

# Hydrogen Production by Oxidative Steam Reforming of Methanol over Ni/CeO<sub>2</sub>–ZrO<sub>2</sub> Catalysts

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## Abstract

Single  $\text{ZrO}_2$  and mixed  $\text{CeO}_2$ - $\text{ZrO}_2$  oxides with different  $\text{CeO}_2/\text{ZrO}_2$  ratios were prepared by the sol-gel method and the  $\text{CeO}_2$  by precipitation. The prepared support were impregnated with an aqueous solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at an appropriate concentration to yield 3 wt. % of nickel respectively in the catalysts. Catalytic materials were characterized by BET ( $\text{N}_2$  adsorption-desorption), SEM (scanning electron microscopy), EDS (energy dispersive X-ray spectroscopy), XRD (X-ray diffraction) and TPR (temperature-programmed reduction). The oxidative steam reforming of methanol (OSRM) reaction was investigated on these catalysts for  $\text{H}_2$  production as a function of temperature. Depending of the  $\text{CeO}_2/\text{ZrO}_2$  ratio; the catalysts have a significant influence on the surface area (BET), reduction properties and methanol conversion. XRD patterns of the Ni-base catalysts showed well defined diffraction peaks of the metallic Ni except on the Ni/ $\text{CeO}_2$  catalyst, suggesting that on this sample all of the active phase was highly dispersed. Ni/Ceria-rich catalysts were vastly active for OSRM, giving a total  $\text{CH}_3\text{OH}$  conversion at  $325\text{ }^\circ\text{C}$  with  $\text{GHSV}=0.3 \times 10^5\text{ h}^{-1}$ . They also showed close selectivity toward  $\text{H}_2$ , with high selectivity to  $\text{CO}_2$  in all range of temperature, this suggest that reverse WGS reaction did not occurred on these samples. It seems that the nickel is the phase mainly responsible of hydrogen production although the  $\text{CeO}_2/\text{ZrO}_2$  support reduces the CO formation.

**Author Keywords:** Nickel catalyst; Hydrogen production; oxidative steam reforming of methanol;  $\text{ZrO}_2$ ;  $\text{CeO}_2$ , TPR, XRD

## 1. Introduction

Hydrogen fuel cells are promising candidates for the generation of electrical power for mobile applications. Conventional hydrogen production methods use gasoline or natural gas reforming. From the different feed stock fuels available, alcohols are very promising candidates because they are easily decomposed in the presence of water and generate a hydrogen-rich mixture at relatively low temperatures. An advantage of using methanol for  $H_2$  production is their high hydrogen/carbon ratio, this makes the steam reforming of methanol energetically favorable and has the advantage of reduction of soot formation due to the absence of carbon–carbon bonds, which may otherwise lead to catalyst deactivation [1, 2]. On the other hand, methanol is easy to store and transport as it is in a liquid form at room temperature. Instead of handling  $H_2$  under high-pressure or cryogenic conditions, steam reforming of methanol (MSR) can be used to produce hydrogen on board [3, 4]. A large variety of catalytic materials for the reforming of methanol have been reported in the literature [5-17]. Among them, copper-containing catalysts such as Cu/ZnO and Cu/ZnO/ $Al_2O_3$ , which are traditionally used for methanol synthesis and low-temperature water gas-shift reaction, have been the most frequently studied systems [6, 16, 18, 19]. Therefore, the development of new efficient catalyst systems that exhibit an improved long-term stability and selectivity toward hydrogen production are highly desired. Liu et al. [20] reported that CuO/ $CeO_2$  is very effective for steam reforming of methanol (SRM). It has been shown that the catalytic activity of CuO– $CeO_2$  catalyst in SRM is considerably affected by the copper content. Oguchi et al. [21] found that the optimum amount of CuO in CuO/ $CeO_2$  was 80 wt. % having an accelerating effect in the SRM with the addition of  $ZrO_2$ . In the same way, Udani et al. [22] found that the 70 wt.% CuO– $CeO_2$  catalyst had the

highest activity in the temperature range of 160–300 °C for both SRM and OSRM. On Cu/CeO<sub>2</sub> catalysts [11] was reported that samples with 2 and 6 wt.% of copper had the best catalytic activity on the OSRM than the catalyst with 10 wt.% of copper. On the other hand, Shimokawabe et al. [23] have reported that highly active Cu/ZrO<sub>2</sub> catalysts for the steam reforming of methanol could be prepared by impregnation method. They found that the Cu/ZrO<sub>2</sub> catalysts exhibited significantly higher activities than their silica-supported counterparts. Yao et al. [24] found that the catalyst with higher specific copper surface area and component dispersion shows higher activity for methanol conversion at lower temperature and low CO production. Breen and Ross [25] studied the steam reforming of methanol on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. They found that using zirconia as a support for Cu and ZnO produces a more active catalyst than Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> for the SRM reaction. Biswas and Kunzru [26] studied the effect of Ni on CeO<sub>2</sub>-ZrO<sub>2</sub> supports and found that the reforming capability of Ni/Ce<sub>0.16</sub>Zr<sub>0.84</sub>O<sub>2</sub> and Ni/Ce<sub>0.41</sub>Zr<sub>0.59</sub>O<sub>2</sub> catalyst was low, whereas the highest activity was obtained on 30% Ni/Ce<sub>0.74</sub>Zr<sub>0.26</sub>O<sub>2</sub> sample at 600 °C. The high ethanol conversion observed on the 30% Ni/Ce<sub>0.74</sub>Zr<sub>0.26</sub>O<sub>2</sub> sample for SR was attributed at the higher amount of reduced nickel available for reaction. However, all catalysts tested, produced significant amount of acetaldehyde at lower temperatures due to the dehydrogenation of ethanol. On Cu/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts during OSRM reaction was observed highest catalytic activity and less CO production on the Cu/CeO<sub>2</sub>-rich catalysts, while the lowest performance was obtained on the Cu supported on mixed ZrO<sub>2</sub>-CeO<sub>2</sub> oxides with > 50 wt.% of ZrO<sub>2</sub> in the support [13].

In this work we studied the catalytic properties of nickel supported on CeO<sub>2</sub>-ZrO<sub>2</sub> with different ZrO<sub>2</sub>/CeO<sub>2</sub> ratios in the OSRM reaction for H<sub>2</sub> production as a function of temperature. Catalytic materials were characterized by BET (N<sub>2</sub> adsorption–desorption),

SEM (scanning electron microscopy), EDS (energy dispersive X-ray spectroscopy), XRD (X-ray diffraction) and TPR (temperature-programmed reduction).

## **2. Experimental**

### ***2.1. Catalysts Preparation***

Single ZrO<sub>2</sub> oxide was prepared by the sol-gel method from Zirconium (IV) propoxide (Fluka) as a precursor in n-propanol (Aldrich) solution and basic catalyst (NH<sub>4</sub>OH) (Fluka) with constant stirring. Mixed oxides CeO<sub>2</sub>-ZrO<sub>2</sub> (10, 50, 90 wt. % of ZrO<sub>2</sub> in mixed oxides) were prepared as follow: (C<sub>6</sub>H<sub>9</sub>CeO<sub>6</sub> at an appropriate composition was dissolved at room temperature in n-propanol then Zr-propoxide was added and finally the NH<sub>4</sub>OH. The solution was processed at reflux temperature (85 °C) and water was drop wise added to the solution. The reflux temperature was maintained for 1 hour and the resultant mixture was cooled at room temperature ageing it for 24 h. The residual liquid was removed by decanting. The molar ratio used for the synthesis was: propoxide/alcohol/H<sub>2</sub>O/NH<sub>4</sub>OH = 1:4:4:0.33 [13, 27-29]. The xerogel was obtained after heating the mixture in an oven at 100 °C for 24h in static air using a temperature ramp of 5 °C/min. Under an air stream the xerogel was heated at 100°C for 1 hour and then calcined at 600 °C for 5 hours. The CeO<sub>2</sub> synthesis was done using the precipitation method of the C<sub>6</sub>H<sub>9</sub>CeO<sub>6</sub> in NH<sub>4</sub>OH at 50 °C. The solid obtained was calcined at 600 °C for 5 h in air stream. The prepared supports were impregnated with a solution of NiCl<sub>2</sub>•6H<sub>2</sub>O at an appropriate concentration to yield 3 wt. % of Ni in all catalysts. The samples were dried at 100 °C for 1h followed by calcination at

500 °C for 2h in static air and then reduced with H<sub>2</sub> stream (60 mL/min) at the same temperature for 2h before characterization and activity test. The labeling of different catalysts will be referred as Ni/ZrO<sub>2</sub>, Ni/CeO<sub>2</sub> and Ni/CZn, where C=CeO<sub>2</sub>, Z=ZrO<sub>2</sub>, n=10, 50, 90 wt. % of ZrO<sub>2</sub> in the samples respectively. The actual Ni content was determined by ICP and it was 2.82, 2.82, 2.85, 2.86 and 2.84 for Ni/ZrO<sub>2</sub>, Ni/CZ90, Ni/CZ50, Ni/CZ10 and Ni/CeO<sub>2</sub> respectively.

## **2.2. Characterization**

Single point Brunauer–Emmett–Teller (BET) surface area of catalysts was determined by the dynamic pulsing technique on a multitask RIG-100 instrument from ISRI equipped with a Thermal Conductivity Detector (TCD) with output to a computer, employing nitrogen physisorption at liquid nitrogen temperature. Prior to each measurement, the sample was degassed at 120 °C by passing 30 % N<sub>2</sub>/He for 30 min. Temperature-Programmed Reduction (TPR) experiments was performance on a multitask RIG-100. The oxidized catalyst (0.1 g) was placed in the reactor and purged with UHP Ar at room temperature and then the TPR measurement was performed using 5% H<sub>2</sub>/Ar gas mixture (40 mL/min). The temperature was increased at a rate of 10 °C/min from room temperature to 600 °C. The effluent gas was passed through silica gel to remove water before measuring the amount of hydrogen consumed during the reduction of the catalysts in a TC detector. The signal was calibrated by 0.5 ml pulses of 5 % H<sub>2</sub>/Ar at the end of the experiment. Also TPR analysis of the samples after catalytic activity was performance. For this, the surface of the spend catalysts was cleaned by a He stream (40 mL/min) for 30 min at 375 °C and cooled at room temperature, then the sample was purged with UHP Ar flow and the TPR was done. X-ray

diffraction (XRD) powder patterns were recorded in a Siemens D-5000 diffractometer, using Cu K $\alpha$  ( $\lambda=0.15406$  nm). The morphology and chemical composition of the samples were determined in a Philips XL-30, with resolution of 3.5 nm, fitted with an energy dispersive X-ray Spectrometer (EDAX) at an acceleration voltage of 25 kV, obtaining the images with the backscattering electron signal. Before the analysis, the samples were fixed on aluminium specimen holder with an aluminum tape.

### ***2.3 Catalytic Reaction***

The steady-state activity in the oxidative steam reforming of methanol reaction was performed in a conventional fixed-bed flow reactor (8 mm i.d.) using a commercial flow system RIG-100-ISRI. The catalytic test was evaluated in a temperature range from 250 to 375 °C with less of 5 % of the error in the curves, at atmospheric pressure with 0.1 g of the catalyst placed in the reactor with a thermocouple in contact with the catalytic bed to control the temperature inside the catalyst. The sample was first activated in a stream of H<sub>2</sub> (60 mL/min) from room temperature to 500 °C with a heating rate of 7 °C/min and held at this temperature for 1h. The catalyst was brought up to the reaction temperature in He and the reaction mixture was introduced. For the OSRM reaction, O<sub>2</sub> (5%)/He mixture was used and the total flow rate was kept at 60 mL/min (GHSV= 30,000 h<sup>-1</sup> based on the total flow). This gas was added by means of a mass flow controller (RIG-100) and bubbled through a tank containing mixture of water and methanol; the partial pressure of CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> was 73.59, 12.75 and 22.44 Torr respectively. The effluent gas of the reactor was analyzed by gas-chromatography (Gow-Mac 580 instrument) equipped with a two columns system

(molecular sieve 5 Å and Porapak Q columns), double injector controlled by Clarity software V.2.6.04.402 and TCD. The first column was used to separate the gaseous products such as H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and CO. The second column was used to separate water, methanol, methyl formate (MF) and CO<sub>2</sub>. The Ni/CeO<sub>2</sub>-rich catalysts after catalytic reaction were tested again in a second cycle in the OSRM reaction. So at the end of the reaction (375 °C) the spent catalyst was cleaned with He for 30 min, then the sample was cooled at the reaction temperature and the catalytic activity was performed. All the reported data were collected during 3 h of run time. The following equations were used to determine the methanol conversion and selectivity:

$$X(\%) = \frac{C_{in} - C_{out}}{C_{in}} * 100$$

$$S_{H_2}(\%) = \frac{nH_{2-out}}{nH_{2-out} + nCH_{4-out} + nCO_{out} + nCO_{2-out}} * 100$$

$$S_{CO_2}(\%) = \frac{nCO_{2-out}}{nH_{2-out} + nCO_{2-out} + nCO_{out} + nCH_{4-out}} * 100$$

The subscripts in and out indicate the inlet and the outlet concentrations of the reactants or products.

### 3. Results and discussion

#### 3.1 Crystalline phases (XRD)



XRD patterns of the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts are presented on Fig. 1. It can be seen on the Ni/ZrO<sub>2</sub> catalyst, the tetragonal and monoclinic phases of the zirconia. The addition of CeO<sub>2</sub> to ZrO<sub>2</sub> on mixed oxides causes a reduction in the intensity and a broadening of the diffraction peaks. This finding was associated with the reduction of crystallinity, as well as a reduction in the particle size of the support [13, 28, 30, 31]. Adding 10 wt. % of the CeO<sub>2</sub> to zirconia stabilized the tetragonal phase of the ZrO<sub>2</sub> as was reported for other materials [13, 28, 31]. However, on the Ni/CZ50 sample, a mixture of solid solution was observed and it corresponding to the tetragonal Zr<sub>0.84</sub>Ce<sub>0.16</sub>O<sub>2</sub> and cubic Zr<sub>0.4</sub>Ce<sub>0.6</sub>O<sub>2</sub> phases [13]. Typical ceria cubic structure was present on the XRD patterns of the Ni/CeO<sub>2</sub> and Ni/CZ10 catalysts. In addition, diffraction peak of the metallic Ni was observed in all samples; but the intensity of this peak was higher on the Ni/ZrO<sub>2</sub>-rich samples than on the Ni/CeO<sub>2</sub>-rich catalysts; suggesting that CeO<sub>2</sub> support promote the dispersion of Ni and make its crystallite size smaller. The XRD patterns of the Ni/ZrO<sub>2</sub> and the Ni/CZ50 samples post-reaction showed changes in the crystalline structure. The intensity of the tetragonal phases of the ZrO<sub>2</sub> and the Zr<sub>0.84</sub>Ce<sub>0.16</sub>O<sub>2</sub> diminished on the Ni/ZrO<sub>2</sub> and Ni/ZC50 catalysts respectively, whereas the intensity of the monoclinic structure of zirconia and cubic Zr<sub>0.4</sub>Ce<sub>0.6</sub>O<sub>2</sub> phase was increased on the same samples. This phenomenon was observed previously on Cu/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts during OSRM reaction [13]. So the tetragonal structure was transformed to a monoclinic phase in the case of the Ni/ZrO<sub>2</sub> sample and a cubic structure in the case of the Ni/ZC50 catalyst, thus the increase of the monoclinic and cubic phases was at the expense of the tetragonal phase. On the other samples, those crystalline structures were almost unaffected by the reaction. Bi et al. [32] reported the same phenomena on Pt-Ru/ZrO<sub>2</sub> catalysts after OSR of the ethanol reaction; they observed that the tetragonal phase diminished and the monoclinic structure of ZrO<sub>2</sub> increased.

### ***3.2 Textural properties***

The surface area of the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts calculated by the BET method from N<sub>2</sub> adsorption-desorption through the single point method are summarized in table 1. CeO<sub>2</sub> support exhibited a high value of the specific surface area (ca. 53 m<sup>2</sup>/g) than ZrO<sub>2</sub>. On the other hand, the addition of the CeO<sub>2</sub> to ZrO<sub>2</sub> caused and increased in the specific surface on the mixed oxide. When the ceria content goes up to 90 and 50 wt.% on the mixed oxide the surface area values were higher than ZrO<sub>2</sub>-rich supports. These results are in agreement with those reported on [13, 31], they reported that the surface area of CeO<sub>2</sub>-ZrO<sub>2</sub> supports increased as the zirconium was added to CeO<sub>2</sub>. This finding could be improved the dispersion of the Ni on the support, which is beneficial for the performance of the catalyst. Ni impregnation on the supports causes a decrease in the surface area, this behavior could be attributed to the blockade of the pores in the support by the Ni, as well as to the thermal treatments, but the tendency in the surface area was maintained. Fig. 2 shows the SEM image of the Ni/ZC50 catalyst before catalytic reaction. It can be seen that the sample was constituted by large particles with semispherical tendency and flat particles like a rectangular rods. After catalytic reaction, these kinds of particles remain in all the catalysts as at the beginning of the reaction.

### ***3.3 Temperature-programmed Reduction***

Temperature-programmed reduction profiles of the fresh Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> samples and catalysts after catalytic reaction were performed in order to compare the effect of support

composition on the reducibility of the nickel oxide (Fig. 3). Reduction peaks observed on the catalysts at temperatures close to 350 °C were associated to the reduction of NiO particles strongly bonded with the support [12, 26] and the peak above 500 °C was related to the partial reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  [11, 13, 31]. TPR profiles of the catalysts showed that with increasing  $\text{CeO}_2$  content to  $\text{ZrO}_2$ , the reduction temperature of the Ni-base catalysts supported on the mixed  $\text{CeO}_2$ - $\text{ZrO}_2$  oxides shifted towards higher temperature until ZC-50 support as reported for other catalysts that used  $\text{ZrO}_2$ - $\text{CeO}_2$  oxides as catalytic supports [13, 26, 31]. In addition, it is clear that the TPR profile of the Ni/ZC-50 catalyst showed a combined broad reduction peak indicating heterogeneity in the kinds of NiO species present on the catalysts, this finding could be associated with the strong interaction of Ni with the mixture of solid solution identified on this catalyst than the Ni deposited on the others supports. TPR profiles of the samples after OSRM reaction showed a shift of the reduction peaks at lower temperatures than on the fresh catalysts. This effect was associated with the redispersion of the active phase supported on  $\text{CeO}_2$ - $\text{ZrO}_2$  oxides having highly dispersed species as was reported on literature [11-13]. However, as before the reaction, the  $\text{CeO}_2$ -rich catalyst had high  $\text{H}_2$  consumption. This finding showed that all catalysts were oxidized during catalytic reaction, and that the reducible species present on the surface of the catalysts was present in both oxidized and reduced states, but the metallic state prevails as was confirmed by XRD results of the samples analyzed after catalytic reaction. Turco et al. [33] suggested that there was a zone of the catalytic bed in which the catalyst is oxidized, and another zone in which it was reduced. However, we suggest that some fraction of the metallic surface active phase is partially oxidized and the core of the particles remains in the reduced state. On Cu/ $\text{CeO}_2$  samples after OSRM reaction it was found by EPR technique,  $\text{Cu}^{2+}$  forming a nano-sized two-dimensional structure [11, 34, 35].

Oguchi et al. [21] observed a reduction peak on the CuO/ZrO<sub>2</sub> sample post-reaction. They concluded that the Cu<sub>2</sub>O phase was stabilized during the SRM reaction and confirmed by XRD analysis. The principal peak positions and the percentage of the NiO reduced on each catalyst given by the Ni/H<sub>2</sub> ratio were summarized in Table 1. The H<sub>2</sub> uptake on the fresh Ni/CeO<sub>2</sub>-rich catalysts was higher than the Ni/ZrO<sub>2</sub>-rich catalysts, however on all samples the H<sub>2</sub> consumption was lower than that required for a total reduction of NiO except on the Ni/CZ50 catalyst. The lower value of Ni/H<sub>2</sub> ratio suggests that on ZrO<sub>2</sub>-rich catalysts the interaction of nickel with the support is high avoiding the Ni reduction. However, in the Ni/ZC50 sample the hydrogen uptake was higher than the expected for the total reduction of the NiO present on the sample. This finding could be associated to the fact that, in the TPR study, Ni particles probably cause spill over of hydrogen onto the support inducing a concurrent reduction of both nickel oxide and the surface of the CeO<sub>2</sub> [11, 13, 31]. This shows that the mixed ZC50 oxide had a greater oxygen storage capacity and better oxygen transport capability, which contributes to the hydrogen consumption.

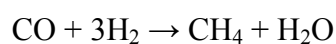
#### ***3.4 Oxidative Steam Reforming of Methanol reaction over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalysts.***

The effect of the reaction temperature between 250 and 375 °C on the catalytic performance of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts during the OSRM reaction is illustrated in Fig. 4. It can be seen that the conversion of methanol was high at the maximum reaction temperature. In addition, it showed that depending of the composition of the support; the catalysts have a significant influence on the methanol conversion. Among them, the Ce-rich catalysts exhibit the highest methanol conversion, whereas nickel supported on Zr-rich

supports gave the lowest conversion. On Ni-base catalyst supported on ZrO<sub>2</sub>-monoclinic the catalytic activity reported was low as on this work [12]. Biswas and Kunzru [26] reported that the best catalyst for the steam reforming of ethanol was the Ni/ZrO<sub>2</sub> catalyst followed by the Ni/Ce<sub>0.74</sub>Zr<sub>0.26</sub>O<sub>2</sub> and Ni/CeO<sub>2</sub> samples respectively. As shown in Fig. 4, the light-off temperature was 250 °C and 300 °C for Ce-rich samples and Zr-rich catalysts respectively. Ni/CeO<sub>2</sub> catalyst showed the highest methanol conversion at temperature below 300 °C, raising the reaction temperature up to 375 °C, the catalytic activity approaches 100 % on Ni/CeO<sub>2</sub>, Ni/CZ10 and Ni/CZ50 samples. While, on the Ni/ZrO<sub>2</sub> and Ni/CZ90 catalysts, the methanol conversion at 300 °C were < 10 % whereas at 375 °C the catalytic activity was close to 70%. Note that the BET surface area of the Ni/Ce-rich catalysts were higher than Ni/Zr-rich samples, thus, the catalytic activity observed on the Ni/Ce-rich catalyst can be correlated with the surface on these samples, as well as, to the quantity of Ni<sup>0</sup> present on the catalysts (Table 1). However, on the Ni/CZ50 sample did not follow this tendency. Even though the reduction degree for this catalyst was higher than Ni/CeO<sub>2</sub>-rich samples, its activity was lower. This could be due to the difference in the nature of phases present as was proposed previously [13] and at the high oxygen storage capacity of the support [26]. Taking in account these findings we analyzed the spent Ni/CeO<sub>2</sub>-rich samples in order to find if the samples had the same catalytic activity. The Ni/CeO<sub>2</sub>-rich catalysts exhibited stable performance during 2 cycles of reaction (Fig. 4) without apparent deactivation, evidenced by the consistent composition of the outlet stream (Table 2).

The products observed on the oxidative steam reforming of methanol reaction over nickel-base catalysts supported on CeO<sub>2</sub>-ZrO<sub>2</sub> were H<sub>2</sub>, CO<sub>2</sub>, CO and H<sub>2</sub>O. However, a small quantity of methyl formate (MF) was observed at temperatures below 325 °C in all the

samples. Above this temperature, the methyl formate was unstable on Ni/Ce-rich catalysts and was not detected. Esposito et al. [36] reported the production of MF on copper-containing ZrO<sub>2</sub> systems, they suggested that it was produced on the support. Fig. 5a showed the hydrogen selectivity as a function of the reaction temperatures during the catalytic test of the Ni-base catalysts. It showed that the hydrogen production started at 275 °C, in addition, it is clear that the Ni/ZrO<sub>2</sub> catalyst had higher selectivity toward H<sub>2</sub> after 325 °C than the others samples; however it had low methanol conversion. At the maximum reaction temperature the H<sub>2</sub> production, gave values near to 45 % on Ni/CeO<sub>2</sub>-rich catalysts. At this temperature the methanol conversion was nearly 100 %. Oguchi et al. [21] reported that the incorporation of zirconia in ceria significantly affects the properties of the ceria–zirconia support and the properties of the copper catalysts on the steam reforming of methanol. They observed that the Cu supported on CeO<sub>2</sub>-10%ZrO<sub>2</sub> had high H<sub>2</sub> production, this phenomena was also observed on the OSRM reaction [13]. In the same way, Biswas and Kunzru [26] observed highest H<sub>2</sub> production on Ni/ZrO<sub>2</sub> sample than Ni/CeO<sub>2</sub>-rich catalysts during SRE reaction. The CO<sub>2</sub> selectivity (Fig. 5b) was important at the beginning of the reaction and at the maximum reaction temperature was close to 50 %. While, the CO selectivity reached a maximum at 300 °C over the Ni/Ce-rich catalysts, after this temperature it decrease (Fig. 5c), although the CH<sub>3</sub>OH conversion was close to 100 %. It is clear that the CH<sub>4</sub> formed during the reaction was expense of CO, because CO<sub>2</sub> selectivity was practically constant. The following reaction could be occurring on these catalysts:



#### 4. Conclusions

Ni-based catalysts supported on  $\text{CeO}_2\text{-ZrO}_2$  were prepared to investigate the effect of the support on the catalytic performance in the methanol steam reforming reaction system. Activity tests showed that the Ni-base catalysts were highly active and stable for oxidative steam reforming of methanol. The Ni/Ceria-rich catalysts presented the best catalytic performance on the OSRM, while Ni/ $\text{ZrO}_2$ -rich catalysts presented poor catalytic activity. The Ni/ $\text{CeO}_2$ -rich catalysts exhibited stable performance during 2 cycles of reaction without apparent deactivation, evidenced by the consistent composition of the outlet stream. High  $\text{H}_2$  selectivity was observed on Ni supported on  $\text{ZrO}_2$  but it no transform all the methanol while, Ni/ $\text{CeO}_2$ -rich samples ( $> 50$  wt. % of  $\text{CeO}_2$  on the mixed oxides) showed close selectivity near to 45 %. The high selectivity of  $\text{CO}_2$  in all range of temperature showed that the reverse WGS reaction did not occurred on these samples. It seems that the nickel is the phase mainly responsible of hydrogen production although the  $\text{ZrO}_2$  support reduces the CO formation.

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## Figure captions

Figure 1. XRD patterns of the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts before and after catalytic activity.

Figure 2. SEM image of the fresh Ni/CZ50 catalyst.

Figure 3. Temperature-programmed reduction profiles of the fresh Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts (solid line), samples after catalytic reaction (thin line).

Figure 4. Effect of temperature on the catalytic performance in the oxidative steam reforming of methanol over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts. (Full symbol corresponds to the second cycle of reaction). Partial pressure of CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> was 75, 12.75 and 25.2 Torr respectively. GHVS=30,000 h<sup>-1</sup>.

Figure 5a. H<sub>2</sub> selectivity as a function of reaction temperature. Partial pressure of CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> was 75, 12.75 and 25.2 Torr respectively. GHVS=30,000 h<sup>-1</sup>.

Figure 5b. CO<sub>2</sub> selectivity as a function of reaction temperature. Partial pressure of CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> was 75, 12.75 and 25.2 Torr respectively. GHVS=30,000 h<sup>-1</sup>.

Figure 5c. CO (open symbol) and CH<sub>4</sub> (full symbol) selectivity as a function of reaction temperature. Partial pressure of CH<sub>3</sub>OH, H<sub>2</sub>O and O<sub>2</sub> was 75, 12.75 and 25.2 Torr respectively. GHVS=30,000 h<sup>-1</sup>.

Table 1. Specific BET area and TPR data of calcined Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts

Sample	Surface area Support (m <sup>2</sup> /g)	Surface area Catalyst (m <sup>2</sup> /g)	Peak 1		H <sub>2</sub> uptake		Reduction	
			T <sub>max</sub> (°C)		(μmol H <sub>2</sub> /g cat)		(% )	
			Before	After	Before	After	Before	After
Ni/ZrO <sub>2</sub>	4	3	342	314	26	8	55	16
Ni/CZ90	4	3	343	290	27	7	55	14
Ni/CZ50	29	20	380	223	58	14	120	28
Ni/CZ10	67	55	355	194	44	34	91	70
Ni/CeO <sub>2</sub>	53	47	348	264	44	36	90	74

**Table 2.** Selectivity of the second cycle of the reaction on the Ni/CeO<sub>2</sub> and Ni/CZ10 catalysts during the OSRM reaction.

Ni/CZ90					Ni/CeO <sub>2</sub>			
Temperature	CO							
°C	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>		H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>
250	0	22	78	0	65	2	33	0
275	29	7	64	0	21	5	73	1
300	37	14	48	0	28	6	66	0
325	34	15	50	1	34	6	60	0
350	38	5	54	2	35	4	60	1
375	40	4	55	2	35	3	61	1

Fig. 1

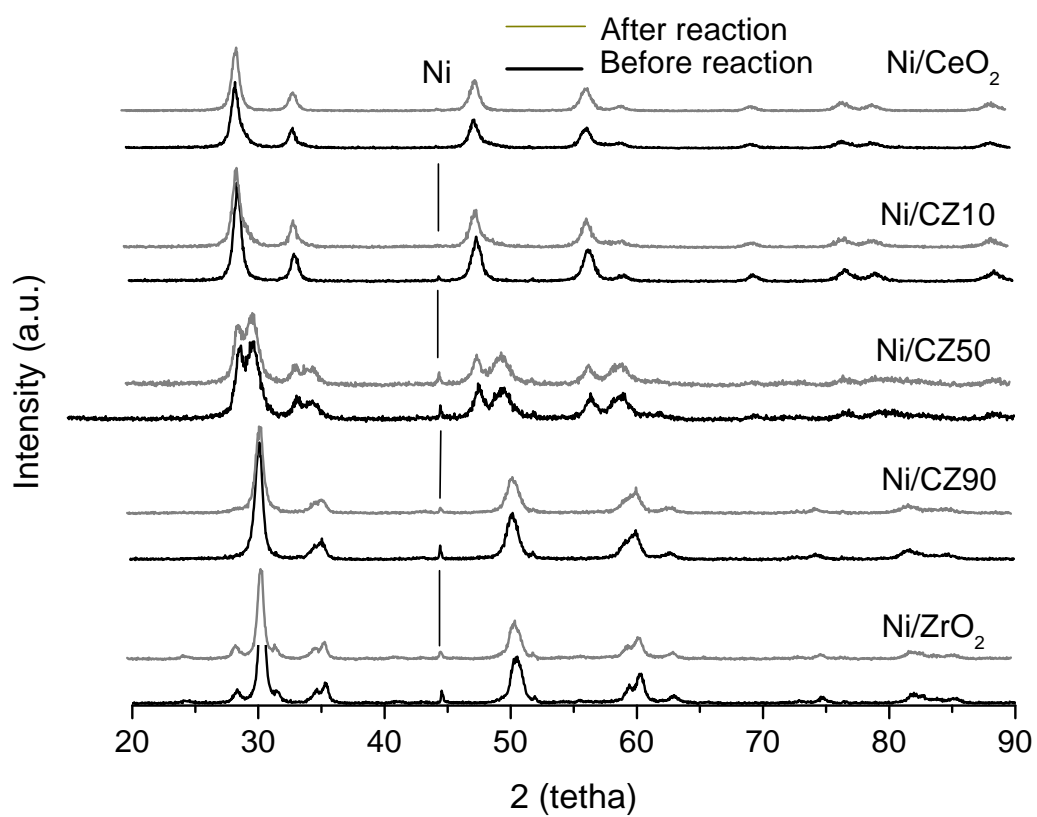




Fig. 2

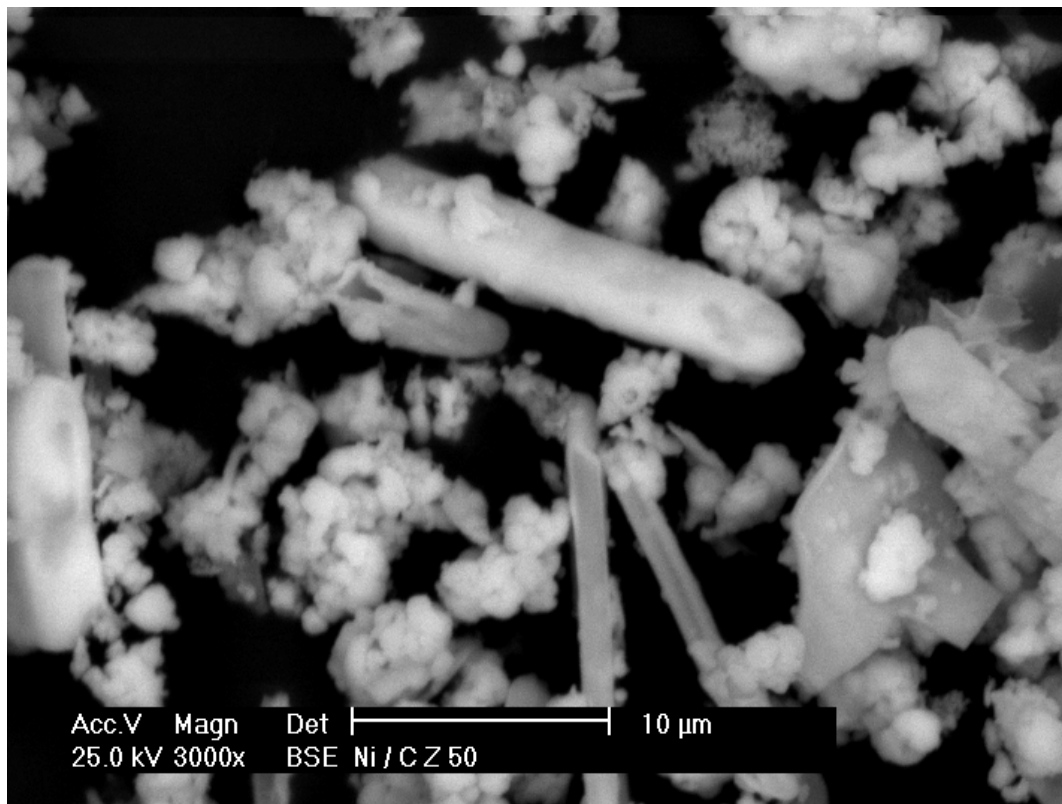


Fig. 3

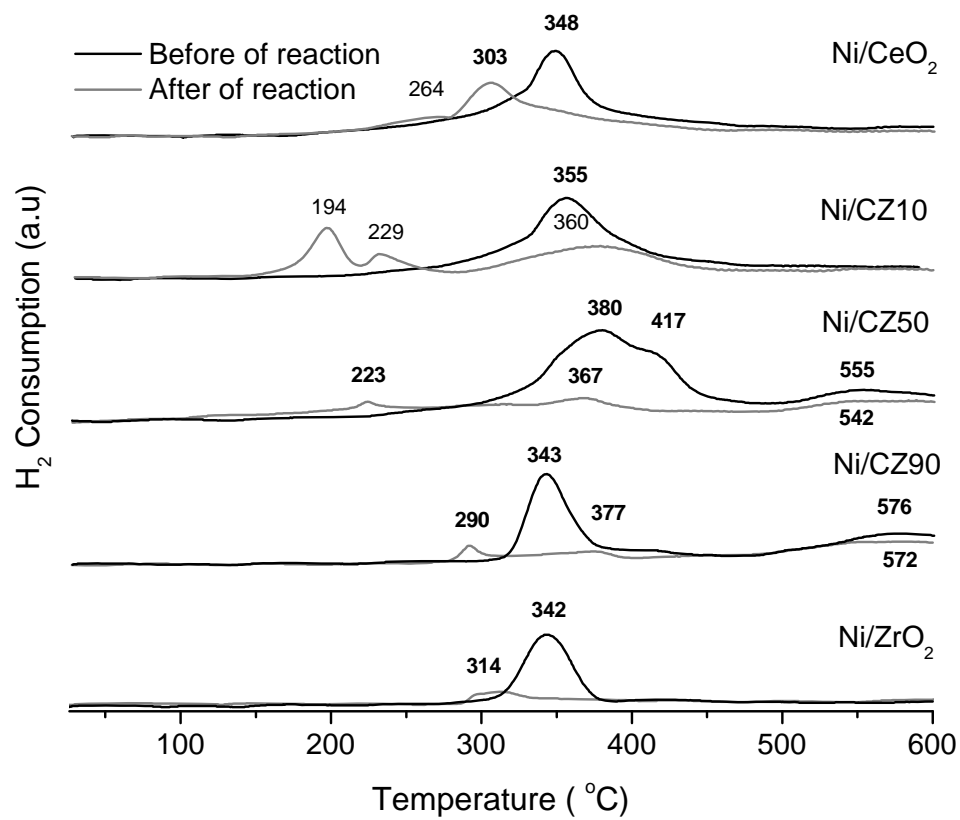


Fig. 4

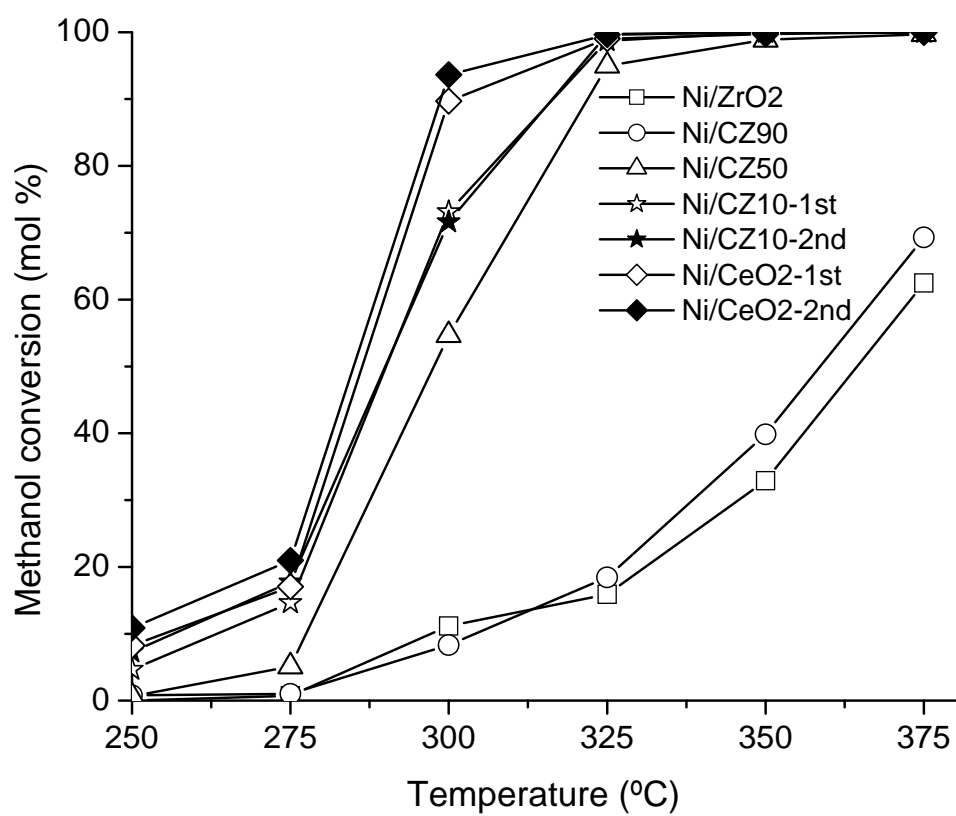


Fig. 5a

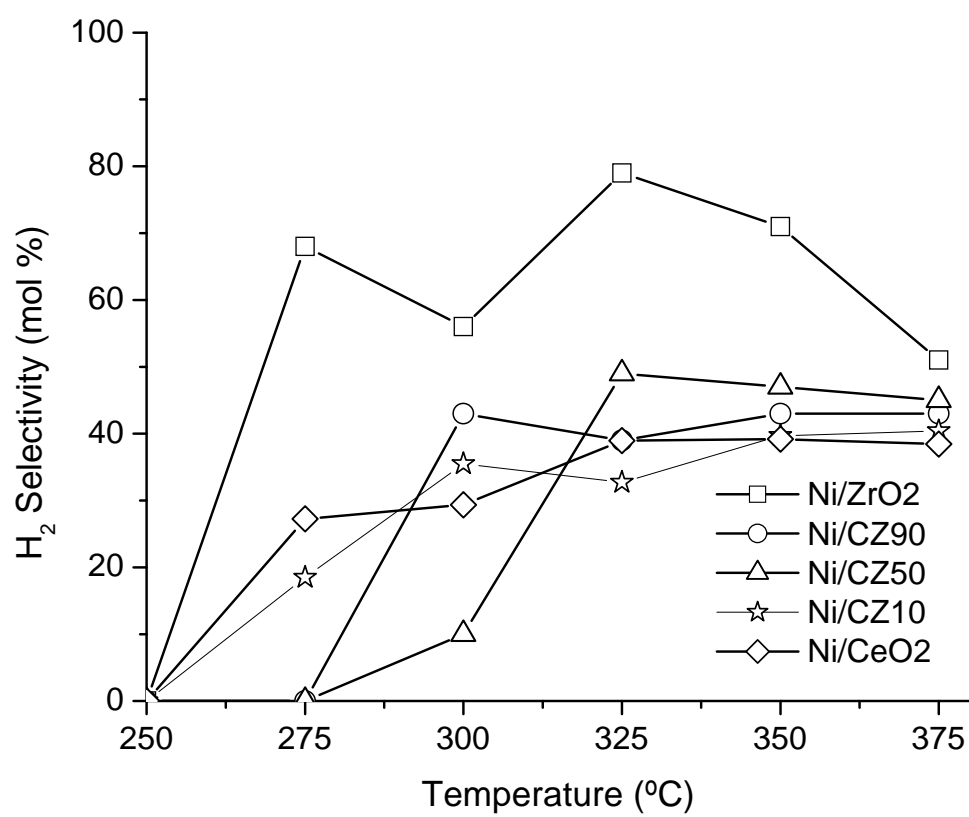


Fig. 5b

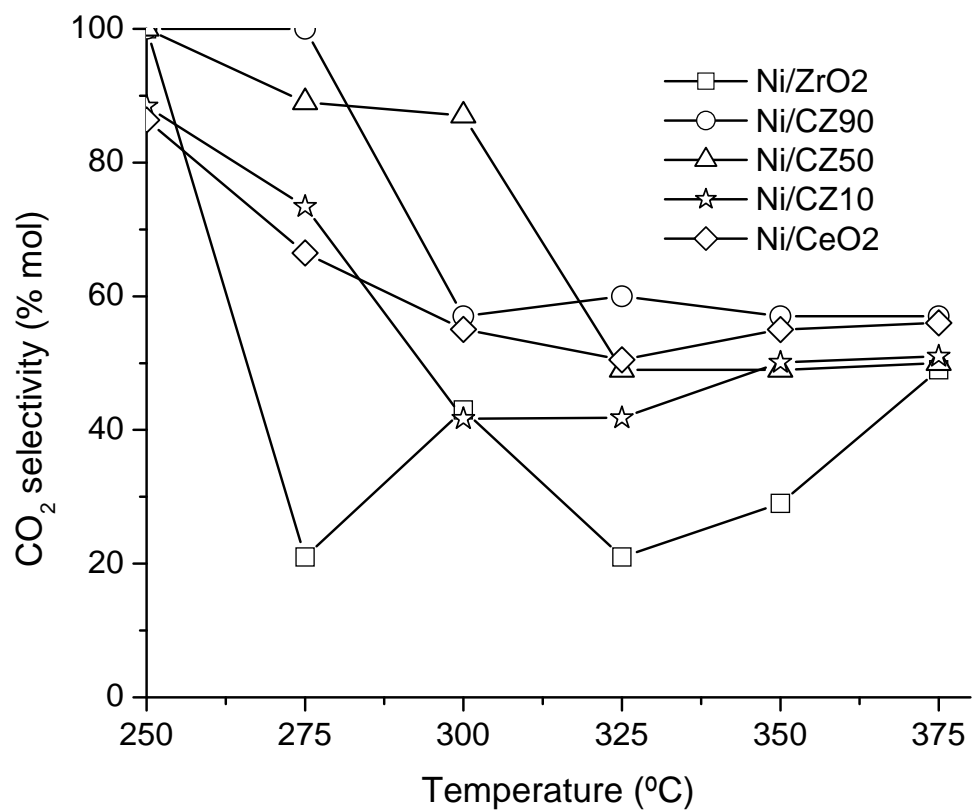


Fig. 5c

