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## Article

# Morphology effect of zirconia support on the catalytic performance of supported Ni catalysts for dry reforming of methane

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## ABSTRACT

An immature pinecone shaped hierarchically structured zirconia (ZrO<sub>2</sub>-ipch) and a cobblestone-like zirconia nanoparticulate (ZrO<sub>2</sub>-cs), both with the monoclinic phase (m-phase), were synthesized by the facile hydrothermal method and used as the support for a Ni catalyst for the dry reforming of methane (DRM) with CO<sub>2</sub>. ZrO<sub>2</sub>-ipch is a much better support than ZrO<sub>2</sub>-cs and the traditional ZrO<sub>2</sub> irregular particles made by a simple precipitation method (ZrO<sub>2</sub>-ip). The supported Ni catalyst on ZrO<sub>2</sub>-ipch (Ni/ZrO<sub>2</sub>-ipch) exhibited outstanding catalytic activity and coke-resistant stability compared to the ones on ZrO<sub>2</sub>-cs (Ni/ZrO<sub>2</sub>-cs) and ZrO<sub>2</sub>-ip (Ni/ZrO<sub>2</sub>-ip). Ni/ZrO<sub>2</sub>-ip exhibited the worst catalytic performance. The origin of the significantly enhanced catalytic performance was revealed by characterization including XRD, N<sub>2</sub> adsorption measurement (BET), TEM, H<sub>2</sub>-TPR, CO chemisorption, CO<sub>2</sub>-TPD, XPS and TGA. The superior catalytic activity of Ni/ZrO<sub>2</sub>-ipch to Ni/ZrO<sub>2</sub>-cs or Ni/ZrO<sub>2</sub>-ip was ascribed to a higher Ni dispersion, increased reducibility, enhanced oxygen mobility, and more basic sites with a higher strength, which were due to the unique hierarchically structural morphology of the ZrO<sub>2</sub>-ipch support. Ni/ZrO<sub>2</sub>-ipch exhibited better stability for the DRM reaction than Ni/ZrO<sub>2</sub>-ip, which was ascribed to its higher resistance to Ni sintering due to a strengthened metal-support interaction and the confinement effect of the mesopores and coke deposition resistance. The higher coking resistance of Ni/ZrO<sub>2</sub>-ipch for the DRM reaction in comparison with Ni/ZrO<sub>2</sub>-ip originated from the coke-removability of the higher amount of lattice oxygen and more basic sites, confirmed by XPS and CO<sub>2</sub>-TPD analysis, and the stabilized Ni on the Ni/ZrO<sub>2</sub>-ipch catalyst by the confinement effect of the mesopores of the hierarchical ZrO<sub>2</sub>-ipch support. The superior catalytic performance and coking resistance of the Ni/ZrO<sub>2</sub>-ipch catalyst makes it a promising candidate for synthesis gas production from the DRM reaction.

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## 1. Introduction

The dry reforming of methane (DRM) has attracted considerable attention because CO<sub>2</sub> is the primary greenhouse that

has brought about significant climate change, and methane as the main component of natural gas used in combustion leads to a great deal of CO<sub>2</sub> emission. Thus, the DRM reaction converts two greenhouse gases to the industrially important synthesis

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gas ( $H_2$  and  $CO$ ), which serves as the platform for downstream liquid fuels and valuable chemicals [1–8].

Although the noble metal catalysts have exhibited high catalytic performance and low carbon deposition, their high cost and low availability limit their large scale application in industry [9–13]. Ni-based catalysts have been established as potential catalysts for industrial application in synthesis gas production from the DRM reaction owing to their low cost and comparable activity and selectivity to noble metal catalysts. Unfortunately, Ni-based catalysts have a bottleneck issue of rapid deactivation due to the carbon deposition as well as the sintering and oxidation of metallic Ni under the harsh reaction conditions [14–22]. Among these, carbon deposition has been accepted as the main reason of catalyst deactivation [23–25]. Many reports have focused on retarding coke deposition [7,26–31]. Typically, the coke can be efficiently suppressed by Ni-support interface tuning [32] and enhancing heat transfer [33,34]. There is agreement in the references that the coke originates mainly from the two reactions of the decomposition of methane and the Boudouard reaction of  $CO$ , which are strongly dependent on the nature of support.

In the references [35–39],  $ZrO_2$  has been widely used as the catalyst support for diverse transformations including DRM, owing to its high thermal stability, unique acid-base properties and surface oxygen mobility. It was found that the crystalline phase, crystalline size, and pore structure of the  $ZrO_2$  support significantly affected the catalytic performance of the supported catalysts [40–42]. Zheng et al. [43] compared the catalytic performance of supported Ni catalysts on a  $ZrO_2$  prepared by flowing nitrogen ( $ZrO_2$ -AN) and air ( $ZrO_2$ -CP). It was found that  $Ni/ZrO_2$ -AN exhibited much higher stability than  $Ni/ZrO_2$ -CP, which was ascribed to the different nature but not to the amount of coke. Change et al. [44] confirmed that the simultaneous alteration of the support and Ni surface of  $Ni/ZrO_2$  with a Ce modifier and a Ca promoter led to a high performance catalyst, mainly ascribed to a synergy effect of the Ca promoter and Ce modifier for coke resistance and high temperature catalyst aging. Gonzalez-Delacruz et al. [3] found that the size of metallic Ni of the  $Ni/ZrO_2$  catalyst can be efficiently tuned by a  $H_2/CO$  treatment, which significantly affects the catalytic performance for DRM. Xu et al. [45] explored the size effect of  $ZrO_2$  support particles on the catalyst and catalytic performance of a  $Ni/ZrO_2$  catalyst for the utilization of natural gas through dry reforming by  $CO_2$ , and found that the supported Ni catalyst on the  $ZrO_2$  support with a smaller particle size exhibited much higher catalytic stability, ascribed to the enhancing effect of reducing the particle size on oxygen transfer ability. It was found that the shape of the supports (e.g.,  $CeO_2$ ,  $ZnO$ , and  $La_2O_3$ ) strongly affected their catalytic performance [47–49]. In many cases, the morphology effect of  $CeO_2$  and doped  $CeO_2$  has been widely used on a catalyst support to promote the activation of  $CO_2$  and oxidative removal of surface carbon species [7,46,49–51]. However, to the best of our knowledge, few reports regarding the morphology effect of the  $ZrO_2$  support on Ni-based catalysts for DRM reaction can be found.

Herein, we successfully prepared two m- $ZrO_2$  supports with different morphologies including an immature pinecone

shaped hierarchically structured zirconia ( $ZrO_2$ -ipch) and a cobblestone-like zirconia nanoparticulate ( $ZrO_2$ -cs), and tested the catalytic performance of the supported Ni catalysts ( $Ni/ZrO_2$ -ipch and  $Ni/ZrO_2$ -cs) on the two supports for the DRM reaction.  $Ni/ZrO_2$ -ip was also prepared and tested for comparison. It was found that the  $Ni/ZrO_2$ -ipch catalyst exhibited much higher catalytic activity than  $Ni/ZrO_2$ -cs or  $Ni/ZrO_2$ -ip, and it also exhibited higher coke-resistant stability. Characterization techniques including X-ray diffraction (XRD),  $N_2$  adsorption measurement (BET), transmission electron microscopy (TEM), temperature-programmed reduction of hydrogen ( $H_2$ -TPR),  $CO$  chemisorption, temperature-programmed desorption of  $CO_2$  ( $CO_2$ -TPD), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) were employed to investigate the morphology effect of the  $ZrO_2$  support on the supported Ni catalyst for DRM. The origin of the high activity and coke-resistant stability of  $Ni/ZrO_2$ -ipch was explored.

## 2. Experimental

### 2.1. Catalyst preparation

All chemicals (Sinopharm Chemical Reagent Co., Ltd) were used as purchased without further purification. For  $ZrO_2$ -ipch, 3.22 g (7.5 mmol) of  $Zr(NO_3)_4 \cdot 5H_2O$  was dissolved in de-ionized water under magnetic stirring, followed by adding 1.5 g (10.7 mmol) of hexamethylenetetramine aqueous solution to the  $Zr(NO_3)_4 \cdot 5H_2O$  aqueous solution. Then  $NH_4F$  was introduced into the above mixture. The resulting solution was transferred into a Teflon-lined autoclave and hydrothermally treated for 24 h. After the autoclave was cooled down to room temperature, the suspension was separated by filtration, washed with de-ionized water several times, and then dried at 105 °C overnight. The solid was subsequently calcinated at 550 °C for 5 h in a muffle furnace, and  $ZrO_2$ -ipch was obtained. For  $ZrO_2$ -cs, a solution containing 3.22 g (7.5 mmol) of  $Zr(NO_3)_4 \cdot 5H_2O$  was transferred into a Teflon-lined autoclave and was hydrothermally treated at the same conditions as above. After the autoclave was naturally cooled down to room temperature (RT), the solid was recovered by filtration, washed with de-ionized water several times, and then dried at 105 °C overnight. The solid was calcined at 550 °C for 5 h in a muffle furnace, and the  $ZrO_2$ -cs sample was obtained. For comparison, a traditional  $ZrO_2$ -ip support was also prepared by the common precipitation method by using 35% ammonia as precipitant.

The supported Ni catalysts on the  $ZrO_2$ -ipch,  $ZrO_2$ -cs and  $ZrO_2$ -ip supports (10% Ni loading) were prepared by using the previously established LA-IWI method [52]. The  $NiO/ZrO_2$ -ipch,  $NiO/ZrO_2$ -cs and  $NiO/ZrO_2$ -ip samples were reduced at 850 °C for 2 h under a mixture of 20%  $H_2$  in 80%  $N_2$  at a flow rate of 30 mL/min to obtain the reduced samples, which were denoted as  $Ni/ZrO_2$ -ipch,  $Ni/ZrO_2$ -cs and  $Ni/ZrO_2$ -ip, respectively.

### 2.2. Catalyst characterization

TEM images were obtained by using a Tecnai F30 HRTEM

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