

# Nanostructured catalysts for carbon dioxide conversion

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**Abstract:** CO<sub>2</sub> reforming of methane into syngas and CO<sub>2</sub> hydrogenation into methane are two of most promising technologies in CO<sub>2</sub> conversion. Ni catalysts are most widely investigated candidates in both technologies. The prime bottleneck of Ni catalysts lies in rapid deactivation due to carbon deposition and/or metal sintering. Herein, several nanostructured Ni catalysts, such as nanoconfined and nanocomposite Ni catalysts, have been designed for CO<sub>2</sub> reforming of methane and CO<sub>2</sub> methanation. The structure-activity relationship of the catalysts was elucidated as well. Our work highlights the significance of the nanostructures and provides guideline for synthesis of novel catalysts for CO<sub>2</sub> conversion.

**Keywords:** Nickel, Nano, CO<sub>2</sub>.

## 1. Introduction

Conversion of CO<sub>2</sub> into useful chemicals is of great importance in both fundamental research and industrial application<sup>1</sup>. Ni catalysts are most widely investigated candidates for CO<sub>2</sub> reforming of methane into syngas and CO<sub>2</sub> hydrogenation into methane. The prime bottleneck of Ni catalysts in both technologies lies in rapid deactivation due to carbon deposition and/or metal sintering. Recently, a number of studies have demonstrated that nanostructured catalysts would deliver exceptional activity and stability<sup>2</sup>. Herein, several nanostructured Ni catalysts have been designed for CO<sub>2</sub> reforming of methane and CO<sub>2</sub> methanation<sup>3-8</sup>.

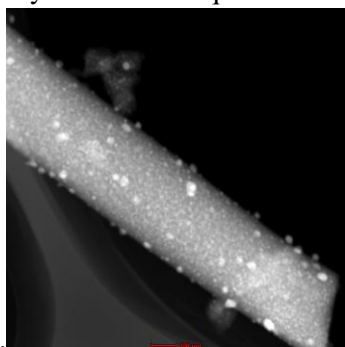
## 2. Experimental

SiO<sub>2</sub> nanofibre confined Ni catalyst was synthesized by the electrospinning technique, being labelled as Ni/SiO<sub>2</sub>-F. The commercial SiO<sub>2</sub> powder impregnated Ni catalyst was prepared as a reference and labelled as Ni/SiO<sub>2</sub>-C. The carbide derived carbon (CDC) layer was grown over SiC surface by exposing the commercial  $\alpha$ -SiC sample to Ar saturated CCl<sub>4</sub> vapor at 800 °C for 1 h. A Ni/CeO<sub>2</sub>-CDC-SiC catalyst was synthesized by a co-impregnation method. A reference catalyst of Ni/CDC-SiC was prepared with a similar procedure without CeO<sub>2</sub> promoter. An Al<sub>2</sub>O<sub>3</sub>-coated SiC, Al<sub>2</sub>O<sub>3</sub>@SiC was synthesized by the evaporation-induced self-assembly (EISA) method. A reference sample, Al<sub>2</sub>O<sub>3</sub>-SiC was synthesized by the deposition-precipitation method. The Ni/Al<sub>2</sub>O<sub>3</sub>@SiC and Ni/Al<sub>2</sub>O<sub>3</sub>-SiC catalysts were prepared by the incipient wetness impregnation method. The catalysts were characterized with N<sub>2</sub> sorption, XRD, SEM, HR-TEM, TG/DTA, XPS and H<sub>2</sub>-TPR/O<sub>2</sub>-TPO/CO<sub>2</sub>-TPD/NH<sub>3</sub>-TPD measurements. The catalytic test was performed under atmospheric pressure in a tubular quartz reactor (i.d. 8 mm). Before reaction the catalyst was reduced in a H<sub>2</sub> stream. The effluent gases were analyzed by an online gas chromatograph.

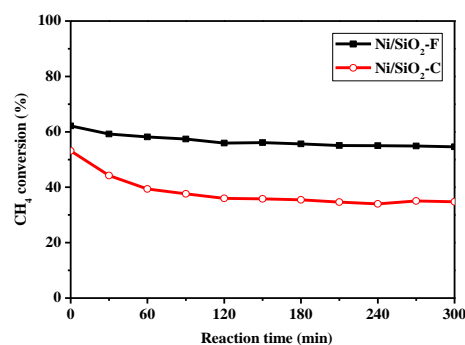
## 3. Results and discussion

STEM image of the fresh Ni/SiO<sub>2</sub>-F catalyst (Figure 1) clearly demonstrated that most of the Ni nanoparticles were confined in the SiO<sub>2</sub> nanofibre. Compared with the Ni/SiO<sub>2</sub>-C counterpart, the Ni/SiO<sub>2</sub>-F catalyst exhibited slightly higher initial activity and much better stability (Figure 2). Structural characterizations revealed that the slightly higher activity was ascribed to the improved dispersion of Ni, and the much better stability was due to the significantly alleviated carbon deposition. The SiO<sub>2</sub> nanofibre confined Ni catalyst possessed much stronger metal-support interaction and more abundant basic sites, leading to an enhanced coke-resistance property. Al<sub>2</sub>O<sub>3</sub> nanofibre confined Ni catalyst with superior

reforming performance was successfully synthesized by the electrospinning technique as well, reflecting the versatility of this technique.



**Figure 1.** STEM image of the fresh Ni/SiO<sub>2</sub>-F catalyst.



**Figure 2.** Catalytic performances of the Ni/SiO<sub>2</sub> catalysts

A ceria-promoted Ni/CDC-SiC catalyst with enhanced activity and improved stability for CO<sub>2</sub> reforming of methane has been successfully synthesized and systematically characterized. N<sub>2</sub> sorption data showed an increased BET specific surface area after the addition of CeO<sub>2</sub> promoter. XRD and TEM results revealed a smaller size of Ni nanoparticles on the CeO<sub>2</sub>-promoted catalyst, which would lead to an enhanced reforming activity. High resolution TEM image and EDX elemental mapping results documented the abundant Ni-CeO<sub>2</sub> interfaces on the CeO<sub>2</sub>-promoted catalyst. High resolution XPS of Ce 3d revealed the presence of Ce<sup>3+</sup> state, implying the defect structure of CeO<sub>2</sub> promoter and the formation of oxygen vacant sites. The excellent redox properties of CeO<sub>2</sub> promoter was proposed to explain the superior coke resistance property, which resulted in an improved stability.

An Al<sub>2</sub>O<sub>3</sub>-coated SiC supported Ni catalyst, Ni/Al<sub>2</sub>O<sub>3</sub>@SiC was designed via the EISA method followed by an incipient wetness impregnation for CO<sub>2</sub> methanation. Compared with the Ni/Al<sub>2</sub>O<sub>3</sub>-SiC and Ni/SiC catalysts, the Ni/Al<sub>2</sub>O<sub>3</sub>@SiC catalyst exhibited enhanced activity. The CO<sub>2</sub> conversion of the Ni/Al<sub>2</sub>O<sub>3</sub>@SiC catalyst reached 72.9% at 300 °C and a maximum of 78.8% at 350 °C. The excellent activity of the Ni/Al<sub>2</sub>O<sub>3</sub>@SiC catalyst was mainly due to the tiny size of Ni nanoparticles and the mesoporous structure of Al<sub>2</sub>O<sub>3</sub> layers on the surface of SiC. Moreover, the Ni/Al<sub>2</sub>O<sub>3</sub>@SiC catalyst exhibited an excellent long-term stability at 350 °C under atmospheric pressure.

#### 4. Conclusions

First, nanoconfined Ni catalysts have been synthesized via the electrospinning technique for CO<sub>2</sub> reforming of methane. Compared with the conventionally impregnated Ni/SiO<sub>2</sub> catalyst, the SiO<sub>2</sub> nanofiber confined Ni catalyst exhibited improved metal dispersion and enhanced metal-support interaction, leading to higher activity and better stability. Second, a nanocomposite Ni/CeO<sub>2</sub>-CDC-SiC catalyst consisting of Ni-CeO<sub>2</sub> interfaces on a nanoporous carbide-derived carbon (CDC) layer over SiC support was designed with improved coke resistance and better stability. Third, an Al<sub>2</sub>O<sub>3</sub>-coated SiC, Al<sub>2</sub>O<sub>3</sub>@SiC was designed via the EISA method to serve as a nanocomposite support for Ni catalysts in CO<sub>2</sub> methanation. The Ni/Al<sub>2</sub>O<sub>3</sub>@SiC catalyst exhibited excellent initial activity and superior long-term stability in CO<sub>2</sub> methanation due to high metal dispersion and proper physiochemical properties.

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