

CeO₂ and W Modified Mesoporous Ni/Al₂O₃ Catalysts for Hydrogen Production by Steam Reforming of Diesel Fuel

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Highlights

- High GHSV lead to high side product formation and low GHSV enhances coke deposition.
- CeO₂ incorporation enhances H₂ production by diminishing Ni^o crystal size
- W incorporation significantly reduced coke deposition during DSR by WC formation

1. Introduction

On-site production of hydrogen from diesel through steam reforming (DSR) reaction for fuel cell powered stationary auxiliary power unit applications (APUs) draw interest for medium term operations. The main reasons of selecting diesel as the hydrogen source are its easy accessibility and easy transportation. DSR (R.1) provides very high hydrogen concentration (70-80% in volume base), but requires high reaction temperatures.



Before the application of this technology in APUs, the main problem of catalyst deactivation due to coke and sulphur deposition should be eliminated. Ni/Al₂O₃ catalysts which are active in reforming reactions and stable at high temperatures can be modified with the addition of promoters to address coke and sulphur deposition problem. CeO₂ is preferred in reforming reactions as a promoter, due to its high oxygen mobility, high coke resistivity and strong interaction with nickel [1]. W also attracts attention with its good redox potential and coke resistive properties [2].

This study focuses on the optimization of catalyst composition and operating conditions for the purpose of achieving maximum hydrogen production and minimum coke deposition. Catalysts were characterized before and after the reaction tests to understand the effects of harsh reaction conditions on the materials and select the best operating conditions and catalysts for diesel steam reforming reaction.

2. Methods

Syntheses of new mesoporous Al₂O₃ catalyst supports containing CeO₂ and/or W were performed by modifying the evaporation induced self-assembly method [3]. Six different catalyst supports were synthesized through direct synthesis with Al₂O₃ by using 10wt.% or 20 wt.% CeO₂, 10 wt.% or 20wt.% W, and 10wt.% W together with 10 wt.% CeO₂. Synthesized materials were calcined at 900°C and then nickel was impregnated (10 wt.%). Catalysts that were calcined and reduced at 900°C were characterized and tested for their activity in DSR reaction at 800°C and at optimum GHSV and H₂O/C ratio which were selected according to the results of the optimization experiments.

3. Results and discussion

Parametric investigation experiments showed that, side product formation increased at high values of GHSV (25000, 17000 h⁻¹), due to low contact time between the feed and the catalyst. Decreasing GHSV enhances

hydrogen production, but too much decrease ($<5000 \text{ h}^{-1}$) lead to higher coke deposition. Further experiments were performed at a GHSV value of 7500 h^{-1} . Investigation of effect of $\text{H}_2\text{O}/\text{C}$ ratio on diesel steam reforming reaction showed that increase of this ratio decreased coke deposition and enhanced H_2 production mainly by promoting water gas shift reaction. A medium value of $\text{H}_2\text{O}/\text{C}$ ratio was selected as 2.5 for further experiments considering energy economy. Characterization results of the catalysts showed that incorporated metals interacted with each other and formed different crystal structures. For ceria incorporated metals, this effect was observed as the formation of CeAlO_3 structures. Analyzing effect of incorporated ceria amount (10wt.% and 20wt.%) on the catalytic properties of the catalysts showed that low ceria loading is more beneficial in terms of H_2 production capability of the catalyst due to lower Ni^0 crystal size. As it can be seen in Fig.1, the best catalytic activity was observed with $\text{Ni}@10\text{CeO}_2\text{-Al}_2\text{O}_3$. Tungsten incorporation significantly reduced Ni^0 presence according to XRD results which has been known as the active component in reforming catalysts, by forming Ni_4W crystals. Tungsten incorporated catalysts were less active towards diesel steam reforming reaction compared to Al_2O_3 and $\text{CeO}_2\text{-Al}_2\text{O}_3$ supported catalysts. However, coke formation was lower for these materials due to formation of WC crystals according to XRD results of spent catalysts and probably due to low solubility of carbon in Ni_4W crystals.

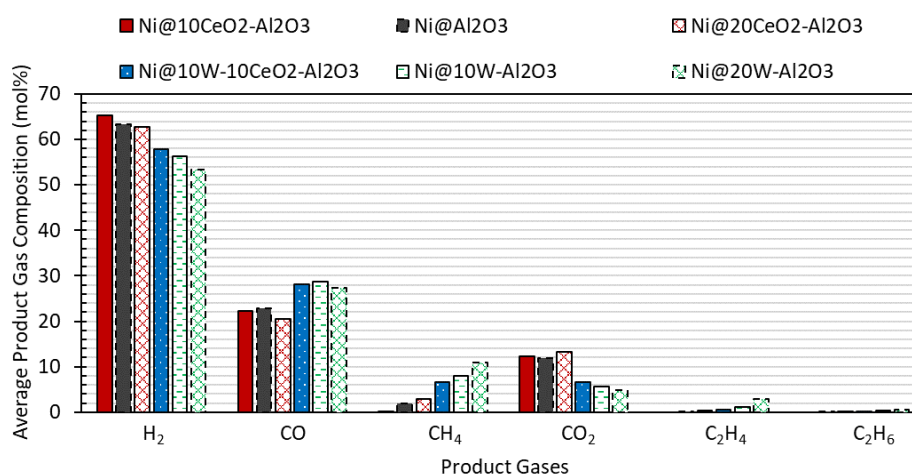


Figure 1. Effect of catalyst composition on average product gas composition during DSR experiments (GHSV= 7500 h^{-1} , $\text{H}_2\text{O}/\text{C}=2.5$, 800°C).

4. Conclusions

Addition of CeO_2 to $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts was proven to be effective at low loading amounts in terms of H_2 production. On the other hand, W addition was shown to have a negative effect in terms of H_2 production, but it has a positive effect in terms of coke deposition which influences catalyst lifetime. Optimum GHSV and $\text{H}_2\text{O}/\text{C}$ ratio for DSR reaction were found as 7500 h^{-1} and 2.5, respectively.

References

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Keywords

Diesel steam reforming; tungsten-alumina, ceria-alumina, hydrogen