CHARACTERIZATION OF IRON-BASED CATALYSTS SUPPORTED ON SBA-15 APPLIED IN THE FISCHER-TROPSCH SYNTHESIS: A REVIEW

PRODUÇÃO DE CATALISADORES SUPORTADOS COM FERRO PARA APLICAÇÃO NA SÍNTESE DE FISCHER TROPSCH

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Abstract: Synthesis processes using simple compounds become attractive for offer alternatives routes from fuel production. Iron-based catalysts have wide applicability in the Fischer Tropsch process. This work aims to evaluate the catalyst Fe/Cu/K/SBA-15 in the Fischer Tropsch synthesis. The catalyst was prepared with the molecular sieve SBA-15 synthesized by hydrothermal method with rice husk ashes, treated by heat and chemical processes, as silica source and simultaneous incorporation of metals by wet impregnation of molar ratio 100Fe/5Cu/18K/139SiO2. The catalyst was submitted to heat treatment under nitrogen and synthetic air flow. The Fischer Tropsch synthesis was carried out in a slurry bed reactor operating at 240ºC, 10 atm and H2:CO molar ratio raging in 1 and 2. The SBA-15 and the catalyst were characterized by XRD, EDX, and nitrogen adsorption, SBA-15 by SEM, and the catalyst for RTP. SBA-15 showed typical morphology traces of mesoporous materials with small specific area of 112m2/g. The catalyst presented the pre-defined composition, maintaining the structure, but with area reduction after impregnation (92m2/g). By RTP results was found the ranges of temperature reduction typical of iron oxides phases. The catalyst showed moderate conversion to liquid hydrocarbons C5+ (54.47%) in the molar ratio H2/CO of 1:1.

Keywords: SBA-15. Iron. Potassium. Rice husk ashes. Slurry bed reactor. Fischer-Tropsch synthesis.

Resumo: Processos de síntese utilizando compostos simples tornam-se atrativos por oferecerem rotas alternativas de produção de combustíveis. Catalisadores à base de ferro têm ampla aplicabilidade no processo Fischer Tropsch. Este trabalho tem como objetivo avaliar o catalisador Fe/Cu/K/SBA-15 na síntese de Fischer Tropsch. O catalisador foi preparado com a peneira molecular SBA-15 sintetizada pelo método hidrotérmico com cinzas de casca de arroz, tratadas por processos térmicos e químicos, como fonte de sílica e incorporação simultânea de metais por impregnação úmida. O catalisador foi submetido a tratamento térmico sob fluxo de nitrogênio e ar sintético. A síntese Fischer Tropsch foi realizada em reator de leito de lama operando a 240ºC, 10 atm e razão molar H_2:CO variando de 1:2. O SBA-15 e o catalisador foram caracterizados por DRX, EDX e adsorção de nitrogênio, SBA- 15 pela SEM e o catalisador da RTP. O SBA-15 apresentou traços morfológicos típicos de materiais mesoporosos com pequena área específica de 112m2/g. O catalisador apresentou a composição pré-definida, mantendo a estrutura, mas com redução de área após impregnação (92m^2/g). Pelos resultados do RTP foram encontradas as faixas de redução de temperatura típicas das fases de óxidos de ferro. O catalisador apresentou conversão moderada em hidrocarbonetos líquidos C_5^+ (54,47%) na razão molar H_2/CO de 1:1.

Palavras-chave: SBA-15; Potassio; Cinzas da casca de arroz; Reator leito de lama; Síntese de Fischer Tropsch.

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1 INTRODUCTION

The Fischer-Tropsch process, used to transform gas into liquid fuels, framed in GTL technology (Gas To Liquid), stands out as a process of transformation of primary sources in commercial value fuels and introduces as a technology to auxiliary traditional production process. The synthesis gas, mixture of carbon monoxide and hydrogen, under suitable temperature and pressure in the presence of catalyst becomes fuels of different molecular weight, and the product can be presented in different fractions in the gaseous phase, liquid or even solid, depending on the conditions. The fuels produced by this process have qualities superior to those obtained by refining the oil when compared to sulfur ratios, nitrogen and even heavy metals (Schulz *et al*., 1999; Steynberg *et al*., 2004; Anderson *et al*., 1984)

The catalysts used in Fischer-Tropsch synthesis are generally formed by metals, prepared by precipitation processes, impregnation or ion exchange. After several years of studies on the development of these materials, iron and cobalt emerge as the most favorable metals FTS process. The ruthenium and nickel also have catalytic activity and considerable performance, but the high cost and the tendency to form methane, respectively, unfavorable for industrial use (Andreson *et al*., 1956).

The Iron, low cost and abundant metal on the planet, has wide application in the FTS process. Adsorbents and catalysts based on iron oxides have been used in various industrial processes. To obtain greater selectivity and activity, alkali metals are usually present as promoters in iron catalysts. The potassium and copper, relatively inexpensive metals, are often employed as promoters for iron catalysts. These metals, when present in the catalyst are in a ionic state, yielding a large part of their valence electrons to the surface of transition metal, which explains the promotion of this metal in the FTS process. Potassium acts on the activity and selectivity of the catalyst product. Copper has significant influence on the speed with which the iron catalyst achieves maximum activity (Zhang *et al*., 2004 Davis *et al*, 2003).

In recent years, various researches on materials used as catalyst support applied FTS have efficient results. High materials area and well-defined mesoporous structure favor the FTS reaction, given that they allow higher metal dispersion and the reagents and products access to the pores of the catalyst. SBA-15 is a new class of mesoporous silicate that has a high thermal and hydrothermal stability when compared to materials belonging to the M41S family, due to the greater thickness of the walls of the pores. The evaluation and the influence of the support as the surface area and the pore size in the mesoporous structure materials enable higher metal dispersion and the reactants and products access to the pores of the catalyst, providing a higher catalytic activity (Griboval-Constanta *et al*, 2002).

The use of molecular sieves produced from alternative sources of silica is presented as a promising technology as it replaces the conventional silica source of high financial value (TEOS) for alternative sources of silica (rice husk ashes) and these sources are found in abundance, and is the raw material of low cost. The ashes have shown to be a great raw material of silica, creating a thin material and high reactivity. Accordingly, the silica obtained from rice husk have been used with great success as a raw material for producing catalysts, demonstrating its high technological potential. However, the use of silica in catalysis requires, in most cases, purification processes for the removal of minor components present. These processes involve, in general, heat treatment and acid (Johnston *et al.*, 1993; Jin *et al*., 2000)

In this study the catalyst Fe/Cu/K/SBA-15 synthesized with rice husk ashes was characterized by X-ray diffraction, X-ray energy dispersion spectrophotometer, N2 adsorption-desorption, temperature-programmed reduction, and scanning electron microscopy. The performance of this catalyst in Fischer-Tropsch synthesis in slurry bed reactor becomes promising to give basis for future research.

2 EXPERIMENTAL

2.1 Rice husk ashes obtainment: Thermal and chemical treatments

Rice husk was subjected to thermal and acid treatments (Rodrigues *et al*.,2012). Heat treatment is a process used to separate the silica from organic compounds of rice husk. The acid treatment is a process to remove impurities of rice husk ashes. The rice husk, previously washed in running water, were put in muffle furnace at a temperature of 600°C, in elevation levels of 100ºC for 4 hours at the final temperature. The rice husk ash, obtained by heat treatment, were treated with hydrochloric acid 1M at temperature of 100°C with stirring in a contact time of 2 hours and ratio of rice husk ashes/volume solution of 25g/500mL. The material was dried in oven for 12 hours at 60°C.

2.2 Preparation of SBA-15 molecular sieve

The SBA-15 molecular sieve was synthesized according to the hydrothermal method (Rodrigues *et al*., 2012), using 10 g of triblock copolymer Pluronic®123 [poly (ethylene oxide) - poly (propylene oxide) -poly (ethylene oxide)] EO20PO70EO20 dispersed in 30g of distilled water. 350ml from hydrochloric acid 2M were added to solution under agitation at 35°C. Subsequently, 21g from rice husk ashes (RHA) as silica source was added, leading to formation of a reactive gel molar composition 1.0 SiO_2 : 0.017 P123 : 5.7 HCl : 193 H_2O. The reactive gel was stirred at 35°C for 24 hours; The gel was transferred to a teflon crucible placed in a stainless steel autoclave. The autoclave was conditioned for 48 hours in oven previously heated at 100°C. The material, after washing and drying in oven at 60°C for 24 hours, was calcined in a muffle furnace to remove the organic driver at 550°C for 5 hours, leaving room temperature under heating rate of 10°C/min.

2.3 *Preparation of Fe/Cu/K/SBA-15 catalyst*

The Fe/Cu/K/SBA-15 catalyst was prepared by wet impregnation method of metals. Was adopted the molar basis 100Fe/5Cu/18K/139SiO_2 using iron nitrate nonahydrate $Fe(NO_3)_3.9H_20$, copper nitrate trihydrate $Cu(NO_3)_2.3H_20$ and potassium bicarbonate $KHCO_3$ as metals sources, and SBA-15 as silica source; 123,32g of iron nitrate were dissolved in distilled water. The solution was placed under stirring on a magnetic stirrer C-MAG HS 4 IKA with heating at 25°C, with addition of 26,25g of SBA-15. A solution containing 3.8g of copper nitrate in distilled water was prepared, as too solution containing 5,67g of potassium bicarbonate in distilled water. Reached the homogenization of the mixture containing iron nitrate and SBA-15, the solutions prepared from copper nitrate and potassium bicarbonate were added. After 30 minutes stirring, the mixture was stored in an oven at 60°C for 24 hours to dry. The calcination process was conducted in synthetic air atmosphere following a procedure in two stages; Initially, from 25ºC to to 100ºC under heating rate of 5ºC/min, remaining for 10 minutes, followed by heating rate of 10ºC/min from 100ºC to 300°C,remaining at this temperature for 5h.

2.4 *Characterization of the Samples*

- *X-Ray Diffraction (XRD)*: Powder diffraction patterns were measured on a Shimadzu XRD 6000. The operational conditions were: Copper Kα radiation at 40 KV/30 mA, goniometer velocity of 2□/min with a step of 0.02□ over the 2θ-range from 2º to 80º. The average diameter of the sample crystallites was determined by the Scherre equation.

- *X-ray energy dispersion spectrophotometer (EDX)*: Elemental analysis was determined through energy dispersive X-Ray spectrophotometry, in a Shimadzu EDX-700 instrument.
- *Nitrogen Adsorption (BET method)*: The textural characteristics of the catalyst were investigated by isothermal gas adsorption/desorption of N_2 at -196ºC using a Micrometrics ASAP 2020 equipment. The adsorption and desorption N_2 isotherms were obtained in the range of relative pressure (P/P_0) between 0.02 and 1.0. The values of the average pore diameter and surface area (S_{BET}) were obtained by the proposed method (BET).
- *Scanning Electron Microscopy (SEM):* The micrographs of the samples were determined through a scanning electron microscope (XL30 EDAX).
- *Analysis by Temperature Programmed Reduction (RTP)*: The temperature programmed reduction tests were carried out in an RTP equipment ChemiSorb 2720, Micromeritics, with measurements obtained using a reducing mixture containing 1.5% H_2 in air with a flow rate of 30 ml/min using high purity argon as reference gas in the same flow.

2.5 Fischer-Tropsch Reaction

The reaction of the Fischer-Tropsch synthesis were carried out in a slurry bed reactor (PARR Model) wrapped in a thermal blanket, fed with 3g of catalyst and 150ml of hexadecane used with inert liquid phase; CO and H_2 gases were added in proportions H_2: CO 2:1 (first running) and 1:1 (second run) in gas flow batch governed by the ideal gas law, fed by mass flow controllers; the agitation of the magnetic coupling system allowed the reactor recirculation gas phase through the slurry bed set at 760rpm. The temperatures and pressures in the tests were set at 240°C and 10atm, respectively; the catalysts were activated in situ; after achieving reaction temperature, the synthesis proceeded for a period of 4 hours.

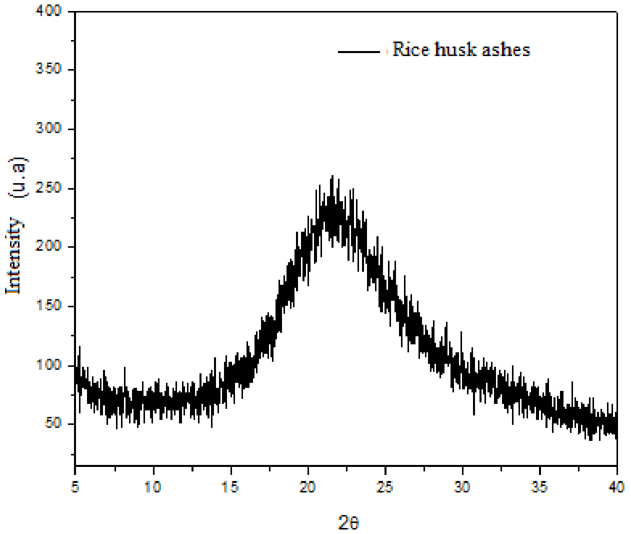
2.6. Data Analysis

Gaseous products were analyzed on line using a gas chromatograph (Thermos Ultra). Samples from the liquid phase were withdrawn after reactor cooling and also analyzed by chromatography. The chromatographic analysis was performed using a column of thermal conductivity detectors (TCD) and a flame ionization detector (FID). On chromatographic analysis, the results of gaseous and liquid products formed in the Fischer-Tropsch synthesis the fractions were separately identified with a subsequent normalization of the produced hydrocarbons.

3 RESULTS AND DISCUSSION

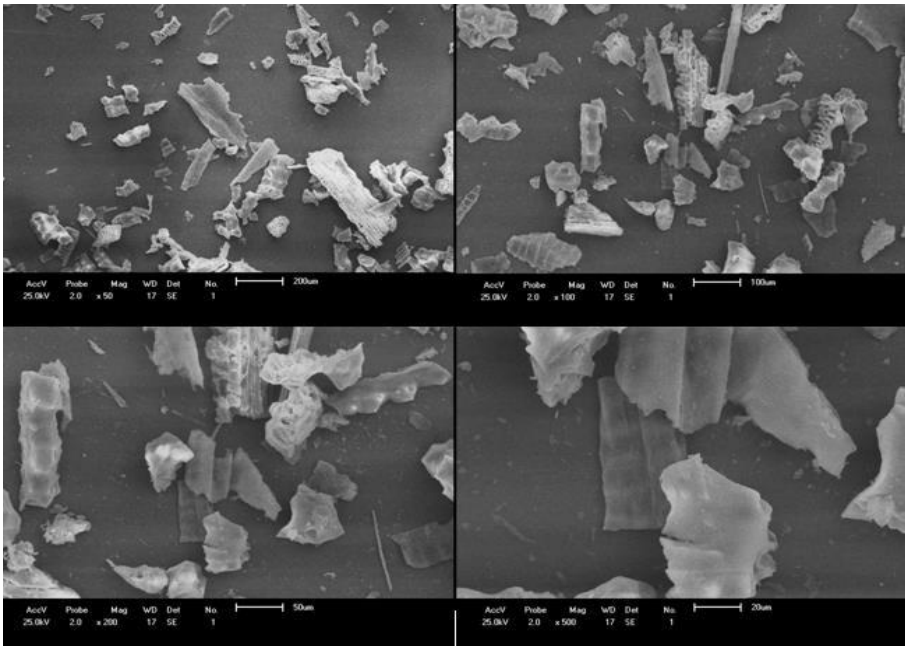
In Figure 01 is shown the ash standard X-ray diffraction rice husk after heat treatment and acid.

Figura 01 - XRD pattern from rice husk ashes



Silica present in the ash remained predominantly amorphous. A diffuse peak around 22º begins to highlight indicating the presence of silica in the form of disorderly cristobalite (Davis, 2003). The crystallization phenomenon was not observed due to the lower temperatures applied were 800°C, is the most likely initiation temperature of the silica present in RHA crystallization (Jin *et al*., 2000). The results of chemical composition, it is found that the composition of the rice husk ashes is essentially silica in the 96.2%. In Figure 02, images of scanning electron microscopyfrom the ashes of rice husk at different magnifications are arranged.

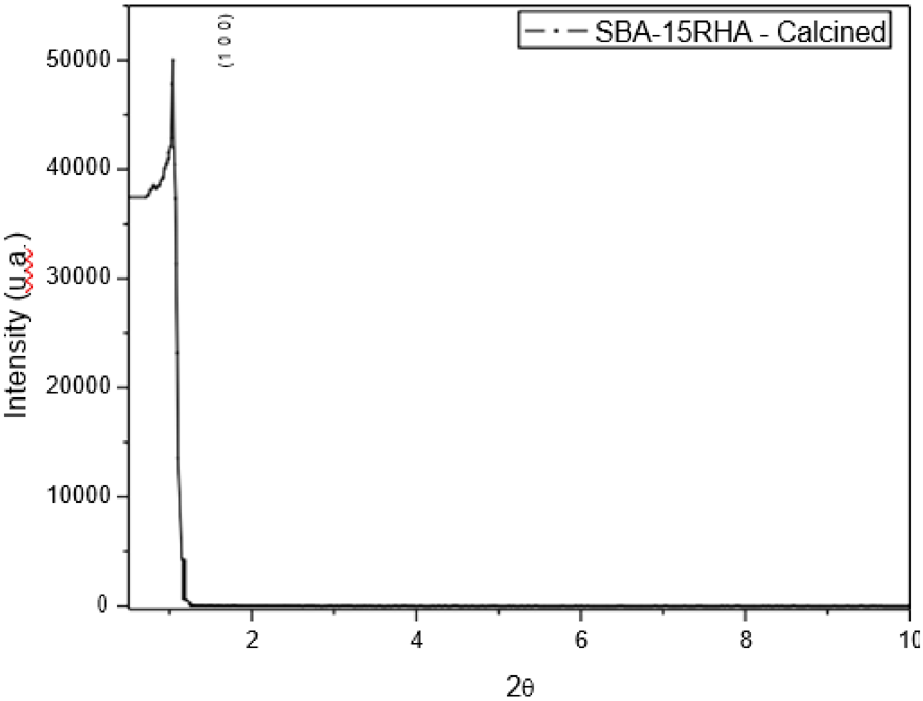
Figure 02 - Images obtained by electron microscopy from the rice husk ashes



It is found that silica obtained from treatments, thermal and acid, applied to the rice husk has particle elongated and twisted leaves; is also visible detail waving external epidermis in denser areas of regions. In the inner regions, there is the formation of a porous cell structure known as silica skeleton resulting from the removal of lignin and cellulose during firing (Rodrigues, *et al* 2012.). The silica concentration tends to be higher in the outer skin due to this gap caused by removal of organic compounds of the shell structure.

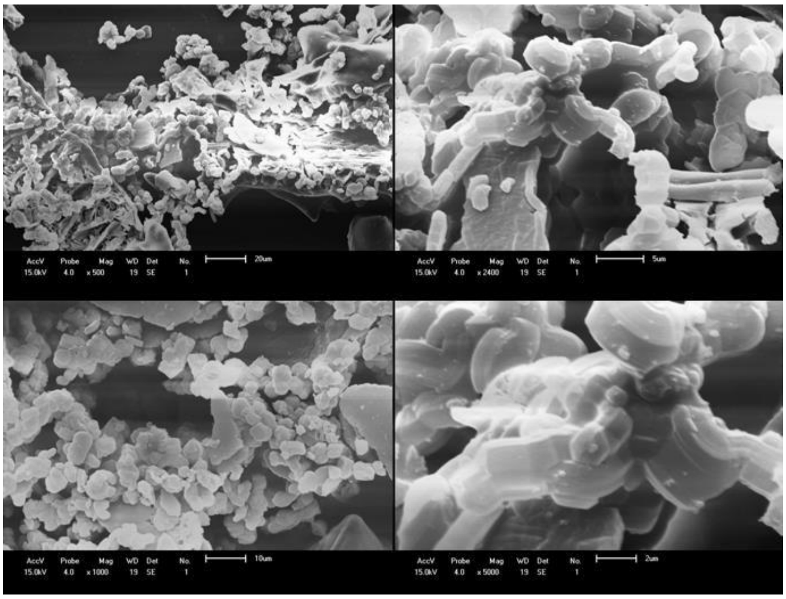
In Figure 03 it’s shown the result of X-ray of SBA-15 molecular sieve calcined.

Figure 03 - X-ray diffraction of SBA-15 molecular sieve calcined



It can be observed pattern formation characteristic of the structure of a two-dimensional hexagonal symmetry typical p6mm SBA-15 (Zhao *et al*., 1998). The main diffraction peak, with Millerindex of (100), referring to the crystal planes, characteristic of this type of material can be observed by XRD. After calcination, the SBA-15 shown high silica content of 97.8%, scheduled for this type of material synthesized with rice husk ashes with a high percentage of silica. In Figura 04, are presented images of microscopy molecular sieve SBA-15.

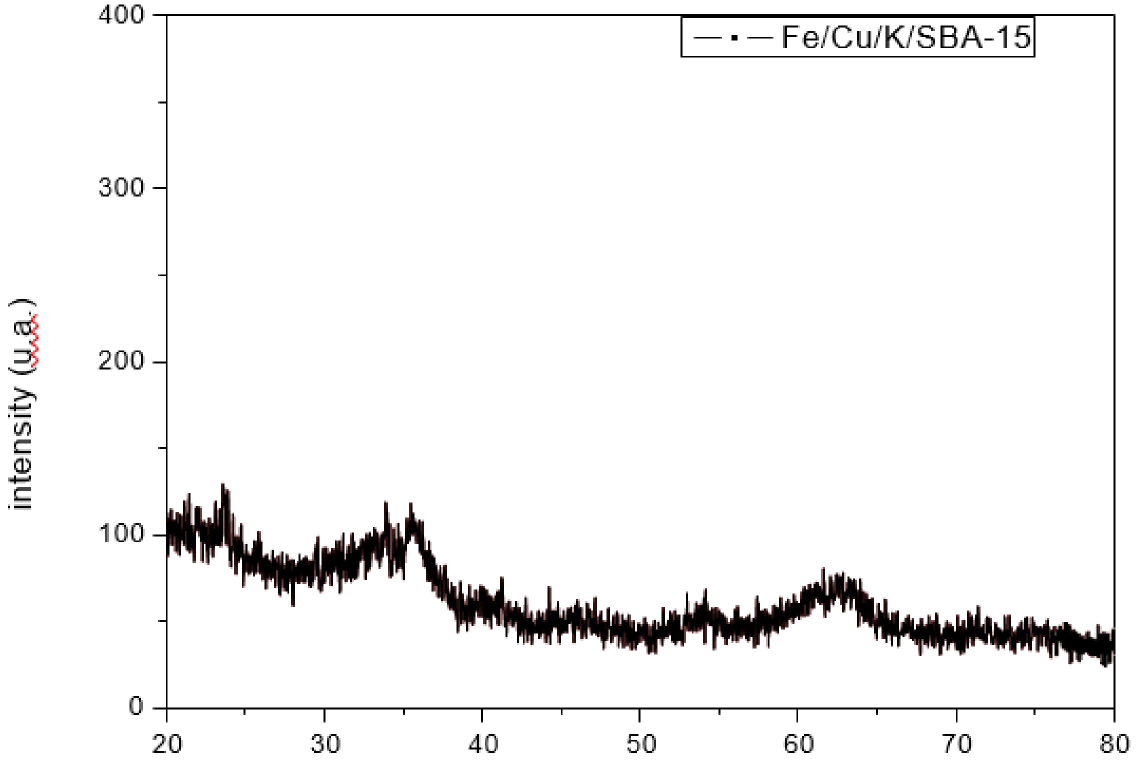
Figura 04 - Scanning electron microscopy of SBA-15



Are observed silica nodule formations in micrometric dimensions joining to each other by smaller particles forming collars interlocking, characteristic of SBA-15 molecular sieve. It is also observed, not typical formations SBA-15; the fibrous exoskeleton, characteristic of the inner epidermis of rice husk ash, presents around of SBA-15 micrometric nodules, indicating the presence of primary silica morphology, also characterized by the presence of external epidermis of rice husk ash. These particles hinder the process of forming the molecular sieve because their structures do not "frame" the organic driver and possibly reduce the fraction of silica in the form of SBA-15 sieve.

Figure 05 shows the x-ray diffraction of the catalyst Fe/Cu/K/SBA-15 after the impregnation and calcination process, in the range of 2θ between 20º and 80º.

Figura 05 - X-ray diffraction of the catalyst Fe/Cu/K/SBA-15 after the impregnation and calcination

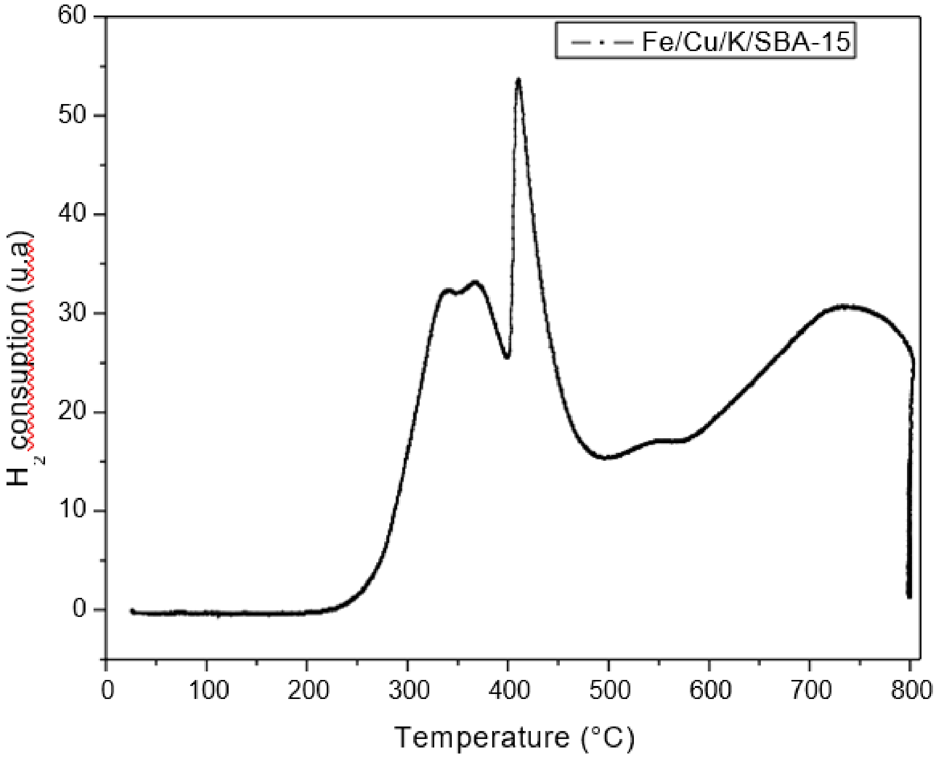


The analysis of the XRD patterns presented, the iron should be well dispersed in the structure of SBA-15 molecular sieve, which favors the thermal stability of the catalyst. This points to the low degree of crystallinity of the catalyst and small metal particle sizes in the structure, characterized as a material with dispersed iron nanoparticles and semi-crystalline (Wang *et al.*, 2005).

The catalyst Fe/Cu/K/SBA-15 showed iron oxide, copper oxide and potassium oxide basis weight values of 51.3%, 2.7% and 4.7%. In the metal, the mass percentage values for the catalyst were 36.01%, 1.83% and 3.98% of iron, potassium and copper, respectively, indicate convergence with the pre-set values for molar basis 100Fe/5Cu/18K /139SiO2.

In Figura 06 it's shown the Reduction Temperature Programmed profile from Fe/Cu/K/SBA-15 catalyst.

Figura 06 - Reduction Temperature Programmed profile from Fe/Cu/K/SBA-15 catalyst



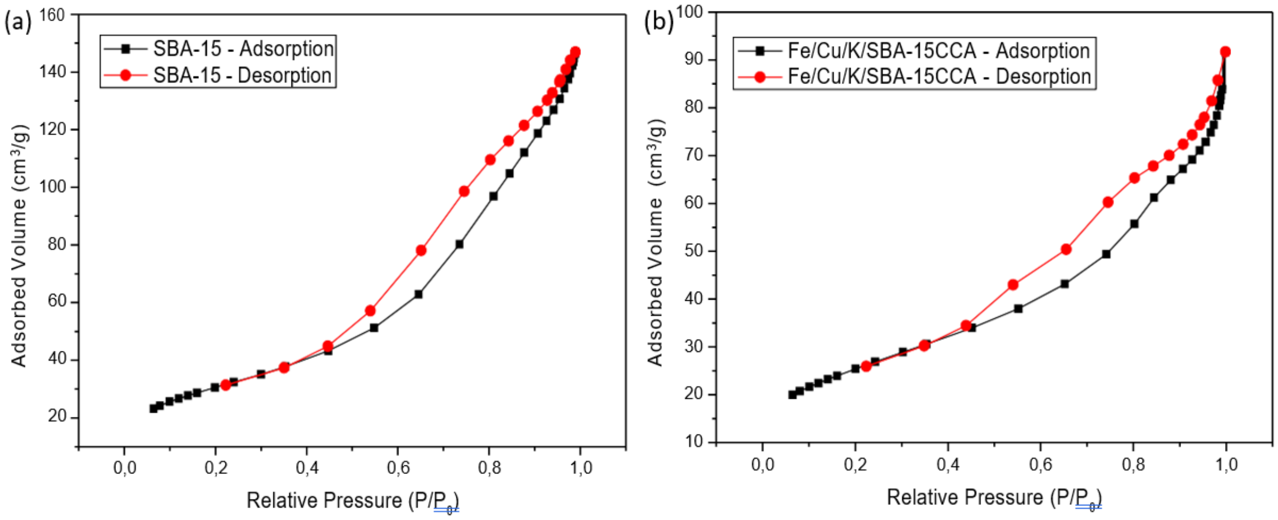
The addition of chemical promoters such as potassium and copper facilitates reduction of the catalyst and the adsorption and dissociation of H_2 on the catalyst surface. The presence of the copper facilitates reduction of iron oxide, especially in the transformation of hematite to magnetite. Potassium has a pronounced effect on TPR analyzes, due to interactions between the promoter (potassium) and the support (SBA-15), and between the support (SBA-15) and metal (iron) (Zhao *et al.*, 1998).

Iron catalysts, copper and potassium supported on silica, three reduction stages are identified: magnetite to hematite phase, magnetite to iron carbide phase and / or wustita, in the third stage the transformation occurs to the metal layer ($Fe2O3 \rightarrow Fe3O4 \rightarrow FeO \rightarrow Fe$). The silica support reduces the mobility of the phases of iron while avoiding sintering process at the RTP experiments and improves thermal stability of the catalyst (Rodrigues *et al*., 2012). There is the occurrence of the characteristic peaks of reduced iron oxides phases; Hematite reduced to magnetite (300°C to 450°C) (Hamad *et al*., 1981)) and Magnetite reduced to metallic iron (with possible formation of intermediate phases) (600ºC to 800ºC).

As expected (Rodrigues *et al*., 2012), the highest hydrogen consumption was found to reduce the conversion of magnetite to metal phase, which occurs at high temperatures; As mentioned, copper has pronounced effect on the transformation of hematite magnetite phase to phase; copper oxides are reduced to metallic copper between 300°C and 400°C, which can be seen that peak reduction. It is also observed that after the reduction of copper, hematite is reduced to magnetite, showing the influence of the promoter in the reduction of the iron catalyst.

In Figure 07 are presented the N_2 adsorption-desorption isotherms at -196°C related to SBA-15 molecular sieve (a) and Fe/Cu/K/SBA-15 catalyst (b) calcined.

Figura 07 - N_2 adsorption-desorption isotherms at -196°C related to SBA-15 molecular sieve (a) and Fe/Cu/K/SBA-15 catalyst (b) calcined



It is found through analysis of N_2 adsorption-desorption isotherms of type IV and H1 hysteresis type, comprising two vertical branches over a range of 0.5 to 0.8 (P/P0) on the abscissa axis. This behavior is characteristic of mesoporous materials of which the SBA-15 is part and it is checked before and after impregnation of the metals in SBA-15. Although the isotherms are type IV, there is a tendency of type III isotherms training, which characterizes formation of non-uniform pores in the material. The textural properties obtained by adsorption of N_2 of the SBA-15 (a) and Fe/Cu/K/SBA-15 catalyst are presented in Table 01.

Table 1 - Textural properties of SBA-15 and catalyst Fe/Cu/K/SBA-15

Sample	***^{a}SBET (m^2/g)***	***^{b}VPtotal (cm^3/g)***	***^{c}e (nm)***
SBA-15	112	0,22	8
Fe/Cu/K/SBA-15	92	0,12	-

[a]specific area calculated by BET method, [b]the total pore volume and [c]wall thickness.

It is seen that there was a decrease in pore volume of 42.6% and a surface area of 18.1%when compared to the synthesized molecular sieve. With the inclusion of metals in used rate, it was expected that reduction area. The attempted synthesis with the ashes of the rice husk is not discarded because they are obvious indications of formation of molecular sieve, creating a material with similar properties (morphology, crystallinity, mesoporosity, type IV isotherms) the synthesized with conventional sources silica, but with lower pore volume, and resulting lower specific area. As supports for metals, these materials obtained are attractive because they provide catalysts of the same chemical composition, but differ in physical properties, verified by the area variation, morphology and structure, and which are fundamental to a study of the influence of these properties in a catalytic reaction system such as Fischer- Tropsch.

In the Table 2 are presented the conversion range of values from synthesis gas to hydrocarbons.

Table 2 - Results of Fischer-Trospch synthesis using catalyst Fe/Cu/K/SBA-15 at 240° C and 10atm

Amostra	T (ºC)	P (atm)	H2:CO	C1-C4 (%)	C5-C9 (%)	C10+ (%)
Fe/Cu/K/SBA-15	240	10	2:1	61,50	25,87	12,63
	240	10	1:1	45,53	47,20	7,27

Iron based catalysts are highly dependent of the ratio of hydrogen/carbon monoxide (H_2/CO) in the syngas when is desired a high conversion of hydrocarbons. When there is a syngas with a relative low H_2/CO must work with an iron catalyst supported on silica (or alumina). The activity of the Water Gas Shift (secundary reaction) also results in a low coke formation in the transformation process gas to liquid fuels (Van der Laan *et al*, 2002; Davis *et al*., 2003). It has been found that the reaction water produced in the Fischer-Tropsch synthesis (FTS) functions as an inhibitor for the primary reaction (Zhao *et al*., 1998; Zhao *et al*, 1998). Therefore, iron catalysts reactions are favored at lower synthesisgas molar ratio (H_2/CO).

The catalyst showed good performance in gas conversion to heavier hydrocarbon fractions, especially from 55% of $C5^+$ in optimum synthesis gas (H_2:CO of 1:1); the ratio of gas (H2:CO 2:1) this catalyst was disadvantaged nevertheless showed 40% of $C5^+$ production.The iron catalyst employed, promoted with potassium and copper supported on SBA-15, with satisfactory increase in the index that represents the length of hydrocarbon chain; potassium content is used that favors higher degree of polymerization for the iron catalyst supported in relation to other lower concentration promoter, seen in the literature (Davis, 2003).

4 CONCLUSIONS

The material obtained by the hydrothermal method using rice husk ashes as silica source showed typical features of SBA-15 molecular sieve, but with low specific area for this type of material; The catalyst showed metal contents in the form of oxides near the predefined values while keeping the hexagonal structure after impregnation of the metals, with iron in good dispersion of the mesoporous structure.

The catalyst Fe/Cu/K/SBA-15 decreased specific area of 18% compared to the synthesized SBA-15 related to the possible formation of the oxides phases in the pores of the molecular sieve; The influence of copper on iron reduction catalyst, wherein the hematite is reduced after the reduction of the promoter, was observed.

In the Fischer-Tropsch catalyst Fe/Cu/K/SBA-15 showed moderate selectivity for $C5^+$ production at 240°C temperature and pressure of 10atm; the molar ratio of synthesis gas had a significant influence on the concentration profiles obtained from the Fischer-Tropsch reaction; Tests have shown that iron catalyst reactions are favored at lower synthesis gas molar ratio (H_2/CO).

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