



# Nickel based mesoporous silica-ceria-zirconia composite for carbon dioxide reforming of methane



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## ARTICLE INFO

### Article history:

Received 25 December 2015

Received in revised form 4 April 2016

Accepted 19 April 2016

Available online 21 April 2016

### Keywords:

Mesoporous

Silica-ceria-zirconium composite

Oxygen vacancy

CO<sub>2</sub> reforming

Stability

## ABSTRACT

A series of mesoporous silica-ceria-zirconia composite (Si-MCeZr) with variable Si/(Ce + Zr) molar ratios are prepared by improved evaporation induced self-assemble strategy (EISA). TEM and XRD measurements show that the Si-MCeZr frameworks are made of ceria-zirconia solid solutions crystalline nanoparticles and the amorphous silica that serves as glue connecting the nanocrystals. The further heating treatment (700 °C) reveals that the thermal stability of Si-MCeZr is higher than that of Si free mesoporous ceria-zirconia solid solution (MCeZr). This might be due to the key role of the introduction of Si, which improves the thermal stability via inhibiting the growth of nanoparticles and crystallization of ceria-zirconia solid solution nanoparticles. Furthermore, the Si-MCeZr materials are applied as support to prepare nickel based catalysts (Ni/Si-MCeZr) for CO<sub>2</sub> reforming of CH<sub>4</sub>. The XPS analyses show that the concentration of surface oxygen vacancies in Ni/Si-MCeZr increases with the increasing of Si/(Ce + Zr) molar ratios. The long term reforming test demonstrates that the catalytic stability of Ni/Si-MCeZr is improved compared to Si free nickel based catalyst (Ni/MCeZr). The obtained results indicate that enhanced durability may originate from the higher concentration of oxygen vacancies, more rapid oxygen mobility and improved nickel dispersion in Ni/Si-MCeZr, which contribute largely to higher catalytic activity and decoking ability in reforming reaction, as confirmed by TG-DSC and XRD characterizations of catalysts before and after stability tests.

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## 1. Introduction

Carbon dioxide reforming of methane (methane dry reforming of carbon dioxide) has attracted extensive attention by virtue of its vital function to reduce greenhouse gases (carbon dioxide and methane) and alleviate global warming [1–4]. The dry reforming production syngas with low H<sub>2</sub>/CO ratio is more appealing to the synthesis of higher alcohols, oxygenates chemicals [5–7], and 1, 2-dimethoxyethane [8]. The VIII transition metals (Fe, Co, Ni, etc.) and noble metals (Ru, Rh, Pd, Ir, Pt, etc.) have been extensively investigated as catalytic active components in dry reforming reaction [9–17], among which the nickel-based catalysts are most commonly used due to their high activity, low price and wide availability. Unfortunately, in dry reforming reaction, nickel based catalysts suffer from severe deactivation by active metal sintering and carbon accumulation on active sites.

It has been demonstrated that the support is critical for enhancing catalytic performance of nickel based catalysts, and the typical examples are that CeO<sub>2</sub> and Ce-containing mixed oxides are widely employed as supports for methane dry reforming of carbon dioxide [18–20]. CeO<sub>2</sub> can store and/or release a large amount of oxygen via a facile reaction reversibly, i.e., 2CeO<sub>2</sub> ↔ Ce<sub>2</sub>O<sub>3</sub> + 1/2O<sub>2</sub> [21], and the reduced Ce<sub>2</sub>O<sub>3</sub> are prone to being oxidized by CO<sub>2</sub> in the process: Ce<sub>2</sub>O<sub>3</sub> + CO<sub>2</sub> → CeO<sub>2</sub> + CO. In addition, the CeO<sub>2</sub> can remove the carbon deposited on the surface of the catalysts via the reaction: 2CeO<sub>2</sub> + C → Ce<sub>2</sub>O<sub>3</sub> + CO, which promotes the removal of carbon to maintain the accessibility of the metal sites to the reactants [22,23]. However, such good property of CeO<sub>2</sub> will be suppressed as the reaction temperature increases to 350 °C due to the poor thermal stability of the pure CeO<sub>2</sub> [24,25], which leads to the decrease in surface area. It has been reported that the addition of ZrO<sub>2</sub> into CeO<sub>2</sub> could improve oxygen storage capacity, thermal stability and metal dispersion [26–28]. The oxygen storage capacity (OSC), one of the most important requirements of a catalyst in dry reforming reaction, is closely related to the Ce/Zr molar ratios in Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>, and the Ce/Zr ratio at 1 generally

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gives higher OSC than the other molar ratios [29–32]. Our previous work has verified that the carrier ( $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ) with Ce/Zr molar ratio of 1 behaved the highest catalytic activity among all Ce/Zr molar ratios in the dry reforming reaction [33]. Furthermore, the oxygen vacancy is vital in the dry reforming reaction because  $\text{CO}_2$  dissociates over the oxygen vacancies to produce CO and O species and the surface carbon species can be consumed by the interfacial reaction between the carbon and O species [34]. It was found that the incorporation of  $\text{Zr}^{4+}$  into  $\text{CeO}_2$  can induce extrinsic defects associated with oxygen vacancy, stated in Kröger–Vink notation as:  $\text{ZrO}_2 = \text{Zr}''_{\text{Ce}} + \text{V}_\text{O}^{\bullet\bullet} + 2\text{O}_\text{O}^\times$ . The oxygen vacancy can be also created by the surface interactions with oxygen in the ceria-zirconia solid solutions ( $2\text{CeCe}^\times + \text{OO}^\times = 2\text{CeCe}' + \text{V}_\text{O}^{\bullet\bullet} + 1/2\text{O}_2$ ) [35]. In order to further improve the catalytic performance and thermal stability, doping the third component such as transition metal oxide and rare earth oxide into the  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  is confirmed to be effective [36–38]. Adding manganese (Mn) into the  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  can remarkably enhance the catalytic activity and stability due to the increase in migration of lattice oxygen and surface oxygen species [39]. Doping yttrium (Y) into  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  solid solution can improve the oxygen mobility and storage capacity, and the  $\text{CeO}_2$ – $\text{ZrO}_2$ – $\text{Bi}_2\text{O}_3$  solid solution boost the OSC, promoting the catalytic activity [40].

It is well known that the active Ni nanoparticles with smaller sizes have better decoking ability in dry reforming reaction. The mesoporous materials have been widely applied to maintain the small size of active metal under severe reaction condition because the confined space of the mesopores could protect the metal nanoparticles from aggregating and sintering. The application of mesoporous MCM-41 [41], SBA-15 [42], Ordered Mesoporous Ce-Al Oxide Materials [43] to support Ni particle for the improvement of catalytic performance has been reported. It was also demonstrated that both the strong interaction between the supports and active metals and the confined effect of the mesoporous structure make the NiO crystallites dispersed uniformly on the ordered mesoporous  $\text{NiO}$ – $\text{Al}_2\text{O}_3$  composite oxides, ordered mesoporous alumina and mesoporous Ni–Ln (Ln = Ce, La, Sm, Pr)–Al–O composite oxides [44–46].

Hence, the mesoporous  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  may be a promising candidate to support Ni nanoparticles for the dry reforming reaction. However,  $\text{CO}_2$  reforming of  $\text{CH}_4$  is commonly carried out at high temperature of 700 °C, at which the mesoporous structure of  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  support is difficult to retain in that the porous network of  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  will collapse at 650 °C [47]. In this regard, improving the thermal stability of mesoporous structure of  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  is highly desirable for its successful use in reforming reaction. It is noticeable that the introduction of silica into mesoporous materials can enhance their structural stability. For instance, the stability of the ordered mesoporous  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  can be enhanced greatly with the threshold temperature up to 1000 and 900 °C when Si is introduced into their frameworks, respectively [48,49].

In this work, a class of silicon-introduced mesoporous  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  (Si-MCeZr) with variable Si/(Ce + Zr) molar ratios (0–0.4) were prepared by improved evaporation-induced self-assembled methods. The introduction of silica significantly improves the thermal stability of  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  in high temperature (700 °C). Furthermore, the Si-MCeZr support was used to synthesize nickel based catalysts (Ni/Si-MCeZr) by incipient wetness impregnation strategy for  $\text{CO}_2$  reforming of  $\text{CH}_4$ , and the resultant Ni/Si-MCeZr exhibits higher reforming stability compared to Si free catalyst (Ni/MCeZr). The reasons for the improvement in catalytic stability induced by the Si incorporation are also investigated.

## 2. Experimental

### 2.1. Synthesis of the mesoporous silica-ceria-zirconia composite

The mesoporous silica-ceria-zirconia composite, denoted as Si-MCeZr- $x$  ( $x$  refers to the molar ratio of Si/(Ce + Zr), ranging from 0 to 0.4), were prepared by the improved evaporation-induced self-assembly (EISA) strategy reported in the literature [50]. Typically, 1.8 g F127 was dissolved in 20 g ethanol with vigorous stirring at room temperature. Then 2.17 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 1.61 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and different amount of tetraethyl orthosilicate were added to the solution successively. After stirring for at least 4 h at room temperature, the solution was transferred to a Petri dish covered with PE film. Then the Petri dish was put into an oven with desired temperature and humidity (temperature 40 °C, relative humidity 50%) to age for 48 h, the gel product was further dried at 100 °C for another 24 h. Calcination was carried out by slowly increasing the temperature from room temperature to 500 °C for 5 h with ramping rate of 1 °C  $\text{min}^{-1}$ . The synthesis of silica free mesoporous ceria-zirconia solid solution (MCeZr) was similar to that of Si-MCeZr except without the addition of tetraethyl orthosilicate.

### 2.2. Catalyst preparation

Nickel based catalysts with 7 wt% Ni were prepared by incipient impregnation method using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as nickel source and Si-MCeZr- $x$  as supports. After 3 h ultrasound treatment, the samples were dried in an oven at 60 °C for 24 h. The final catalysts (denoted as Ni/Si-MCeZr- $x$  for the silicon-based catalysts and Ni/MCeZr for the Si-free catalyst) were obtained via calcining the precursors from room temperature to 500 °C for 5 h with ramping rate of 1 °C  $\text{min}^{-1}$ .

### 2.3. Catalyst characterization

The X-ray diffraction patterns (XRD) were recorded on X'Pert Pro multipurpose diffractometer (PANalytical, Inc.) with Ni-filtered  $\text{Cu K}\alpha$  radiation (0.15046 nm) at room temperature from 10.0 to 90.0. The nitrogen adsorption and desorption isotherms were performed on an Autosorb-iQ analyzer (Quantachrome Instruments U.S.) at –196 °C. Prior to the tests, all the samples were degassed at 200 °C for 4 h. The specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) method in the relative pressure ranging from 0.05 to 0.3. The single-point pore volume was calculated from the adsorption isotherm at a relative pressure of 0.990, and the pore size distributions were calculated using adsorption branches by Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDX) measurements were carried on the TECNAIG<sup>2</sup>F20 under a working voltage of 200 kV. Raman spectra were collected on the Raman spectrometer (LabRAM ARAMIS, Horiba Jobin Yvon) using 532 nm laser. X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo Scientific ESCALAB250xi spectrometer. For XPS test, the fresh catalyst was pressed into wafer with tablet press machine. All binding energies were calibrated to the C 1s signal at 284.8 eV.  $\text{H}_2$  temperature-programmed reduction ( $\text{H}_2$ -TPR) measurements were performed on an Autosorb-iQ analyzer (Quantachrome Instruments U.S.). The samples (0.1 g) were loaded in a U-shaped quartz reactor. Before TPR measurements, samples were treated at 200 °C for 1 h in flowing He gas (40  $\text{mL min}^{-1}$ ) to remove any moisture and other adsorbed impurities. After cooling the reactor to 40 °C, a 5%  $\text{H}_2$ –Ar gas (40  $\text{mL min}^{-1}$ ) mixture was introduced. The catalyst was heated to 850 °C at a rate of 10 °C  $\text{min}^{-1}$ , and the  $\text{H}_2$  gas consumption was measured using a TCD detector. Thermogravimetric-differential scanning calorimetry (TG-DSC)

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