

Activity and Stability of Yolk-Shell Nanotube Catalysts for Tri-Reforming of Methane

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Abstract

Activity and stability of the NiCe@SiO₂ multi-yolk-shell nanotube catalysts are investigated for tri-reforming of methane (TRM), as a point of source CO₂ conversion technology. The yolk-shell catalysts prepared at different yolk sizes can maintain high activity for TRM. Small yolks can lose its activity due to the re-oxidation of active Ni component under oxidizing feed gas conditions. These results confirm that the morphology of the multi-yolk-shell nanotube catalyst can be engineered to maintain a high TRM activity at different feed gas composition.

Keywords

Tri-reforming, yolk-shell, CO₂, CH₄.

Introduction

Catalytic tri-reforming is a unique process that can be used to utilize CO₂ emissions directly from a combustion source using natural gas as the primary reactant. The tri-reforming reaction involves synergetic combination of dry reforming (DR), steam reforming (SR), and partial oxidation of methane (POM). (Song, 2000) In the tri-reforming process, most of the CO₂ content of the flue gas can be converted to syngas by DR. Coupling DR, SR, and POM can provide an advantage to adjust the H₂/CO molar ratios between 1 and 2.5 in the product stream. Several metals ranging from noble to base metals (Ni, Co) have been investigated for reforming reactions. In particular, Ni has been preferred for hydrocarbon reforming reactions as it can exhibit high catalytic activity compared to the expensive noble metals. Due to the severe reaction conditions of high temperature and pressure in the tri-reforming reactions, Ni can sinter or agglomerate, and coke can be deposited on the Ni active site during the reaction, which leads catalyst to be deactivated. Supports (CeO₂, ZrO₂) having strong metal-support interaction (SMSI), and high oxygen storage capacity (OSC) can influence the catalytic activity. In reforming reactions, SMSI can contribute to the high stability of Ni, and promote CO₂ and H₂O adsorption on the support, leading to an increase in CO₂ conversion. (García-Vargas et al., 2012) One way to increase SMSI and optimize the fraction of interfacial sites is to prepare metal nanoparticles (core) surrounded by oxide

shells. The core-shell structures can be synthesized with various compositions in the core and shell, and their properties can be modified by tuning their morphologies. The core-shell particles can also be synthesized with a cavity inside the shell (yolk-shell). The yolk-shell structures can be formed in different geometries such as spherical or nanotube structures, and can improve the mass and heat transfer inside the shell.

The unique advantages of yolk-shell nanoparticles make them excellent candidate for tri-reforming, as the particle size, dispersion, and sintering of Ni can be controlled to enhance the catalytic activity for tri-reforming. In this work, NiCeO₂@SiO₂ yolk-shell nanotube catalysts were synthesized with different sizes and their activities were evaluated for the tri-reforming reaction.

Methods

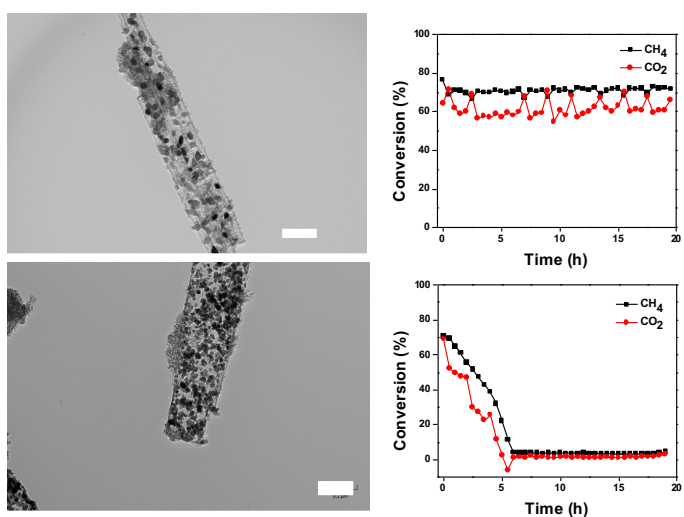
The NiCeO₂@SiO₂ yolk-shell nanotube structures are synthesized using the reverse microemulsion methodology. First, a surfactant with hydrophilic and hydrophobic sites are dispersed into an oil phase solution. Next, precursors of Ni and Ce, and a reducing agent in water solution are added into the oil solution dropwise so that a micelle structure is formed. Finally, SiO₂ source is added to encapsulate the metal particles and the yolk-shell template is aged to form the nanotube structure. The weight percentage of Ni and Ce

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in overall catalyst will be fixed at 10% and 5%, respectively. The activity of yolk-shell catalysts for tri-reforming is tested under oxidizing conditions in a quartz reactor at 750°C. Water is injected into an evaporator tube via a peristaltic pump and mixed with the reaction gases (CH₄, CO₂, O₂, and N₂). The amount of CH₄, CO₂, CO, and H₂ is measured with a gas chromatograph. Fresh and spent catalyst are characterized using x-ray diffraction (XRD), H₂-temperature programmed reduction (TPR) and transmission electron microscopy (TEM).

Results and discussion

The morphologies of the NiCeO₂@SiO₂ yolk-shell nanotube structures are tuned by changing the ratio of hydrophilic and hydrophobic sites during the synthesis. As



shown in Figure 1a, lower hydrophilic site concentrations resulted larger yolk size with a mean particle size of 33 nm. These structures have shown stable activity for tri-reforming with CH₄ and CO₂ conversions of 70% and 60%, respectively. On the other hand, smaller yolks is obtained for the structures synthesized at high hydrophilic site concentrations. The tri-reforming activity of smaller yolks decreased with the time and is completely deactivated after 5 h on stream. The XRD analysis of the fresh catalysts show that NiO and CeO₂ are forming inside the amorphous SiO₂ shell. The analysis of the spent catalysts using XRD and TEM indicates that Ni is oxidized and the structure of SiO₂ shell is not maintained in the smaller yolk structures. In the case of larger nanotube structures, the morphology of the catalyst does not change, and Ni is maintained at the reduced state leading to a high tri-reforming activity.

Conclusions

In this work, the morphologies of the NiCeO₂@SiO₂ yolk-shell nanotube structures are tuned for high tri-reforming activity. Stable nanotube geometries are obtained

at lower hydrophilic site concentrations under tri-reforming conditions. The deactivation of the catalyst is found to be related with Ni oxidation and deformation of the SiO₂ shell.

References

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