Hydrogen production through glycerol steam reforming using Co catalysts supported on SBA-15 doped with Zr, Ce and La

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The steam reforming of glycerol has been studied at 500 and 600°C using Co/SBA-15 and Co/M/SBA-15 (M: Zr, Ce, or La) promoted catalysts. The prepared materials were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray powder diffraction (XRD), hydrogen temperature-programmed reduction (H₂-TPR), ammonia temperature-programmed desorption (NH₃-TPD), nitrogen physisorption analysis (N₂-BET), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The incorporation of promoters like Zr, Ce and La on SBA-15 support and successive Co impregnation led to smaller cobalt crystallites improving metal dispersion. Besides, stronger metal-support interactions between Co species and M/SBA-15 supports were observed. Thanks to the incorporation of Zr, La and mainly Ce, promoted catalysts present higher glycerol conversion than Co/SBA-15 along 5 h of time on stream. Besides, at 600°C, Co/M/SBA-15 (M: Zr, Ce, or La) catalysts produce higher hydrogen amounts than Co/SBA-15.

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1. Introduction

Hydrogen, together with biofuels and renewable energies, can contribute to the increasing diversification of the power sources scenario and, they are gaining more and more importance as a potential non-carbon based energy systems that can replace fossil fuels, which greatly contribute to climate change and global warming [1–3]. In this sense, hydrogen can be considered as the alternative fuel that can be generated by steam reforming of clean and green sources like bioethanol and glycerol [4,5]. Glycerol is a by-product of the emerging biodiesel industry and several attempts are being developed to consume the excess of glycerol and produce value added products, in order to reduce biodiesel production costs [6]. Currently, glycerol is used in personal care, food, tobacco, polymers, and pharmaceutical industries. Thus, an incipient use of glycerol is the steam reforming to produce renewable hydrogen [7].

Several papers have been published comparing catalysts with different active phases for hydrogen production by steam reforming [8–10]. While Ni catalysts were widely studied in the last decade, the alternative use of Co catalysts has been less explored despite Co-based catalysts provide high catalytic activity at moderate temperatures where water gas shift (WGS) reaction is favored by increasing hydrogen production [11]. However, the main drawback of cobalt catalysts lies in their deactivation by surface oxidation and sintering of the Co metal species [12]. This last fact is greatly affected by the choice of the catalytic support because it is reported how cobalt interacts strongly with Al₂O₃ and TiO₂ carriers, leading to a high dispersion of Co species, but the formation of cobalt aluminates and titanates results in less Co species reduced. On the contrary, a weaker interaction of cobalt with silica support improves the reducibility of the cobalt oxides but promote the agglomeration of cobalt particles during the calcination and reduction steps [13,14].

Since the metal-support interaction plays a very important role in the dispersion and reducibility of metallic species. The very high surface area characteristic of mesostructured materials like SBA-15, should allow to get good dispersions as compared with conventional amorphous silica. Besides, the presence of a uniform pore-size distribution in SBA-15 may avoid the formation of large Co clusters and catalysts deactivation by metal sintering [15].

On line with this, it has been reported that the incorporation of promoters like Zr, Ce and La to Ni-based catalysts can modify the size and dispersion of metallic particles and, therefore their catalytic performance during ethanol steam reforming [15–17]. La₂O₃ may prevent metal sintering and decrease coke deposition since oxycarbonate species like La₂O₂CO₃ can react with carbon deposits releasing CO and regenerating La₂O₃. CeO₂ is used as promoter due to its redox properties, and high oxygen mobility which may re-

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duce carbon deposits in steam reforming reactions [18]. ZrO2 addition to Ni/Al2O3 catalyst showed the capacity to inhibit the metal sintering in the presence of water at high temperatures, besides ZrO2 favors the steam adsorption and then the spillover of steam from the support to the active metallic centers improving the gasification of surface hydrocarbons and/or carbon deposits [19]. For the above mentioned reasons, the literature has reported the incorporation of Ce, Zr, and La to Ni-based catalysts used in ethanol steam reforming [16,20,21]. However, the promotion effects of Ce, Zr and La over Co/SBA-15 samples have been scarcely studied. These modified cobalt catalysts have been previously used in Fischer–Tropsch synthesis, methanol decomposition and benzene oxidation [22–24], but there are no references about their use in glycerol steam reforming. Taking into account the above mentioned reasons, this work studies the glycerol steam reforming over Co/SBA-15 and promoted Co/M/SBA-15 (M: Ce, Zr, La).

The incorporation of dopant elements to the calcined SBA-15 support was carried out by incipient wetness impregnation using aqueous solutions of Zr(NO3)2·6H2O (Aldrich), Ce(NO3)2·6H2O (Aldrich) and La(NO3)3·6H2O (Scharlau) with the proper concentration to get SBA-15 loaded with 8.5 wt% of Ce, Zr or La. These modified supports were characterized by TG analyses in order to select a calcination temperature, high enough to decompose Zr, Ce and La precursors (see Supplementary material). After calcination at 600 °C, the active phase was added to the support by incipient wetness impregnation using an aqueous solution of Co(NO3)2·6H2O (Aldrich), with the proper concentration to get 7 wt% Co loading in the reduced catalysts. To get calcined materials, the as-prepared catalysts were kept at 550 °C for 5 h with a heating rate of 1.8 °C/min. These samples were reduced under flowing of pure hydrogen (30 mL/min) at 600 °C for 4.5 h with a heating rate of 2 °C/min.

2. Experimental

2.1. Catalysts preparation

Catalysts containing 7 wt% Co were prepared over bare SBA-15 and modified SBA-15 mesoporous material. The synthesis of SBA-15 was carried out by hydrothermal method as described by Zhao et al. [25]. In a typical synthesis, 32 g of block-copolymer Pluronic 123 (Aldrich) as the structure-directing agent were dissolved under stirring in 1.1 HCl 1.9 M at room temperature. The resultant micellar solution was heated to 40 °C and then 70 g of tetraethyl orthosilicate (Aldrich) were added as the silica source. The mixture was maintained at that temperature under stirring for 20 h. Next, it was loaded into an autoclave to be aged under static conditions and autogenous pressure at 100 °C for 24 h. Thereafter, the solid product was recovered by filtration and air-dried overnight. Subsequent air calcination at 550 °C in static conditions for 5 h (1.8 °C/min heating rate) allowed eliminating the template agent.

2.2. Catalytic tests

The glycerol steam reforming reactions were accomplished on a MICROACTIVITY-PRO unit (PID Eng &Tech. S.L.) as described elsewhere [26]. The reaction temperatures (500 and 600 °C) were fixed for each experiment and catalytic tests were carried out isothermally at atmospheric pressure. Previous to the reaction, catalyst was in situ reduced under flowing pure hydrogen (30 mL/min) at 600 °C for 4.5 h with a heating rate of 2 °C/min. After the catalyst activation, the water–glycerol liquid mixture was firstly vaporized at 200 °C and further eluted by N2 (60 mL/min) using (water/glycerol) molar ratio of 6 and WHSVglycerol = 7.7 h⁻¹ (defined as the ratio between the inlet feed mass flow rate of glycerol and the mass of catalyst). The composition of the output gas stream was determined online using a gas chromatograph Varian CP-3380 with a Hayesep Q and a Molecular sieve columns and a thermal conductivity detector (TCD). Condensable vapors were trapped in a condenser at 4 °C and analyzed in a Varian CP-3900 chromato-

Fig. 1. Nitrogen adsorption-desorption isotherms (a), and pore size distributions (b) of calcined catalysts.
graph equipped with a CP-WAX 52 CB column and flame ionization detector (FID). The results of these analyses evidenced the lack of reaction products in the liquid outlet stream. The amount of carbon deposited during reaction ($\Delta m$) was evaluated from thermogravimetric (TGA) (see next Section 2.3).

2.3. Catalysts characterization

Catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray powder diffraction (XRD), hydrogen temperature-programed reduction ($H_2$-TPR), ammonia temperature-programed desorption (NH$_3$-TPD), nitrogen physisorption analysis (N$_2$-BET), transmission electron microscopy (TEM), thermogravimetric analysis (TGA).

ICP-AES technique was used to measure the total metal content in the catalysts using a Varian VISTA-PRO AX CCD simultaneous ICP-AES apparatus. Catalysts samples were previously dissolved by acidic digestion with HF and H$_2$SO$_4$. XRD data were acquired on a Philips X’Pert PRO diffractometer equipped with high-temperature chamber, using Cu $K\alpha$ radiation. The patterns were recorded with a 2$\theta$ increment step of 0.020° and a collection time of 2 s. Computer file storage made possible to compare the obtained XRD patterns with those of known compounds taken from JCPDS index. Mean metallic crystallite diameters were calculated by applying the Scherrer equation. $H_2$-TPR measurements were performed on a Micromeritics AUTOCHEM 2910, placing the calcined catalyst in a fixed-bed quartz tube under 10% $H_2$ in argon flow (35 mL/min) with a heating rate of 5°C/min from 25 to 900°C. Effluent gas is forced to flow through a cold trap to remove water produced before reaching the thermal conductivity detector (TCD). Samples were previously degassed under dry argon flow (35 mL/min) at 110°C for 30 min with a heating rate of 15°C/min. NH$_3$-TPD was used to determine the acid properties of the catalysts in the same apparatus described for TPR. Samples were previously outgassed under a He flow (50 NmL/min) at 560°C for 30 min. After saturation of the sample with ammonia and removal of the physisorbed fraction by flowing He at 180°C, NH$_3$ was desorbed from the sample by increasing temperature up to 550°C with a heating rate of 15°C/min, and this temperature kept constant for 30 min. NH$_3$ concentration in the effluent stream was monitored using a TCD. Textural properties were measured by liquid N$_2$ adsorption/desorption analyses, using a Micromeritics TRISTAR 3000 sorptometer. Prior to the nitrogen-adsorption, samples were outgassed under vacuum at 200°C. Catalyst particles were observed by TEM using a Philips TECNAI 20 microscope equipped with W filament and an accelerating voltage of 200 kV. The apparatus has also the possibility to perform elemental microanalysis by energy dispersive X-ray spectroscopy (EDX). Samples were prepared by powder dispersion of the material, finely divided, in acetone and subsequent deposition on a copper grid with carbon support. TGA measurements were performed in airflow on a TA instruments SDT 2960 thermobalance with a heating rate of 5°C/min up to 1000°C.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 shows N$_2$ adsorption/desorption isotherms and pore size distributions of calcined catalysts. Both Co/SBA-15 and promoted samples showed type IV isotherm with type H1 hysteresis cycle, indicating a mesoporous structure with hexagonal array typical of SBA-15 material used as support. The modification of SBA-15 by adding promoters like Ce, Zr and La keeps almost unaltered its mesoporous structure. In fact, all materials showed narrow pore size distributions. A summary of physicochemical properties is shown in Table 1, together with those corresponding to the bare SBA-15. In comparison to the Co/SBA-15 sample, the addition of Zr, Ce and La leads to catalysts with lower BET surface areas, pore volumes and narrower pores, mainly in the case of Zr and La.

Fig. 2 shows the X-ray patterns of calcined and reduced catalysts. In Fig. 2(a) characteristic peaks of cubic Co$_3$O$_4$ spinel ap-
Table 1. Physicochemical properties of Co/SBA-15 and promoted Co/M/SBA-15 (M: Zr, Ce, La) catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co (wt%)</th>
<th>M (wt%)</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_{\text{mes}}) (cm(^3)/g)</th>
<th>(D_{\text{pore}}) (nm)</th>
<th>(D_{\text{Co},\text{O}}) (nm)</th>
<th>(D_{\text{Co}}) (nm)</th>
<th>(D) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>–</td>
<td>–</td>
<td>581</td>
<td>1.00</td>
<td>8.7</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Co/SBA-15</td>
<td>7.0</td>
<td>–</td>
<td>539</td>
<td>0.86</td>
<td>8.2</td>
<td>9.4</td>
<td>7.3</td>
<td>13.2</td>
</tr>
<tr>
<td>Co/Zr/SBA-15</td>
<td>7.0</td>
<td>8.5</td>
<td>458</td>
<td>0.72</td>
<td>7.9</td>
<td>9.2</td>
<td>5.4</td>
<td>17.8</td>
</tr>
<tr>
<td>Co/Ce/SBA-15</td>
<td>7.0</td>
<td>8.4</td>
<td>478</td>
<td>0.73</td>
<td>7.8</td>
<td>9.2</td>
<td>5.6</td>
<td>17.1</td>
</tr>
<tr>
<td>Co/La/SBA-15</td>
<td>6.9</td>
<td>8.2</td>
<td>421</td>
<td>0.69</td>
<td>7.8</td>
<td>7.8</td>
<td>5.2</td>
<td>18.6</td>
</tr>
</tbody>
</table>

\(^a\) ICP-AES measurements.
\(^b\) Determined at \(P/p_0=0.97\).
\(^c\) Maximum of the BJH pore size distribution.
\(^d\) Mean crystallites size calculated from the (3 1 1) reflection of Co\(_2\)O\(_4\) in XRD patterns of calcined samples (see Fig. 2a).
\(^e\) Mean crystallites size calculated from the (1 1 1) reflection of Co\(^0\) in XRD patterns of reduced samples (see Fig. 2b).
\(^f\) Co dispersion calculated as \(D=96/D_{\text{Co}}\) taken from Ref. [27].

Fig. 3. TEM images of calcined catalysts: (a) Co/SBA-15, (b) Co/Zr/SBA-15, (c) Co/Ce/SBA-15 and (d) Co/La/SBA-15.

pear at \(2\theta=31.3^\circ, 36.9^\circ, 44.8^\circ, 55.6^\circ, 59.4^\circ\) and \(65.3^\circ\) (JCPDS42-1467). As it can be observed, promoted catalysts show broader and less intense Co oxide peaks, indicating smaller Co\(_2\)O\(_4\) crystallites. Furthermore, in the case of the Co/Ce/SBA-15 catalyst peaks corresponding to cubic CeO\(_2\) at \(2\theta=28.4^\circ, 33.0^\circ, 47.3^\circ, 56.1^\circ\) and \(68.2^\circ\) are also observed (JCPDS81-0792). On the contrary, no peaks corresponding to ZrO\(_2\), La\(_2\)O\(_3\) were observed, so very small crystallites not detectable by XRD were formed. In Fig. 2(b) it can be seen that the peaks corresponding to Co\(_2\)O\(_4\) are replaced by those corresponding to Co\(^0\) (\(2\theta=44.0^\circ\) and \(51.4^\circ\) [JCPDS-15-0806]) after catalyst reduction. However, CeO\(_2\) particles are not reduced since their XRD peaks remain in the diffraction pattern of reduced Co/Ce/SBA-15 catalyst.

Table 1 shows the mean crystallites size of Co\(_2\)O\(_4\) and Co\(^0\) found on these catalysts calculated with the Scherrer equation. Cobalt dispersion values \((D)\) are also included, they were calculated from Co crystallites sizes \(D_{\text{Co}}\) (nm) applying the equation \(D=96/D_{\text{Co}}\) [27], which assumes a spherical geometry for metal particles, and a Co surface density of 14.6\,atm/nm\(^2\). According to these data, Co/SBA-15 sample has the largest Co\(^0\) crystallites while they become smaller in samples promoted with Ce, Zr and mainly in the case of La.
Fig. 3 shows the TEM images of calcined catalysts where it can be observed the hexagonal array of the SBA-15 pores in spite of the decrease of textural properties produced by Ce, Zr and La incorporation (Table 1).

As can be seen in the magnification of Fig. 3(a), calcined Co/SBA-15 sample contains particles (~80 nm) composed of smaller Co3O4 crystallites (9–19 nm). However, promoted catalysts present smaller and better-dispersed particles, which according to EDX analysis are made up of both Co3O4 crystallites very close to the oxide crystallites of ZrO2, La2O3, or CeO2.

Fig. 4 shows the H2-TPR profiles of the calcined samples. Co/SBA-15 sample shows two reduction peaks with maxima located at 234–256 °C and 315 °C, which correspond to the two-step reduction process where the Co3O4 are firstly reduced to CoO and then to Co[15]. The third reduction peak above 500 °C can be assigned to other surface-Co oxide species in intimate contact with the SBA-15 support, whose interaction degree is proportional to the temperature [29,32,35].

As explained above, promoted samples present smaller Co3O4 crystallites which are going to interact greatly with the support, so it is reasonable to find these reduction peaks shifted towards higher temperatures [29–31,35]. In this sense, promoted catalysts present the first cobalt oxide reduction peak at 240–245 °C [11] and the second around 325–330 °C. Therefore, it is reasonable to think that these smaller cobalt oxide crystallites are hardly reduced in comparison with larger ones found on Co/SBA-15. On line with this, the relative contribution of the third reduction peak to the overall reduction profile increased in promoted samples. In this case, the high temperature has the contribution of surface-Co oxide species interacting with SBA-15 support together with promoter’s oxides crystallites as evidenced by EDX analysis explained above. The promotion of metal oxides having strong interaction with the support by Ce and Zr incorporation has been also reported in literature [33,34]. In the case of the Co/La/SBA-15 catalyst the temperature of this third reduction peak is higher (around 665 °C) and may also due to the reduction of the LaCoO3 perovskite species [36].

In summary, from the catalysts characterization, it can be concluded that higher metal dispersion and stronger interaction between the Co phase and the support were obtained by the incorporation of Zr, Ce and La to the SBA-15 support. A similar behavior has been reported for Cu-Ni/SBA-15 catalysts modified by Ce and La [15], for Co/SBA-15 modified with Ca and Mg [35], and for Co/SiO2 catalysts modified by Zr and La [34].

Finally, NH3-TPD analysis (Supplementary material) showed negligible acidity for these catalysts, except for the Co/Zr/SBA-15 sample (0.12 meq-NH3/g).

3.2. Glycerol steam reforming: catalytic tests

Fig. 5 compares the glycerol conversion values obtained with Co/SBA-15 and Co/M/SBA-15 (M: Ce, Zr, La) promoted catalysts at 500 and 600 °C along time on stream.

As can be seen, Co/SBA-15 deactivates in a higher extent than promoted catalyst, mainly at 500 °C where glycerol conversion drops from 98% to 75% in a couple of hours (from 1 to 3 h of time on stream). On the contrary, Co/Co/SBA-15 catalyst keeps almost constant the initial glycerol conversion next to 100%, along the 5 h of time on stream. Due to CeO2 redox properties and high oxygen mobility, which may reduce carbon deposits in steam reforming reactions [18], Co/Co/SBA-15 sample does not produce more coke than Co/SBA-15 despite its higher conversion, as can be seen in Table 2. The higher stability of Co/Co/SBA-15 sample may be also
related with its higher textural properties (see Table 1) which are going to difficult the deactivation by active sites plugging or foul- ing joined to coke deposits.

Regarding products distribution, Co/CeSBA-15 catalyst gives higher CO and very low CO amounts, because as mentioned before, ceria improves oxygen mobility and water reactivity, which favors water gas shift, while methane steam reforming may be slightly reduced [15]. Therefore, Co/CeSBA-15 produces more hydrogen than Co/ZrSBA-15 and Co/LaSBA-15. Table 2 also shows that acid sites from zirconium oxide catalyze dehydration reactions giving ethylene, which is responsible of the highest coke amount deposited on Co/ZrSBA-15 during glycerol steam reforming at 500°C.

By increasing reaction temperature up to 600°C, the initial glycerol conversion given by CoSBA-15 catalyst is lower than that at 500°C. On the contrary, promoted catalysts keep glycerol conversion near 100% along time on stream. This fact can be explained since at 600°C larger Co crystallites measured by XRD on CoSBA-15 (7.3 nm) are less active than smaller (5.6–5.2 nm) and better dispersed Co crystallites found on promoted catalysts (see Table 1). Regarding products distribution, it is noticeable how promoted catalysts improve hydrogen formation in comparison with CoSBA-15, because according to reduction profiles shown in Fig. 4, promoted catalysts require temperatures above 520–530°C to get strongly interacted cobalt species completely reduced. Glycerol steam reforming tests done at long time on stream (50 h), as observed in Fig. 6, confirmed the higher stability of Co/CeSBA-15 sample with glycerol conversion values near 100% while CoSBA-15 gave 90%. In both cases, the hydrogen content in the gas outlet stream decreased with time while methane increases (not shown). Besides, coke deposition is also growing. So, it is reasonable to think that a secondary reaction like C + 2H2 ↔ CH4 is taking place at the same time [37].

4. Conclusions

Co/M/SBA-15 (M: Ce, Zr, La) catalysts have the typical ordered mesoporous structure of SBA-15 support, although the incorporation of promoters reduces the textural properties of original CoSBA-15, mainly in the case of Zr and La. X-ray patterns of calcined catalysts show that La avoids the growth of large CoO crystallites. After reduction step, Co crystallites deposited on promoted catalysts were smaller than those deposited on CoSBA-15, improving metal dispersion. On line with this, stronger metal-support interactions between Co species and M/SBA-15 supports were observed through the shift of H2–TPR profiles of promoted catalysts towards higher temperatures. At 500°C, CoSBA-15 catalyst suffers a severe glycerol conversion drop along time on stream, to overcome this drawback, La, Zr and Ce were incorporated to SBA-15 support. In this sense, Co/M/SBA-15 (M: Ce, Zr, La) catalysts present higher stability and glycerol conversion than CoSBA-15. Regarding products distribution, it is noticeable how at 600°C promoted catalysts improve hydrogen formation in comparison with CoSBA-15, because promoted catalysts require temperatures above 520–530°C to get strongly interacted cobalt species completely reduced.

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Supplementary Materials

Supplementary material associated with this article can be found, in the online version, at http://doi.org/10.1016/j.jjchtem.2016.09.001.

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