Sandwiched Core-shell Ni-SiO$_2$@CeO$_2$ catalyst for coke-free Dry Reforming of Methane: Performance & Mechanism Study

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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.

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

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$^\circ$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$^\circ$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$^\circ$C and CH$_4$/CO$_2$ = 3:2, the Ni-SiO$_2$ catalyst deactivated within 22 h by bed blocking from coke.
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$_{\text{coker}}$/$g_{\text{cat}}$ 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].

4. Conclusions

A novel core-shell structured Ni-SiO$_2$@CeO$_2$ 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.

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References