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TEZĂ DE DOCTORAT

Sinteza selectivă Fischer-Tropsch a olefinelor

Fischer-Tropsch selective synthesis of olefins

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Doctoral School of Applied Chemistry and Materials Science

Department of Bioresources and Polymer Science

Fischer-Tropsch selective synthesis of olefins

Thesis summary

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Key words: Fischer-Tropsch, microwave field, olefins, catalyst, promotor, syn-gas, nickel, iron, cobalt, dielectric properties, penetration depth, carbon, hydrocarbons

NOTE; Chapter, subchapter, figure and table notations in this document are written as they are in the thesis.

Objectives and thesis structure

As fossil fuels have a negative impact on the environment and their processing becomes more and more expensive due to their exhaustion, alternative solutions for these raw materials have been sought, such as: Fischer-Tropsch synthesis, hydrogen use as a fuel, Alternatives (wind, geothermal, etc.). In this work, it was proposed to approach hydrocarbon synthesis by the Fischer-Tropsch process and especially the synthesis of olefins and especially lower olefins (ethene, propene). Lower olefins are of particular importance in the industry for the synthesis of many intermediate compounds that are applicable in the pharmaceutical, petroleum and chemical industries.

The general objectives and purpose of this paper are:

- ➢ Preparation and characterization of a series of catalysts for the F-T process;
- ➢ Construction of a F-T lab setup capablel of synthesizing lower olefins at atmospheric pressure;
- ➢ Catalyst testing on the setup;
- ➢ Determination of the dielectric properties of the unused, used catalysts and their support in order to see the fesability of mnicrowaves on this process;

The paper is divided into 2 parts, containing a study that was made on the basis of sources available from the literature, and a part consisting of the original research.

The first part, the Literature Study, is structured in 6 chapters.

Chapter 1.1. Is a short summary of the history of the Fischer-Tropsch process in which the evolution of this process is presented.

Chapter 1.2. Presents a more detailed history of the process and what installations were used in the world and the current state of the process in industry.

Chapter 1.3. Refers to the reactions present in the process, the reaction mechanisms encountered, and how chain-growth occurs in the Fischer-Tropsch process.

Chapter 1.4. Shows the most used catalysts in the industry.

Chapter 1.5. Describes the synthesis of olefins and under what conditions their yield can be maximised.

Chapter 1.6. Covers the microwave side where it is mentioned about how microwave energy interacts with various materials and some basic notions about microwaves in general.

Part II includes:

Chapter 2.1. Where a method for determining hydrocarbons obtained through the Fischer-Tropsch process has been developed. The method used was Gas Chromatography, and determinations were made for retention times, calibration curves, and component identification.

Chapter 2.2. Describes the laboratory facilities described in this thesis as well as the improvements made.

Chapter 2.3. Talks about the catalysts used in the process, how they are prepared and how they are characterized.

In **Chapter 2.4.** We have the results obtained by testing different catalysts both by conventional heating and by microwave heating. Also here is the dielectric characterization of some catalysts used in the Fischer-Tropsch process. These experiments were conducted over a three-month research period at the University of Nottingham, United Kingdom, based on the POSDRU / 159 / 1.5 / S / 132397 program.

This paper also contains some of the conclusions and perspectives of development and application of the research results, which highlighted the way in which the proposed objectives were achieved and the way in which the subject studied could be improved in the future.

Literature study

1.1)   Short history

Gasification of coal and its conversion into hydrocarbons was originally set up by Friedrich Bergius in 1913 and used coal that was hydrogenated at temperatures of 400 ° C and pressures of 200 atm. Bergius began with the hydrogenation of coal under high pressure in 1910. The process involved the use of coal with a carbon content of less than 85%. It was crushed and ground, and then it was dissolved in mineral oil to form a paste. This paste reacts with hydrogen at a pressure of 200 atm and a temperature of 400 ° C resulting in liquid hydrocarbons. In 1925 he sold his patent to BASF, and from 1925 to 1930 Mattias Pier worked to improve the yield and quality of hydrocarbons. [1]

The Fischer-Tropsch process was discovered as a response to Germany's oil shortage. A decade after Bergius, Franz Fischer and Hans Tropsch, they devised a process that converts synthesis gas, a mixture of carbon monoxide (CO) and hydrogen (H_2) into liquid hydrocarbons [2]. The process was put in place in the 1920s. They oxidized coal with insufficient oxygen to give rise to CO. It was further mixed with hydrogen and passed through a catalyst bed at a temperature slightly lower than that used by Bergius (180-200 ° C) and a pressure of 1-10 atm. The catalyst used was one based on iron stumps having Kieselgur filling. [3]

But Germany was not the only country to research coal liquefaction. In the UK, the British synthetic fuels program evolved from a pilot plant in a laboratory that began at the University of Birmingham in 1920 to a refinery located in Billingham which have an annual capacity of 1.28 million barrels of synthetic oil Being able to equate Germany's then capacity, but because of competition with fossil fuels, it remained the only artificial fuels plant in the UK. [4]

The United States Bureau of mines began to turn their attention towards research on the Fischer Tropsch in 1927, but not made much progress until after the Second World War when there were worries about the growing consumption of oil, one in hand, and secondly, they have been able to access Germany's Fischer Tropsch technology. In total, four F-T pilot stations were made in the US, but none reached the maximum potential due to technical problems. Further, the crisis of the 1970's and with oil prices, refineries producing F-T compounds by have ceased all over the world except for SASOL in South Africa. [5]

South Africa has been and still remains among the few countries where Fischer-Tropsch synthesis is used on an industrial scale. The first plant, SASOL 1, was commissioned in 1955 in Sasolburg (south of Johannesburg). Two other factories were opened in 1973 and 1976 in Secunda. [6]
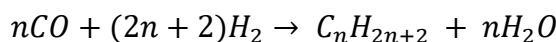
Until the 90's, the interest in the F-T process was low due to the low cost of fossil fuels. But after the 1990s, the scientific world began to investigate the process more thoroughly due to two main reasons. The first was the rise in oil prices caused by the embargo on Arab oil imports. The second reason was an abundance of natural gas market presence [7].
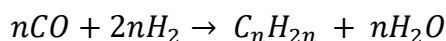
## 1.3)   Reactions, chain growth, mechanism

1.3.1) Reactions:

$$CO + H_2 \rightarrow -(CH_2) - + nH_2O \qquad \Delta H^0_{250°C} = -158.5 \, kJ/mol(n = 1)$$

This reaction can lead towards paraffin formation

$$nCO + (2n + 2)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

Or towards olefin formation

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

The formation of hydrocarbons can be determined by the following reaction conditions. If an insufficient amount of hydrogen is used, the catalyst can be deactivated much faster. [58] This can be observed by the following equation:

$$2nCO + 2nH_2 \rightarrow C_nH_{2n} + nCO_2$$
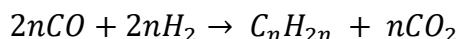
The reaction above is followed by another secondary reaction where carbon monoxide reacts with the water vapors initially generated from the reaction and leads to the formation of CO_2 and H_2 [59] This reaction also known as "water gas shift" occurs both in the case of an H_2 ratio: CO that is large enough to prevent the formation of CO_2 as well as in the case of a low H_2: CO ratio resulting in carbon black formation) which leads to deactivation of the catalyst. [60]

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$nCO + nH_2 \rightarrow C_nH_{2n} + nC$$
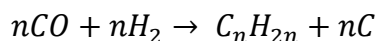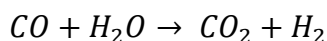
The stoichiometry of the Fischer-Tropsch reaction is also given by the consumption rate for H_2 and CO. [61] This stoichiometry is strongly influenced by both the types of catalysts used and the reaction conditions. [62]

1.3.2) Chain growth

The Anderson-Schulz-Flory mathematical model refers to the chain-growth of compounds obtained by the Fischer-Tropsch process. Each compound is favored by a growth factor (α) that dictates the length of the carbon chain or its mass fraction (wn). [65]

The mass fraction of the product containing n carbon atoms (Wn) can be calculated by:

$W_n = n \, (1- \alpha)^2 . \, \alpha^{n-1}$

The growth parameter (α) can be controlled under certain conditions by changing working parameters (temperature, pressure, catalyst, raw material mixture, etc.). [66] In the industry, a high α-value of 0.7-0.9 is preferred to reach hydrocarbons in the range of petrol or diesel. [67]

	Chain growth probability	Olefin selectivity	Parrafin selectivity	Light Hydrocarbon selectivity
Temperature ↑	↓	↑	↓	↑
Pressure ↑	↑	*	↓	↑
H2/CO ratio ↑	↓	↑	↓	↑
Conversion ↑	*	↓	↑	↓
Space velocity ↑	*	↑	↓	↑

	Heavy hydrocarbon selectivity	Carbon formation	Methane selectivity	Oxygenated compounds
Temperature ↑	↓	↑	↑	↑
Pressure ↑	↓	*	↓	↑
H2/CO ratio ↑	↓	↓	↑	↑
Conversion ↑	↑	↑	↑	*
Space velocity ↑	↓	*	↓	*

Fig 8. Formation conditions for various componds that can be obtained in the F-T process

For all catalysts, as the temperature rises, α decreases, which means a shift in product distribution to lower molecular masses. The Fe catalyst has a selectivity that can be influenced by the presence of alkaline promoters such as K_2O, while the Co promoter catalyst does not change the distribution of the products. [74] For the Fe catalyst, it does not depend on the total pressure, for the Co catalyst, α increases with pressure up to 20 at, after which the pressure effect is low.

1.3.3) Mechanism

1.3.3.1) Methylenic mechanism

The mechanism involves a dissociative adsorption of carbon monoxide as well as hydrogen. Freshly formed carbohydrate on the surface of the catalyst is hydrogenated to form a CH_2 group. [75] Propagation of the reaction by increasing the carbon chain occurs by coupling the CH_2 groups. The termination of the reaction takes place by an additional hydrogenation of the chain or by the dissociation of a hydrogen atom leading to the formation of alkenes. [76]

1.3.3.3) Alkenylic mechanism

The alkenyl mechanism involves the formation of methylidene (-CH$_2$-) radicals at the surface of the catalyst and involves the formation of α-olefins. [82] The initiation of the reaction occurs by generating a vinyl species by attaching the methylidene groups to generate allylic radicals. These allyl radicals can continue to grow or stop growing by forming α-olefins by reacting an atomic hydrogen at the surface of the catalyst. [83]

1.3.3.3) Enolic mechanism

Many of the mechanisms proposed for the Fischer-Tropsch process over the years were based on the hypothesis that an intermediate containing oxygen in the builder group was needed rather than a carbide monomer. In the enolic mechanism, the carbon monoxide adsorption is undissociated. [84] After the reaction of carbon monoxide adsorbed with hydrogen, a HC * OH intermediate is formed as the structural unit-repeating unit. Coupling the 2 blocks leads to water removal and thus the chain-growing process. The termination is similar to the carbide mechanism. [85]

1.3.3.4) CO insertion mechanism

Another mechanism used in Fischer-Tropsch synthesis is the CO insertion mechanism. Like the enolic mechanism, the one by CO insertion is based on oxygen containing intermediates. [86] The base intermediate is formed after the reaction of a CO molecule with a hydroxyl group and leads to the formation of a CH$_3$O * compound that is attached to the surface of the catalyst. The reaction is propagated by the addition of another molecule of CO and other 2 molecules of hydrogen. The termination takes place like in the carburic and enolic mechanisms. [87]

1.4) Catalysts

A suitable catalyst for the F-T process should have a good capacity to support the carbon monoxide hydrogenation activity to produce hydrocarbons. [91]
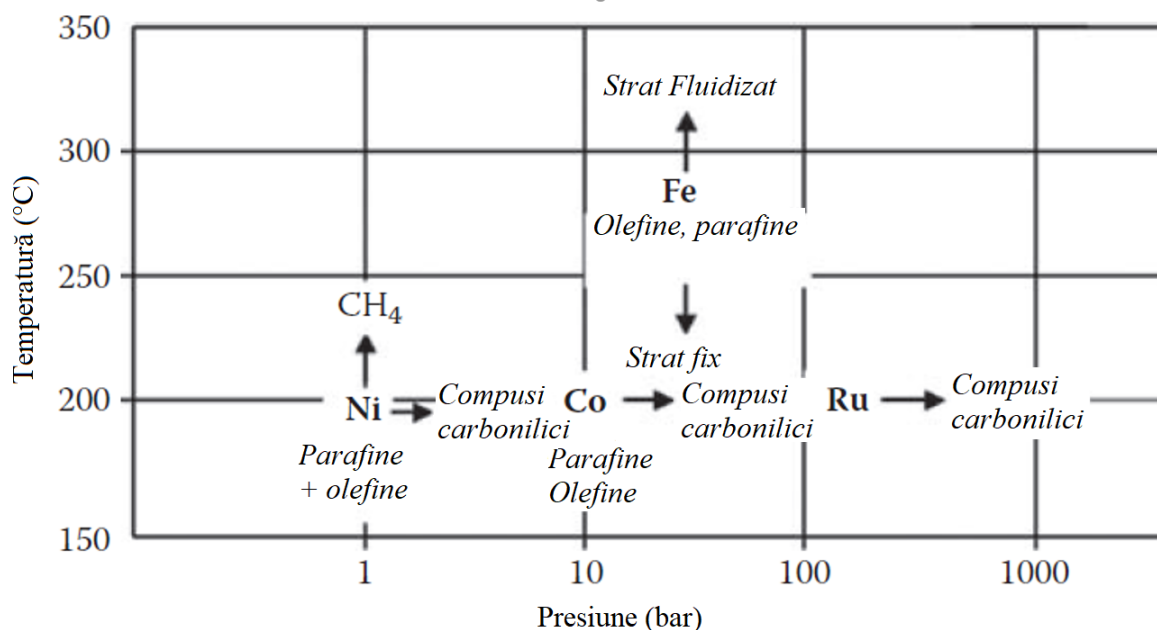
Fig 14. Reaction conditions for the most used metals in the F-T process and their selectivity

There have been many metals treated in literature for the Fischer-Tropsch process, but the most used metals in industry are:

1) Iron
2) Cobalt

   1.4.1) Iron:

Iron catalysts are the cheapest and most accessible category of catalysts for this process. Fe may exist in the form of magnetite, Fe carbide and α-Fe inside the catalyst. Each of these allotropic forms has an impact on final conversion as well as on selectivity for end products. [95]

Cobalt

Cobalt catalysts have a high activity and can achieve CO conversion of 60-70%. [101] In addition to high activity, stability and selectivity can also be found, which can be controlled by addition of other promotional metals or changing working parameters. Higher stability is due to the low selectivity for cobalt to form water in the gas, which leads to the premature deactivation of the catalyst from the iron where the reaction is present and must be removed by raising the temperature. Cobalt has a high methanation capacity and high selectivity to olefins at temperatures above 250 ° C. [102]

1.5)   Olefin formation

Olefins or alkenes are unsaturated hydrocarbons of very high industrial importance. These compounds are also used as intermediates in various branches of the chemical industry (plastics, paints, pharmaceuticals, surfactants, etc.). [106] The importance of olefins increases as the size decreases. Small olefins such ethylene or propene type have a much larger usage than their higher equivalents (pentene, hexene, etc.) because they can be more easily processed into macromolecular compounds. [107] Normally lower olefins are synthesized by pyrolysis of light naphtha, catalytic cracking of "gas-oil" fractions, catalytic dehydrogenation of alkanols, or dehydration of alcohols, but these methods pose serious environmental problems or by various economic factors that put into question their feasibility. The use of the Fischer-Tropsch process to produce light olefins may reduce the carbon footprint of refineries to cracking or pyrolysis-like processes. [108]

1.6)   Microwaves and their interaction with matter

The properties of any material in relation to the radiation in the microwave field are described by its permissiveness ε^*.[116]

$$\varepsilon^* = \varepsilon' - i * \varepsilon''$$

The real part (ε') or the dielectric constant defines the capacity of a material to store the electric energy, and the imaginary part (ε'') is the dissipation factor of the permittivity and reflects the ability of the material to dissipate or reflect the energy.

The components of the dielectric properties can be calculated using Debye's equations.

$$\varepsilon' = \varepsilon'_\omega + \frac{\varepsilon'_0 + \varepsilon'_\omega}{1 + \omega^2 * \tau^2}$$

$$\varepsilon'' = \frac{(\varepsilon'_0 - \varepsilon'_\omega)\omega\tau}{1 + \omega^2 * \tau^2}$$

Where ε'_0 is the static dielectric constant, representing the constant at a high frequency, ω is the angular frequency, and τ represents the relaxation time that characterizes the rate of increase and decrease in the polarization of the field. [118] The relaxation time shows how the material can behave in a microwave field by orienting the dipole moments and changing them in the case of liquids, and by orienting the crystals or their arrangement for solids. [119]

Unlike conventional heating, microwave heating is volumetric. Because of this, the permitivitty of a material is crucial to see how well you can heat a material in a microwave field. The more a body or a material has a better absorbance of the microwaves, the lower the penetration depth. The penetration depth (D_p) refers to the distance that microwave radiation travels through when it passes through a material to the point where it dissipates in its volume. [120] At that time, situations can be encountered in which only part of the material is heated and the other part remains cold or may become warm due to the conduction effect present in

the material with two different temperatures. Literature is also described as the point where energy can penetrate until it drops to about 40% of its original value. [121]

The penetration depth (D_p) can be calculated as follows:

$$D_p = \frac{\lambda * \sqrt{\varepsilon'}}{2 * \pi * \varepsilon''}$$

Where λ is the microwave wavelength.

2) Experimental part

2.1) Hydrocarbon determination via Gas-Chromatography:

Initially, the analytical methods for the compounds that might have resulted from the process had to be developed, after which the installation of the Fischer Tropsch setup.

2.1.1) Apparatus description

Concentrations of the Fischer Tropsch process components were analyzed using gas chromatography. The analyzes were performed using a Buck model 910 GC.

The device is designed to detect and separate H_2, O_2, N_2, NO_x, methane, ethane, propane, butane, pentane, hexane, heptane, octane as well as their derivative compounds and isomers.
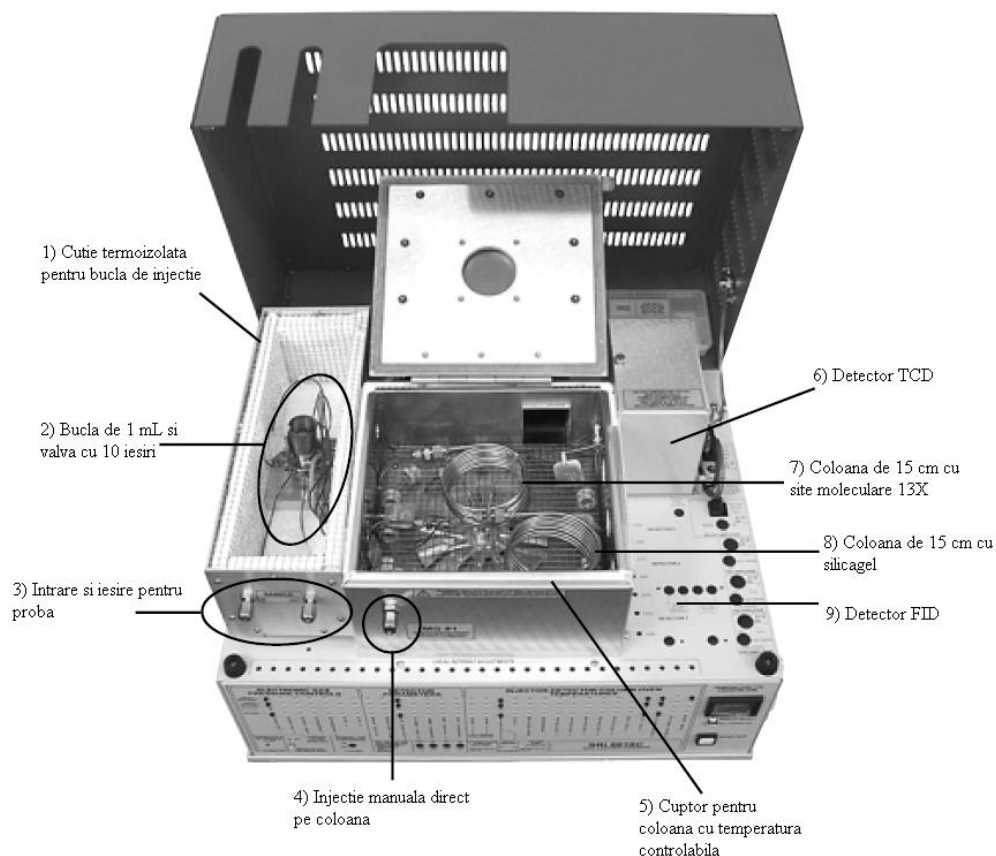
Fig 15. Buck 910 type GC used for the hydrocarbons resulted from the Fischer-Tropsch process

The GC analysis for this type of device proceeds as follows:

First the sample is injected into the injection loop. After the analysis starts, the loop switches from the position where it is in contact with the external environment to the position with the assay medium. After switching the loop, the sample first passes through the molecular column because it can separate the lighter compounds first such as CO, N_2, CH_4 etc ... after which the gaseous sample passes through the silica gel column and finally the sample passes first through The TCD detector then through the FID detector.

In order to have an efficient separation, the column temperature is varied according to a precise program and proceeds in the following way:

1) The column temperature remains at 40 ° C for 6 minutes

2) The temperature rises to 220 ° C with a ramp of 10 ° C / min.

3) The temperature remains at 220 ° C until the analysis is stopped.

2.1.2) Hydrocarbon identification

The pure gas samples as well as the reaction samples were sampled using TEDLAR hermetic bags with a maximum capacity of 1L (normal conditions).

CO, CO_2, Propylene and Isobutene were derived from cylinders containing these compounds having a high purity (99.99%) and ethylene was obtained in the laboratory according to the ethanol dehydration method using sulfuric acid [136], see Fig. 17.

Tab 9. Retention time for compounds resulted from the F-T reaction

Compound	Retention time (min)	Compound	Retention time (min)
CO	3.266	Propylene	11.133
CO_2	7.383	n- buthane	12.1
Methane	3.533	Isobuthane	13.133
Ethane	7.216	Isobuthylene	13.916
Ethylene	7.683	1- buthylene	14.2
Propane	10.366	2- buthylene	14.466

2.1.3) Establishing the calibration curves

For the determination of the amounts of the reaction compounds it is necessary to determine the area of some compounds of different concentrations known by plotting a calibration curve.

Several mixtures obtained by successive dilutions were made to obtain a calibration curve on which we can determine the concentrations of compounds in our samples.

Tab 17. Equations for the calibration curves

$y=a+b1*x+b2*x^2$	CO	CO_2	Methane
a=	0	0	0
b1=	-7,59647E-6	1,61192E-5	1,94296E-6
b2=	2,58166E-9	3,60335E-8	1,90418E-11

Knowing the equations to determine the concentration of a compound from an unknown sample, the conversion of carbon monoxide and the selectivity with which each component is formed was determined. Based on the conversion and selectivity, the yield of each component in the system was determined.

Based on the calibration curve equations, the selectivity, conversion and yield for each compound were determined.

$$Conv = \frac{C_{ico} - C_{fco}}{C_{ico}} * 100$$

$$Sel_x = \frac{C_x}{C_{ico} - C_{fco}} * 100$$

$$\eta = \frac{Sel * Conv}{100}$$

C_{ico} = initial concentration of CO (%)

C_{fco} = final concentration of CO (%)

C_x = Percentage of CO transformed in x

η = yield

2.4)   Results and discussion

2.4.3) Cat Fe-Ni, 4 : 6 with γ-Al$_2$O$_3$, SAPO 34, ZSM 5, MCM-41, SBA-15 supports

Samples of non-impregnated support, fresh catalyst as well as catalyst that was subjected to the Fischer-Tropsch reaction were kept. These samples were analyzed for their structural properties, specific surface area, pore volume and pore diameter. Also, SEM analyses for fresh and used catalysts were performed to observe eventual deposits of carbon and metal deposits on the catalyst surface. They were carried out using EDAX with which the SEM was provided and some elemental analyzes on the catalyst surface. However, carbon deposits were carried out using a thermogravimetric analysis (TGA).

For each sample, at least 3 measurements were made to see the stability of the catalyst. It has been observed that between 300 ° C and 350 ° C there was a partial deactivation of the catalyst which can be expressed by stagnation of the conversion. This has been observed for all

5 catalysts that have undergone the F-T reaction. The most active catalysts were ZSM-5, MCM-41 and SBA-15, reaching 55% conversion for SBA-15, 60% for ZSM-5 and 65% for MCM-41.
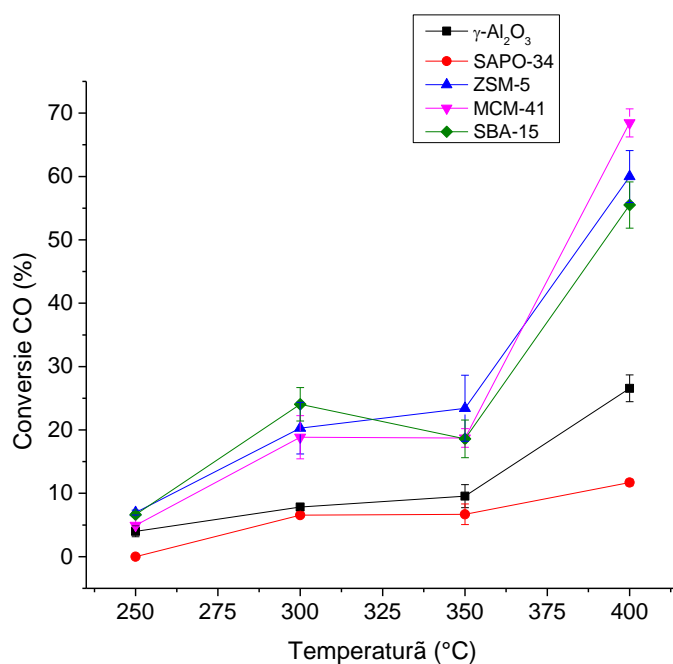

Fig 37. CO conversion for catalysts after they have been impregnated with metal after shaping the support
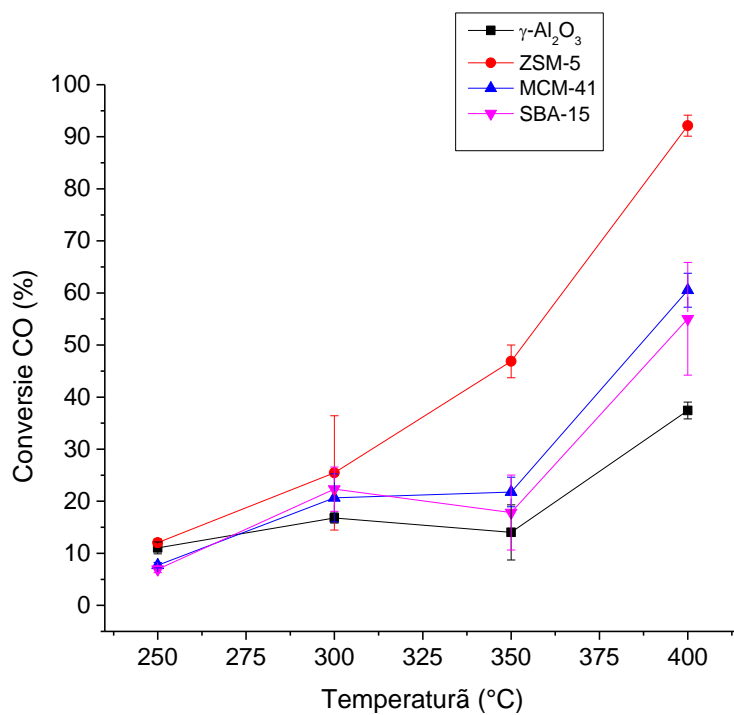

Fig 42. CO conversion for catalysts after they have been impregnated with metal prior to support shaping

Compared to the type of impregnation, better conversions were obtained for catalysts that were impregnated with metal before being formed. This method aimed at a more uniform deposition of the metal in the volume of the catalyst than by impregnation after the support was shaped and extruded with the binder. In the case of impregnation catalysts prior to shaping, a significant increase in CO conversion and yields for useful compounds relative to the other catalysts was observed.

2.4.4) Cat Co Mn Ca at a 10:1:1 molar ratio with AlSBA-15 support having a 20% metal content

After testing a series of different (γ-Al₂O₃, ZSM-5, SAPO-34, MCM-41 and SBA-15) catalysts, each impregnated with a Fe: Ni ratio of 4: 6, An Al-SBA15 support, and a metallic component was chosen as a cobalt catalyst that was used together with two other manganese and calcium promoters. The reason why it was chosen to use cobalt as process metal was its selectivity for a lower temperature range than iron. In literature, iron generally operates at 300-350 °C, while cobalt is used at 200-250 °C. The role of manganese and calcium was to reduce CO_2 formation. But this also means a drop in yield for the other hydrocarbons produced.
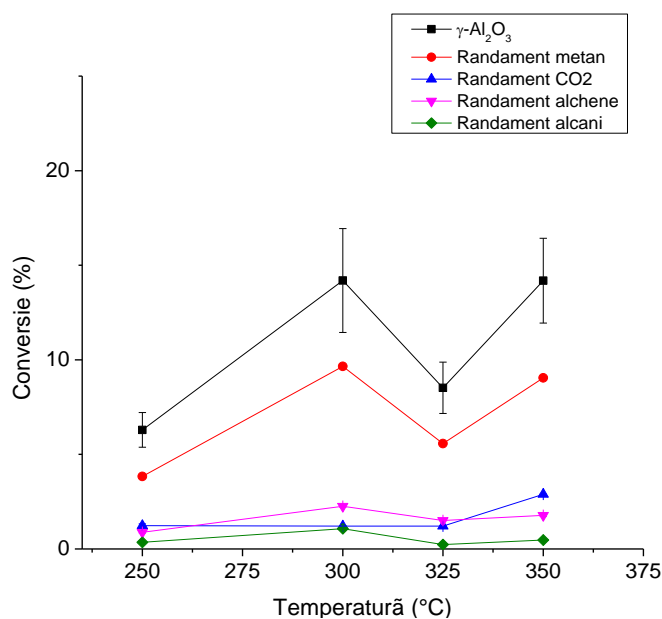
Fig 48. Catalyst activity at a CO:H₂ 1:1,25 molar ratio

During the experiments with a ratio of 1: 1,25 a variation in conversion was observed which also affected the yields of the other components, but especially methane. An increase in yields from 250 °C to 300 °C was observed, followed by a decrease to 325 °C. Similar trends were observed for the Fe-Ni based catalyst at the 300 and 350 °C range. This may be due to partial deactivation. It is assumed that initially, the catalyst consisting of the activated metal would react with carbon monoxide to form the carbide of the metal. After this incipient phase,

the catalyst would enter the second activation step where it is assumed to have the highest yield for the alkene. As observed in both cases, the catalyst remained active for a relatively long period compared to the first activation step.
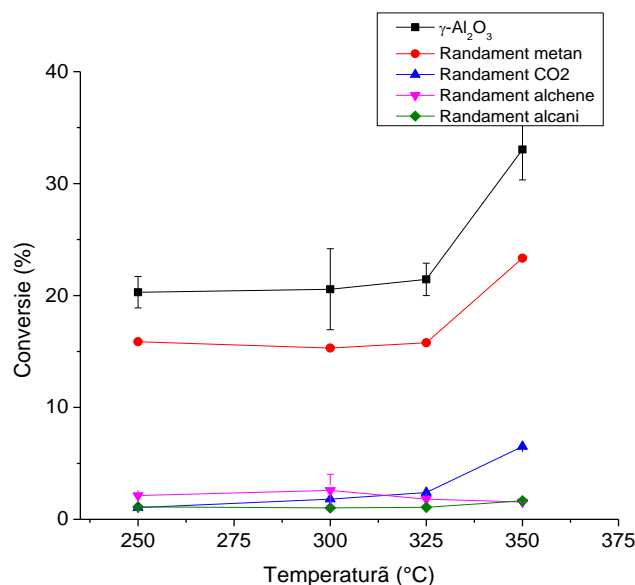
Fig 49. Catalyst activity at a H_2:CO 1:1,25 molar ratio restesting

After the experimental series were performed at molar ratios of 1: 1; 1: 1,25; 1: 1,5; 1: 2 a repeat was made for the ratio of 1: 1.25 where there was an increase in conversion. However, this increase did not affect the selectivity for alkenes or alkanes, which remained constant. What changed was methane yield, however, increasing from a 4-9% initial rate to 16% for 250, 300, 325 °C, and 22% for 350 °C. The carbon dioxide yield also increased to 6% at 350 °C compared to 2% originally recorded.

2.4.5) Cat Co Mn Ca with 10:1:1 ratio and AlSBA-15 support at 20% metal content MW.

After conventional Co: Mn catalyst testing: As impregnated on an AlSBA-15 support, the catalyst was tested in the microwave field, based on the dielectric properties of the catalyst.
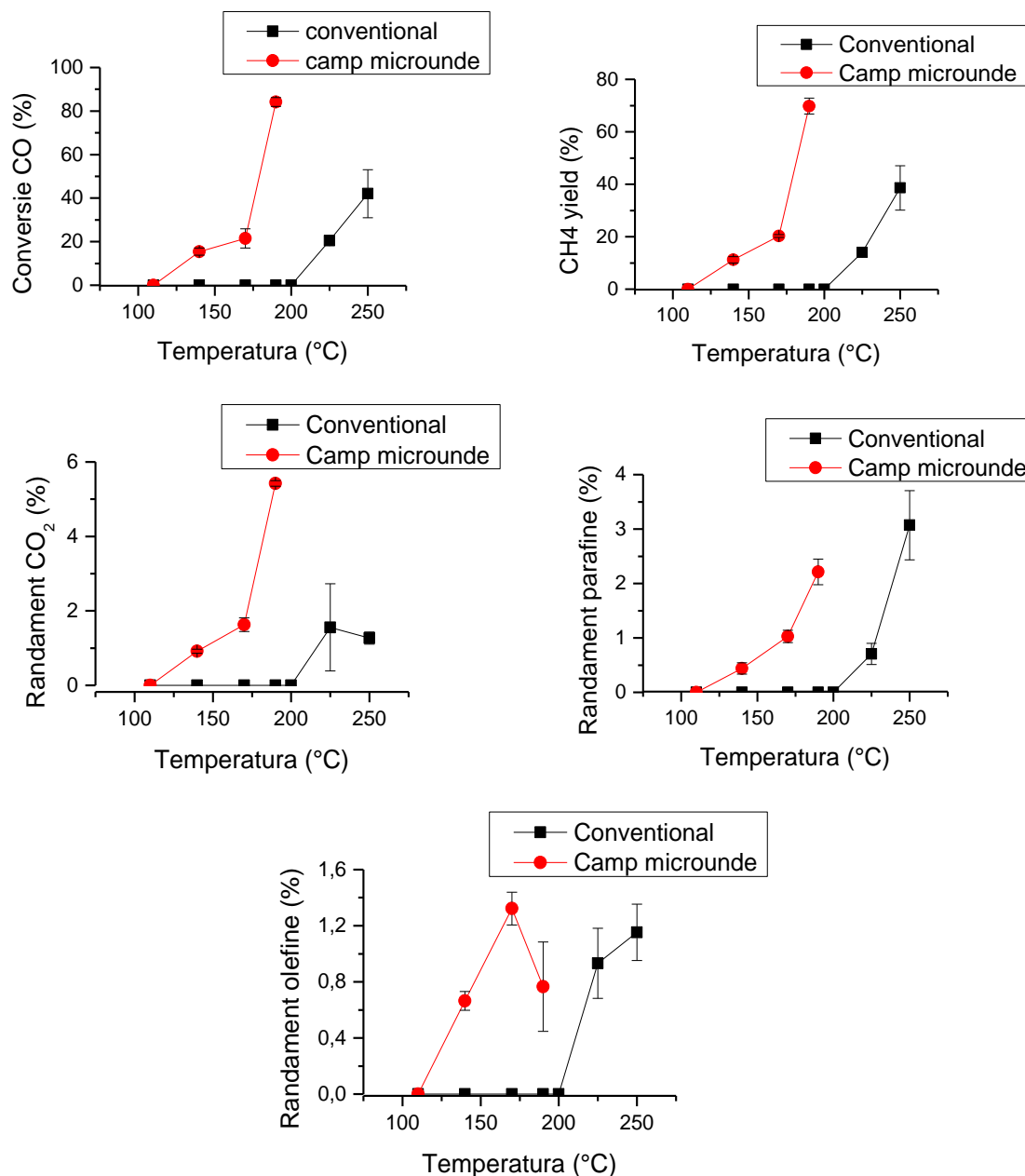
Fig 52. Catalyst yields at a H_2:CO 4:1 molar ratio

Initially, in the catalyst tests, determinations were started at a CO: H_2 molar ratio of 1: to minimize the deactivation of the catalyst and continued with 1: 2 and 1: 1,25.

Compared to conventional heating, microwave heating (MU) was noted by a much higher conversion, 80% for MU versus 45% for conventional heating. Compared to previous catalysts, the only component that had a higher yield was methane, with a yield of 70% for MU versus 40% for conventional heating. This increase in yield was due both to the use of a much higher amount of hydrogen in the reaction mixture as well as to the operation of microwave heating. The fact that microwave energy selectively heats component elements in a material could be the cause of increasing methane yield. Since in the Fischer-Tropsch reaction, the hydrocarbon length is due to the temperature and reaction time on the CO and H_2 catalyst surface,

microwaves would favor the formation of methane through a short reaction time on the catalyst surface.

2.4.6) Dielectric properties of used and fresh catalysts

The dielectric properties of the γ-Al$_2$O$_3$, ZSM-5, MCM-41 and SBA-15 catalysts impregnated with the molar 4: 6 Fe-Ni mixture were studied to see if these measurements can provide an indication Easier deposition of carbon on different catalysts compared to the techniques already used. In Fig. 56 no major differences were observed between support and the fresh catalyst in the temperature range 20 and 420 ° C for the γ-Al$_2$O$_3$ and SBA-15 catalysts. However, for MCM-41 and ZSM-5 slight differences were observed in the variation of the dielectric constant between the support and the fresh catalyst in the high temperature region. By impregnating the metal support, there have been some alterations in the molecular response that MCM-41 and ZSM-5 have when they are under the influence of an external electromagnetic field. In the case of the fresh MCM-41 catalyst, the values are slightly reduced, while the ZSM-5 values increase.

By comparison, all the catalysts used showed both higher values and a lower variation in the dielectric constant at that temperature for the support and the fresh catalyst. Both effects are associated with the deposition of carbon on the surface of the catalyst during use. Since carbon is a material with good microwave absorption, it has been found that this was the reason for the variation between the dielectric properties of the used, fresh catalysts, and the support.

912 MHz
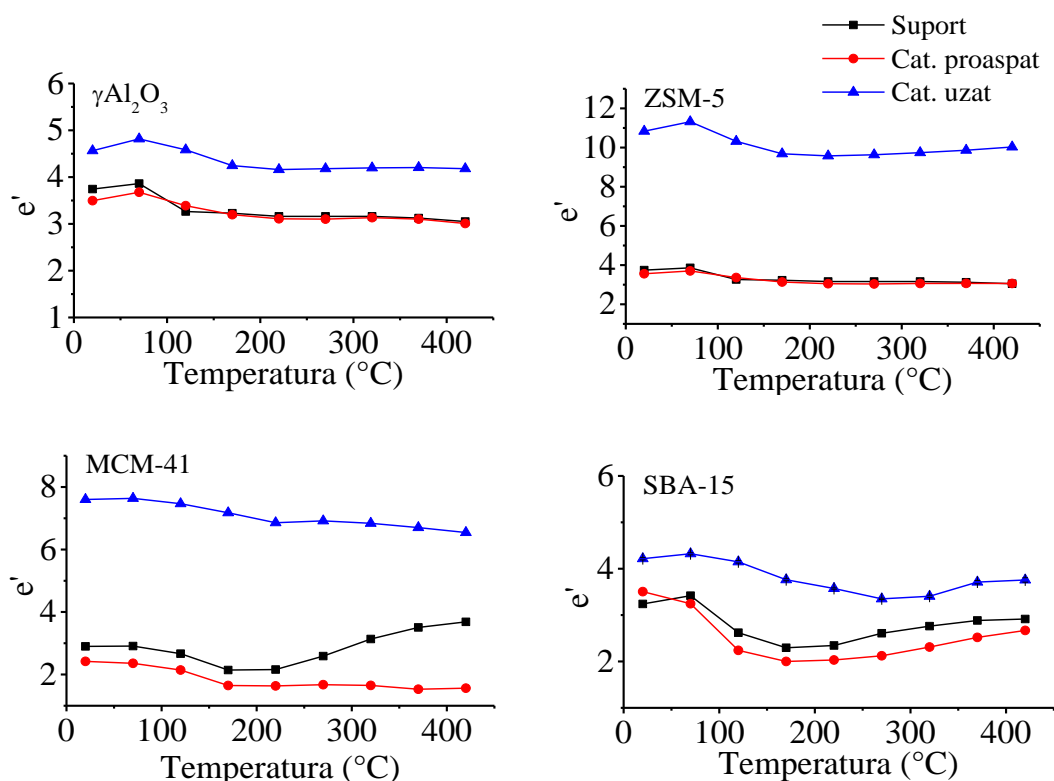
Fig 56. Dielectric constant for Fe-Ni catalysts at 912 MHz

Property	Catalytic support			
	γ-Al₂O₃	ZSM-5	MCM-41	SBA-15
Carbon content (%)	4.4	10.8	8.9	5.6
Carbon contribution on the real component of permitivitty ($\Delta\varepsilon$') at 912 MHz	1.1	6.8	5.2	1.2
Carbon contribution on the real component of permitivitty ($\Delta\varepsilon$') at 2470 MHz	0.97	5.8	4	0.93
Carbon contribution on the imaginary component of permitivitty ($\Delta\varepsilon$'') at 912 MHz	0.35	2.97	2.1	0.23
Carbon contribution on the imaginary component of permitivitty ($\Delta\varepsilon$'') at 2470 MHz	0.33	2.48	1.69	0.22
CO conversion (%)	14.2	46.9	21.8	17.8
Carbon formation aspect	Short fibers	Long fibers	Long fibers	Particles

Tab 20. Carbon desposit influnce on the dielectric properties for the catalysts

Tab. 20 shows the data obtained for 912 MHz and 2470 MHz which are correlated with thermogravimetric (TGA) data on spent catalysts where it does not represent the carbon contribution to the dielectric constant of the spent catalyst which was calculated as a difference between ε 'for the spent catalyst And the fresh catalyst at a reaction temperature of 350 °C.

3) Conclusions and original contributions

The effects of using different supports on a Fe and Ni containing catalyst on the synthesis gas conversion and the selectivity of its conversion to lower olefins have been tested.

The use of supports with different structures had a pronounced effect on the type of compounds obtained. The use of nickel, however, seems to have a great impact on favoring methane formation. As a future objective, a solution is sought to use nickel in a lower amount of catalyst or, if possible, to completely avoid its use.

To maximize the olefin continuity in the Fischer-Tropsch process, the working temperature should be between 300 °C and 350 °C, the pressure used should be atmospheric, the CO: H_2 ratio used should be between 1: 1 and 1 : 1,5 and the space velocity must be high enough to avoid long hydrocarbon formation.

Experimental data obtained on a ZSM-5 support would indicate that it would be a suitable candidate for the process, but due to the high degree of methanation and the selectivity of CO_2, the catalyst composition should be rethought.

The most prominent results were observed for catalysts that had a MCM-41 and SBA-15 support, which also had the highest selectivity for alkenes.

Four Fe and Ni based catalysts impregnated on different supports were prepared and coextruded with hydroxylated alumina at a mass ratio of 1: 1 to obtain granules which are easy to process. These were tested in the Fischer-Tropsch process on a temperature range of 250 °C to 400 °C. The molar ratio of CO and H_2 in the raw material was 1: 1 to favor inferior olefin formation. It has been discovered that with the increase in temperature, CO conversion was also increased. In addition, the ZSM-5 support catalyst showed the highest conversion at 350 °C, but at that temperature, the dominant hydrocarbon was methane with low selectivity to olefins (C1, C2, C3, C4). Thus, these catalysts did not have a reliable selectivity for the production of olefins. Moreover, at this CO: H_2 molar ratio formation of some carbon deposition species on the surface of the catalyst was observed. Investigation of the dielectric properties of supports, fresh catalysts and spent catalysts showed the greatest influence of dielectric properties on spent catalysts, which also had deposited carbon deposits. Although the dielectric properties of the support and the fresh catalyst were almost identical, those of the spent catalysts exhibited much higher values. From the real component (ε ') and the imaginary component (ε"), the actual component was considered more explicative to show the behavior in a microwave field for the catalysts used. Moreover, the data constant shows that this method, which is used for the determination of the dielectric constant (ε '), is relatively accurate given the correlation of the determined value with the existing carbon content. Although the correlation of data was not linear, differences in carbon content increased as carbon content increased. Therefore, in the case of real process monitoring, a calibration curve related to dielectric properties can be made to show the true percentage of existing carbon. The data presented showed that the measurements did not depend on the different types of carbon morphologies that were on the surface of the catalyst, so this method could have a wider scope. As carbon deposits grew, it was observed that the penetration depth of MU decreased much. It has also been observed that

using a lower frequency, both dielectric constant and dielectric loss varied which ultimately led to an increase in penetration depth (~ 10%).

Thus, dielectric monitoring has shown that it can have significant potential to allow accurate determination of the level of contamination a catalyst has, and this could allow optimization of process conditions to maximize catalyst use time. In addition, the method is non-invasive, ie the sample is preserved and is not consumed at the time of measurement, which allows the implementation of this method as a non-invasive analytical method that could be easily applied at industrial level.

Process pressures may vary from one to several atmospheres; A high pressure favors the growth of the hydrocarbon chain. Analyzes were performed on a cobalt-based catalyst and impregnated on a high porosity AlSBA-15 support that was used to obtain light olefins. It has been adopted to use atmospheric pressure to see if the process can be used on an industrial scale and can be cost-effective. When using atmospheric pressure, large amounts of CO_2 are formed. The optimal conditions where the selectivity of CO_2 is low and the maximum olefin content was recorded at 325 °C and a CO: H_2 ratio of 1: 1,25.

Based on this cobalt catalyst, a cobalt catalyst with manganese and calcium promoters was synthesized in a molar ratio of 10: 1: 1 Co: Mn: Ca impregnated on an AlSBA-15 support and was Subjected to the Fischer Tropsch reaction at atmospheric pressure. The experiments were carried out both in conventional and microwave fields, and temperatures were chosen in order to obtain comparable results for CO conversion and hydrocarbon yields. Therefore, for the microwave, temperatures of 110 °C, 140 °C, 170 °C and 190 °C were used, and temperatures of 200 °C, 225 °C and 250 °C were used for the conventional regime. The molar ratios used by CO: H_2 were 1: 4; 1: 2 and 1,25: 1. These reports were chosen to reduce catalyst deactivation and prolong its life. The residence time in the reactor was $0,1 s^{-1}$, and the main products were methane together with very small amounts of both saturated and unsaturated C2-C4 hydrocarbons.

In microwave mode, higher CO and higher CH_4 yields at much lower temperatures (170° C-190 °C) than conventional (225 °C-250 °C) were recorded. The highest results were recorded in the H_2: CO ratios of 4: 1 and 2: 1, respectively.

The low temperature (170 °C) required at atmospheric pressure together with an H_2: CO ratio suggests using unconventional heating as a much milder methanisation process than the Sabatier method, requiring a nickel catalyst and temperatures of 400 °C.

4) Perspectives of development and application of research results

The use of microwaves can be used for a heterogeneous solid-gas system.

The effect of high pressure on the process under microwave heating should be studied.

Concerning the catalyst, a future idea would be to focus on supports having a channel structure such as AlSBA-15 and a pore size greater than 10 nm.

Studies on dielectric properties can be implemented as a method of detecting the degree of coking of a catalyst in various industrial processes, not just the Fischer-Tropsch.

Preliminary research into the microwave field metanisation effect can lead to the implementation of research on the development of the process to give it a practical application on a larger scale.

5) Publication and conference list:

Publications

- Utilization of Dielectric Properties Assessment to Evaluate the Catalytic Activity and Rate of Deactivation of Heterogeneous Catalysts Tudor I. Sibianu, Georgios Dimitrakis, Juliano Katrib, Cristian Matei, Daniela Berger, Christopher Dodds, Adrian V. Surdu, Ioan Calinescu, Derek J. Irvine, Industrial and Engineering Chemistry Research; 56(8); 2017; 1940-1947; Factor impact 2,567

- Microwave Assisted Fischer-Tropsch Synthesis at atmospheric pressure; Tudor I. Sibianu, Daniela Berger, Cristian Matei, Ioan Calinescu; Revista de Chimie; 68(5); 2017; 1040-1044; Factor impact 0,956

- Fischer-Tropsch synthesis using a Co- based catalyst deposited on AlSBA-15 under atmospheric pressure; Tudor I. Sibianu, Daniela Berger, Cristian Matei, Ioan Calinescu; Buletinul Stiintific al Universitatii Politehnica Bucuresti; 78(3); 2017; 39-46

- Study of the olefin selectivity of a Fe-Ni catalyst for Fischer-Tropsch synthesis; Tudor I. Sibianu, Ioan Calinescu, Petre Chipurici; Buletinul Societatii de inginerie chimice din Romania; 3(1); 2016; 47-57

Conferinces:

- Cea de-a 19-a conferință internațională romană a chimiei și ingineriei chimice (RICCCE); 2-5 sept 2015, Sibiu, România. Study of the olefin selectivity of a Fe-Ni catalyst for Fischer-Tropsch synthesis; Tudor I. Sibianu, Ioan Călinescu, Petre Chipurici;

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