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Nickel-based doped ceria-supported catalysts for steam reforming of methane at mild conditions

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ABSTRACT

Hydrogen is widely considered a promising green energy vector. It may be produced by steam reforming of methane which may be obtained from renewable resources such as biogas or biomass gasification. Nickel catalysts supported in ceria oxides doped with La, Pr, or Zr were used. Catalysts were prepared by wet impregnation of supports previously obtained by coprecipitation using the urea method and subsequent calcination at 600°C. Solids were then characterized by Brunauer–Emmett–Teller, X-Ray diffraction, and oxygen storage capacity/oxygen storage capacity complete measurements. Catalysts have shown both effectiveness and stability in methane steam reforming reaction at 600°C with a steam/methane ratio close to the stoichiometric.

KEYWORDS

Ceria; nickel; steam methane reforming

1. Introduction

Taking into consideration both fossil fuel depletion and increasing ecological consciousness, several environmental friendly energy sources are being explored. Among these, hydrogen production for fuel cell operation is a promising approach. One of the most studied processes to produce hydrogen *in situ* is steam reforming of methane obtained from renewable sources. Both biogas, which is obtained as a result of anaerobic degradation of biomass (Ashrafi et al., 2008), and the exit current of biomass gasification contain mainly methane, carbon oxides, and some light hydrocarbons (Grierson et al., 2009). The reforming of this type of current being the objective of the study, methane was chosen as a representative molecule because its stable chemical structure makes it the most difficult compound to reform (Rostrup-Nielsen, 1984).

Since methane steam reforming (MSR) is a well-known industrial reaction, catalysts were extensively studied and nickel-based ones are preferred because of their reasonably high activity and low cost. Traditionally, Ni is supported on alumina because of their superior thermal and mechanical stability. However, coking, sulfur poisoning, and sintering are still frequent inconvenients in these solids (Sehested, 2006). In consequence, developing new active, stable, and cheap catalysts for MSR is an attractive challenge.

High oxygen mobility and storage capacity of ceria were reported to reduce carbon formation through rapid oxidation of coke precursors (Huang and Wang, 2007). In addition, ceria doping has been reported to enhance its ability to transport oxygen and also promote nickel dispersion (Trovarelli, 2002). Consequently, in the present work, the use of ceria-based supports is proposed to enhance nickel-based catalyst stability in MSR.

Steam methane reforming is, due to its endothermicity, traditionally carried at high temperatures (over 700°C), while steam/methane ratio over 3 is usually employed to avoid coke formation with nickel/alumina catalysts (Roh et al., 2003). Both elevated temperatures and steam partial pressure imply an energy cost which is desirable to reduce. In this sense, alternative supports are studied in this work to operate at mild conditions. Doped ceria supports were prepared by coprecipitation of Ce with La, Pr, or Zr using the urea method. Catalysts were prepared by impregnation of these doped supports with nickel and further calcined at 600°C. Samples were characterized and tested in MSR reaction at the same temperature with varying steam/methane feed ratios (0.5 to 3).

2. Experimental

2.1. Supports and catalyst preparation

Supports were prepared by coprecipitation of Ce with La, Pr, or Zr using the urea method (Jobbágy et al., 2006); atomic doping percentage of La, Pr, or Zr was always 5%. The urea to total cation ratio was kept at 10, temperature was 90°C, and reaction time was 24 h in every case. The obtained precipitate was washed and centrifuged three times, dried overnight at 80°C, and finally calcined at 600°C for 5 h. Supports were named CeM₅, with M indicating the dopant (M = La, Pr, or Zr). Afterward, supports were impregnated with a nickel nitrate solution, the concentration of which was calculated to obtain 5 wt% in the final catalyst, dried overnight at 80°C, and finally calcined at 600°C for 5 h. Catalysts were named 5% Ni/CeM₅.

2.2. Characterization and activity tests

BET area measurements were performed in an ASAP 2020–Micromeritics apparatus, using N₂ at –196°C and previous degassing of the samples in Ar for 24 h. XRD patterns were obtained in a Siemens D-501 diffractometer, with CuK α radiation and Ge (1 1 1) monochromator (45kV y 35 mA). OSC/OSCC measurements were performed in an AutoChemII–Micromeritics apparatus; the procedure being followed was the one conventionally used for three-way catalysts (Yao et al., 1984).

Activity tests were carried out in an isothermal tubular fixed-bed reactor. Both the entrance and exit of the reactor was analyzed by gas chromatography employing a Shimadzu GC 14-B chromatograph equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) detectors. Before each activity test, the catalysts were pretreated with 5% H₂ in N₂ at 500°C for 60 min before rising the temperature up to 600°C in N₂. All catalytic tests were performed with constant contact time ($W = 100$ mg, $F = 100$ Nml/min, $W/F = 1$ g.min/Nml) and the following composition at reactor entrance: CH₄ (12.5%), H₂O/CH₄ (0.5, 1, 1.5, or 3), and N₂ as balance. Time-on-stream was 4 h for every catalytic test since this period was enough for methane conversion and CO and CO₂ selectivity stabilization. Methane conversion, CO and CO₂ selectivity, and hydrogen yield (Y_{H_2}) were calculated by the usual definitions. In addition, in order to quantify catalyst deactivation, methane conversion diminution during 4 h time-on-stream is calculated by: $\alpha = 1 - x_{CH_4}^{final}/x_{CH_4}^{initial}$ (α equals 1 when deactivation is complete or 0 if no deactivation is observed).

3. Results and discussion

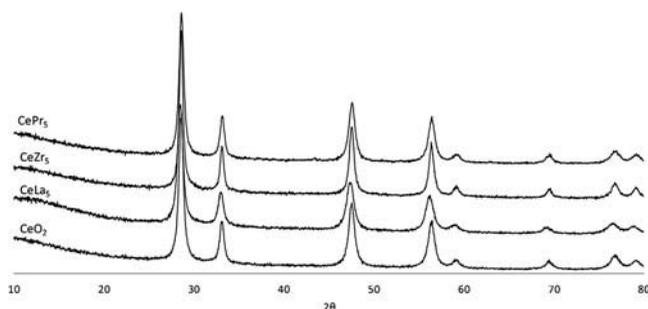
3.1. BET and XRD measurements

BET surface area results for supports calcined at 600°C presented in Table 1 show that all the values are around 50 m²/g. With the synthesis conditions employed in this work, pure ceria had the largest surface area.

Table 1. Structural characterization of supports.

Support	S_{BET} [m ² /g]	d_{BET} [nm]	d_{XRD} [nm]	a_{XRD} [Å]	a_{Kim} [Å]	$a_{\text{Hong et al.}}$ [Å]
CeO ₂	53.8	15	21	5.411 (5.410)	5.413	5.411
CeLa ₅	49.0	17	17	5.426 (5.428)	5.453	5.441
CePr ₅	49.6	17	21	5.412 (5.413)	5.412	NA
CeZr ₅	44.8	19	25	5.410 (5.410)	5.399	NA

NA (not available). Hong and Virkar (1995) equation is used for trivalent dopants.

**Figure 1.** XRD patterns of supports.

Supports XRD patterns shown in Figure 1 allowed typical ceria fluorite structure identification in every sample with no phase segregation, which is consistent with the low dopant percentage used. Lattice parameters experimentally estimated (shown in Table 1) were in accordance with relative atomic radii between host (cerium) and dopant cation, i.e., lattice expansion is only expected for zirconium-doped ceria since Zr⁴⁺ radii is greater than that of Ce⁴⁺. In addition, these values agree with the ones calculated following theoretical correlations established by Kim (Kim, 1989) and Hong et al. (Hong and Virkar, 1995). Catalysts XRD patterns (not shown) did not evidence any NiO diffraction peak. Catalysts lattice parameters are also shown in Table 1 in parentheses, next to support values. If nickel had been inserted in the ceria lattice, appreciable cell contraction would be expected because nickel radii is even smaller than that of Zr⁴⁺. Therefore, since nickel insertion in the lattice is rejected, these results indicate that nickel crystallites did not agglomerate on the supports (due to the low content) remaining indiscernible.

Table 1 also contains information about crystallite size estimated both from XRD (using Scherrer equation) and from BET area measurements (assuming spherical particles) for which similar values were obtained, indicating low crystal agglomeration at this calcination temperature.

Table 2. OSC and OSCC of catalysts and supports.

Samples	OSC [μmol CO ₂ /g]	OSCC [μmol CO ₂ /g]
<i>Supports</i>		
CeO ₂	48	123
CeLa ₅	48	122
CePr ₅	63	147
CeZr ₅	82	202
<i>Catalysts</i>		
5% Ni/CeO ₂	123	409
5% Ni/CeLa ₅	123	492
5% Ni/CePr ₅	164	633
5% Ni/CeZr ₅	209	661

3.2. OSC/OSCC measurements

Table 2 resumes oxygen storage capacity results where differences are observed between the different solids, in particular for the ones containing zirconium and praseodymium.

Doping ceria with non-reducible aliovalent ions such as La^{+3} originate intrinsic vacancies so the solid remains electroneutral. These vacancies, in the doping range considered, have a positive effect on oxygen storage capacity and its mobility. In the case of zirconium-doped ceria, OSC increase is associated to defects generated by differences between host and dopant radii. After nickel impregnation, oxygen storage capacity increases considerably, which can be explained in terms of Ni particles acting as portholes to facilitate oxygen supply. When considering catalyst samples, the ones supported on Pr- and Zr-doped ceria show the highest OSC and OSCC values as seen with supports.

3.3. Activity test

Two main deactivation causes are carbon formation and sintering. The first one is expected to prevail at low steam/methane ratios, while the second one is more likely to occur at high steam partial pressures (Sehested et al., 2006). In line with this behavior, a minimum for deactivation ratio is expected at an intermediate steam content which, as the results in Table 3 show, occurs at $R = 1.5$ for samples employed in this work. Deactivation for neat ceria-supported catalyst is the highest at every feed condition. It should be emphasized that, considering our reaction conditions, deactivation registered with $\text{H}_2\text{O}/\text{CH}_4 = 1.5$ is extremely low for all catalysts.

Reaction mechanisms presented in literature for metallic catalysts supported on oxides with redox activity suggest that water and the support itself serve as oxygen sources in the catalytic cycle (Huang et al., 2005). At water-deficient conditions, i.e., low steam/methane feed ratio, the main oxygen source will be the support. Therefore, higher hydrogen yields are encountered in catalysts which supports have higher OSC/OSCC values.

Regarding CO and CO_2 selectivities, increasing steam partial pressure at the feed diminishes the first one and increases the second one, which may be explained by water gas shift equilibrium displacement toward products. Regarding methane conversion, some authors have reported a non-monotonic behavior of steam reforming activity when varying steam partial pressure (Elnashaie et al., 1990), the appearance of which is caused by water and methane competition for catalytic sites; this behavior is only registered for 5% Ni/Ce. For doped ceria-supported catalysts, both methane conversion and hydrogen yield augment with increasing

Table 3. Activity results of catalysts tested ($T = 600^\circ\text{C}$, $W/F = 1 \text{ g min/Nml}$, time-on-stream = 4 h).

Catalyst	$\text{H}_2\text{O}/\text{CH}_4$	x_{CH_4} [%]	S_{CO} [%]	S_{CO_2} [%]	Y_{H_2} [%]	α
5% Ni/CeO ₂	0.5	26.6	57.3	22.3	17.3	0.560
	1	51.1	51.4	28.0	34.0	0.311
	1.5	70.4	48.9	36.4	51.4	0.087
	3	54.9	39.3	56.3	47.1	0.217
5% Ni/CeZr ₅	0.5	36.1	56.4	20.0	22.5	0.477
	1	38.5	49.9	38.0	29.0	0.186
	1.5	60.4	39.2	42.2	43.2	0.066
	3	71.8	59.7	46.5	65.5	0.130
5% Ni/CePr ₅	0.5	29.2	60.8	21.4	19.6	0.508
	1	26.6	44.9	50.0	22.2	0.272
	1.5	67.5	42.7	39.2	48.1	0.031
	3	72.4	41.7	52.1	60.4	0.147
5% Ni/CeLa ₅	0.5	27.1	60.8	29.6	20.4	0.263
	1	52.1	47.3	35.3	36.9	0.094
	1.5	53.9	49.2	34.3	38.4	0.021
	3	67.4	38.5	49.3	52.6	0.049

steam/methane ratio in the range studied. Highest hydrogen yields were obtained with 5% Ni/CePr₅ and 5% Ni/CeZr₅.

4. Conclusions

It was seen that supports with higher OSC showed better stability and hydrogen yield, in particular when operation takes place in water-deficient conditions. Among them, zirconium- and praseodymium-doped ceria showed the best results. Nickel catalysts supported on ceria-based materials demonstrated high methane conversion and stability operating at mild conditions which represent substantial energy saving.

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