Co/Ru/SBA-15 CATALYSTS SYNTHESIZED WITH RICE HUSK ASHES AS SILICA SOURCE APPLIED IN THE FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

Synthesis processes using simple compounds become attractive as they offer alternative routes for fuel production. Cobalt-based catalysts have wide applicability in the Fischer Tropsch process. This work aims to evaluate the catalyst Co/Ru/SBA-15 in the Fischer Tropsch synthesis. The catalyst was prepared with the molecular sieve SBA-15 synthesized using the hydrothermal method with rice husk ashes, treated by heat and chemical processes, as silica source; and incorporating, simultaneously, metals by wet impregnation of molar ratio 100Co/5Ru/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 240°C, 10 atm, and H₂:CO molar ratio ranging between 1 and 2. The SBA-15 and the catalyst were characterized by X-ray diffraction- XRD, X-ray energy dispersion- EDX, and nitrogen adsorption. The SBA-15 was characterized using scanning electron microscopy- SEM, and the catalyst was characterized by temperature programmed reduction - TPR and transmission electron microscopy - TEM. SBA-15 showed typical morphology traces of mesoporous materials with a small specific area of 627 m²/g. The catalyst presented the pre-defined composition, maintaining the structure, but with area reduction after impregnation (339 m²/g). The ranges of temperature reduction typical of iron oxides phases were found using RTP results. The catalyst showed high conversion to liquid hydrocarbons C₅⁺ (88.20%) in the molar ratio H₂/CO of 1:1.

KEYWORDS

SBA-15; cobalt; ruthenium; rice husk ashes; slurry bed reactor; Fischer-Tropsch synthesis

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1. INTRODUCTION

Fischer-Tropsch synthesis- FTS- is an important catalytic process discovered in 1923. Then, it was used in the production of hydrocarbons from syngas, a mixture of hydrogen and carbon monoxide (Eq.1), which can be obtained from biomass, coal, and natural gas by gasification and/or reforming (Schulz & Claey, 1999; Steynberg & Dry, 2004; Anderson, 1984; Espinoza et al., 1999; Andreson, 1956; Laan & Beemackers, 1999).

The FTS process can be catalyzed by certain transition metals. In the process, Co, Fe, Ni, and Ru have been used in mainly three different reaction systems, such as fixed-bed, slurry, and bubbling fluid bed, to improve syngas conversion in liquid fuels. Cobalt-based FTS catalysts have been widely studied because of their high conversion rates, high selectivity to linear paraffins, and low water–gas shift (WGS) activity (Zhang et al., 2004; Luo et al., 2003; Das et al., 2014).

In recent years, various researches on materials used as catalyst support applied in FTS have shown successful results. High material areas and well-defined mesoporous structure favor the FTS reaction, given that they allow higher metal dispersion and grant reagents and products access to the pores of the catalyst. SBA-15 is a new class of mesoporous silicate that has 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 (Reza et al., 2009). The influence and evaluation of the support show that the surface area and the pore size in the mesoporous structure materials enable higher metal dispersion, granting the reactants and products access to the pores of the catalyst and providing a higher catalytic activity (Griboval-Constant 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). These new sources raw materials from silica are found in abundance and at a low cost. The ashes, create a thin material and produce high

reactivity. Accordingly, the silica obtained from rice husk has been used with great success as a raw material for producing catalysts, which demonstrates its high technological potential. However, the use of silica in catalysis requires, in most cases, the employment of pre-purification processes for removing minor components. These processes involve, in general, heat treatment and acid (Real et al., 1996; Krishnarao et al., 2001; Cook, 1986; Nakata, 1989; Rodrigues et al., 2013; Zhao et al., 1998).

Noble metals such as Ru, Re, and Pt have been employed with Co-based catalysts to increase the reduction degree of cobalt. The use of small amounts of noble metals associated with cobalt oxide has increased the reduction degree of Co-based catalysts by almost two-fold compared to non-promoted Co-based catalysts. In particular, the use of Ru enhances the interaction between Co and Ru. The presence of this noble metal leads to bimetallic crystallite formation, which is an excellent approach to decrease the reduction temperature (Luo et al., 2003; Reza et al., 2009; Griboval-Constant et al., 2012).

Study conducted by Luo et al. (2003) shows that both FTS activity and C_5^+ hydrocarbon selectivity increase with an increase in Ru content. The increase in activity and selectivity were attributed to the higher number of active sites resulting from higher reducibility, as well as, the synergetic effect of Ru and Co.

Rodrigues et al. (2012) evaluated the catalytic properties of a Ruthenium promoted Cobalt/SBA-15 for FTS. The increase in activity and selectivity were attributed to the increased number of active sites resulting from higher reducibility and the synergetic effect of Ru and Co. Ru/Co/SBA-15 catalysts showed a moderate conversion (40%) and high selectivity towards the production of C_5^+ (80% w/w).

In this study the catalyst Co/Ru/SBA-15 synthesized with rice husk ashes was characterized by X-ray diffraction, X-ray energy dispersion spectrophotometer, N_2 adsorption-desorption, temperature-programmed reduction, and scanning electron microscopy. The performance of this catalyst in Fischer-Tropsch synthesis in slurry bed reactor becomes promising for future research.

2. EXPERIMENTAL

2.1 Rice husk ashes (RHA) obtainment: Thermal and chemical treatments

Rice husk was subjected to thermal and acid treatments (Nakata, 1989). 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, was put in muffle furnace at a temperature of 600°C, in elevation levels of 100°C for 4 hours at the final temperature. The rice husk ash, obtained by heat treatment, was 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 described by Zhao et al. (1998) and adapted by Rodrigues et al. (2012), using 10 g of triblock copolymer Pluronic®123 [poly (ethylene oxide) -poly (propylene oxide) -poly (ethylene oxide)] EO20PO70EO20 dispersed in 30mL of distilled water. Then, 350ml from hydrochloric acid 2M were added to the solution under agitation at 35°C. Subsequently, 21g from rice husk ashes was added as silica source, leading to formation of a reactive gel molar composition 1.0 SiO₂ : 0.017 P123 : 5.7 HCl : 193 H₂O. 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 Ru/Co/SBA-15 catalyst

The Ru/Co/SBA-15 catalyst was prepared by co-impregnation of SBA-15. First, a 0.1 mol/L aqueous solution of cobalt nitrate [Co(NO₃)₂.6H₂O] was used to deliver the amount of cobalt to the support. Afterwards, the impregnation of Ru was carried out using an aqueous of ruthenium-nitrosyl. The Co/Ru/SBA-15 catalyst was calcined using the same

procedure described for the production of the Ru/Co/SBA-15. The impregnation was carried out at room temperature for 30 min under continuously stirring. The mixture was dried at 80°C for 24 h. The solid material was calcined at 200 °C under a nitrogen flow rate of 100 mL/g_{cat} min, with a heating ramp of 10 °C/min starting from room temperature, and kept at the final temperature for 1 h. After this period, the nitrogen flow was replaced by synthetic air and the sample was heated again at 2 °C/min from 200 to 450 °C, and kept at this temperature for 2 h.

2.4 Characterization of the samples

X-ray energy dispersion spectrophotometer (EDX): Elemental analysis was determined through energy dispersive X-Ray spectrophotometry, in a Shimadzu EDX-700 instrument.

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

Temperature Programmed Reduction (TPR): samples were characterized by RTP using ChemiSorb 2720, Micromeritics, under a mixed flow of H₂-N₂ (5% H₂ 30 mL.min⁻¹). Approximately 20 mg of each sample was heated at 10 °C.min⁻¹ over the range 20°C-1000°C. Before beginning data acquisition, the samples were subjected to a pre-treatment process that consisted of heating the material from room temperature up to 200 °C (at 10 °Cmin⁻¹) and, then, maintaining this temperature for 1 hour under a N₂ flow (30 mL.min⁻¹).

Nitrogen Adsorption (BET method): The textural characteristics of the catalyst were investigated by isothermal gas adsorption/desorption of N₂ at 77 K using a Micromeritics ASAP 2020 equipment. The adsorption and desorption N₂ isotherms were obtained in the range of relative pressure (P/P₀) 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).

Transmission electron microscopy (TEM): The analyses were performed on JEOL equipment Model JEM-1200 EX II Instrument with the technique of embedding in Araldite resin and, then, cut with Sorvall MT 5000 ultramicrotome.

2.5 Fischer-Tropsch reaction

The reaction of the Fischer-Tropsch synthesis was 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 H₂ gases were added in proportions H₂: CO 2:1 (first run) 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, and 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 the chromatographic analysis, the results of gaseous and liquid products formed in the Fischer-Tropsch synthesis the fractions were identified separately with a subsequent normalization of the produced hydrocarbons.

2.7 Conversion and hydrocarbon selectivity

The conversion of syngas into hydrocarbons was determined by mass balance of CO, assayed using the same temperature programming with a Supelco Q-Plot capillary column (30 m × 0.25-mm i.d. × 0.25-μm film). A microcomputer used for performing data acquisition and process control also controlled automatic chromatograph sampling.

The FTS product distribution was determined by mass balance of carbon species, which has considered the conversion of syngas and the mass

fractions of hydrocarbon species in gas and liquid phases.

The conversion of carbon monoxide into hydrocarbons (X_{CO}) was determined based on the analysis of the data obtained by the TCD and applying the equation (2):

$$X_{CO}(\%) = \frac{n_{CO}^o - n_{CO}}{n_{CO}^o} \times 100 \quad (2)$$

Where, X_{CO} (%) is the conversion of carbon monoxide into hydrocarbons; and n_{CO}^o and n_{CO} are the initial and final concentration of carbon monoxide in the reactor, respectively.

The selectivity of hydrocarbons was calculated by the following equation (3):

$$S_{Cn}(\%) = \frac{Area(Cn)}{\sum Area(Cn)} \times 100 \quad (3)$$

Where, S_{Cn} is the selectivity of a hydrocarbon with n carbons and Area (C_n) is the peak area of a hydrocarbon with n carbons.

3. RESULTS AND DISCUSSION

Figure 1 shows the standard X-ray diffraction pattern of rice husk ashes after thermal and acid treatment.

The silica present in the ash remained predominantly amorphous. A diffuse peak around 22° indicates the presence of silica in the form of disorderly cristobalite (Hamad, & Khattab, 1981). The crystallization phenomenon was not observed due to the lower temperatures applied. 800°C is the most likely initiation temperature of the silica present in RHA crystallization (Nakata, 1989). The results of chemical composition show that the composition of rice husk ash is essentially silica in the 96.2%.

Figure 2 provides images of scanning electron microscopy from the ashes of rice husk at different magnifications. It shows how the material is arranged.

The silica obtained from the treatments, thermal and acid, applied to the rice husk has elongated particles and twisted leaves. The waving external epidermis in denser areas of regions is

Figure 1. XRD pattern of rice husk ashes after thermal and acid treatment.

Figure 2. Images obtained by electron microscopy from the rice husk ashes after thermal and acid treatment.

also visible. 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 (James & Rao, 1985). 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 3 one can see the result of X-ray of SBA-15 molecular sieve calcined.

Looking at the images, one can observe the pattern formation characteristic of the structure of a two-dimensional hexagonal symmetry typical p6mm SBA-15 (Zhao et al., 1998; Wang et al.,

2005; Yang et al., 2005). The main diffraction peak, with Miller index of (100), referring to the crystal planes, is characteristic of this type of material and can be observed by XRD. After calcination, the SBA-15 shows high silica content of 97.8%, scheduled for this type of material synthesized with rice husk ashes with a high percentage of silica. Figure 4 presents images from a microscopy molecular sieve SBA-15.

Silica nodule formations in micrometric dimensions joining each other by smaller particles forming collars interlocking can be observed, characteristic of SBA-15 molecular sieve. Non-

Figure 3. X-ray diffraction of SBA-15 prepared with rice husk ashes after thermal and acid treatment.

Figure 4. Scanning electron microscopy of SBA-15 prepared with rice husk ashes after thermal and acid treatments.

typical formations of SBA-15 are also observed. The fibrous exoskeleton, characteristic of the inner epidermis of rice husk ash, present around of SBA-15 micrometric nodules, indicates 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, possibly reducing the fraction of silica in the form of SBA-15 sieve.

Figure 5 shows the X-ray diffraction of the catalyst Co/Ru/SBA-15 after the impregnation and calcination processes, in the range of 2θ between 25° and 75° .

Figure 5. X-ray diffraction of the catalyst Co/Ru/SBA-15 RHA after the impregnation and calcination.

Figure 6. X Reduction Temperature Programmed profile from Co/Ru/SBA-15 RHA catalyst.

After impregnation with Co and co-impregnation with Ru, the X-ray diffraction profiles are almost unchanged, exhibiting high diffraction peaks at low angles, reflecting that SBA-15 maintains its ordered structure after impregnation of cobalt and ruthenium.

Cobalt nitrate is decomposed into cobalt oxide during calcination under synthetic air environment (Hua et al., 2000; Ghampson et al., 2010). At temperatures above 200 °C, cobalt nitrate decomposes releasing NO_x and the Co²⁺ ions which are converted into Co₃O₄, as reported by

Ghampson et al. (2010). The presence of peaks indicating the formation of Co₃O₄ species in the Co/SBA-15 catalyst was identified using the JCPDS-ICDD library (International Centre for Diffraction Data). The presence of peaks at 31.3°, 36.9°, 45.1°, 59.4°, and 65.4° (2θ angles) indicates that the cobalt species (after calcination at 450 °C) were primarily in the crystalline Co₃O₄ spinel form (Figure 5).

Figure 6 shows the Reduction Temperature Programmed profile from Co/Ru/SBA-15 catalyst.

Figure 7. N₂ adsorption-desorption isotherms at -196°C related to SBA-15 RHA molecular sieve (a) and Co/Ru/SBA-15 RHA catalyst (b).

The TPR profiles of the catalysts are shown in Figure 4. For Co/Ru/SBA-15 catalyst, three reduction peaks located at 209, 357, and 395 °C, respectively, were observed. The first reduction peak at 209 °C can be attributed to the first reduction step of Co₃O₄ (Co₃O₄→CoO). The second reduction peak at 357 °C can be attributed to the reduction of intermediate CoO phase (CoO→Co⁰). The temperature reduction peak at 395 °C can be attributed to reduction of barely reducible cobalt silicates (Co₂SiO₄) formed due to a strong interaction between cobalt and the siliceous support (Dry, 2002; Davis, 2003).

Figure 7 presents the N₂ adsorption-desorption isotherms at -196°C related to SBA-15 molecular sieve (a) and Co/Ru/SBA-15 catalyst (b).

The isotherms for the calcined SBA-15 sample were of type IV, and exhibited a well-defined H1 hysteresis loop according to the IUPAC classification relative to the mesoporous materials (Anderson, 1956). The isotherms for the catalysts showed similar profiles, typically of type IV. The desorption curve for this catalyst also showed an H1 hysteresis loop for partial pressures (P/P₀)

between 0.6 and 0.8, which can be attributed to capillary condensation and evaporation in the internal mesoporous structure of the tubes (Anderson, 1984; Rodrigues et al., 2012).

The pore volume increased with heating time, as described in the literature. This can be explained by the existence of micropores in the walls. As the synthesis time increases, the micropore volume decreases. This is due to the partial dehydration of the PEO blocks at elevated temperatures. Consequently, it decreases the interaction between micelles through the PEO chains so that these become less occluded into the silica wall, resulting in microporosity reduction (James & Rao, 1985).

The textural properties obtained by adsorption of N₂ of the SBA-15 and Co/Ru/SBA-15 catalyst are presented in Table 1.

There was a decrease in pore volume and in surface area if compared to the synthesized molecular sieve. With the inclusion of metals in used rate, the area reduction was expected. The attempted synthesis with the ashes of the rice husk is not discarded because they are obvious

Table 1. Textural properties of SBA-15 and catalyst Co/Ru/SBA-15 RHA.

Sample	^a S _{BET} (m ² /g)	^b VP _{total} (cm ³ /g)	^c e (nm)
SBA-15 RHA	627	0.98	8
Co/Ru/SBA-15 RHA	339	0.68	-

^aspecific area calculated by BET method, ^btotal pore volume. and ^cwall thickness.

Figure 8. Micrographs of the catalyst Co/Ru/SBA-15 RHA.

indications of molecular sieve formation, creating a material with similar properties (morphology, crystallinity, mesoporosity, type IV isotherms) to the synthesized with conventional sources silica, but with lower pore volume, and lower specific area. As supports for metals, these materials obtained are attractive because they provide catalysts of the same chemical composition, but with different physical properties, verified by the area variation, morphology and structure, which are fundamental to a study of the influence of these properties in a catalytic reaction system such as Fischer-Tropsch.

The representative TEM images of the catalysts after reduction are shown in Figure 8. Cobalt was distributed in the interior surface of the support and particle size distribution was wide. The small dark spots, marked with black arrows, corresponded to cobalt oxide located inside the pores. For such high cobalt loading, cobalt presented itself in the form of clusters. Some of these clusters had agglomerated forming islands consisting of many small particles. However, not all channels in this sample were filled by cobalt oxide. It was not possible to obtain the cobalt particle size from the TEM micrographs because the contrast between the metal and the support was not

sufficiently clear (Ghampson et al., 2010).

Table 2 presents the conversion range of values from synthesis gas to hydrocarbons.

The performance of the catalyst in the FT synthesis is presented in Table 2. The catalyst with Ru promoter displayed lower methane selectivity and higher C_5^+ hydrocarbon selectivity compared to the catalyst prepared without ruthenium, as verified by (Rodrigues et al., 2012). The conversion of syngas into hydrocarbons has increased slightly with the addition of ruthenium to the catalyst.

The increase in the amount of heavy hydrocarbons is related to the formation of a hydrocarbon film around the catalyst particle and to the partial saturation of the pores of the catalyst with hydrocarbons. Hydrogen acts as reactant and also as chain transfer agent in carbon polymerization. Excess hydrogen tends to form hydrocarbons with low carbon number (light gases). The formation of a hydrocarbon film prevents easy access of hydrogen to the active sites of the catalyst and, thus, the termination of the hydrocarbon chains. As a result, the amount of heavy hydrocarbons increases as the reaction progresses, until reaching a steady state (about 7 to 8 h of reaction) (Dry, 2002; Davis, 2003).

Table 2. Results of Fischer-Tropsch synthesis using catalyst Co/Ru/SBA-15 at 240° C and 10 atm, 40% conversion.

Sample	T (°C)	P (atm)	H ₂ :CO	C ₁ -C ₄ (%)	C ₅ ⁺ (%)
Co/Ru/SBA-15 RHA	240	10	1:1	11.8	88.2

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.

The catalyst Co/Ru/SBA-15 showed a decrease in specific area compared to the synthesized SBA-15 related to the possible formation of the oxide phases in the pores of the molecular sieve. One could observe a hematite reduction after reducing the promoter due to the influence of copper on iron reduction catalyst.

However, one of the most interesting facts to be pointed out is that the use of this catalytic system for the catalyst prepared with alternative and inexpensive silica source showed high selectivity in liquid products, that is, in hydrocarbons with C_5^+ chains and no formation of products was oxygenated in this reaction. The Co/Ru/SBA-15 catalyst showed selectivity for a C_5^+ range around 88.2%. The performance of this catalyst may have been due to the presence of ruthenium as catalyst promoter, favoring a reduction of cobalt species in the presence of hydrogen, promoting its dispersion as well as increasing the selectivity of C_5^+ hydrocarbons.

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