Chemical Engineering Journal 156 (2010) 380–387

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Effect of different promoters on $Ni/CeZrO_2$ catalyst for autothermal reforming and partial oxidation of methane

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ARTICLE INFO

*Article history:*
Received 15 July 2009
Received in revised form 19 October 2009
Accepted 21 October 2009

*Keywords:*
Promoters
Methane
Autothermal reforming
$Ni/CeZrO_2$

ABSTRACT

$Ni/CeZrO_2$ catalysts promoted by Ag, Fe, Pt and Pd were investigated for methane autothermal reforming and partial oxidation of methane. The catalysts properties were determined by BET surface area, X-ray diffraction (XRD), $H_2$ temperature-programmed reduction (TPR), temperature-programmed desorption of $CO_2$ ($CO_2$-TPD) and UV–vis diffuse reflectance spectroscopy (DRS). Nickel dispersions were evaluated using a model reaction, the dehydrogenation of cyclohexane. BET surface area results showed that the catalysts prepared by successive impregnation presented lower surface area which favored the smaller nickel dispersion. XRD analysis showed the formation of a ceria–zirconia solid solution. TPR experiments revealed that the addition of Pt and Pd as promoters increased the reducibility of nickel. $CO_2$-TPD results indicated that the AgNiCZ catalysts presented the best redox properties among all catalysts. The autothermal reforming of methane showed that, among different promoters, the sample modified with silver, AgNiCZ, presented higher methane conversion and better stability during the reaction. These results are related to the good reducibility and to the higher redox capacity observed in TPR and $CO_2$-TPD analysis. Samples prepared by successive impregnation technique resulted in a smaller catalytic activity. For partial oxidation of methane, just as happened in autothermal reforming, AgNiCZ also presented the best performance during the 24 h of reaction and the addition of silver by successive impregnation resulted in a lower methane conversion, probably, due to the smaller metal dispersion.

## 1. Introduction

In recent years, there has been much interest in hydrogen production for high efficiency generation of electricity in fuel cells [1]. Special attention has been given to fuel cells technology due to the fact that it does not have harmful emissions compared to other energy conversion systems [2]. Among all the potential sources of hydrogen, natural gas, composed largely by methane, offers many advantages: it is very abundant, clean and it can be easily converted to hydrogen [3].

Among several processes used to obtain hydrogen, steam methane reforming (SMR) shows the highest $H_2$-yield. However, it requires high energy input. On the other hand, catalytic partial oxidation (CPOX) releases energy, despite of a lower $H_2/CO$ ratio. Since autothermal reforming (ATR) integrates both processes, it has attracted more attention in the last years. Seo et al. [4] analyzing the process of methane reforming to produce hydrogen through computer simulations, verified that partial oxidation and autothermal reforming of methane are more attractive than steam reforming, because they require less energy to produce the same amount of hydrogen.

Nickel supported on alumina catalysts are traditionally used for methane reforming reactions especially due to their low cost. However, these catalysts suffer severe deactivation generally because of the formation of carbon deposits on the surface. In order to improve the stability of these $Ni/Al_2O_3$ catalysts, $CeO_2$ and $CeZrO_2$ have been tried as supports since their oxygen storage properties help to avoid the accumulation of coke on the surface [5,6]. Recently, Chen et al. [7] studied the effect of preparation methods on structure and performance of $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts for dry methane reforming, while Xu and Wang [8] analyzed the activity and coking resistance of $Ni/Ce_xZr_{1-x}O_2$ catalysts in partial oxidation of methane reaction. Both groups reported promising results for the use of nickel- and ceria-based catalysts for methane reforming reactions. Escritori et al. [9] investigated $Ni/Al_2O_3$, $Ni/CeO_2/Al_2O_3$, $Ni/CeZrO_2/Al_2O_3$ and $Ni/CeZrO_2$ samples for autothermal reforming of methane. They verified that $Ni/CeZrO_2/Al_2O_3$ catalysts were active at lower temperatures than $Ni/Al_2O_3$, since the mixed oxide offers more actives sites for the reaction.

Besides changing the support, another form to avoid coke deposition is the use of dopants such as noble metals [10,11]. It has been reported in the literature that the use of promoters such as Pt on $Ni/Al_2O_3$ for methane reforming with $CO_2$ and $O_2$ can increase

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doi:10.1016/j.cej.2009.10.047

the activity and the stability of these catalysts [12]. Recently, Dias and Assaf [1] investigated the use of small amounts of palladium as a promoter for $Ni/Al_2O_3$ catalysts during the methane autothermal reforming. They verified that palladium is a good promoter since the catalytic activity was considerably increased. The use of silver as promoter was investigated by Parizotto et al. [13] and the results showed that this metal can contribute to the control of coke accumulation during methane reforming on nickel-based catalysts. The effect of the preparation methods on the properties of 0.3%Pt–10%Ni/$Al_2O_3$ catalysts was evaluated by Tomishige et al. [12]. They verified that a sample prepared by successive impregnation showed higher activity at lower temperatures than the bimetallic catalyst prepared by co-impregnation and the monometallic catalyst in the autothermal reforming of methane.

In order to try to combine the advantages of the use of a ceria-based support and the use of dopants to improve the performance of a nickel-based catalysts, we decided to study the effect of promoters such as platinum, palladium, silver and iron, on the properties and on the catalytic performance of Ni/$CeZrO_2$ for partial oxidation and autothermal reforming of methane.

## 2. Experimental

### 2.1. Catalyst preparation

The support, $CeZrO_2$, with atomic Ce/Zr ratio equals to 1, was prepared by co-precipitation technique, using $(NH_4)_2Ce(NO_3)_6$ and $ZrO(NO_3)_2$ as precursors and calcination at 773 K during 4 h. In order to evaluate the effect of the method of addition of the dopant we used two preparation methods: co-impregnation and successive impregnation. Co-impregnation was performed using an aqueous solution of nickel, silver, iron, platinum and palladium nitrates (10 wt.% for Ni and 0.1 wt.% for promoters). Then, the samples were dried at 393 K for 2 h and calcined in air at 723 K during 4 h. For the successive impregnation method, 10 wt.% nickel was added to the $CeZrO_2$ support and calcined. Then, successively, another impregnation was performed using a silver nitrate solution to obtain samples containing 0.1 and 1 wt.% of silver. The samples were dried and calcined as the catalysts prepared by co-impregnation method. The catalysts synthesized and the nomenclatures used in the present work are listed in Table 1.

### 2.2. Catalysts characterization

BET surface areas of the catalysts were measured using a Quantasorb Jr. apparatus equipped with a thermal conductivity detector. Before nitrogen adsorption, samples were pre-treated at 423 K, during 12 h. $N_2$ adsorption was carried through at liquid nitrogen temperature (77 K).

X-ray diffraction measurements were made using a RIGAKU diffractometer with a CuKα radiation. XRD data were collected at 0.04°/step with integration times of 1 s/step between $2\theta = 25^\circ$ and $65^\circ$.

**Table 1**
Nomenclature used for the catalysts.

| Catalyst | Used nomination |
|---|---|
| 10%Ni/$CeZrO_2$ | NiCZ |
| 0.1%Ag–10%Ni/$CeZrO_2$ | AgNiCZ |
| 0.1%Fe–10%Ni/$CeZrO_2$ | FeNiCZ |
| 0.1%Pt–10%Ni/$CeZrO_2$ | PtNiCZ |
| 0.1%Pd–10%Ni/$CeZrO_2$ | PdNiCZ |
| 0.1%Ag–10%Ni/$CeZrO_2$ (successive impregnation) | AgNiCZ-s |
| 1%Ag–10%Ni/$CeZrO_2$ (successive impregnation) | 1AgNiCZ-s |

Nickel dispersion was estimated through cyclohexane dehydrogenation, a structure insensitive reaction [14]. The samples (25 mg) were submitted to the same pretreatment (drying and reduction) as described in $CO_2$-TPD. After the reduction step, the sample was cooled in hydrogen flow to 523 K and the flow was increased to 100 mL/min. The reaction mixture was obtained by bubbling hydrogen through a saturator containing cyclohexane (99.9%) at 285 K ($H_2$/cyclohexane = 13.2). Reaction temperatures varied between 523 and 573 K. At these conditions, no mass transfer or equilibrium limitations were observed. The composition of effluent gas phase was measured by online gas chromatograph (Shimadzu) equipped with a thermal conductivity detector and a Chrompack CP-WAX 57 CB column.

Temperature-programmed reduction (TPR) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). A mixture of 2% $H_2$ in Ar flowed through the sample (300 mg) at 30 mL/min, raising the temperature at a heating rate of 10 K/min up to 1273 K. $H_2$ consumption was obtained from the integrated peak area of the reduction profiles relative to a calibration curve.

$CO_2$ temperature-programmed desorption ($CO_2$-TPD) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The samples were reduced under $H_2$ flow (30 mL/min), increasing the temperature up to 773 K at 10 K/min. The temperature remained at 773 K for 3 h, the $H_2$ flow was replaced by He and the sample was heated up to 1073 K. Then, the samples were cooled to room temperature and the He flow was replaced by a mixture of 20%$CO_2$/He for chemisorption. After $CO_2$ chemisorption was completed, the reactor was purged with He and $CO_2$-TPD measurements were carried out increasing the temperature up to 1073 K at 20 K/min. $CO_2$ desorbed and CO produced were obtained from the integrated peak areas of the profiles relative to a calibration curve.

The samples were characterized at room temperature between 200 and 800 nm in a VARIAN-Cary 500 UV–vis spectrophotometer equipped with a diffuse reflectance accessory (Harrick). $CeZrO_2$ was used as reference, and the Kubelka–Munk function F(R) was calculated.

### 2.3. Autothermal reforming of methane

Before catalytic tests, the sample was reduced as described in the $CO_2$-TPD. After the reduction, the sample was heated to 1073 K under He (30 mL/min). The catalytic tests were carried out using 12 mg of catalyst and a total flow of 180 mL/min. The feed composition was $2CH_4{:}1H_2O{:}0.5O_2$. Effluent gases from the reactor were analyzed by a gas chromatograph (Shimadzu) equipped with a Hayesep column.

### 2.4. Partial oxidation of methane

Before catalytic tests, the sample was reduced as described in the $CO_2$-TPD. After the reduction, the sample was heated to 1073 K under He (30 mL/min). The catalytic tests were carried out using 6 mg of catalyst and a total flow of 300 mL/min. The feed composition was $2CH_4{:}1O_2$.

## 3. Results and discussion

Table 2 summarizes BET surface areas, NiO particle sizes and nickel metal dispersions obtained for all synthesized samples. The value of BET area of the $CeZrO_2$ support is similar to values previously reported in the literature [15]. The addition of metals to $CeZrO_2$ did not change significantly the total area. The samples prepared by successive impregnation method showed lower