



# The influence of the support modification over Ni-based catalysts for dry reforming of methane reaction

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## ABSTRACT

5 wt.%Ni/CeZr0.5 wt.%Me (Rh,Ru) catalysts were synthesized by mixed sol–gel and impregnation method. Their catalytic activity was examined in dry reforming of methane reaction (DR) and compared with CeZrMe (Rh,Ru) parent catalysts prepared by sol–gel method. The as prepared fresh catalysts were characterized by XRD while the aged catalysts by XRD, TPO, TEM and Raman. It was found that the Rh and Ru were well incorporated into CeZr fluorite structure. Nickel was present in NiO form.

Ni/CeZrRh catalyst demonstrated the highest activity reaching at 800 °C CH<sub>4</sub> conversion near thermodynamic one.

Ageing of the catalysts shows that the introduction of Rh into CeZr structure results in high activity and good stability even without Ni addition. However for CeZrRu catalyst deactivation is observed. The subsequent impregnation of Ni over CeZrRu catalyst leads to the considerable increase in its stability.

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## 1. Introduction

The natural gas can be enriched through its transformation into synthesis gas (CO + H<sub>2</sub>) by several routes. One of them is dry reforming of methane (DR), which allows the utilization of the excess of CO<sub>2</sub> present in some natural gas streams. The equilibrium composition of an endothermic DR reaction is influenced by the presence of the reverse water gas shift (RWGS) reaction and by coke formation. The occurrence of RWGS results in a decrease in H<sub>2</sub>/CO ratio providing the ratios below thermodynamically admissible value of 1.

Coking is the principal way of deactivation of DR catalysts. It can be accomplished via Boudard reaction and/or CH<sub>4</sub> decomposition [1].

To minimize coke formation two approaches can be taken into account. The first one can be executed by working at high temperatures [2], low space velocities [3] or diluting reaction mixture [4]. The second approach can be allied with the modifications in catalysts composition. CeZr seems to be very attractive as a support due to its good thermal resistance and high mobility of oxygen what can facilitates the reaction with adsorbed carbon species [5]. It was demonstrated that the incorporation of small amount of metal into CeZr structure [6,7] results in shifting of reduction temperature of active metal and CeZr support to lower values what in the end can

influence the hindering of CH<sub>4</sub> decomposition reaction and thus coke formation.

It is generally known that nickel-based catalysts are very interesting in DR reaction due to their lower cost and higher availability [2,8–10]. Nevertheless, these catalysts are needed to be improved in terms of deactivation due to coke formation. Noble metals (i.e. Rh, Ru) reach high activity with a high coke resistance but they are less attractive in view of their costs [11]. The addition of noble metals assists Ni reducibility acting through a hydrogen spill-over [12], which brings H-atoms to the active metal [13,14].

The aim of this paper is to investigate the promoting effect of incorporation of small amount (0.5 wt.%) of noble metals (Ru and Rh) into CeZr structure and its impact over Ni-impregnated CeZrMe (Rh,Ru) catalysts. The influence of modification in Ni catalysts over its activity, coke formation and ageing process is evaluated.

## 2. Experimental

### 2.1. Catalyst preparation

Two different synthesis methods were involved into catalysts' preparation. The CeZr support as well as modified by 0.5 wt.% of noble metal CeZrRh and CeZrRu parent catalysts were developed by using pseudo sol–gel method based on thermal decomposition of metallic propionates [6,15,16].

The introduction of 5 wt.% of Ni was conducted by wet impregnation in the excess of the solvent. The precursor used was nickel (II) nitrate hexahydrate. The obtained dry residue was calcined in air at 750 °C during 4 h. The catalysts formulations are sum-

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marized as follows  $\text{Ce}_2\text{Zr}_2\text{O}_8$  (CeZr),  $\text{Ce}_2\text{Zr}_{1.97}\text{Rh}_{0.03}\text{O}_{8-\delta}$  (CeZrRh),  $\text{Ce}_2\text{Zr}_{1.97}\text{Ru}_{0.03}\text{O}_{8-\delta}$  (CeZrRu), 5 wt.%Ni/Ce<sub>2</sub>Zr<sub>1.97</sub>Rh<sub>0.03</sub>O<sub>8-δ</sub> (Ni/CeZrRh) and 5 wt.%Ni/Ce<sub>2</sub>Zr<sub>1.97</sub>Ru<sub>0.03</sub>O<sub>8-δ</sub> (Ni/CeZrRu).

## 2.2. Catalysts' characterization

The catalyst phase composition was determined by Powder X-Ray Diffraction (XRD) on Bruker D8 Advanced diffractometer with Cu K $\alpha$  radiation.

Thermoprogrammed oxidation (TPO) was conducted over aged catalysts heated from room temperature to 900 °C with a slope 15 °C/min in the oxygen/helium mixture. CO<sub>2</sub> formation was analyzed by Mass Spectrometer Pfeiffer Vacuum. The catalyst surface was previously pre-heated in helium to decompose possible carbonates presented on the surface and to be sure that all CO<sub>2</sub> formed during TPO comes only from the carbon oxidation.

Transmission Electron Microscopy images were collected by TOPCON EM-002B apparatus with accelerating voltage 200 kV. The specimens for TEM were prepared by the dispersion of a small amount of the samples in ethanol and depositing them on membrane supported on copper grids.

Raman spectra were recorded using a Micro-Raman set-up (DILORXY), back-scattering geometry.

## 2.3. Catalytic activity

The catalytic activity measurements were performed in a fixed bed quartz reactor. Prior to CO<sub>2</sub>/CH<sub>4</sub> reaction, 0.1 g of catalyst was reduced in 5% H<sub>2</sub>–95% Ar at 750 °C for 4 h (0.0025 L/min). After the pre-treatment, a feed mixture consisted of CH<sub>4</sub>/CO<sub>2</sub>/Ar 10/10/80 was introduced into reactor. The total space velocity was equal to 30 Lh<sup>-1</sup> g<sup>-1</sup>. The reforming tests were studied with an increase of temperature from 550 °C to 800 °C with the stabilization of 2 h at each temperature. Some steady-state experiments at 750 °C were also performed to study the stability of the catalysts. The effluent gases were analyzed by micro Gas Chromatograph (Agilent) equipped with two columns: Poraplot U and Tamis 5A.

## 3. Results and discussion

### 3.1. Catalysts characterization

XRD diffractograms of the freshly prepared catalysts and support (Fig. 1) show the patterns matching well to face-centered cubic structure of solid solution of Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> (JCPDS 38-1439). The patterns characteristic to ruthenium or rhodium oxides were not detected in the catalysts prepared by sol–gel method. The ionic radii of Rh (Rh<sup>3+</sup> 67 pm) is close to ionic radii of Zr (Zr<sup>4+</sup> 84 pm). Sol–gel preparation facilitates the incorporation of metal in low concentration into CeZr structure [6,7]. As the ionic radii of Ru<sup>3+</sup> is 68 pm the insertion of this metal into CeZr structure was also observed.

It should be noticed also that for the impregnated catalysts the patterns characteristic of nickel oxide (JCPDS 01-089-7131) are present (Fig. 1). For impregnated catalyst all Ni is outside the CeZr structure containing Rh and Ru what can be confirmed by the lack of change in lattice parameters compared to CeZr alone with the same Ce/Zr ratio (5.30 Å).

### 3.2. Catalytic activity measurements

It was demonstrated that the optimal Ce to Zr ratio was equal to 50:50 to obtain catalysts with high activity and good stability [6]. Fig. 2A shows the comparison of CH<sub>4</sub> conversion versus temperature for CeZr, CeZrMe (Rh,Ru) and 5 wt.%Ni/CeZrMe (Rh,Ru)

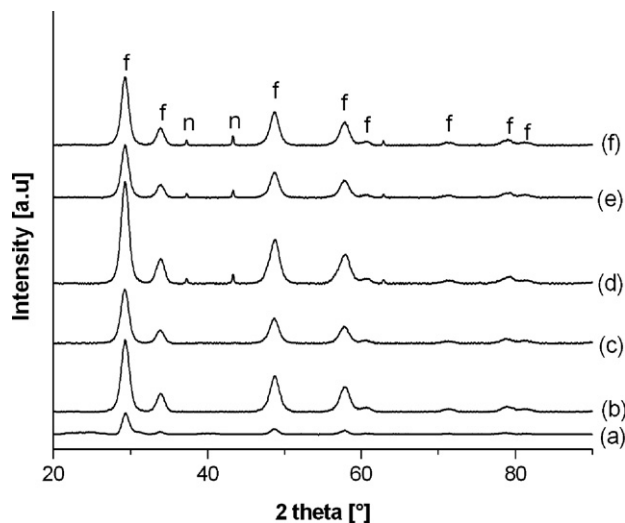


Fig. 1. XRD of freshly prepared catalysts (a) CeZr, (b) Ni/CeZr, (c) CeZrRh, (d) CeZrRu, (e) Ni/CeZrRh and (f) Ni/CeZrRu; f – face centered cubic fluorite structure, n – NiO species.

catalysts with the thermodynamic curve. The conversion values corresponding to thermodynamic equilibrium were obtained by the simulation (minimization of Gibbs energy) using program ProSim Plus. It can be seen that the conversions obtained experimentally are always below thermodynamic values. The introduction of Ru or Rh into CeZr fluorite structure results in augmentation in catalyst activity. The increase in CH<sub>4</sub> conversion at 750 °C from 2% in the case of CeZr support to 59% for CeZrRu and 82% for CeZrRh catalyst was observed. It can be seen that the insertion of Rh leads to the highest changing in catalytic properties, achieving the activity close to the thermodynamic equilibrium. The impact of Ni impregnation over CeZr and CeZrRu and CeZrRh parent catalysts shows a subsequent increase of activity up to 76% and 85% respectively while for Ni/CeZrRh slightly to 87%. The methane consumption is generally lower than one of CO<sub>2</sub> what can be assigned to the occurrence of reverse water gas shift reaction (RWGS) appearing simultaneously with dry reforming of methane. Donazzi et al. [17] suggests that dry reforming of methane is a combination of steam reforming and RWGS reactions. This can be confirmed by H<sub>2</sub>/CO ratio curves (Fig. 3). Their growth with the increase of temperature can be explained by the augmentation in selectivity towards hydrogen. In the case of CeZrRh, Ni/CeZr and Ni/CeZrRu catalysts the hydrogen to carbon monoxide ratio is higher than unity what can be associated with the presence of methane decomposition and/or steam reforming of methane. Some long term tests were also performed to study the stability and deactivation of CeZrRh, CeZrRu, Ni/CeZr, Ni/CeZrRu and Ni/CeZrRh catalysts (Fig. 2B). The experiments were performed at 750 °C during 90 h (for Ni/CeZr only 70 h due to its rapid deactivation). The catalysts exhibit a good stability in CH<sub>4</sub> conversion except CeZrRu and Ni/CeZr for which drop of more than 40% was observed. The introduction of Rh into CeZr structure results in good stability even without Ni addition. However for CeZrRu the impregnation of Ni leads to the considerable increase in its stability compared to CeZrRu parent catalyst.

### 3.3. Characterization after test

#### 3.3.1. Physico-chemical characterization

After catalytic tests the fluorite structure is always present without changing in lattice parameters (ca. 5.30 Å). The diffraction patterns (Fig. 4) at 2 $\theta$  = 45° and 50° are indexed as Ni metal for Ni-

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