



# Ceria-Zirconia supported Ni catalysts for partial oxidation of methane to synthesis gas

A.S. Larimi, S.M. Alavi\*

Department of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

## HIGHLIGHTS

- ▶ Highly active and coking resistant Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> (x = 0, 0.25, 0.5, 0.75 and 1) catalysts prepared by precipitation method.
- ▶ The catalyst performance increase with an increase in Zr loading.
- ▶ All catalysts have shown stable performances in the typical operation period of approximately 7 h.
- ▶ Ni/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> catalyst shows the better performance than the others.

## ARTICLE INFO

### Article history:

Received 23 April 2011

Received in revised form 28 May 2012

Accepted 7 June 2012

Available online 27 June 2012

### Keywords:

Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub>

Methane partial oxidation

Nickel catalysts

Solid solution

## ABSTRACT

In this study, 5%Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> (x = 0, 0.25, 0.5, 0.75 and 1) catalysts were prepared by precipitation method and tested for methane partial oxidation. The structures of the catalysts were examined by N<sub>2</sub> adsorption and X-ray diffraction. The catalytic activity and stability were also investigated. The incorporation of Zr into the CeO<sub>2</sub> lattice was found to promote the redox properties. The methane oxidation activity of the mixed oxides was found to be dependent on the Ce:Zr ratio, which relates to the degree of reducibility. The catalytic activity increased with an increasing Zr content. 5%Ni/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> was reported to exhibit the highest BET surface area, activity, stability, and H<sub>2</sub> and CO selectivity for partial oxidation of methane. The catalytic activities and selectivities were also affected by CH<sub>4</sub>/O<sub>2</sub> ratio in the feed stream.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

In recent years, a catalytic partial oxidation of methane has attracted much attention because the reaction can produce H<sub>2</sub>/CO ratio of 2 which is suitable for methanol synthesis and Fischer-Tropsch reaction. On the other hand, much attention has been paid to the high efficiency generation of hydrogen. Hydrogen is now produced by steam reforming of hydrocarbons. Natural gas, composed largely of methane, is used more widely as the raw hydrocarbon due to its abundance and cleanliness. Since steam reforming of methane requires high energy input, catalytic partial oxidation of methane releases energy and requires less energy to produce the same amount of hydrogen. It is well known that high methane conversion, H<sub>2</sub> and CO selectivities can be obtained over catalysts containing transition metals (Ni, Co, Cu and Fe) [1–3], noble metals (Pt, Pd, Rh, Ru and Ir) [4–6] and metal oxides [7–9]. Among those, the catalysts based on noble metals are more active than Ni-based catalysts. However, because of the very high cost of

noble metals, Ni-based catalysts are traditionally used for methane reforming reactions especially due to their low cost.

On the other hand, it is well known that CeO<sub>2</sub>–ZrO<sub>2</sub> solid solutions also have a high oxygen storage capacity which plays the important role of enhancing catalytic activity under reducing and oxidizing conditions [10]. Moreover, zirconia improves the thermal stability of ceria by decreasing the rate of the crystallite growth process [11].

In this study, we report on the activity, selectivity and stability of Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> (x = 0, 0.25, 0.5, 0.75 and 1) catalysts for methane partial oxidation to synthesis gas over the temperature range of 450–850 °C at atmospheric pressure.

## 2. Experimental

### 2.1. Catalyst preparation

Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> (x = 0, 0.25, 0.5, 0.75 and 1) catalysts were prepared by the co-precipitation method. Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (98.5% Merck), ZrOCl<sub>2</sub>·8H<sub>2</sub>O (99% Merck) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99% Merck) solids were dissolved in distilled water in a ratio corresponding to

\* Corresponding author. Tel.: +98 21 77240496; fax: +98 21 77240495.

E-mail address: [alavi.m@iust.ac.ir](mailto:alavi.m@iust.ac.ir) (S.M. Alavi).

the desired final composition. NaOH aqueous solution was added slowly under stirring until the PH of mixture reached 11. The precipitate was washed with distilled hot water, dried in an oven at 90 °C for 24 h and calcinated in air at 750 °C for 4 h. The Ni content was 5 wt.% for all the catalysts.

## 2.2. Catalyst characterization

BET surface area was determined by N<sub>2</sub> adsorption at –196 °C (a three point Brunaur–Emmett–Teller (BET) method using a Quantachrome Corporation Autosorb). Samples were pre-treated at 250 °C for 5 h.

X-ray diffraction (XRD) profiles were recorded on a Philips PW1800 diffractometer by using Cu K $\alpha$  radiation and a power of 40 kV  $\times$  30 mA.

The morphology of the coke formed by the reaction was observed on a Jeol 100X equipment.

Temperature-programmed reduction (TPR) was performed to determine the reduction behavior of catalysts. The experiments were performed on the Micromeritics Pulse Chemisorb 2705 equipment, using 50 mg of catalyst and The temperature was increased from 35 °C to 1000 °C at a heating rate of 10 °C/min. 25 cm<sup>3</sup>/min of 5% H<sub>2</sub> in Ar gas mixture was allowed to flow through the reactor.

## 2.3. Catalytic reaction

Catalytic tests were carried out in a fixed-bed flow reactor, operated isothermally at atmospheric pressure. The reactor was made with a quartz tube of 4 mm inner diameter. The reactor was heated with an electric oven equipped with temperature controller. About 300 mg of each catalyst was loaded into a reactor. The catalyst was tableted, pulverized into 25–45 mesh, set in the reactor, and then *in situ* pretreated in a pure H<sub>2</sub> stream at 700 °C for 2 h. After the catalyst was cooled, the reactant gas mixture containing CH<sub>4</sub> and O<sub>2</sub> with the molar ratio of 2 and 17 mol% N<sub>2</sub> was allowed to flow at GHSV = 149000 h<sup>-1</sup>. The product gases were analyzed by an on-line Teif gostar 101-B chromatograph equipped with a molecular sieve and propack q columns and a TCD, and using He with flow of 15 ml/min as carrier.

The methane conversion and selectivities reported in this work were calculated in the following way:

$$\text{CH}_4 \text{ Conversion : } \%X_{\text{CH}_4} = \frac{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}}{\text{CH}_4^{\text{in}}} \times 100 \quad (1)$$

$$\text{H}_2 \text{ Selectivity : } \%S_{\text{H}_2} = \frac{\text{H}_2^{\text{out}}}{2(\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}})} \times 100 \quad (2)$$

$$\text{CO Selectivity : } \%S_{\text{CO}} = \frac{\text{CO}^{\text{out}}}{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}} \times 100 \quad (3)$$

## 3. Results and discussion

### 3.1. BET surface area

Table 1 summarizes BET surface areas for all synthesized samples. The BET surface area of the catalysts which are based on mixed oxide is higher than those of both based on pure ceria and pure zirconia. The BET surface area of the mixed oxides increased with an increase in Zr loading. This is due to the substitution of a Zr<sup>4+</sup> ion which has a smaller cationic radius, in the Ce<sup>4+</sup> lattice location. A decrease of crystal size would usually be expected to accompany an increase in surface area [12]. Ceria has low thermal

**Table 1**  
The results of BET surface area.

Catalyst	BET Surface area (m <sup>2</sup> /g)
Ni/CeO <sub>2</sub>	72
Ni/Ce <sub>0.25</sub> Zr <sub>0.75</sub> O <sub>2</sub>	160
Ni/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>	128
Ni/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	112
Ni/ZrO <sub>2</sub>	87

stability and is sinter during the calcinations process. Since sintering occurs due to the crystallite growth [12], it could be said that ZrO<sub>2</sub> improves thermal stability of ceria by decreasing the rate of the crystallite growth process.

BET results are higher than those reported by Xu and Wang [13]. By using ZrOCl<sub>2</sub>·8H<sub>2</sub>O instead of ZrO<sub>2</sub> as a starting metal salt, more gasses will release during the calcination process, So prosity will increase and it is resulted in increasing BET surface area.

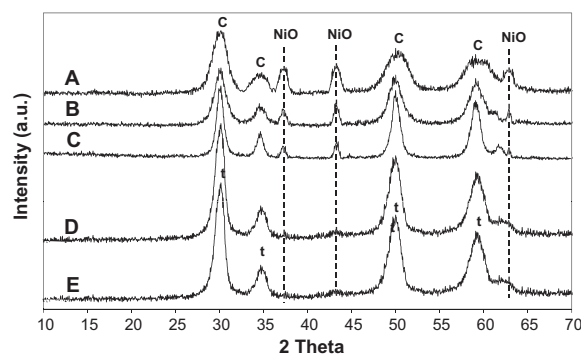
### 3.2. XRD

Fig. 1 presents XRD patterns of calcined catalysts. Ni/CeO<sub>2</sub> sample showed visible peaks at  $2\theta = 28.73^\circ, 33.34^\circ, 47.42^\circ$  and  $56.28^\circ$  which represent the indices of (111), (200), (220) and (311) planes, respectively. This indicates a cubic structure. The XRD pattern of Ni/ZrO<sub>2</sub> sample showed characteristic peaks of tetragonal phase. No evidence for extra peaks due to non-incorporated ZrO<sub>2</sub> was observed in any XRD patterns of Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> ( $x = 0.25, 0.5$  and  $0.75$ ) catalysts. This suggests that ZrO<sub>2</sub> will be incorporated into the CeO<sub>2</sub> lattice to form a solid solution.

It should be noted that the diffraction peaks were shifted to higher degrees with the increasing amounts of ZrO<sub>2</sub>. This observation was attributed to shrinkage of lattice due to the replacement of Ce<sup>4+</sup> (1.09 Å) with a smaller cation radius Zr<sup>4+</sup> (0.86 Å). The results are similar to those observed by Xu and Wang [13], Pengpanich et al. [14] and Alifanti et al. [15].

The small diffraction patterns at  $2\theta = 37.2^\circ, 43.2^\circ$  and  $62.8^\circ$  indexed as NiO, with (101), (012) and (110) planes can also be observed. The intensity of NiO diffraction patterns differs and increases with the increase in Ce content due to the competition between larger Zr<sup>4+</sup> (84 pm) and smaller Ni<sup>2+</sup> (69 pm) cations in the Ce–Zr structure. The highest intensity of NiO diffraction patterns was observed for the catalysts enriched in Ce.

The NiO peaks indicating that NiO was not well dispersed on CeO<sub>2</sub>. In the case of Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> ( $x = 0.25, 0.5, 0.75$ ) catalysts, XRD patterns showed all peaks corresponding to cubic-fluorite structure of NiO/CeO<sub>2</sub>–ZrO<sub>2</sub> solid solution. For the Ni/Ce<sub>(1-x)</sub>Zr<sub>x</sub>O<sub>2</sub> ( $x = 0.25, 0.5, 0.75$ ) catalysts, intensity of the peaks corresponding



**Fig. 1.** X-ray diffraction profiles for Ni/CeO<sub>2</sub> (A), Ni/Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> (B), Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> (C), Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> (D), Ni/ZrO<sub>2</sub> (E).

Download English Version:

<https://daneshyari.com/en/article/6643475>

Download Persian Version:

<https://daneshyari.com/article/6643475>

[Daneshyari.com](https://daneshyari.com)