ-graft (15.8%)>Ni/AZ-mix (15.6%)>Ni/γ-Al₂O₃ (15.5%). It is concluded that the well-developed tetragonal phase of ZrO₂ and the high dispersion of ZrO₂ on the surface of γ-Al₂O₃ were responsible for the enhanced catalytic performance of Ni/AZ-graft. A new interaction between nickel and ZrO₂ inhibiting the incorporation of nickel into the lattice of γ-Al₂O₃ through the formation of a favorable Al₂O₃-ZrO₂ composite structure was also responsible for the enhanced catalytic performance of Ni/AZ-

graft.

CONCLUSIONS

An Al₂O₃-ZrO₂ support was prepared by grafting a zirconium precursor onto the surface of γ-Al₂O₃. For the purpose of comparison, a physical mixture of Al₂O₃-ZrO₂ was also prepared. Ni/Al₂O₃-ZrO₂ catalysts were then prepared by an impregnation method for use in the hydrogen production by steam reforming of LNG. The effect of ZrO₂ and preparation method of Al₂O₃-ZrO₂ on the performance of supported nickel catalysts in the steam reforming of LNG was investigated. The highly dispersed ZrO₂ inhibited the incorporation of nickel species into the lattice of γ-Al₂O₃ through the formation of a favorable Al₂O₃-ZrO₂ composite structure in the Ni/AZ-graft catalyst. In the hydrogen production by steam reforming of LNG, the LNG conversions and hydrogen compositions were decreased in the order of Ni/AZ-graft>Ni/AZ-mix>Ni/γ-Al₂O₃, in good agreement with the trend of reducibility. The well-developed tetragonal phase of ZrO₂ and the high dispersion of ZrO₂ on the surface of γ-Al₂O₃ played an important role in the adsorption of steam and the subsequent spillover of steam from the support to the active nickel in the Ni/AZ-graft catalyst.

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