

High H₂ Production From The Reforming of CH₄ by Hydrogen Sulphide Using Mo-Cr Supported on Heterogeneous Catalysts

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ABSTRACT

Catalytic steam reforming has been for a long time the principal method for the production of hydrogen. According to this method, hydrogen is generated by the reaction of steam with methane (CH₄) at quite high temperatures from 923 to 1223 K requiring the removal of hydrogen sulphide (H₂S) present in natural gas streams or light hydrocarbons.

Alternative processes for hydrogen production have been studied. A proposed method is the reforming of CH₄ by H₂S. With this process, the removal of H₂S in natural gas streams is no longer necessary and sulfur, usually considered as a strong pollutant on liquid fuels in refineries, is used as a reagent in H₂S form of hydrodesulphurization processes.

This research involved the synthesis of modified SBA-15 support with zirconia dioxide; achieving the mechanical resistance, chemical stability and redox properties of zirconia improving the textural characteristics. Furthermore, lanthanum oxide incorporation in zirconia was carried out allowing increase of its surface area with enhanced thermal stability. The supports were impregnated with molybdenum as active phase and chromium as promoter.

The materials were evaluated in a quartz reactor at range temperatures of 873 – 1123 K, feed molar ratio CH₄:H₂S of 1:12. Synthesized materials were characterized before and after reaction by X-Ray diffraction, nitrogen physisorption, thermogravimetry techniques and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). All techniques confirm the mechanical and thermal stability of the supports and their textural properties.

Molybdenum supported on zirconia-lanthanum catalyst showed better catalytic performance, achieving high selectivity to hydrogen (64%).

Keywords: reforming, hydrogen, modified supports



1. Introduction

Currently, 80-85% of the hydrogen produced in the world is obtained from the reforming of methane with steam (SMR) of natural gas streams [1]:



Hydrogen production by this route requires great energy consumption. It also requires the removal of sulfur compounds present in natural gas streams. This extra cleaning step in the process, with its additional cost is necessary because the catalysts are quickly poisoned by sulfur compounds. In the petrochemical and refining industry, the removal of hydrogen sulfide from natural gas and refinery gas streams has increased its importance due to the environmental and economic damage caused by the processes used today impact. The gas sweetening process is to remove contaminants, H_2S and carbon dioxide (CO_2), received the sour wet gas producing wells. This process involves the selective absorption of contaminants, using an aqueous, a base formulation amine solution which circulates in a closed circuit where it is regenerated for continued use. The acid gas ($\text{H}_2\text{S} + \text{CO}_2$), from sweetening process goes through a thermal reactor (combustor), and then passes two catalytic reactors, where finally the conversion of H_2S to elemental sulfur (S) is achieved, this process known as Claus [2]:



Sulfur is recovered at the end of the processes in liquid phase and is to be sent "hot" boat market, thus the sum of costs associated with the extraction, transport heating operation and risks make unprofitable marketing especially with prices ranging around \$ 40 per ton [3]. In México, National Industry of Petroleum announced that the daily production of sulfur subsidiary in Gas and Basic Petrochemicals and Refining amounts to about three thousand 500 ton/day, which makes this element becomes a problem logistics due to its high production, low capacity of some gainful sale and export, because sulfur should be kept in liquid phase at a temperature of 403 K in special pools and if it takes the sale, then the process train is saturated, so you would have to reduce or stop the production of gas and fuel.

Additionally, a thermodynamic study by Sitja and Bravo in relation to the conditions of non-stoichiometric operation of a sulfur recovery plant, it is concluded that it cannot comply with the provisions of the EPA (Environmental Protection Agency), as it have atmospheric emissions of 440 and 705 lbs of sulfur dioxide (SO_2) / ton of sulfur produced as the Claus process does not allow full exploitation of the hydrogen sulfide to convert sulfur and hydrogen [4]. This problem requires solving by developing new processes that remove sulfur from gas streams, avoiding the Claus process. He has been investigating the reaction of hydrogen sulfide content in the acid gas with methane for direct hydrogen production (considered as the fuel of the future) [5] and carbon disulfide, which has a market price four times higher the sulfur. Methane and hydrogen sulfide react in a temperature range of 743-960 K at atmospheric pressure, to produce hydrogen and carbon disulfide, according to the following reaction [6].



Catalytic reforming of CH_4 and H_2S to produce H_2 and CS_2 is proven by experimental evidence scant research done over the years. However, these investigations are based on tests with extreme operating conditions (high temperature and vacuum pressure), which generate extra economic cost, to achieve good conversions. Moderate operating conditions (optimum reaction system) have achieved only low conversions of the desired products; it is believed that this deficiency is due to the use of bulk catalysts or simple supports that, given their catalytic properties do not meet the needs of activation, selectivity and / or stability required for this reaction [7]. Therefore, it is a



priority need to extend the search for catalysts that possess characteristics that generate high conversion potential at moderate operating conditions.

In this work, the mesoporous support SBA-15 was synthesized by modifying its micellar dioxide zirconia (ZrO_2) structure, this combination can seize the mechanical strength, chemical stability and redox properties posed zirconia increasing their low surface area and porosity [8]. Further, the zirconia is synthesized changing its micelle structure with lanthanum oxide (La_2O_3) with this increasing their surface area and forming a mesoporous solid with enhanced thermal stability [9]. The supports were impregnated with molybdenum (Mo) as the active phase and chromium (Cr) as promoter [11, 10, 6, 4, 3, 7].

2. Experimental

2.1 Synthesis of materials

The synthesis of mesoporous material SBA-15 was carried out in acidic medium from clear solutions ($\text{TEOS}/\text{H}_2\text{O}$) and Pluronic-123 ($[\text{OE}]_{20} - [\text{OP}]_{70} - [\text{OE}]_{20}$ PM 5838 g/gmol, where EO: ethylene oxide PO: polyethylene oxide). In a typical synthesis 4 g of Pluronic P123 was weighed and dissolved in 140 ml of water (H_2O). Subsequently 7.5 ml of hydrochloric acid (HCl) is added. The solution is transferred into a cell at 318 K and stirred for 2 to 3 h. 9.6 ml of TEOS was added dropwise with constant stirring is added and let stand with stirring for a period of 24 hours. It is placed in the oven at 363 K for 24 hours. Following this, the solid formed is filtered and washed, placed in the oven to complete drying for 12 hr. Subsequently, calcined at 393 K for 1 hr and then at 823 K for 6 h in air flow. The modification of the support SBA-15 was made via metallic chemical grafting, as the source of zirconium is zirconium propoxide used IV, Zr (Npro) 4, 70% in 1-propanol.

The composite oxide, $\text{ZrO}_2 - \text{La}_2\text{O}_3$ was prepared by co- precipitation of a solution of zirconium oxychloride (ZrOCl_2) and lanthanum nitrate hexa- hydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), with ammonia solution. The pH during the precipitation was controlled. The precipitate was collected by filtration and washed with deionized water until no Cl⁻ detecting anions. The gel was dried at 378 K for 24 hours and then calcined in flowing air for three hours at 823K [9].

Impregnation of active stages and the synthesized media promoters was conducted by the incipient wetness method. The substrate is heated to dry the pores and then soak it in enough solution of ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) [12] and nano hydrated chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), to fill the pores with the desired amount of active component, stirring for one hour at 343 K. The pores are filled with the correct amount of salt solution. The solvent is removed by evaporation and the resulting samples are dried for 23 hours at 393 K. Catalytic materials are calcined in air flow at 673 K for 2 hours.

Mesoporous supports were modified under a 1:1 ratio, while the load of Mo and Cr was 15% and 5% by weight respectively.

2.2. Physicochemical Characterization

The textural properties of the catalyst were characterized by a surface area analyzer ASAP-2405, Micromeritics brand, with a liquid nitrogen temperature of 77K, and a degassing temperature of 573 K. Measuring patterns XRD for phase identification was performed using a Siemens D-500 diffractometer, Cu wavelength $\text{K}\alpha_1$, $2\theta = 1518$ Angstroms.



2.3. Catalytic tests

The catalytic evaluation of materials was carried out in a micro plant where they were subjected to the conversion reactions of CH_4 and H_2S to H_2 . The system is mainly constituted by three sections, 1st feed section consists of a gas supply control, H_2S , CH_4 .

The second section reaction system, consisting of a vertical reactor, equipped with an oven termolyne 11000 with internal temperature controller. 3rd Section of identifying reaction products, has a gas chromatograph Varian Star 3400 equipped with a capillary column Pora-Q bond with a length of 25.0m, 0.32mm, 5 μm , #CP7361.

Catalyst at 393 K were dried for 2 hours under nitrogen (N_2) using a flow of 6,838 L/h. Continuing with the same gas flow N_2 - H_2S gas (5.95 L/h) was added raising the temperature to 723 K at a rate of 353 K/h keeping it under these conditions for 4 hours in order to ensure the formation of the sulfur materials molybdenum disulfide (MoS_2) and chromium sulphide III (Cr_3S_2). Then, the flow of N_2 gas was changed through the gas flow helium (He) at a rate of 6.84 L/h starting increased from 723 to 873 K at a rate of 353 K/h.

With the ratio CH_4 : H_2S 1:12 proceeded to change the flow of He gas and CH_4 gas was fed from the top side of setting a flow 0.189 L/h, and the H_2S gas from the top of a flow 2.47 L/h. The temperature reaction began to 873 K and it was increased at 973, 1073 and 1123 K each 2 h, maintaining the reaction state work for 2h, 3h and 5h respectively assaying gas chromatograph the product at time zero and every 0.5 h. Before releasing the product gases into the atmosphere, the gases are sent through a scrubber 2 liter containing a solution of sodium hydroxide (NaOH, 6M) and hydrogen peroxide (H_2O_2), that to remove them, effectively, the H_2S and other sulfur gases.

3. Results and discussion

3.1 Structural properties

Figure 1 was obtained on diffraction angle in order to provide evidence of the presence of the SBA-15 in Mo/ZrO_2 -SBA15 and CrMo/ZrO_2 -SBA15 phases. The SBA-15 is characterized by three main peaks corresponding to the planes (100, 110, 200). The materials studied showed the characteristic intense reflection in the plane (100) of the hexagonal mesoporous structures of high symmetry. The absence of the plane (110), indicative of the order of 2-D pores, and the level (200), which shows the regularity of pore arrangement, is due to the addition of ZrO_2 in its structure micelles.

Figure 2 evidence the characteristic peaks of the elements comprising the materials Mo/ZrO_2 -SBA15 and CrMo/ZrO_2 -SBA15 respectively to high angle and calcinations temperatures in the range of 873 to 1073 K. The results confirm the assumption of the impregnation of molybdenum oxide species and chromium oxides were appropriate. Thus, the diffraction peaks corresponding to the reflection of the ortho- rhombic Mo_4O_{11} phase, being the characteristic peaks of monoclinic phase $\text{Cr}_2(\text{MoO}_4)_3$ in the diffractogram of the catalyst CrMo/ZrO_2 -SBA15. Zirconia (ZrO_2) pure cubic phase transforms tetragonal is stable up to $\sim 1240^\circ\text{C}$, and finally, at lower temperatures, down to room temperature, the monoclinic phase is stable [13]. It is known to stabilize the stable tetragonal ZrO_2 phase within a glassy matrix containing silicon oxide IV (SiO_2). In this composite, the presence of SiO_2 in the matrix has a double effect: first inhibits the formation of cubic phase in favor of the tetragonal phase and moreover inhibits transformation tetragonal ZrO_2 to monoclinic ZrO_2 . The diffractograms show the stabilization of the tetragonal ZrO_2 to calcination temperatures of 823 K as a result of the addition of SBA-15 by modifying its micelle structure giving higher thermal stability and mechanical. As temperature increases, the characteristic peaks of SBA-15 at low angles disappear and SiO_2 structure changes to monoclinic zirconium silicate (ZrSiO_4). Upon reaching the temperature of 1073 K peak intensity and appear ZrSiO_4 near it monoclinic phases of ZrO_2 , breaking the stability achieved. Similarly, Figure 3, shows the peaks characteristic of the elements $\text{CrMo/La}_2\text{O}_3$ - ZrO_2 and the $\text{Mo/La}_2\text{O}_3$ - ZrO_2 materials. Unlike ZrO_2 -SBA15 mesoporous support, it is seen in that even under the presence of monoclinic ZrO_2 , no phase changes occur that modify the structure of the support by increasing the temperature, showing no formation of



new elements and/or collapsing structures. This confirms that the addition of La_2O_3 support provides the constant thermal and mechanical stability to temperature deltas [13].

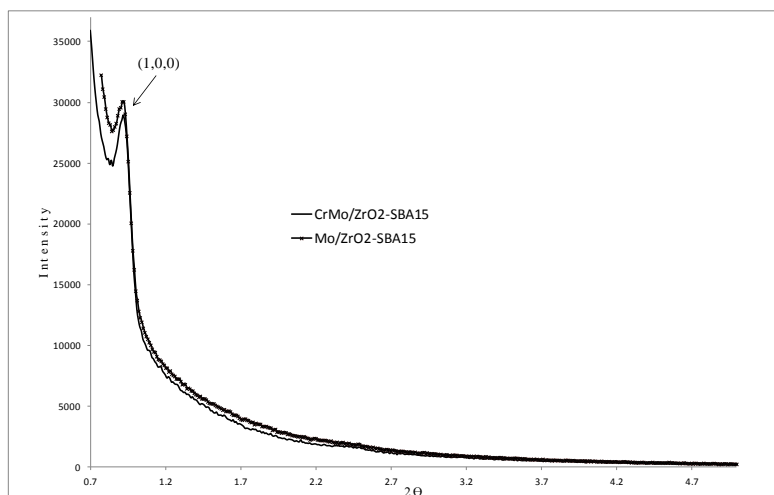


Figure 1. X-Ray Diffraction patterns (small angle) of $\text{CrMo/ZrO}_2\text{-SBA15}$ and $\text{Mo/ZrO}_2\text{-SBA15}$ catalysts.

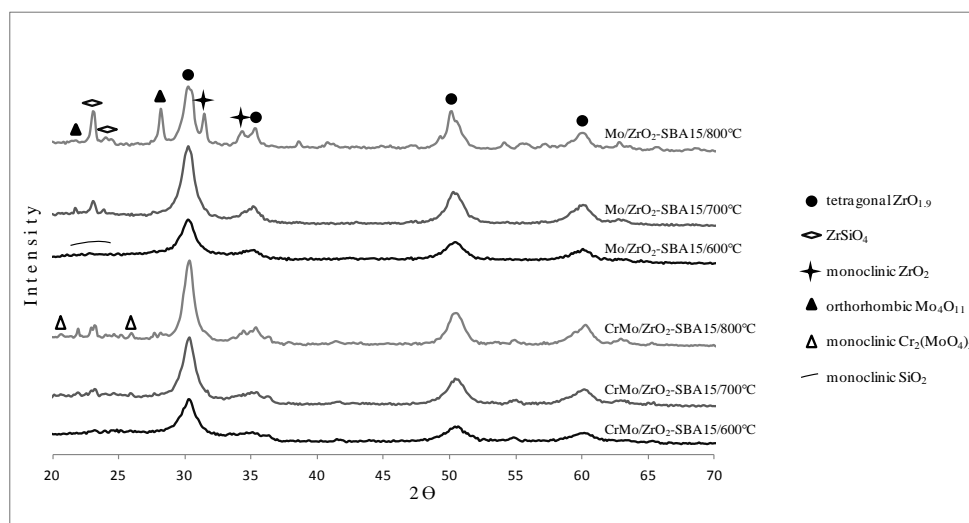


Figure 2. X-Ray Diffraction patterns (wide angle) of $\text{CrMo/ZrO}_2\text{-SBA15}$ and $\text{Mo/ZrO}_2\text{-SBA15}$ catalysts.



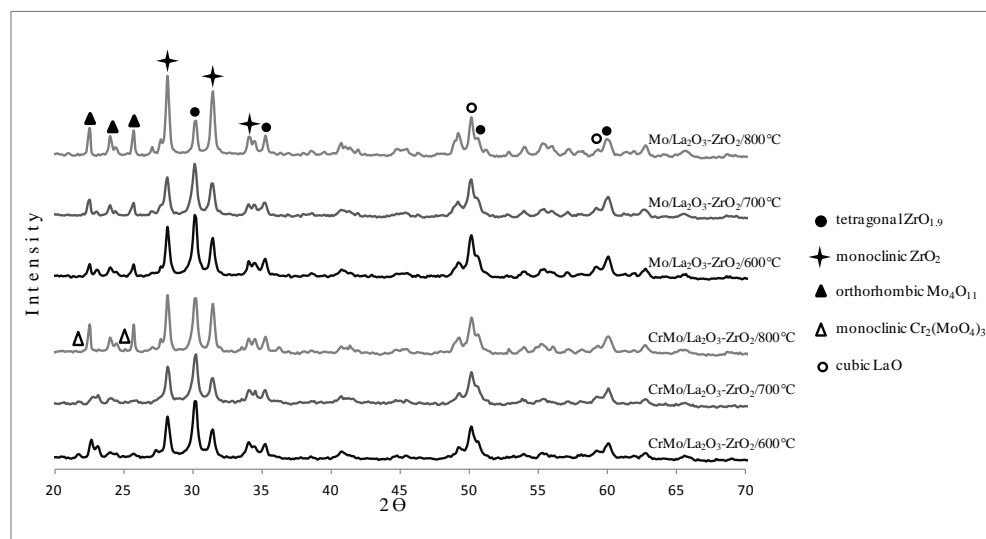


Figure 3. X-Ray Diffraction patterns of Mo/La₂O₃-ZrO₂ y CrMo/La₂O₃-ZrO₂ catalysts at different temperatures of synthesis.

3.2 Textural properties

The analysis by nitrogen physisorption generated the results shown in Table 1 on the textural properties of the sintered materials, they are classified as mesoporous at the discretion of the IUPAC because the pore diameters are in the range of 20-500 Å calculated according to the method Barrett- Joyner- Halenda of (BJH) [14]. Surface areas obtained for Mo/La₂O₃-ZrO₂ and CrMo/La₂O₃-ZrO₂ are characteristic of these types of catalysts. Won Kim et al. mentioned that the incorporation of transition metals, particularly noble metals, it provides the ZrO₂ increased catalyst activity and stability, further confirmed by experimental results that the impregnation of the second metal in the ZrO₂ support encourages sintering considerably modified to low temperature [9-15]. The remaining catalysts make structural advantage provided by the natural properties of SBA-15 in the modification of ZrO₂ support, thus increasing its low surface area.

Table 1. Textural properties of source catalysts.

Materials	Surface area (m ² /g)	Pore volume (cc/g)	Pore diameter (Å)
CrMo/La ₂ O ₃ -ZrO ₂	13,68	0,042	122,87
CrMo/ZrO ₂ -SBA15	197,78	0,263	53,22
Mo/La ₂ O ₃ -ZrO ₂	9,67	0,032	133,49
Mo/ZrO ₂ -SBA15	239,61	0,297	49,53

The adsorption isotherms Mo/La₂O₃-ZrO₂ and CrMo/La₂O₃-ZrO₂ (Fig. 4a), are type II according to the IUPAC classification, feature a macro porous solid type H3 hysteresis behavior that is related to solid aggregates particle with recesses in which no pores of uniform size and shape, as is verified in the pore diameter (Fig. 4b).



Furthermore, the adsorption isotherm Mo/ZrO₂-SBA15 and CrMo/ZrO₂-SBA15 catalysts (Fig. 5a) are type IV according to the classification of the IUPAC, typical of mesoporous solids with a hysteresis type behavior H1 that is related to the presence of pores of uniform size and shape to form cylindrical channels open, as corroborated by the graphs of the pore diameter (Fig. 5b), which show a narrow distribution of pores with a character and a behavior monomodal uniform. Importantly, the trend of behavior obtained is attributed to the textural properties provided by the SBA-15 present in the materials.

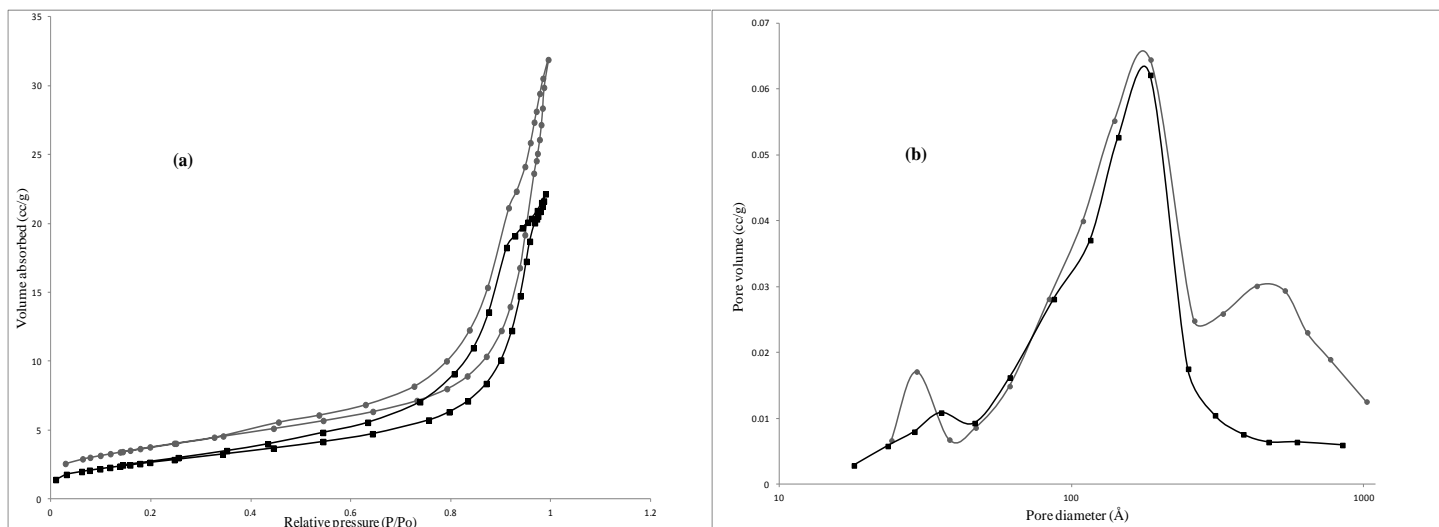


Figure 4. Adsorption-desorption isotherm of N₂ (a) and Pore size distribution of (b) Mo/La₂O₃-ZrO₂ ■ and CrMo/La₂O₃-ZrO₂ ●

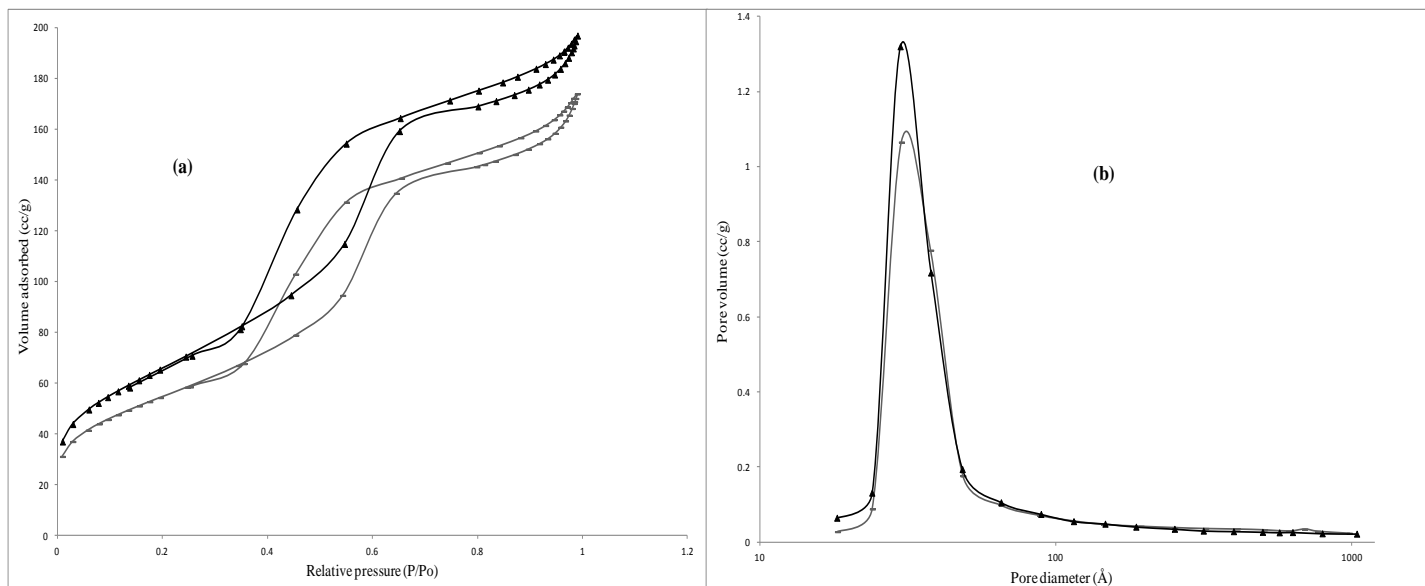


Figure 5. (a) Adsorption-desorption isotherm and (b) Pore size distribution of Mo/ZrO₂-SBA15 ▲ and CrMo/ZrO₂-SBA15 ✕



3.3 Catalytic Activity

The reforming of methane with hydrogen sulfide (R1) proceeds via H_2S thermal decomposition of H_2S (R2) and methane pyrolysis (R3):



The results of evaluating the catalysts in the reforming process of methane with hydrogen sulfide in the pilot plant shown in Figure 6 to Figure 9.

The synthesized catalysts are classified as bifunctional both, the support and the supported phase activate different elementary steps of the chemical reaction, following different catalytic schemes.

In the case of the supported metals, the reaction takes place initially in the metal, resulting in an intermediate which is subsequently converted by the action of the support. Molybdenum disulfide (MoS_2), obtained from the sulfurization step in the tubular reactor before the reaction stage, has proven to be a highly effective catalyst for the decomposition of hydrogen sulfide reaching conversions higher than 95% at temperatures above 600 °C [10].

High conversion (92 to 99%) of H_2S in R2 is observed in Figure 7, the lower magnitude correspond to the materials $\text{CrMo/La}_2\text{O}_3\text{-ZrO}_2$ and $\text{CrMo/ZrO}_2\text{-SBA15}$ as a consequence that the Cr_2S_3 is only effective for the catalytic decomposition of hydrogen sulfide at temperatures below 600°C. The performance of these metal salts is based on the presence of incompletely coordinated atoms containing *d* orbitals available.

The $\text{ZrO}_2\text{-SBA15}$ and $\text{La}_2\text{O}_3\text{-ZrO}_2$ support, lacking of free electrons, produce an ionic intermediary during the catalytic process (carbonium ion type), necessary for carry out the disintegration of hydrocarbons.

The mesoporous silicates are inert materials. They do not possess acid-base or redox properties. Figures 6 and 7 confirm this fact by obtaining lower average CH_4 conversions in R1 and R3 and of H_2S in R1 at 600°C for $\text{CrMo/ZrO}_2\text{-SBA15}$ and $\text{Mo/ZrO}_2\text{-SBA15}$ materials. It is necessary to note that as temperature increases reflected a significant increase in conversions R1 and R3 for those materials, the cause relates to the disappearance of the characteristic peaks of SBA-15 and the consequent transformation of SiO_2 monoclinic structure on zirconium silicate thereby increasing the acidity of the supports.

On average, maximum conversions are achieved at short reaction times (~ 10h), in general, the stability is reached at 800°C. Maximum conversions in reaction R3 (in the order of 95-100%) are achieved at reaction time upper than 15h and a temperature of 850°C, under these operating conditions the selectivity to carbon (C) decreases significantly (Figure 9), therefore, a higher amount of H_2 is produced. Thermodynamic calculations have shown that with a greater amount of H_2S than stoichiometric at temperatures of 950-1000°C, carbon formation is avoided.

The material efficiency distinction confirms the characteristic of La_2O_3 , which, it being a transition metal provides a higher activity and stability to ZrO_2 .

In Figure 8, the percentage of selectivity to CS_2 (16%) and the hydrogen production (64%) are detected, these values increase as the reaction time and temperatures enhance. Molybdenum supported on zirconia-lanthanum catalyst showed better catalytic performance, achieving high selectivity to hydrogen, corresponding to the effectiveness of MoS_2 in the decomposition of hydrogen sulfide. Furthermore, $\text{Mo/ZrO}_2\text{-SBA15}$ reached maximum selectivities to CS_2 at lower reaction time and temperature.

As shown in Figure 9, high selectivity to carbon occurs in the first hours of reaction at a temperature of 600°C, conditions in which the pyrolysis of methane is taking place without the reforming reaction; as the reaction time and temperature are increased selectivity to C decreases significantly to 82% as the lower limit. High selectivity of H_2S to S_2 is achieved, an intermediary to the reforming process of methane with hydrogen sulfide.



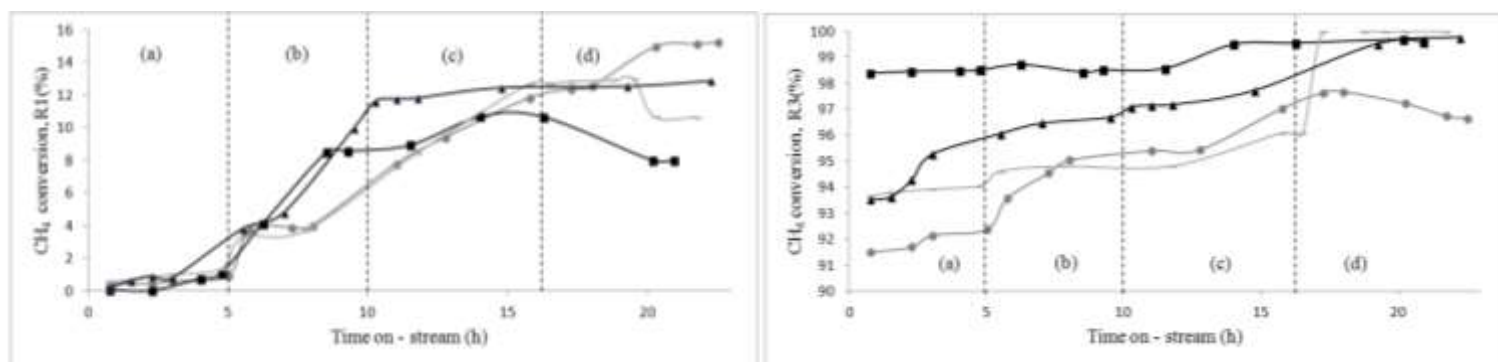


Figure 6. Conversion of CH₄ in R1 and R3 at (a) 873 K, (b) 973 K, (c) 1073 K and (d) 1123K using the catalysts: \blacksquare Mo/La₂O₃-ZrO₂, \bullet CrMo/La₂O₃-ZrO₂, \blacktriangle Mo/ZrO₂-SBA15 and $+$ CrMo/ZrO₂-SBA15.

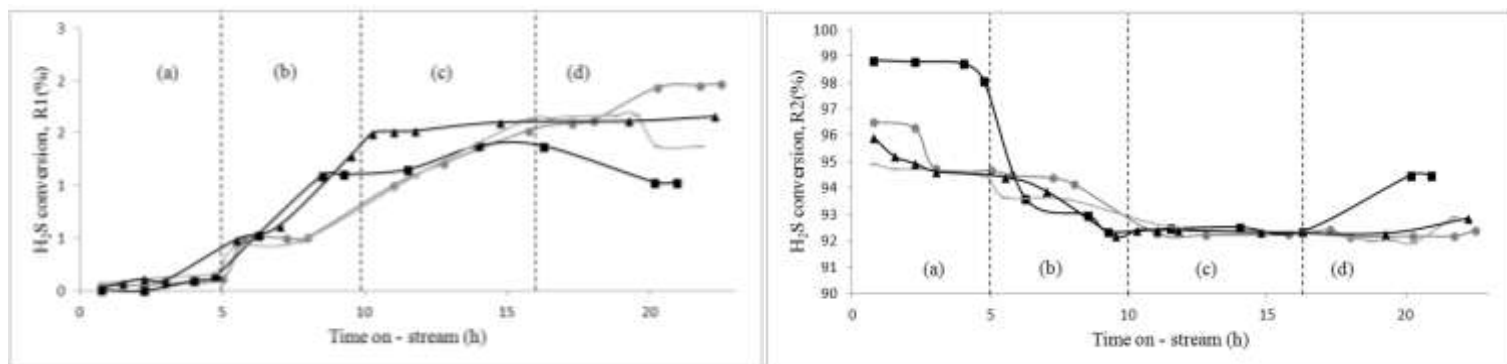


Figure 7. Conversion of H₂S in R1 and R2 at (a) 873 K, (b) 973 K, (c) 1073 K and (d) 1123K using the catalysts: \blacksquare Mo/La₂O₃-ZrO₂, \bullet CrMo/La₂O₃-ZrO₂, \blacktriangle Mo/ZrO₂-SBA15 and $+$ CrMo/ZrO₂-SBA15

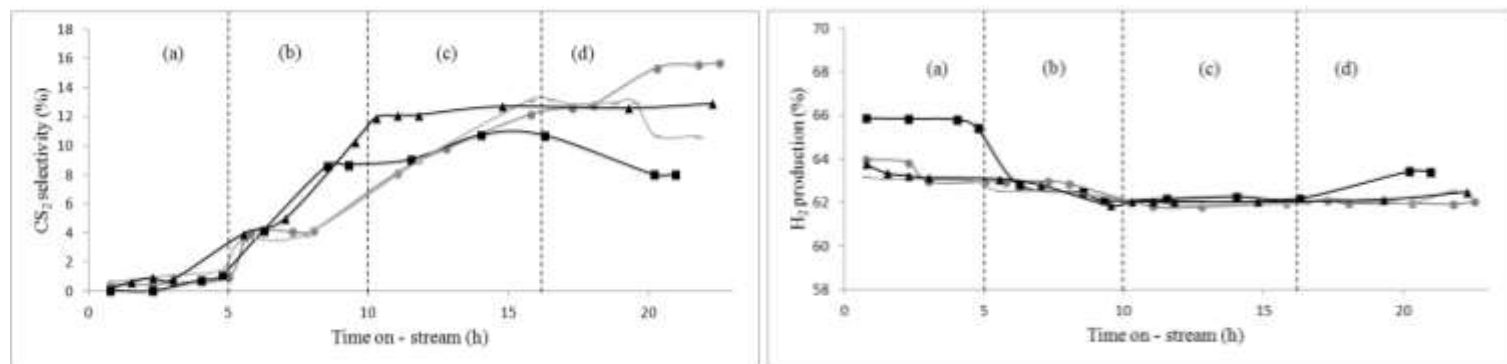


Figure 8. Selectivity of CS₂ and production of H₂ at (a)873K, (b) 973K, (c) 1073K and (d) 1123K using the catalysts: \blacksquare Mo/La₂O₃-ZrO₂, \bullet CrMo/La₂O₃-ZrO₂, \blacktriangle Mo/ZrO₂-SBA15 and $+$ CrMo/ZrO₂-SBA15



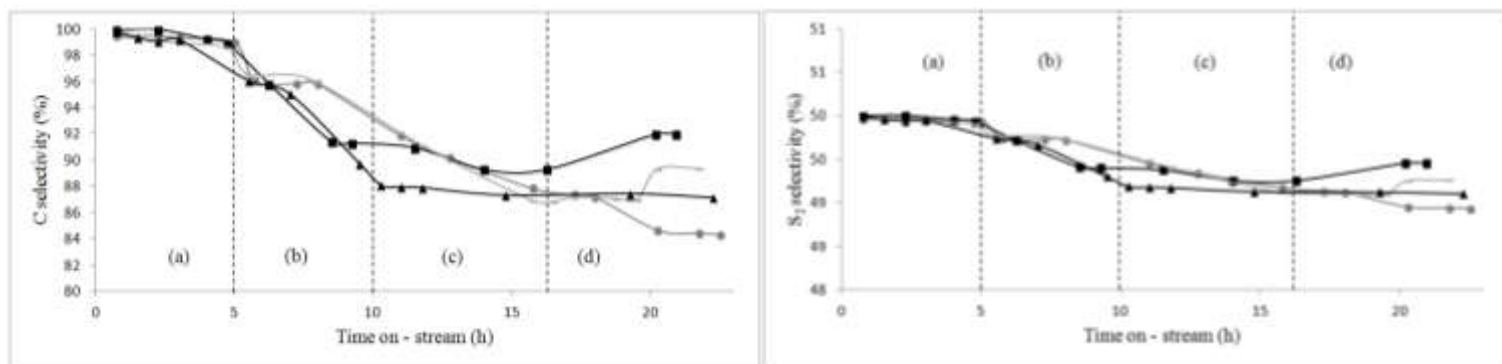


Figure 9. Selectivity of C and S₂ at (a)873K, (b) 973K, (c) 1073K and (d) 1123K using the catalysts: \blacksquare Mo/La₂O₃-ZrO₂, \bullet CrMo/La₂O₃-ZrO₂, \blacktriangle Mo/ZrO₂-SBA15 and $+$ CrMo/ZrO₂-SBA15

Fig 10 show the comparison of diffractograms obtained before reaction (BR) and after reaction (AR) of CrMo/ZrO₂-SBA15 and CrMo/La₂O₃-ZrO₂ materials. The appearance of new elements is observed due to the thermal decomposition of H₂S and the methane conversion on transition metal sulfides and carbides generated respectively. Some characteristic peaks of ZrO₂ remained present after reaction with a visible decrease in intensity. In Section 3.1 of this document, it was mentioned that the impregnation of a second metal on the support of ZrO₂ modified greatly encouraged to low sintering temperature [9, 15], providing strength and resistance to catalyst. This is explained by the observed peaks with increased intensity and frequency in the diffraction patterns after reaction of those catalysts impregnated with chromium, however the greater the presence of carbides thus decreasing the catalytic activity, but the presence of coal was found.

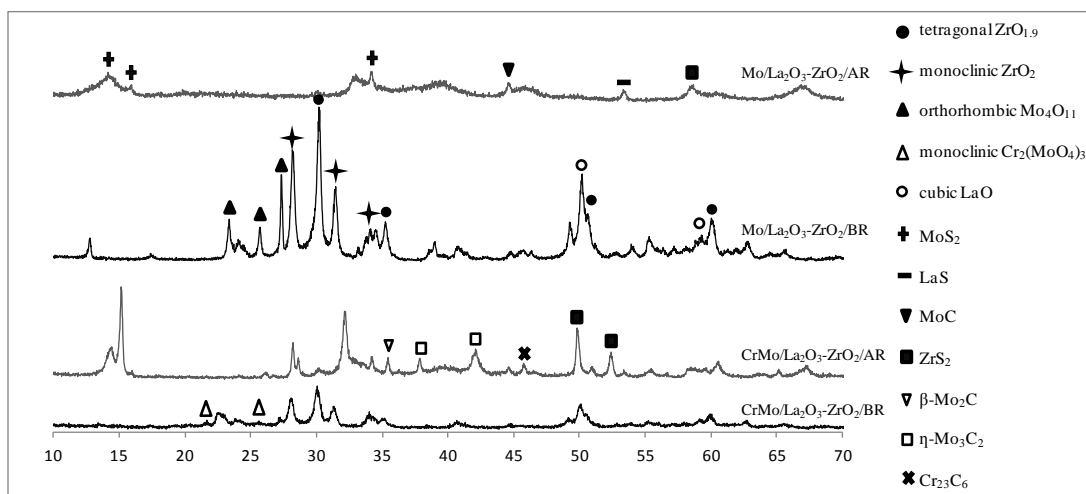


Figure 10. X-Ray Diffraction patterns of Mo/La₂O₃-ZrO₂ and CrMo/La₂O₃-ZrO₂ materials: before reaction (BR) and after reaction (AR).



Figure 11 confirms the presence of carbon deposits on the catalyst; flow of dry air and the presence of high temperatures during the diffuse reflectance infrared Fourier Transform spectroscopy generates the formation of characteristic spectra of CO_2 (2349.3 , 720.5 , 667.3 cm^{-1}). SO_2 bands (1308 - 1340 and 1135 - 1160 cm^{-1}) suggest the molecular oxidation of S_2 on the catalyst, decrease in intensity with increasing temperature.

The resulting spectra using the KBr pellet technique for handling solid samples spectrometry often present, bands at $3,450$ and $1,640 \text{ cm}^{-1}$ due to the absorbed moisture.

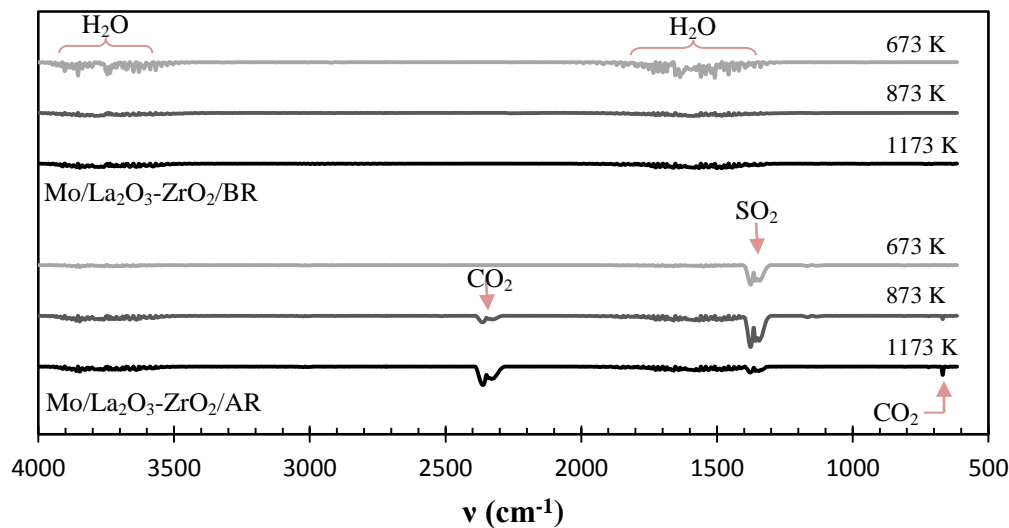


Figure 11. Infrared spectrograms of $\text{Mo/La}_2\text{O}_3\text{-ZrO}_2$ material: before reaction (BR) and after reaction (AR).

4. Summary and perspectives

Catalysts were synthesized with defined characteristics to achieve high conversions of H_2 by reforming of CH_4 with hydrogen sulfide addition to low energy, lowering costs.

The ZrO_2 support with high chemical resistance but poor mechanical stability and surface area, porosity and thermal stability, was modified SBA-15 (1:1) and La_2O_3 (1:1) respectively in order to counteract these deficiencies. In addition to this, metals were impregnated to provide greater activation reaction (15 % Mo and Cr 5 wt% respectively).

The graphs resulting from the catalytic activity of the materials in the pilot plant confirmed providing these characteristics to achieve high yields of H_2 (64%) at temperatures from 973 K with great stability. The catalyst showed better performance was $\text{Mo/La}_2\text{O}_3\text{-ZrO}_2$, because they managed to times and lower temperatures, high conversions and yields to the desired products.

However, in the low range of temperatures studied, the conversion of methane in the reaction R1 and CS_2 selectivity in this reaction are low. There is also a notable selectivity to carbon; negative consequences on the catalyst.



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