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Hydrogen Production by Ethanol Steam Reforming on Ni/SiO_2 Catalysts: Effect of Ce and Zr Incorporation

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1 Introduction

Energy sustainability and CO_2 emissions are currently one of the major challenges and much effort has been done to diminish our dependence on fossil fuels and reduce greenhouse gas emissions. Hydrogen has been projected as a potentially very attractive energy carrier since its combustion and use in a fuel cell produce only water and energy [1]. The conventional methods for hydrogen production are based on gasoline or natural gas reforming, but the environmental goal of decreasing atmospheric CO_2 needs the use of renewable resources. In this sense, steam reforming of bio-ethanol is a very interesting alternative among the various processes proposed for hydrogen production, because ethanol is abundantly available from biomass, is easy to store and non-toxic [2, 3].

The steam reforming of ethanol has been widely investigated over several catalytic materials. Supported nickel catalysts provide good activity and high selectivity to H_2 and CO_x [2-8]. Besides Ni active phase, the nature of the support significantly affects the activity, selectivity and stability of catalysts [9]. In a previous work, we concluded that Ni supported on SiO_2 showed good catalytic performance, but coke formation was relatively high. On the other hand, although silica exhibits high surface area, when exposed to high temperature in the presence of steam, it may aggregate so silica-supported catalysts would decrease their surface area, probably leading to active metal sintering, loss of activity and promotion of coke formation. Several attempts have been done in order to reduce Ni supported catalyst deactivation. According to the literature, ceria has an excellent ability to store, release and transport oxygen, which may favor carbon oxidation/gasification [10-12]. Moreover, the ability of materials based on CeO_2 and/or ZrO_2 to resist carbon deposition has been described [14-16]. In fact, it was reported that the addition of zirconia to silica increased its steam resistance [13]. However, the main drawback of using ZrO_2 and CeO_2 as supporting materials is their low surface area.

The aim of the present work is to investigate steam reforming of ethanol over Ni/SiO_2 modified with 10 % Ce or Zr. The main objective was to study the effect of the support composition on the catalytic activity and products distribution.

2 Experimental

2.1 Catalysts preparation

In order to study the effect of Ce and Zr addition on Ni/SiO_2 catalysts used in ethanol steam reforming, a series of catalysts containing 10 wt% Ce or Zr and 7 wt% Ni have been prepared. The importance of Ni addition before or after Ce or Zr has also been studied. In both cases, metals were incorporated by incipient wetness impregnation using mixed aqueous solutions of the metal precursors, $Ce(NO_3)_3 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot xH_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Scharlab), with the proper concentration to obtain the nominal contents in the final solid. After the incorporation of the first metal, the materials were air-dried overnight and calcined at 500 °C for 5 h with a heating rate of 1.8 °C/min. Then, addition of the second metal was performed following the same impregnation and calcination procedures described above. A Ni/SiO_2 catalyst was also prepared as the reference material.

Prior to the steam reforming reaction all the catalyst were reduced in the fixed-bed reactor used for catalytic tests under flowing pure hydrogen (30 NmL/min) at 550 °C for 4.5 h with a heating rate of 2 °C/min.

Catalysts have been denoted as $Y/X/SiO_2$, where X is the metal that is firstly incorporated and Y is added in the second place.

2.2 Catalysts characterization

Catalysts were characterized by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Nitrogen Adsorption-Desorption at 77 K, X-ray Powder Diffraction (XRD), Ammonia Temperature Programmed Desorption (NH_3-TPD), Hydrogen Temperature Programmed Reduction (H_2-TPR) and Transmission Electron Microscopy (TEM).

ICP-AES technique was used to determine the actual cerium, zirconium and nickel content in the catalysts on a Varian VISTA-PRO AX CCD-Simultaneous ICP-AES spectrophotometer. Catalysts textural properties were measured in a Micromeritics TRISTAR 2050 sorptometer. Surface areas were calculated according to BET method. The acid properties of the supports were determined by NH_3-TPD in a Micromeritics AUTOCHEM 2910 equipment. Adsorbed NH_3 was determined by increasing temperature up to 550 °C with a heating rate of 15 °C/min, keeping this temperature constant for 30 min. H_2-TPR measurements were carried out with the same apparatus described for TPD. The samples were analyzed under 10 % H_2 in Ar flow (35 NmL/min) with a heating rate of 5 °C /min from 25 °C to 800 °C. TEM micrographs were acquired on a Phillips TECNAI 20 equipped with LaB_6 filament and an accelerating voltage of 200 kV.

2.3 Catalytic test

Catalysts were tested for ethanol steam reforming reaction on a MICROACTIVITY-PRO unit, as described elsewhere [17].

The catalyst (around 315 mg) was placed in the reactor and in situ reduced using the method described above. After the catalyst activation, the reaction temperature was fixed at 600 °C and catalytic test was carried out at atmospheric pressure under nitrogen-diluted conditions. A liquid water/ethanol reaction mixture with 3.7 molar ratio was introduced at a flow rate of 0.075 mL/min, vaporized at 150 °C and further eluted by N_2 (30 NmL/ min). WHSV defined as the ratio between the inlet feed (water + ethanol) mass flow rate and the mass of catalyst, was fixed at 12.7 h^{-1}.

The composition of the output gas stream was determined online by a gas chromatograph. Condensable vapours (ethanol, water and acetaldehyde) were trapped in the condenser and later analysed in the chromatograph.

Carbon deposited during reaction was evaluated from thermogravimetric analyses (TGA) on a TA instruments SDT 2960 thermobalance using an air flow of 100 mL/min and a heating rate of 5 °C/min up to 700 °C.

3 Results and Discussion

3.1 Catalysts characterization

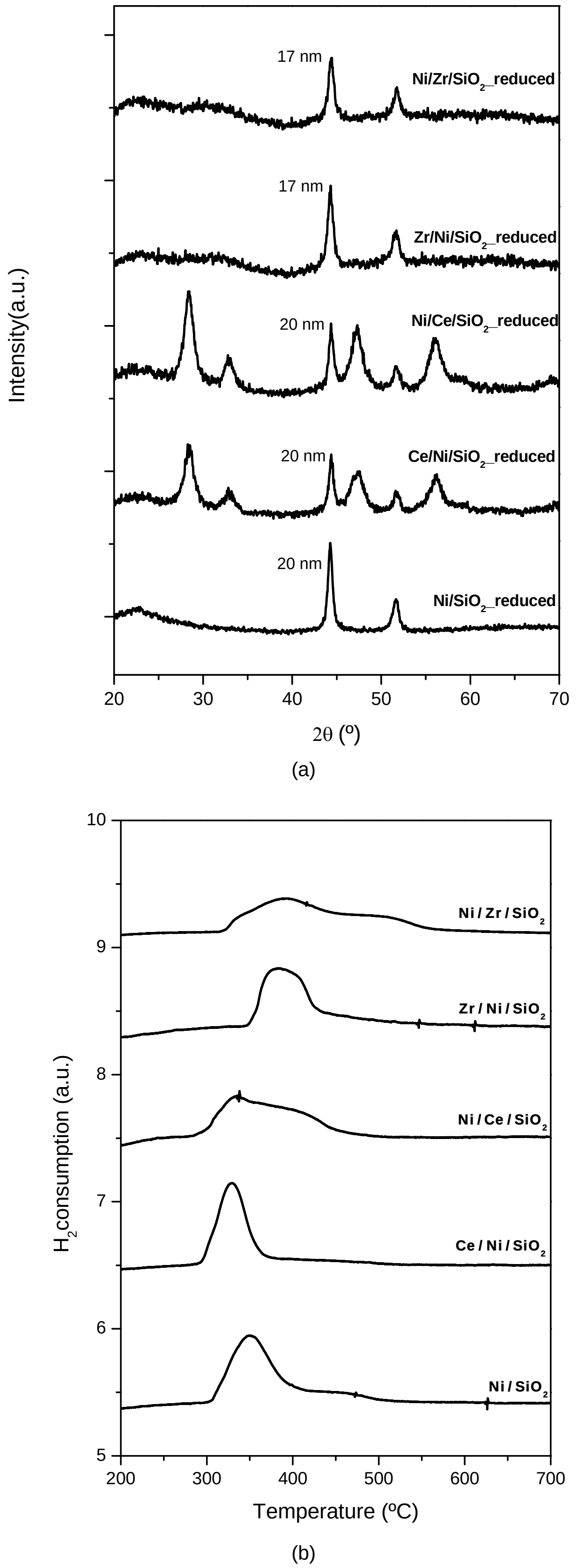
The physicochemical properties of the prepared Ni catalysts are summarized in Table 1. ICP analysis revealed that silica support was loaded with the desired amounts of Ni and Ce or Zr. Regarding textural properties, all the catalysts present high surface area and pore volume. The incorporation of Ce and Zr slightly decreased the surface area and pore volume in comparison to the Ni/SiO_2 catalyst. Table 1 also shows that Zr incorporation into silica support results in the appearance of a little population of acid sites.

Table 1: Catalysts physicochemical properties.

	Ni[a] (wt %)	**Ce[a] (wt %)**	**Zr[a] (wt %)**	**S_{BET} (m^2/g)**	**V_p[b] (cm^3/g)**	**Acidity[c] (meq NH_3/g)**
Ni/SiO_2	7.81	-	-	263	1.07	-
$Ce/Ni/SiO_2$	6.70	8.74	-	228	0.95	-
$Ni/Ce/SiO_2$	6.73	9.22	-	204	0.93	-
$Zr/Ni/SiO_2$	6.74	-	9.43	236	0.88	0.144
$Ni/Zr/SiO_2$	6.77	-	8.87	211	0.87	0.133

[a] ICP-AES measurements
[b] Determined at $P/P_o = 0.98$
[c] Calculated from ammonia TPD measurements

Fig. 1.a. shows the XRD patterns of the reduced samples, together with Ni metal particles size calculated by means of the Scherrer equation. All samples presented diffraction peaks at 2θ = 44.4°, 51.8° and 76.3°, corresponding to cubic Ni (JCPDS 01-070-1849). For samples containing Ce peaks at 2θ = 28.5°, 33.0°, 47.4° and 56.3° were also observed, corresponding to cubic CeO_2 (JCPDS 00-034-0394). No diffraction peaks of Zr species can be seen, suggesting that the ZrO_2 crystallites are too small to be detected, which agrees with the results of Navarro et al. [18] in Zr/Al_2O_3, because for Zr loadings up to 6.6 µmol Zr/m^2 , Zr ions exists in atomic dispersion. The formation of relatively large Ni crystallites, around 20 nm, was found on all the catalysts, although they are slightly smaller on the Zr-modified catalysts. This indicates that the addition of ZrO_2 can promote the dispersion of the Ni species.



(a)

(b)

Figure 1: X-ray difractograms (a) and H_2-TPR profiles (b) of Ni-catalysts.

The reducibility of catalysts is determined by H_2-TPR experiments. Fig. 1.b. gives the reduction profiles of Ni catalysts. For the Ni/SiO_2 catalyst, one reduction peak appears around 350 °C, due to reduction of Ni^{2+} to Ni°, as well as a broad small shoulder around 450 °C, which may be caused by a part of the Ni phase with stronger metal-support interaction.

After addition of Ce and Zr to Ni/SiO_2 catalysts similar profiles were obtained with a main peak and a broad shoulder. However, the reduction temperature shifts to lower value in the case of $Ce/Ni/SiO_2$ sample, indicating the promotion of Ni reducibility by CeO_2 incorporation to the silica supported Ni catalysts, effect typically found for lanthanide elements [12]. On the contrary, $Zr/Ni/SiO_2$ sample reduces at higher temperatures, which may be related with a higher NiO interaction with the support as a consequence of its smaller crystal size.

On the other hand, when Ni was impregnated after the Ce or Zr oxides incorporation, plateau-shaped profiles are obtained and reduction occurs in a broad temperature range. This indicates that several types of NiO phases differing in the metal-support interaction strength are present within each sample. Profile corresponding to the $Ni/Zr/SiO_2$ sample reaches higher temperatures probably due to easier contact of NiO with the ZrO_2 phase, which is well dispersed over the support, unlike the CeO_2 particles evidenced in the XRD patterns, found on the $Ni/Ce/SiO_2$ sample (Figure 1a).

3.2 Effect of Ce and Zr incorporation on catalytic performance

Table 2 shows the catalytic results obtained in ethanol steam reforming at 600 °C after 8 hours of reaction.

Ethanol conversion over all catalysts was total at the beginning of reaction, however for Ni/SiO_2 sample, slight deactivation can be observed with reaction time, while this is lower in the case of the $Ce/Ni/SiO_2$ sample and negligible for the rest of catalysts. Although hydrogen selectivity is similar for all the samples (around 80 mol%), some differences can be observed relating products selectivities. The presence of CeO_2 increases the CO_2/CO ratio, since it favours water-gas shift reaction [19, 20]. On the other hand, $Zr/Ni/SiO_2$ catalyst, gives small amounts of C_2H_4 and C_2H_6, considered as undesired products, due to the acidic nature of this catalyst. It is well-known that ethanol is dehydrated by the acid sites producing ethylene and ethane, the product of ethylene hydrogenation [21]. Although these products could no be detected on the $Ni/Zr/SiO_2$ sample, they were probably formed, but rapidly converted into another product, presumably coke.

Regarding the impregnation order of Ni and Ce/Zr, it can be observed that the incorporation of Ni after Ce or Zr leads to lower selectivity to intermediate products and, thus, higher selectivity towards the main products (H_2 and CO_2) after 8 hours on stream. This may be ascribed to higher nickel-support interaction detected by H_2-TPR (see Fig. 1), which would prevent nickel sintering under reaction conditions.

Results about coke formation are also shown in Table 2. Values indicate that coke formation occurs at much higher rate on Zr-modified catalysts. The amount of coke formed on these samples is a consequence of their acidity promoting the dehydration of ethanol to ethylene, which acts a hard precursor for the coke formation [21]. Although, the highest coke amount was found on the $Ni/Zr/SiO_2$ sample, no deactivation was observed, since carbon nanofibres typically formed on this kind of catalysts do not embed metal particles and the high surface area of the supports can accommodate high amount of coke [22]. On the other hand, the presence of CeO_2 in Ni/SiO_2 catalyst diminishes coke formation, mainly if we consider that higher ethanol conversion was obtained over Ce-modified catalysts. This may be a consequence of enhancement of carbon gasification by CeO_2, mainly when added over Ni/SiO_2 [10-12].

Table 2: Catalytic results on ethanol steam reforming reaction.

	$X_{Ethanol}$ (mol %)	Selectivity (mol %)							Coke (g coke/ g cat h)
		H_2	CO_2	CO	CH_4	CH_3CHO	C_2H_4	C_2H_6	
Ni/SiO_2	97.1	82.6	50.9	33.7	13.9	1.5	0	0	0.37
$Ce/Ni/SiO_2$	98.5	82.0	49.6	29.9	19.5	1.0	0	0	0.23
$Ni/Ce/SiO_2$	100	84.4	55.9	25.6	18.5	0	0	0	0.37
$Zr/Ni/SiO_2$	100	79.2	43.5	29.1	21.2	0	4.9	1.3	0.57
$Ni/Zr/SiO_2$	100	82.5	62.8	27.1	10.1	0	0	0	0.62

4 Conclusions

Ethanol steam reforming reaction has been studied over Ni/SiO_2 catalysts modified by Ce and Zr. Regarding to catalysts characterization, the incorporation of ZrO_2 on silica or Ni/SiO_2 increases the interaction between Ni and the support, which may be a consequence of the lower Ni crystallites size obtained by XRD. Meanwhile, for Ce-modified catalysts, the presence of CeO_2 favors the reducibility of NiO.

In addition, all catalysts present high activity (hydrogen selectivity around 80 %) and stability (ethanol conversion close to 100 % along the 8 hours of time on stream). Cerium addition to silica or Ni/SiO_2 enhances WGS reaction and coke gasification leading to higher selectivity towards methane and carbon dioxide with lower coke deposition. However, coke generation is higher on Zr modified samples due to the formation of ethylene (a known coke precursor) on acid sites provided by ZrO_2. Concerning to impregnation order, the incorporation of Ce and Zr prior to nickel on silica support gives steam reforming catalysts with better performance.

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