Sandwiched Core-shell Ni-SiO_2@CeO_2 catalyst for coke-free Dry Reforming of Methane: Performance & Mechanism Study

Sonali Das [a], **Ashok Jangam** [a], **Nikita Dewangan** [a], **Kus Hidajat** [a], **Sibudjing Kawi** [a] *

[a] *National University of Singapore, Department of Chemical and Bimolecular engineering, Singapore, 119077*

**Corresponding author: (65) 6516 6312, chekawis@nus.edu.sg*

Abstract: In this study, a novel core-shell structured Ni-SiO_2@CeO_2 catalyst was designed that showed exceptionally high activity and resistance to coke deposition in dry reforming of methane. The high carbon resistance of the core-shell catalyst is attributed to the confinement effect of the ceria shell that prevents nickel sintering at reaction conditions, and the participation of oxygen species in ceria in gasification of carbon species. The ceria shell also helps in increasing Ni dispersion, thereby improving activity. *In-situ* DRIFTS study shows that the ceria shell also changes the reaction pathway to a bi-functional redox mechanism in Ni-SiO_2@CeO_2, that favors less coke.

Keywords: Dry Reforming of Methane, Core-shell catalyst, in-situ DRIFTS.

1. Introduction

Global warming due to anthropogenic CO_2 emissions has led to an increased focus on CO_2 utilization and cleaner fuels. Dry reforming of methane/ natural gas with CO_2 provides an attractive strategy to consume two major greenhouse gases to form synthesis gas that can be used for efficient power generation, higher chemical synthesis or as a hydrogen source.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^o = 247.3\ kJ\ mol^{-1}$$

However, a major challenge in this process is the fast deactivation of catalysts due to the deposition of coke. The coke formation becomes even more severe while working at lower temperatures and high CH_4/CO_2 ratio, as is present in alternate fuels like bio-gas. Nickel based catalysts show high reforming activity but poor stability due to coking[1]. In this study, we have designed an innovative sandwiched core-shell structured Ni-based catalyst, that shows high resistance to coking while maintaining high activity.

2. Experimental

Catalyst Synthesis: Ni-SiO_2 catalyst was synthesized using a Ni-phyllosilicate precursor. Ceria was deposited on Ni-phyllosilicate nano-spheres by a precipitation method and reduced in H_2 to make Ni-SiO_2@CeO_2. Ni-CeO_2 was synthesized by wetness impregnation of nickel salt on ceria support.

Catalyst Characterization: Fresh and spent catalysts were characterized using TEM, XRD, H_2-TPD, XPS, BET, ICP-OES & TGA. In-situ DRIFTS was done to identify role of ceria in the reaction mechanism.

Catalyst Performance Test: Catalysts were tested for dry reforming of methane in a 4mm quartz tube at 600 –750°C, GHSV of 200 L h^{-1} g^{-1} and CH_4/CO_2 ratio of 1:1 and 3:2. Stability test was conducted at 600°C.

3. Results and discussion

Fresh Catalyst Characterization: TEM analysis of the fresh & reduced Ni-SiO_2@CeO_2 catalyst showed a uniform coating of ceria covering all the nickel particles supported on silica (Fig. 1b). The confinement of Ni by ceria was further confirmed by XPS. Interestingly, the reduced Ni-SiO_2@CeO_2 catalyst showed the smallest Ni particle size of 3-5 nm compared to Ni-SiO_2 (7 nm) and Ni-CeO_2 (20 nm) (Fig 1a-c). This result was also supported by XRD results. H_2-TPR (Fig. 1d) showed that the ceria coating enhanced the reducibility of the core-shell catalyst compared to Ni-SiO_2.

Catalyst Activity & Coke Resistance: The core-shell Ni-SiO_2@CeO_2 catalyst showed the highest CH_4 and CO_2 conversion activity followed by Ni-SiO_2 and Ni-CeO_2 at all temperatures (Fig. 2a). In a 72 h stability test at 600°C and CH_4/CO_2 = 3:2, the Ni-SiO_2 catalyst deactivated within 22 h by bed blocking from coke

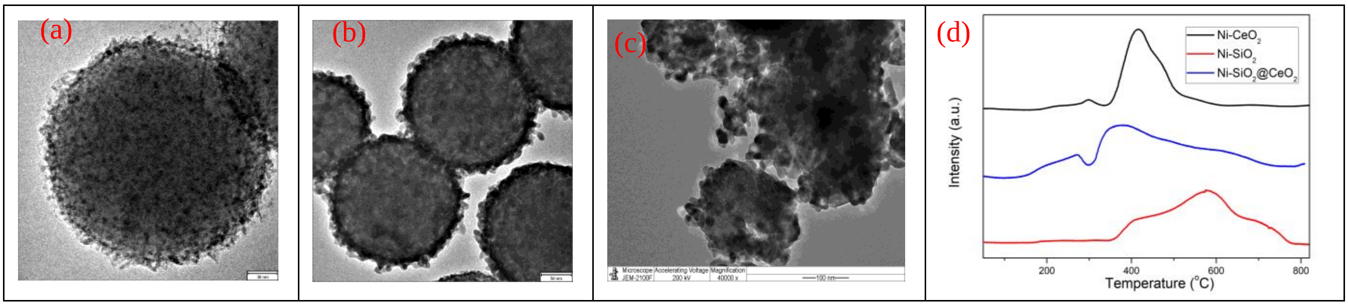

Figure 1. (a-c) TEM image of reduced (a) Ni-SiO_2 (b) Ni-SiO_2@CeO_2, (c) Ni-CeO_2. (d) H_2-TPR profile for all catalysts.

while the Ni-SiO_2@CeO_2 showed the highest activity and a stable performance throughout the 72 h run (Fig. 2b). The Ni-CeO_2 also showed a stable performance but at very low activity. Coke deposition on the spent catalyst was analyzed from TEM, TGA and XRD analysis. No coke was observed on the core-shell catalyst while Ni-SiO_2 and Ni-CeO_2 showed 1.39 and 0.04 g_{coke}/g_{cat} coke respectively (Fig. 2c).

Mechanism Study: In-situ DRIFTS was performed to gain insights into the reaction mechanism. A clear difference was observed in the DRIFTS spectra for Ni-SiO_2 and Ni-SiO_2@CeO_2 catalyst. A strong peak for adsorbed CO on Ni was observed for Ni-SiO_2 but completely disappeared for the ceria coated catalyst. By pulsing CH_4 over reduced Ni-SiO_2@CeO_2, peaks for CO, CO_2 and carbonates were observed, suggesting that the oxygen in ceria is involved in carbon oxidation. From DRIFTS study, it can be inferred that the ceria coating on the core-shell catalyst changes the reaction mechanism from a mono-functional route in Ni-SiO_2 to a bi-functional redox mechanism with active participation of ceria, that helps in coke elimination[2].

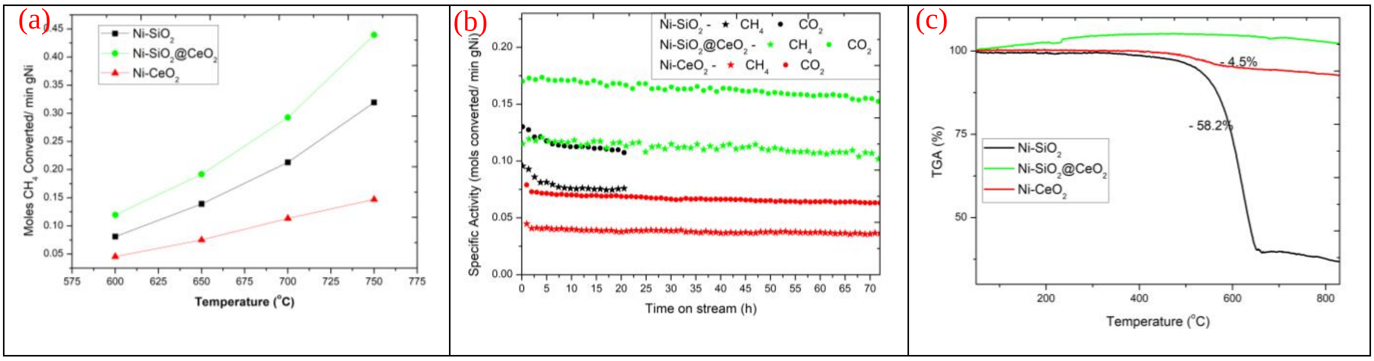

Figure 2. (a) CH_4 reforming activity of all catalysts at different temperature, (b) 72 hr stability test at 600°C and CH_4/CO_2 =3/2, (c) TGA for spent catalyst after stability test.

4. Conclusions

A novel core-shell structured Ni-SiO2@CeO2 catalyst with Ni nanoparticles sandwiched between silica and ceria was developed, that showed very high activity for dry reforming of methane at low temperature and no coke deposition after 72 h time on stream. The ceria shell not only provides a confinement effect on Ni, preventing its sintering, but also supplies mobile oxygen species to gasify carbonaceous species. The activity is also enhanced due to the ability of ceria to further disperse nickel on silica through metal-support interaction to produce smaller nanoparticles.

Acknowledgement The authors gratefully thank the National University of Singapore, National Environmental Agency (NEA-ETRP Grant RP No. 279-000-333-490) and Agency for Science, Technology & Research (AME IRG Grant no. A1783c0016) for generously supporting this work.

References

1. S. Kawi, Y. Kathiraser, J. Ni, U. Oemar, Z. Li, E. T. Saw, ChemSusChem 8(21) (2015) 3556.
2. N. Laosiripojana, W. Sutthisripok, S. Assabumrungrat, Chem. Eng. J., 112(1-3) (2005) 13.