Sustainable production of hydrogen via steam reforming of furfural (SRF) with Co-catalyst supported on sepiolite

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Abstract

Natural sepiolite is a mineral very abundant in Spain, being the main producer worldwide. This material is presented by the first time as promised support to prepare cobalt catalysts with high activity and hydrogen selectivity in the steam reforming of furfural (SRF). Two methods for cobalt incorporation on natural sepiolite, precipitation (PP) and incipient wetness impregnation (IWI), are explored and their influence in the preparation of catalysts highly active and selective in the SRF is studied. PP method makes possible to synthesize a catalytic material with high catalytic performance (high conversion of furfural, > 95%, and high hydrogen selectivity, 70%). Furthermore the production of non-desired byproducts such as CO, CH₄ and acetone, decrease significantly in the catalyst prepared by PP (CoSep). Characterization by N₂ adsorption-desorption to determine surface area, XRD, TPR and TEM shows that PP method favors the formation of smaller metallic particles of Co with a high dispersion. These differential physicochemical properties seem to explain the better catalytic performance exhibited by the sepiolitic catalyst prepared by the PP method (CoSep). In addition, this catalyst exhibits also a higher resistance to deactivation after 24 hours of reaction time. This fact seems to be related to the lower coke deposition on the catalyst prepared by precipitation and particularly, with the lower sinterization of the metallic Co particles during the steam reforming of furfural.

Keywords: Steam reforming, Cobalt Catalyst, Natural Sepiolite, Hydrogen Production, Furfural.

1. Introduction.

Humanity is between despair and hope for the climatic challenges it faces. The youth leads a current that demands drastic changes in society at all levels to minimize CO₂ emissions and try to mitigate the possible effects of climate change. Considering this panorama, hydrogen could be one of the most important alternative fuel on a near future. The use of oil, natural gas, and coal is characterized in recent years for the crescent scarcity of these not renewable energy sources, the increment of their price and, particularly, for the high levels of CO₂ emissions generated during their combustion. In this last aspect is where the use of hydrogen as fuel takes an special importance, since its combustion does not produce pollutants, only produce water as byproduct [1]. Currently, hydrogen is produced industrially from natural gas reforming, a non-renewable feedstock. Thus, renewable and environmentally friendly sources for the sustainable production of hydrogen would be need [2,3]. The use of biomass-derived compounds could be an interesting option. Among them, furfural can be considered a promising hydrogen source since it is widely produced worldwide (300,000 tons/year) [4] from different agricultural byproducts such as corncobs, oat, wheat bran, sawdust, rice husk [5, 6]. Furfural can be also obtained as byproduct in the fast pyrolysis of biomass [7]. The bio-oil obtained in fast pyrolysis can be separated into two phases, an oil fraction suitable to produce hydrocarbons or products with high added value and a non-useful aqueous phase containing a complex mixture of organic compounds where furfural can be considered one of the most representative compounds. Currently, several studies focused on the development of catalysts for the steam reforming of the oil phase to produce hydrogen can be found [8-10]. However, the catalytic reforming of the aqueous phase has not been properly considered yet. An approximation to the study of the steam reforming of the aqueous phase would be the separated study of some of its components in the steam reforming reaction. Thus, the study of the steam reforming of furfural (SRF) as model compound to develop efficient catalysts for the steam reforming of the aqueous phase would be an interesting option.

The main reaction in the steam reforming of furfural is presented in equation (1). In addition, other side reactions, as presented in the equations (2) and (3), can also take place.

As it can be seen, hydrogen can be product and reagent. In addition, the thermal decomposition or cracking of different byproducts can compete with the SRF reaction and carbon deposition can occur by different routes such as Boudouard reaction, ethene polymerization, and CO and CH₄ decomposition [11, 12]. Thus, the development of SRF catalyst is of paramount importance to decrease the formation of these byproducts, to avoid the occurrence of side reactions and, especially, to increase the production of hydrogen.

Precious metals and transition metals such as nickel and cobalt supported on oxides have been thoroughly studied in the steam reforming reaction [12-21]. The present work is based on the use of cobalt supported on natural sepiolite as alternative to the more widespread use of precious metals. Co has an optimal performance at moderate temperatures and the substitution of precious metals by Co supposes a great advantage from the economic point of view. The optimal performance of Co is related to the facility that this metal has to carry out the scission of the C-C and O-H bonds [22-40]. In general, the adequate catalytic performance of one catalyst is determined by three main parameters: activity, selectivity, and stability. A multitude of factors around the catalyst affects significantly these three parameters such as the selected active metal phase, the precursor used for the incorporation of the metal phase in the support, the chosen support, the catalyst synthesis method, the operating conditions and the incorporation of additives. Among them, support is one of the most important factors to consider. Nature of the support is crucial to synthesize highly active, selective and stable steam reforming catalysts, because it can favor high dispersions of the active metal phase of the catalysts and favor metal-support interactions that improve the catalytic performance [39-41]. The method to incorporate the active phase (metals) is another important issue to synthesize efficient catalysts. Specifically, the method of incorporation of the metal phase into the support can influence dramatically the catalytic behavior of the synthesized catalyst [14]. Depending on the method chosen, high dispersions of the metal phase and support metal interactions can be favored [14]. In addition, acidic support seem to promote the formation of coke precursors (ethylene), which can affect the stability of the catalyst during the steam reforming reaction [39-48]. In this work, we show by the first time the use of Co-based catalysts supported on natural sepiolite in the production of hydrogen via furfural steam reforming. Two routes have been explored to incorporate cobalt in the sepiolitic support (PP and IWI) and their influence over the physicochemical characteristic of the synthesized catalysts has been studied in the steam reforming of furfural. The catalytic results show that the method of incorporation of Co has a significant impact on the activity, selectivity and stability of the furfural steam reforming catalyst. Characterization by XRD, TPR, surface area (BET) and TEM has helped to know that this impact is related

to the particular characteristics presented by the metallic particles of cobalt supported such as their size, dispersion and reducibility.

2. Experimental.

2.1. Catalyst preparation.

The incorporation of Co over natural sepiolite (Tolsa Group, Pangel S9) was performed by incipient wetness impregnation (IWI) and precipitation (PP) methods. For IWI an aqueous solution containing the required amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sigma-Aldrich) was used to achieve a concentration of Co of 15 wt.%. After Co incorporation, the catalyst was dried over night at 100 °C and calcined in muffle oven at 600 °C for 3 h (Co/Sep). In the precipitation method (PP), Co was introduced following the methodology described in literature [49] with some modifications. Specifically, two solutions were prepared. The first one contains $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sigma-Aldrich) as cobalt precursor and HNO_3 to achieve a final pH of 2. The second solution contains the natural sepiolite (0.11 g natural sepiolite/L). The first solution was added to the second one under agitation (rate of 1 mL/min via a perfusion pump). NaOH was added to the final mixture to achieve a pH of 11. After the mixture was filtered, dried at 100 °C for 3 hours and calcined at 600 °C for 3 h (CoSep).

2.2. Catalyst characterization.

Cobalt content in the catalytic material was determined by inductively coupled plasma with optical emission spectrometer (ICP-OES) in a Varian 700-ES Series.

Textural properties of the catalysts were obtained from the nitrogen adsorption isotherms, which were measured using an ASAP 2420 apparatus (Micromeritics) at 77 K. Before the analysis, 200 mg of each pelletized sample (0.25-0.40 mm) were degassed at 673 K with high vacuum ($\sim 5 \times 10^{-6}$ bar) overnight. The BET surface area was calculated by using the Brunauer–Emmett–Teller equation, pore volume was calculated by the t-plot method.

Nature of the crystalline phases present in the catalysts was determined by X-ray diffraction. XRD patterns were obtained at room temperature in a Philips X'pert diffractometer using monochromatized $\text{CuK}\alpha$ radiation.

The size of the Co crystalline particle was determined from XRD data using the Scherrer equation [50] and by transmission electron microscopy (TEM). TEM imaging was conducted using a Philips CM-10 at 100 kV with samples deposited onto holey carbon grids using an ethanol dispersion.

TPR profiles were obtained by passing 5 vol.% H₂/Ar through 20 mg of sample heated at 5 °C min⁻¹ from ambient temperature to 900°C in a Micromeritics Autochem 2910 equipment. About 50 mg of the calcined catalyst was initially flushed with 30 mL min⁻¹ of Ar at room temperature during 30 min. Then a mixture of 10 vol.% of H₂ in Ar was passed through the catalyst at a total flow rate of 50 cm³ min⁻¹ while temperature was increasing up till 900°C at a heating rate of 10 °C min⁻¹. The H₂ consumption rate was monitored in a thermal conductivity detector (TCD) previously calibrated. The reduction degree was determined by TPR experiments comparing the total amount of hydrogen consumed by each catalyst with the theoretical amount of hydrogen that would be necessary to complete the reduction of Co₂O₃ in the catalyst.

Equation $D = 96/d$ (nm) [52, 53] was used to calculate the dispersion of the metallic cobalt particles (D: percentage of dispersion, d: average particle size of the particles of metallic cobalt determined by TEM, in nanometers).

Carlo Erba 1106 analyzer was used to determine the amount of carbon deposited on the used catalysts.

2.3. Catalyst activity evaluation.

Reactions were carried out in a stainless tube, atmospheric pressure reactor between 400 °C and 600 °C, H₂O/FUR = 7-84 (mol/mol), S/C = 1-17 and GHSV of 2300 h⁻¹. The range of S/C chosen to carry out the studies is justified considering the amount of water present in the non-useful aqueous phase obtained during the fast pyrolysis process [10, 15, 54-57]. The reactor was charged with 0.5 g of catalyst and SiC as diluent. The catalyst was pretreated with 100 mL·min⁻¹ H₂ for 2 h at 600 °C. Products were analyzed on stream via a Varian 3800 GC-FIC-TCD with a TRB-5 and CarboSieve SII columns.

Conversion of furfural and products selectivity were calculated on a molar basis using the totals of the observed products, excluding water. Definition here used for selectivity can be found sometime in literature as products selectivity or, more rigorously, as products distribution. The equations to determine conversion and selectivity to the different products are as follow:

$$X_{FUR} (\%, mol) = \frac{(F_{FUR})_0 - (F_{FUR})_f}{(F_{FUR})_0} \times 100$$

$$S_j (\%, mol) = \frac{F_j}{(\sum F_j)_{products}} \times 100$$

Where:

X_{FUR} : conversion of furfural.

$(F_{FUR})_0$: furfural fed ($mol \cdot s^{-1}$).

$(F_{FUR})_f$: non-reacted furfural ($mol \cdot s^{-1}$).

S_j : Selectivity to product j.

F_j : product j ($mol \cdot s^{-1}$).

3. Results and discussion.

3.1. Characterization.

Sepiolite structure and crystalline phases of Co present in the catalysts after calcination and reduction steps have been studied by XRD, Figure 1. As it can be seen, crystalline structure of natural sepiolite (JCPDS 13-595) is damaged after the incorporation of Co and the subsequent calcination at 600 °C. In the calcined cobalt-based catalysts (CoSep cal and Co/Sep cal) several diffraction peaks corresponding to CoO (JCPDS 78-0431), Co₃O₄ (JCPDS 89-4037), Co₂SiO₄ (JCPDS 00-029-0506) and Co₂MgO₄ (JCPDS 98-003-0580) are observed. CoO and Co₃O₄ correspond to the oxidation of the cobalt precursor during the calcination step. Mixed oxides (Co₂SiO₄ and Co₂MgO₄) are also formed during calcination by the interaction of cobalt precursor with the components of the sepiolitic support (MgO and Si₂O).

Figure 1. XRD of sepiolite as it was supplied (Natural Sepiolite) and calcined (CoSep cal and Co/Sep cal) and reduced (CoSep red and Co/Sep red) cobalt-based catalysts.

XRD of the reduced catalysts are also presented in Figure 1. As it can be seen, after reduction at 600 °C, the peaks related to the cobalt oxides (CoO and Co₃O₄) nearly disappear and a peak at 44 degrees, corresponding to metallic Co (JCPDS 00-015-0806), appears as consequence of the reduction process. On the other hand, Co₂SiO₄ and Co₂MgO₄ compounds remain in the catalyst after reduction step, suggesting that higher reduction temperatures would be necessary to reduce the Co presents in these compounds. The size of the metallic Co particles has been also determined from the XRD of the reduced catalyst using the Scherrer equation [50]. Table 1 shows that PP method makes possible to obtain metallic cobalt particles of smaller size than those obtained when the incipient wetness impregnation method is used (8 vs 12 nm, respectively).

Co content and BET surface area of the cobalt-based catalysts (CoSep, Co/Sep) and natural sepiolite are also shown in Table 1. The results of the ICP-OES technique show that the level of cobalt in both catalysts is very similar and close to 15 wt.%. In relation to the textural properties, a decreasing of the BET surface area is detected for the sepiolitic support after the cobalt incorporation and calcination. This fact can be explained considering the loss of the sepiolite structure after the calcination at 600 °C. In addition, the oxides of cobalt formed during calcination could be blocking the micropores of the support contributing also in the observed decreasing of the BET surface area [36]. In fact, when pore volume is determined for the sepiolite before and after the cobalt incorporation, a decrease is detected, supporting the pore blockage hypothesis. On the other hand, similar BET surface areas are presented by the cobalt-based catalysts,

suggesting that the PP and IWI methods do not have a significant impact on the final BET surface area of the sepiolitic catalysts.

Table 1. Content of cobalt, surface area (BET), metallic cobalt particles size determined by XRD and TEM, metallic Co dispersion and reducibility at 600 °C for the catalysts studied in this work.

Sample	Co, (wt.%)	BET area (m ² /g)	Pore Vol. (m ³ /g)	Co ⁰ , XRD (nm)	Co ⁰ , TEM (nm)	Co ⁰ dispersion, (%) ^a	Reducibility %, (600 °C)
Sepiolite	-	157	0.75	-	-	-	-
CoSep	15.0	112	0.63	7	6	16.0	48.5
Co/Sep	14.7	115	0.61	12	11	8.7	76.6

(a) Calculated from $dCo(nm) = 96/D(\%)$, D: dispersion, dCo(nm): metallic Co particle size (TEM).

The size of the metallic particles of cobalt was also determined by TEM to verify the size calculated before by XRD. Sizes are shown in Table 1. As it can be seen, similar sizes have been determined by TEM analysis (6 nm vs 7 nm for CoSep sample and 11 vs 12 nm for Co/Sep sample). However, the distribution of sizes is narrower for the catalyst prepared by PP, indicating that this sample presents a larger homogeneity of the sizes of the metallic particles of cobalt. Therefore, PP method would allow to prepare a sepiolitic catalyst with smaller metallic cobalt particles and with a more homogenous distribution. In addition, it should be noted that the cobalt incorporation by the PP method increases the dispersion of the metallic particles of Co on the sepiolitic support compared to the incipient wetness impregnation method (Table 1). The smaller size present in the catalyst CoSep, prepared by PP, could be associated to a higher metal-support interaction. This fact could be explained considering that it is possible that the PP method favors the housing and stabilization of the metallic cobalt particles in special positions of the sepiolitic support where their sinterization would be prevented during the steps of calcination and reduction. On the contrary, the incipient wetness impregnation method does not seem to avoid successfully the sinterization of the metallic Co particles during the calcination and reduction steps as it can be deduced from the larger size of the metallic particles of cobalt present in this sample (Co/Sep).

Figure 2. TEM images of reduced catalysts.

The reducibility of the catalysts has been also studied by temperature programmed reduction (TPR). TPR profile for each catalyst is shown in Figure 3. As it can be observed the reduction profile of the catalyst prepared by incipient wetness impregnation (Co/Sep) is very different compared to the catalyst prepared by precipitation (CoSep). As it can be seen, Co/Sep sample, prepared by IWI, presents four reduction peaks around 298, 398, 693 and 763 °C. The first two peaks correspond to the reduction of cobalt oxide (Co_3O_4), the third is probably associated to the reduction of Co_2MgO_4 [57], and the last one corresponds to the reduction of Co_2SiO_4 [58], both formed during calcination step. Different reduction profile is exhibited by the sample prepared by precipitation (CoSep). This sample presents three main reduction peaks. In addition, the intensity of the reduction peaks exhibited by this sample was completely different. As it can be seen, CoSep sample presents a wide reduction peak at 325 °C, which would correspond to the first two peaks observed in the sample Co/Sep (reduction of Co_3O_4). Two reduction peaks with high intensity are found at high reduction temperatures (670 and 766 °C), which could be related to a larger concentration of Co_2MgO_4 and Co_2SiO_4 compounds where the Co results very difficult to reduce [57, 58]. The degree of reduction of the oxidized Co phases present in the catalysts at 600 °C has been determined from the TPR profiles (Table 1). In the case of the catalyst obtained by precipitation (CoSep) was found a lower degree of reduction compared to the catalyst prepared by incipient wetness impregnation Co/Sep (49% and 77%, respectively). The differences found between both catalytic materials in the profiles and degree of reduction seems to be related to the size of the cobalt metallic particles (Table 1) and particularly with the presence of Co_2MgO_4 and Co_2SiO_4 where the Co results quite difficult to reduce.

Figure 3. TPR of calcined catalysts. Dotted line corresponds to the temperature used for the reduction of the catalyst before reaction.

In summary, the Co incorporation method to synthesize catalysts based on sepiolite as support seems to have an important impact on the size, dispersion and reducibility of the metallic Co particles present. The precipitation method allows achieving smaller metallic cobalt particles and highly dispersing by favoring stronger interactions between cobalt and sepiolitic support.

3.2. Catalytic activity.

Catalytic activity and carbon balance was determined for each experiment. Carbon balance was found between 93 and 101 % for all the experiments. Furfural conversion and hydrogen selectivity at 400 °C versus contact time is shown in Figures 4a and 4b, respectively. As it can be seen the incorporation of Co by PP method (CoSep) allows to obtain a catalytic material with higher activity than IWI method (Co/Sep). Specifically, furfural conversion values are between 20-95% for the sample prepared by PP (CoSep) and between 2-78% for the sample prepared by IWI (Co/Sep). The greater catalytic activity exhibited by the CoSep catalyst could be explained considering the smaller size of the metallic Co particles present in this sample and their higher dispersion, Table 1. Those results would mean that a larger number of active cobalt sites, where the steam reforming of furfural could occur, would be presented in this sample. This

circumstance supports the importance of the synthesis method to prepare catalytic materials with improved catalytic performance. On the other hand, hydrogen selectivity was found quite similar for both catalysts (60-70%). It seems that the Co incorporation method does not have a significant impact in the production of hydrogen. Other reaction products such as CH₄, CO, CO₂ and C₃H₆O were also studied (Figures 4c, 4d, 4e, and 4f). As it can be seen, the sample prepared by precipitation (CoSep) shows a lower production of CO (Figure 4c). For CO₂ production, Figure 4d shows similar values for both catalysts, with small differences at high contact times. For methane production, Figure 4e shows that it is very low in both catalysts. Nevertheless, lower selectivity is presented by the catalyst prepared by PP. This is an interesting point since the formation of methane consumes hydrogen, diminishing its final production during the steam reforming of furfural. Finally, the acetone selectivity (Figure 4f) was lower for CoSep. The production of acetone is related to secondary reactions like furfural dehydration. Its presence suggests that the steam reforming reaction is not carrying out properly. Carbon balance was determined in all the experiment finding values between 94 and 102 %.

Figure 4. a) Conversion of furfural versus contact time. b) Hydrogen selectivity versus contact time. c) Selectivity to CO versus contact time. d) Selectivity to CO₂ versus contact time. e) Selectivity to CH₄ versus contact time. f) Selectivity to acetone versus contact time. (Reaction conditions: T^a: 400 °C and atmospheric pressure).

According to these results, the PP method could be considered a promising method for the incorporation of cobalt to synthesize sepiolitic catalysts highly active and selective in the steam reforming of furfural to produce hydrogen with low concentration of undesired by-products (CO, CO₂, CH₄ and acetone). The best results of CoSep could be explained considering its physiochemical properties such as the smaller metallic cobalt particles and highly dispersing by favoring stronger interactions between cobalt and sepiolitic support. In literature similar results on steam reforming of different biomass derived substrates (ethanol, glycerol, acetic acid as model for biooil) over Ni and Co catalysts are described, being the smaller size of their metallic particles and their higher dispersion the main responsible of the improved catalytic performance [46, 60-65].

3.3. Catalytic deactivation.

Catalytic stability is an important issue to consider for the properly performance of one catalyst. Stability is related to the deactivation of the catalyst with reaction time, which can be related with the formation of carbon deposits and sinterization of metallic active sites [65-70]. Catalytic activity of the catalyst prepared by PP (CoSep) and by IWI (Co/Sep) after 6 and 24 h of reaction time is shown in Table 2. Reaction conditions were adjusted to achieve similar furfural conversion levels. As it can be seen, deactivation happens in a larger extension for the catalyst prepared by incipient wetness impregnation, what could be explained considering the larger amount of coke presents in this sample (Table 2).

Table 2. Conversion of furfural, carbon content, size and percentage of sinterization of metallic Co particles. Conversion data obtained after 6 and 24 hours of reaction time. Reaction conditions: (1) H₂O/Fur =18 (mol/mol), contact time: 0.72 h, 400 °C and atmospheric pressure, (2) H₂O/Fur =18 (mol/mol), contact time: 1.60 h, 400 °C and atmospheric pressure.

Catalyst	%Conv. 6h	%Conv. 24h	Carbon (wt.%)	Co ⁰ , TEM (nm)	Sinterization, (%)
CoSep ⁽¹⁾	54.9	52.4	17.0	10	36
Co/Sep ⁽²⁾	52.5	44.3	21.2	28	60

Sinterization of metallic Co particles supported on the used catalyst has been also studied by TEM. The micrographs present in Figure 5 show clearly the formation of carbon nanotubes. In addition, it can be observed an increasing in the size of the metallic particles of Co after reaction. The level of metal sintering for the used catalysts has been calculated and presented in Table 2. As it can be seen, it is significantly higher for the catalyst Co/Sep prepared by IWI (60% versus 36%, respectively). The furfural conversion fell a 17.5% in the catalyst prepared by the IWI method, while a 4.5% was the fall of the catalyst prepared by precipitation. Therefore, carbon deposition and sinterization of metallic cobalt particles could be considered the major responsible of the loss of activity detected for the sample prepared by incipient wetness impregnation.

Figure 5. TEM images of catalysts after reaction.

Catalytic results indicate that it has been possible to synthesize a cobalt-base catalyst supported on sepiolite with high catalytic performance in the steam reforming of furfural. In addition, it has been shown that the Co incorporation method has an important impact in the physicochemical properties of the final synthesized catalysts. Particularly, the particle size of the metallic cobalt, its interaction with the support and its reducibility are the most affected parameters. Specifically, it has been showed that the PP method makes possible to prepare a catalytic material based on sepiolite promoted with Co highly active and selectivity in the steam reforming of furfural, with high hydrogen yields, low production of unwanted by-products (CO, CH₄ and acetone) and with high stability (lower deposition of coke and specially, lower sintering of the metallic particles of Co).

4. Conclusions.

Co incorporation on natural sepiolite have carried out by precipitation (PP) and incipient wetness impregnation (IWI) methods. The catalysts obtained have been characterized and studied in the steam reforming of furfural to produce hydrogen. High catalytic activity and hydrogen selectivity is exhibited by the catalyst prepared by precipitation (PP). In addition, selectivity to by-products (CO, CO₂, CH₄, acetone) is also minimized using this catalytic material (CoSep). Characterization data suggests that PP method makes possible to synthesize a cobalt catalyst supported on sepiolite with metallic particles of smaller size and well-dispersed on the sepiolite support. The smaller size and the higher dispersion, together with the high interaction cobalt-sepiolitic support, seem to explain the enhanced catalytic performance presented by the catalyst prepared by PP. In addition, the catalyst prepared by precipitation (CoSep) presented a larger catalytic stability with reaction time. Particularly, this sample exhibited slightly lower carbon deposition and, specially, lower degree of sinterization of the metallic particles of cobalt.

Acknowledgements

Thank you to the Spanish Government (Project RTI2018-102161-I00) and Generalitat Valenciana (PROMETEO/2018/006 grant) for the fanatical supporting. The support of the microscopy service at Universitat Politècnica de València (UPV) for the SEM and TEM analysis is also recognized.

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