

Ni/CeO₂ catalysts for dry reforming of methane: Effect of the support synthesis method and its resulting nanomorphology.

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Introduction

Dry (with CO₂) reforming of methane (reaction 1) to produce syngas is one of the processes that has attracted intense interest in catalysis, as it can be considered as an alternative route for recycling CO₂ emissions, for advanced biogas utilization, and concerns the simultaneous control of emissions of the two main greenhouse gases CO₂ and CH₄.



The syngas (H₂+CO) produced through DRM, with a H₂/CO molar ratio close to unity is an ideal feedstock for Fischer-Tropsch industry to synthesize oxygenated hydrocarbons. However, the co-occurrence of several other side reactions during DRM, such as methane cracking, Boudouard reaction, water gas shift reaction etc, is a critical issue as they can affect catalyst performance and induce deactivation phenomena mainly due to coke deposition [1]. Therefore, the development of efficient DRM catalysts with high resistance to carbon accumulative deposition is challenging. Noble metal-based catalysts are significantly active for the DRM reaction with a serious drawback, however, their high cost [2]. Therefore, the interest shifts to transition metal and especially to nickel, which is also an efficient DRM catalyst [1, 3-4]. However, coke formation is a serious drawback of Ni-based catalysts as a cause of their deactivation. To address this problem, attention has turned to the support component of the catalyst, which plays an equally important role in its DRM performance either by inducing kinetic bifunctionalities or by affecting Ni particles activity through enhanced metal-support interactions. Due to its unique redox properties, cerium oxide has been extensively studied in various catalytic processes, including DRM. In addition, a significantly evolving area of research refers to the development of specific nano-morphologies (shapes) of cerium oxide, such as nanorods, nanoflowers and nanocubes, that seems to further affect its catalytic behavior [3].

Here we report on the DRM catalytic performance of Ni particles dispersed on CeO₂ support prepared by two different synthesis methods. The aim is to study whether the synthesis method and the resulted morphology plays an important role in the performance of the catalysts. In particular, the CeO₂ nanorods (CeO₂-NR) morphology was achieved via the hydrothermal synthesis method, while an irregular nanostructure of CeO₂ (CeO₂-Pr) was obtained via precipitation. Ni deposition (10% wt) was carried out via wet impregnation on these supports. The catalytic evaluation of the obtained Ni/CeO₂-NR and Ni/CeO₂-PR catalysts was conducted at 750°C for 30 hours in continuous flow fixed-bed reactor system. It was found that the Ni/CeO₂-NR catalyst exhibited excellent DRM performance, in contrast to Ni/CeO₂-PR which was almost inefficient catalyst for the reaction under the same conditions. The textural/morphological characteristics of the materials were determined by applying various techniques.

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Experimental

Two synthesis methods, hydrothermal and precipitation, were used to synthesize nanostructures of CeO_2 using an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor: The hydrothermal method led to the formation of CeO_2 -nanorods, while an irregular CeO_2 nanomorphology was obtained via precipitation. Before deposition of the active phase, the aforementioned supports were calcined at 750°C for 2h. The supported Ni catalysts (10wt% Ni) were prepared by wet impregnation followed by reduction at 400°C for 2h under 20% H_2 /Ar flow and then heated up to 750°C for catalytic testing. The various structural and morphological characteristics of the catalysts were determined by BET, XRD, and TEM techniques. The catalytic evaluation of the samples was conducted in a fixed-bed ($m_{\text{cat}}=20$ mg) continuous flow reactor (quartz, i.d. =3mm), equipped with on-line gas chromatography (SHIMADZU 14B-TCD, HayeSep D column), at a feed of 50% CH_4 and 50% CO_2 with a total flow rate of 50 mL/min (WGHSV=150,000 mL/g·h) performing 30 h time-on-stream (TOS) stability experiments at 750°C .

Results

The physicochemical and structural properties of the materials were determined by BET, X-ray diffraction (XRD) and TEM measurements. Fig. 1(a) represents the pore size distribution obtained by the N_2 corresponding adsorption-desorption isotherms of Fig. 1(b) for the two different supports of ceria and the counterpart Ni catalysts. From the XRD results (Fig. 2), both CeO_2 and Ni crystalline phases were evidenced. However, Ni is marginally detectable in the case of the Ni/ CeO_2 -NR catalyst indicating the existence of very small Ni nanoparticles on it; on Ni/ CeO_2 -Pr the XRD diffractogram shows larger Ni particles. The TEM images confirm the successful achievement of the “nanorod” morphology of CeO_2 particles through the hydrothermal method applied (Fig. 3(a)), while precipitation resulted in an irregular, mostly cube-like, nanostructure (Fig. 3(b)).

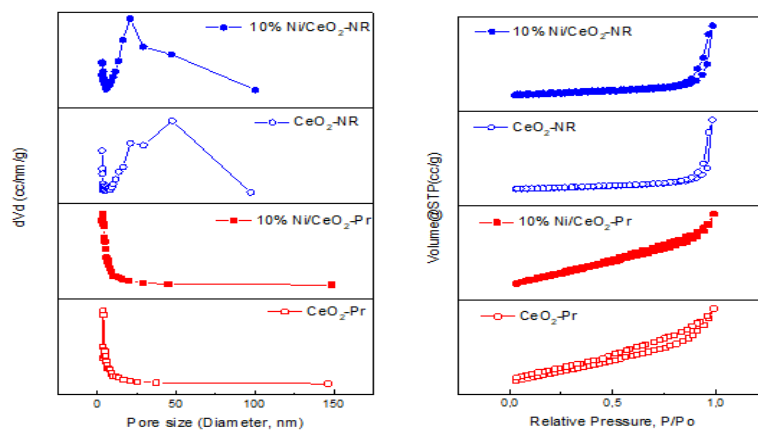


Figure 1: Comparative diagram of pore size distribution (a) and N_2 adsorption-desorption isotherms (b) of CeO_2 -NR, 10%Ni/ CeO_2 -NR and CeO_2 -Pr, 10%Ni/ CeO_2 -Pr

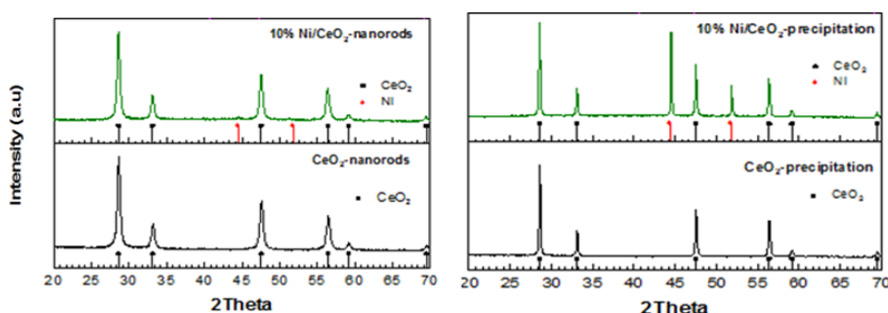


Figure 2: XRD patterns of: (a) CeO_2 -NR and 10%Ni/ CeO_2 -NR, and (b) CeO_2 -Pr and 10%Ni/ CeO_2 -Pr

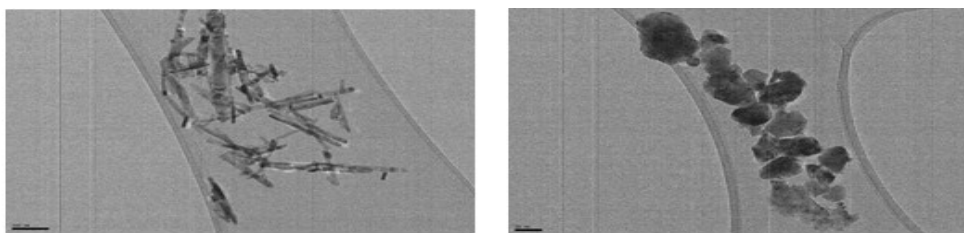


Figure 3: TEM images for the supports of different morphologies: CeO₂-NR (left); CeO₂-Pr (right)

The catalytic stability results carried out for 30 h at 750 °C with CH₄:CO₂ = 50%:50% feed are shown in Fig. 4. As can be seen, the 10%Ni/CeO₂-NR catalyst begins with very high CO₂ and CH₄ conversions of CO₂ and CH₄ (ca. 85%) which are decreased by only ~5-15% after 30 h TOS. In contrast, the 10%Ni/CeO₂-Pr catalyst is almost inefficient for the DRM reaction from the beginning (< ~5% conversions) and become inactive after 10 h TOS.

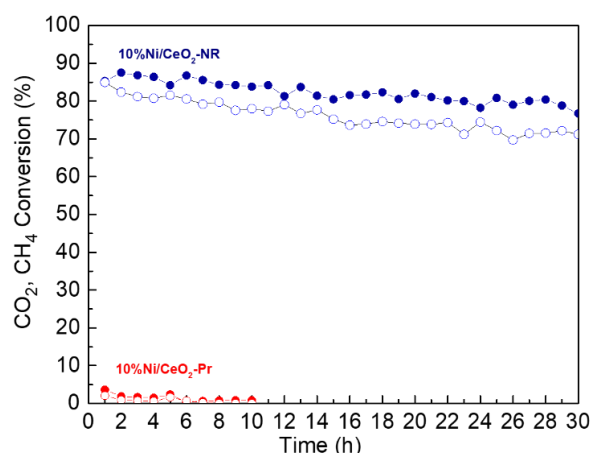


Figure 4: Thirty hours of TOS stability experiments at 750°C for Ni/CeO₂-NR and Ni/CeO₂-Pr catalysts. CO₂ conversion (closed symbols); CH₄ conversion (open symbols). Conditions: CH₄:CO₂ = 50%:50% v/v, p = 1 bar, m_{cat} = 20 mg, F_{t,in} = 50 mL/min (WGHSV=150,000 mL/g·h).

Conclusions

CeO₂ prepared by two different methods (hydrothermal and precipitation) in order to achieve different ceria particle nano-morphologies (nano-rods and irregular cubic-like, respectively) was used as support in Ni/CeO₂ catalysts for DRM reaction. The performance of the obtained Ni/CeO₂-NR and Ni/CeO₂-Pr catalysts on DRM process was extremely different: the former was very active and stable in DRM the second almost inactive. That is, the resulting CeO₂-support nanoparticle differences are strongly influencing the behavior of Ni nanoparticles dispersed on them due to support nanoparticles shape-induced differences on the degree of Ni dispersion and metal-support interactions.

References

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