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Relación de documentos presentados en este archivo:

1) Resumen ejecutivo del proyecto **NICER-BIOFUELS** y resultados relevantes objeto de patente
2) Documentación relativa a la patente
3) Otros méritos e impacto

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SteppiNg towards cIrcular eConomy:

Recycling bio-wastE into heavy transpoRt BIOFUELS

NICER-BIOFUELS. Ref.: PLEC2021-008086

Executive summary

NICER-BIOFUELS was conceived to create a unique knowledge infrastructure that supports the decentralised, sustainable and ***cost-efficient conversion of biomass to sustainable heavy transport biofuels (HTB)*** to contribute towards full transport system decarbonisation. The project targeted the development of disruptive technologies that overcome critical technological barriers, increase process efficiency and reduce marginal costs in the biomass to HTB conversion process. ***Following the spirit of circular economy, the overriding idea of*** NICER-BIOFUELS ***is to combine CO_2 emissions with biomass waste as carbon pool to produce the next generation of HTB.*** Such an ambitious goal has been achieved by integrating advanced gasification strategies, unique catalytic technologies and digital tools to deliver fuel processors which are adaptable to feedstock input and HTB demands. A simplified conceptual diagram is depicted in Fig. 1

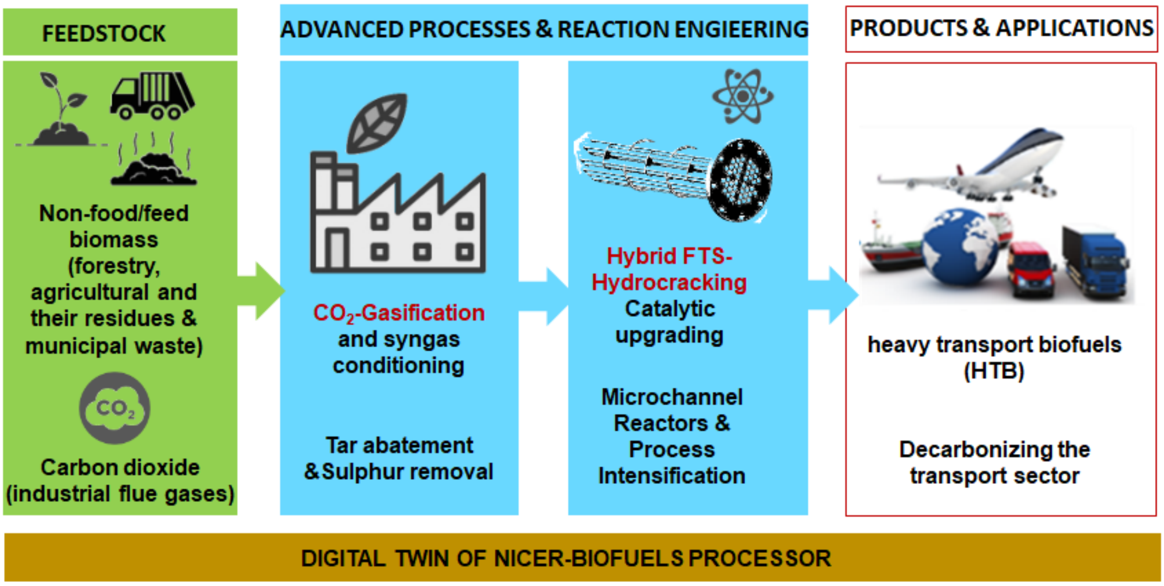

Fig. 1 NICER-BIOFUELS conceptual flow chart

Briefly, waste biomass and textile residues are converted into unconventional of H_2-rich syngas via CO_2 assisted gasification. In a subsequent step syngas will be conditioned (sulphur and impurities removal) prior to its further upgrading in a unique hybrid reactor for Fischer-Tropsch and hydrocracking. Herein syngas is converted into upgraded hydrocarbons mixtures which can be easily customised as HTB (i.e. aviation sustainable fuel, maritime biofuel, heavy duty vehicles fuel, etc). The catalytic syngas upgrading is enabled by multifunctional catalysts and microchannel reactors favouring process intensification. This way we address biomass decentralisation issues allowing flexible production and resulting in an overall carbon fingerprint reduction. Machine learning tools have guided the reaction conditions optimisation to produce biofuels directly from CO_2-rich syngas in a single step.

What makes NICER-BIOFUELS a winning approach? The flexible scalability of these technologies allow their implementation in decentralised processing plants favouring flexibility for production cycles within a circular economy concept. CAPEX and OPEX costs can be remarkably reduced thus decreasing the marginal cost of sustainable high-grade liquid fuels, setting the scene for investment in the increased use of biofuels in aviation and other heavy transport sectors. Beyond the huge market opportunities, the knowledge created under NICER-BIOFUELS's framework will impact the biofuel sector.

One of the major outcomes of NICER-BIOFUELS is an integrated FTS-HCR systems for one-pot conversion of syngas to heavy transport biofuels enabled by a multifunctional catalyst. *Below there is a summary of the results included in the patent (PCT/EP2025/062417)*

- ✓ Successfully developed a tandem catalyst for on-demand hydrocarbon production, including heavy transportation fuels such as sustainable aviation fuels (SAFs), from COx feedstocks.
- ✓ Demonstrated robust conversion above 80 C. % over more than 500 hours.
- ✓ Maintained low methane byproduction (<5 C. %).
- ✓ Achieved high C_5^+ yields (>50 C. % from CO; >70 C. % from CO_2).
- ✓ Enabled tunable liquid fuel composition in the C_5-C_{16} range, covering gasoline and SAFs.
- ✓ Efficiently recycled COx into petrochemicals (e.g., cumene, BTEX, aromatics).
- ✓ Applied statistical and computer-aided tools for process optimization.

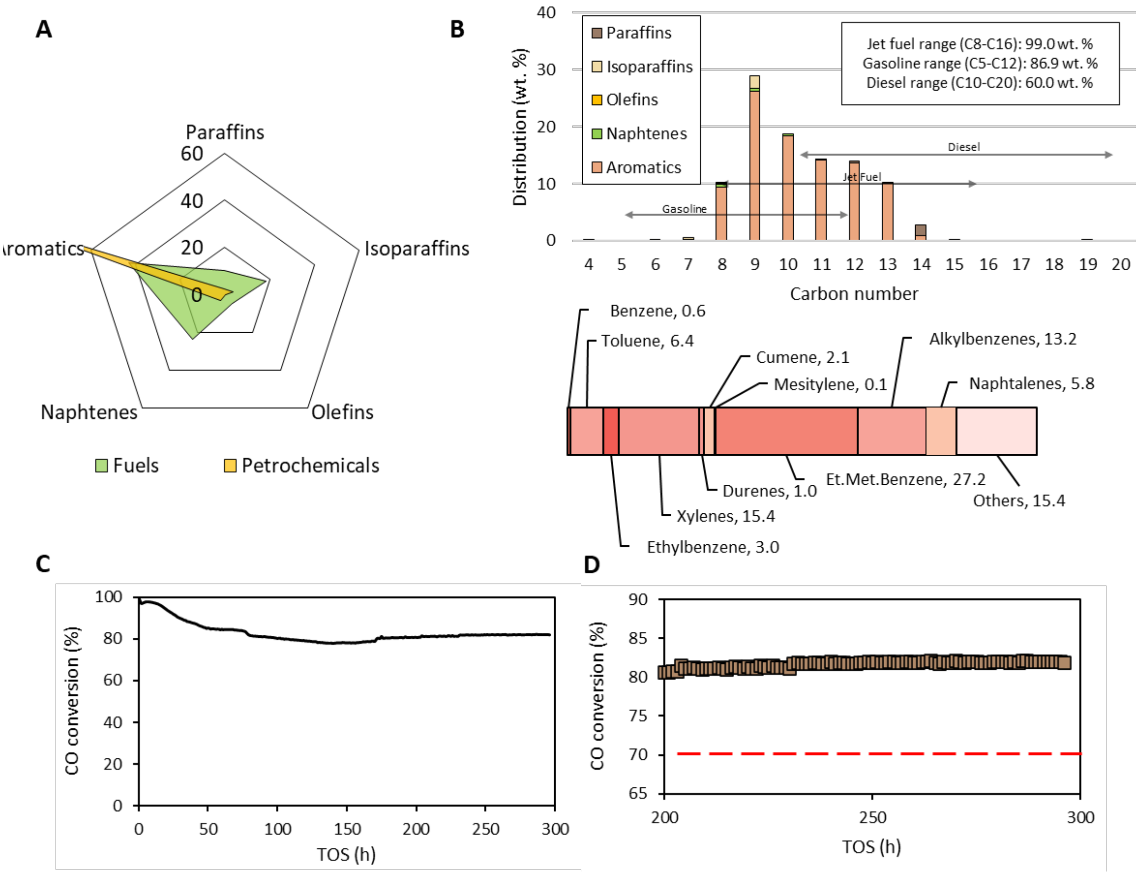

Figure 1. A) Example of liquid product variability for fuel (green) and petrochemical (orange) applications. **B)** Example of selective liquid distribution in the C_8-C_{16} range and corresponding aromatic content**. C-D)** Stability test over 300 hours showing consistent conversion above 80 C. %.

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Capacity: (Representative)

ONE POT PROCESS FOR SYNTHESIZING AROMATICS HYDROCARBON FROM SYNGAS

DESCRIPTION

FIELD OF THE INVENTION

The present invention relates to an improved process of efficiently synthesizing value-added chemicals, i.e. aromatic hydrocarbons, from gas that comprises H_2 and CO in one pot process by metal-based/zeolite composite catalyst. The invention especially relates the manufacturing of lower aromatic hydrocarbons such as benzene, toluene, xylenes (BTX).

BACKGROUND OF THE INVENTION

Aromatic hydrocarbons especially BTX (benzene, toluene, xylene), being conventionally obtained as a by-product of gasoline or ethylene production units through distillate fractions in the petroleum industries, are extensively used as the essential chemical raw materials in aerospace, defense, and energy vector. At present, the major production routes of aromatics divert towards the catalytic reforming of naphtha or steam cracking, hydrolysis, and catalytic cracking of light cycle oil, etc., while adopting the petroleum resources as raw material.

Other source to obtain aromatic hydrocarbon has been natural gas. The patent US10550045 is relates to a method for producing aromatic hydrocarbons from natural gas, which involve producing synthesis gas, converting the same into methanol, producing, from the methanol, in the presence of a catalyst, a concentrate of aromatic hydrocarbons and water, separating the water, air stripping hydrocarbon residues from the water, and separating-out the resultant concentrate of aromatic hydrocarbons and hydrogen-containing gas, the latter being at least partially used in the production of synthesis gas to adjust the ratio therein of H_2:CO 1.8-2.3:1. The disclosed process comprises multiple steps and exhibits low selectivity in the production of aromatic hydrocarbons.

The syngas is also a source to obtain aromatic hydrocarbons. The Canadian patent CA1175073A discloses a process for preparing a hydrocarbon mixture, rich in aromatic hydrocarbons. The syngas is subjected to a catalytic reaction with a mixed catalyst comprising a physical mixture of (1) a palladium catalyst comprising palladium supported on a carrier and (2) a zeolite catalyst, thereby to produce an aromatics-rich hydrocarbon mixture. The method yields a mixture of hydrocarbon wherein the aromatics are lower than 60%.

The production efficiency of these aromatic hydrocarbons is not high enough. Even though, employing different processes of Aroforming, M2 forming process; Z-forming process, Cyclar process of LPG (Liquefied Petroleum Gas) or C_3-C_4 naphtha unit, AROMAX process or RZ-Platformer process etc., could produce aromatics as targeted products, however, still lacking far behind in the yield’s static.

The aromatics production technology directly from biomass or coal derived syngas being regarded as syngas to aromatics (STA), could help in compensating the global consumption of those petroleum derivatives, while alleviating the demand gap of high-value aromatics and the production cost. Since various catalytic processes of utilizing alternative resources for producing value added energy-related products and chemicals have been widely discovered, where the exemplary method of gas to liquid (GtL) through Fischer-Tropsch synthesis (FTS) or methanol synthesis (MTS) processes are highly desirable in the renewable anergy regimes. However, the kinetics control by Anderson-Schulz-Flory (ASF) rule, and extensive number of byproducts ($CO_{2,}$ etc), need to be optimized for improving the overall efficiency of existing technologies.

The effective advancement and appealing strategies in the decades back presented route of STA process by adopting the variety of multi-functional catalyst scheme in a single stage, have significantly invaded the activity barriers (in terms of performance, thermodynamics, and cost etc.) that usually encounter in conventional twostep process. However, limited to the laboratory exploration stage of one-step STA unit, there are still relatively few studies in this era that need the exploration of appropriate solutions for the development of high conversion, stability, and targeted aromatics selective catalytic system. There remains a wide gap of unravelling a rationally designed hybrid catalyst with high activity and high stability to directly transform syngas to highly selective (over

90%) formation of desired aromatic hydrocarbons in a single-stage (one-pot) process.

Various investigations disclosed different methods of improving the catalyst life and aromatics production with a mixture of CO, CO_2, and H_2 reaction gas, however, failing to achieve considerable yield. In most cases, if the catalyst life could sustain longer, the yield of the aromatic hydrocarbon is suppressed to be low level especially at the industrial scale. Some studies have disclosed different methods of catalytic evolution of excellent physiochemical behaviours and oxygen-vacancy-rich spinel structured integrated with HZSM-5 molecular sieves to achieve one-step STA process, where the aromatics selectivity can reach (50%-85%), however either have encountered the low CO conversion levels of 20-40%) or finding relatively high CO_2 generations (30-50%).

While other reaching to the high conversion rate (50%), with more than 80% aromatics selectivity in one-step aromatic synthesis schemes, however, mainly diverging towards higher molecules fractions polymethyl benzene or durene, with reduced light aromatics (BTX) selectivity. Various documents adopting iron-based metal oxide catalysts, find the good initial conversion and aromatics selectivity, but relatively poor stability with sharply dropped catalyst performance with the extension of the reaction time, making a certain distance from the requirements of industrial applications. Therefore, necessary examinations on the catalyst life are direly needed to be carried out for the development of different advanced techniques that should be capable of keeping a high yield of the aromatic hydrocarbon for a long period of time.

SUMMARY OF THE INVENTION

The process referred in the present invention offers a distinct advantage in maintaining a consistently high yield of aromatic hydrocarbons over prolonged durations combined with a high rate of CO conversion level, owing to the sustained efficiency of the catalyst employed throughout the extended operational period.

In the present invention has been development a process to obtain aromatic from a syngas result in a high CO conversion rate of over 96% and while efficiently reaching the aromatics content to 98.72%, with the major fraction of benzene, toluene and xylene (BTX). Another advantage of the present process is that the catalyst maintains the activity for a long period of time. The process is one pot process, this term refers to a multi-step chemical reaction carried out in a reaction vessel.

The composite catalyst used in the process of the invention, that comprises an alkali-Fe- transition metal oxide and a nano molecular sieve zeolite, realizes the enhanced conversion efficiency of the gas and reduces side reactions by effective improvement in the intermediate products. The alkali increases the activity of the catalyst. The bimetallic Fe- transition metal based solid oxide along with the alkali afford the excellent stability and selectivity of the low carbon olefins in the intermediate product that are beneficial in generating the targeted aromatic hydrocarbons.

In the present process the highly selective aromatic synthesis is obtained through the optimization of various reaction parameter.

Therefore, the first aspect of the present invention refers to a process to obtain aromatic hydrocarbons, from a syngas, comprising the steps of:

a) preheating a composite catalyst to a temperature lower than a reaction temperature;
b) reducing the composite material;
c) reacting in a fixed bed the gas at the reaction temperature from 150ºC to 350ºC, at a pressure from $1\cdot10^5$ Pa to $5\cdot10^6$ Pa and at a gas hour space velocity (GHSV) is in a range from 1000 $mLg^{-1}h^{-1}$ to 5000 $mLg^{-1}h^-1$ in the presence of the composite catalyst;

wherein the composite catalyst comprising:
an alkali-Fe- transition metal oxide wherein the Fe is from 50% to 90% by weight relative to the total weight of the alkali-Fe- transition metal oxide and
a nano molecular sieve zeolite;
and wherein the mass ratio of the metal oxide to the nanosized molecular sieve zeolite is (0.1-10):1.

The term syngas a "syngas" or "synthesis gas" means synthesis gas which is the name given to a gas mixture that contains varying amounts of carbon monoxide, hydrogen and/ or carbon dioxide. The raw syngas containing CO_2 and the composition is for example 20.0% H_2, 10.0% CO, 5.0% CO_2, and balance N_2, and the pure syngas does not contain CO_2 and the composition is for example 20.0% H_2, 10.0% CO and balance N_2.

The term "aromatic hydrocarbon" is very well known in the art. Accordingly, the term "aromatic hydrocarbon" relates to cyclically conjugated hydrocarbon, containing at least one benzene moiety; such benzene moieties may be substituted or unsubstituted. Examples of aromatic hydrocarbon are benzene, xylene and toluene.

The term “molecular sieve zeolite” refers to a crystalline aluminosilicate material with a highly ordered structure, characterized by regularly spaced pores of molecular dimensions.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of aiding the understanding of the characteristics of the invention, according to a preferred practical embodiment thereof and in order to complement this description, the following figures are attached as an integral part thereof, having an illustrative and non-limiting character.

The Figure 1 includes a chart showing the effect of time on stream (TOS) on CO conversion, light hydrocarbon selectivity, CO_2 selectivity and liquid product selectivity for an Na modified Fe-Cu based composite catalyst with HZSM-5 zeolite at the reaction conditions of 300° C, 30 bar, and 2000 h^{-1} with syngas (20.0% H_2, 10.0% CO, 5.0% CO_2, and balance N_2).

DETAILED DESCRIPTION OF THE INVENTION

As it is said above the first aspect of the present invention refers to process to obtain aromatic hydrocarbons, from a syngas, comprising the steps of:

a) preheating a composite catalyst to a temperature lower than a reaction temperature;

b) reducing the composite material;

c) reacting in a fixed bed the gas at the reaction temperature from 150ºC to 350ºC, at a pressure from $1 \cdot 10^5$ Pa to $5 \cdot 10^6$ Pa and at a gas hour space velocity (GHSV) is in a range from 1000 $mLg^{-1}h^{-1}$ to 5000 $mLg^{-1}h^{-}1$ in the presence of the composite catalyst;

wherein the composite catalyst comprising:

an alkali-Fe- transition metal oxide wherein the Fe is from 50% to 90% by weight relative to the total weight of the alkali-Fe- transition metal oxide and

a nano molecular sieve zeolite;

and wherein the mass ratio of the metal oxide to the nanosized molecular sieve zeolite is (0.1-10):1.

Preferably the aromatic hydrocarbon obtained in the process is benzene, toluene and/or xylene.

Preferably the metal oxide are irregular particles with a particle size of from 800µm to 400 µm, the pore volume of the metal oxide in the catalyst is 0.03-35 cm^3/g, and the BET (Brenauer Emmett Teller) specific surface area is 20-300m^2/g.

In the present invention the particle size is estimated by transmission electron microscope (TEM) by a Tecnai G220 with an acceleration voltage of 200 KV with a carbon film supported by Cu grid. At least 200 particles were measured to assess the diameter of particles. The volume-surface average diameter was estimated assuming a spherical morphology with the following expression:

$$D_p = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where ni represents the number of particles with diameter di.

In the present invention, the specific surface area and pore volume were estimated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, respectively.

The feature of the nano molecular sieve zeolite; has excellent aromatization activity that can effectively inhibit the formation of carbon deposits and significantly improve the value-added aromatics selectivity.

Preferably the pore volume of the nano molecular sieve zeolite is from 0.04 cm^3/g to 120 cm^3/g, the BET specific surface area is from 50 m^2/g to 500 m^2/g, and the average pore diameter, measured as a ratio of total pore volume is in a range from 1nm to 10nm.

Preferably the alkali metal is selected from: Na, K, Li, Rb, Cs and Fr. More preferably the molar ratio of alkali metal to iron atoms is (0.03-0.20):1.

Preferably the transition metal is selected from: Ti, Va, Cr, Zr, Ru, Rh, W, Pt, Mn, Co, Ni, Cu and Zn. More preferably Co, Ni, Cu, Mn, Zn or Zr.

Preferably the amount of Fe in the alkali-Fe- transition metal oxide is from 60% to 80% by weight relative to the total weight of the alkali-Fe- transition metal oxide.

Preferably the step a) is carried out in contact with a raw material comprising, the H_2 is between 10% to 30% in weight referred to the total weight; CO is between 5% to 15% in weight referred to the total weight; the CO_2 is between 1% to 10% in weight referred to the total weight and balanced with N_2. Preferably the step a) is carried out at a temperature that is not higher than 300ºC, increasing gradually from 150ºC to 280ºC. Preferably the temperature range is from 150ºC to 280ºC.

Preferably the syngas comprises CO_2 from the 10% to 50 % weight CO_2/weight syngas and H_2 and CO in a ratio from 1:1 to 1:3.

Preferably the reduction step b) is carried out at a temperature between 350ºC to 450ºC by reducing with a gas mixture of hydrogen balanced with nitrogen. Particularly the gas mixture of hydrogen balanced with nitrogen is in equal mass flow ratio.

Preferably the temperature of step c) is from 280ºC to 340ºC, more preferably from 290ºC to 340ºC; in this way also is sustained high yields of aromatic hydrocarbons over an extended period.

In the present invention the molecular sieve zeolite preferably is a metal modified nano molecular sieves. Preferably this metal is selected from sodium, potassium, iron, niobium, platinum, nickel or molybdenum. More preferably the metal is impregnated in the molecular sieve zeolite and the metal is from 0.1% to 10% of the weight of the molecular sieve zeolite.

Preferably the molecular sieve zeolite is obtained by hydrothermal method. Preferably the molecular sieve zeolite selected from: MCM-22, MCM-49, BETA, or HZSM-5. Particularly HZSM-5.

Preferably the nano molecular sieve zeolite is a metal modified nano molecular sieves. More preferably the nano molecular sieve zeolite is obtained by hydrothermal method.

Preferably the alkali Fe-transition metal oxide and the nano molecular sieve zeolite are pelletized and mixed uniformly.

Examples

The present invention will be described in more detail with reference to the following examples, but not only limited to these described functions.

Reaction method

A fixed bed flow type reactor was used for the catalyst evaluation. In the following Examples, unless otherwise stated, high-purity gases containing CO and H_2 were used as reaction gases, mixing 10% nitrogen as an internal standard for analysis in an overall feeding rate of 50ml/min, unless otherwise stated.

Described application was in fixed-bed reaction with a double tube fixed bed reactor and a Hastelloy C276 (inner diameter 7 mm), carrying the reaction at the following conditions unless otherwise stated, temperature 300°C, 30 bar pressure with 2000 $mL \cdot h^{-1} \cdot gcat^{-1}$ space velocity and syngas volume ratio of H_2/CO and CO is 2 for the reaction time of 6-72h.

Analysis and Evaluation methods

After the reaction gases material is in full contact with the composite catalyst in the reaction tube, an aromatization reaction occurs, and a sufficient amount of C_2-C_4 olefins and C_5^+ hydrocarbons produced on the metal oxide surface are converted into aromatics into the zeolitic cavities, such as benzene, toluene, xylene, trimethylbenzene and heavy aromatics; the reaction product is separated from gas and liquid, and the liquid phase product contains aliphatic C_5^+ hydrocarbons, methanol, water and the target product aromatics, the gas phase products contain carrier gas, carbon monoxide, low-carbon alkanes, and low-carbon olefins, etc. The reaction products were analysed separately after passing through the gas-liquid separator. The analysis of liquid phase products was carried out by Clarus 580 gas chromatograph of PerkinElmer Company of the United States, and the analysis of gas phase products was carried out by GC900 gas chromatograph produced by Shanghai Tianpu Instrument. The reaction results are shown in Table 3.

Example 1. Process for making the catalyst of the invention

This example describes processes for making and characterizing embodiments of the present catalysts.

In particular, this example describes how to make the catalyst of the invention, and also characterizes their ability to process synthesis gas.

An amount of 0.12mol of $Fe(NO_3)_3(H_2O)_9$ with 0.08mol of copper nitrate $[Cu(NO_3)_2 3H_2O]$ was dissolved in 190mL deionized water to prepare solution A that was acidified with 1mL of nitric acid followed by heating up to 60°C and stirring for 30 minutes to dissolve completely. Then the precipitant sodium hydroxide was dissolved in deionized water to prepare 1.5M solution B, followed by gradually adding solution B dropwise into solution A using a peristaltic pump until the solution pH=8.0 in a vigorous stirring way at 60°C. After the desired pH point, the aging process of the precipitate was carried out with continuous stirring at the constant temperature of 60°C water for 2 hours. The obtained slurry solution after aging was filtered and washed several times with 300mL water until the final mol ratio of sodium ion to iron atom was adjusted to 0.09 in the precipitate. The obtained solid cake after filtration was dried overnight in an oven for 24 h, usually at a temperature of 120°C, followed by calcination thereof in the air by a muffle furnace for 6 h at 600°C to obtain the sodium-modified iron-copper oxides nanocrystals.

The pore volume of the metal oxide was $0.212cm^3/g$, the BET specific surface area was $92.9m^2/g$, and the average pore diameter was 9.1nm.

The zeolite-based oxide solid was synthesized in making a solution A by dissolving a sufficient amount of ethyl orthosilicate, and tetra propylammonium hydroxide in 15mL deionized water at a temperature of 90°C for 48h with another aqueous solution B of aluminum nitrate nonahydrate and sodium hydroxide with the molar ratio of 1:0.3:0.5:0.4:15 for ethyl orthosilicate nonahydrate, aluminium nitrate, tetra propylammonium hydroxide, sodium hydroxide and deionized water, respectively.

The obtained solution B was slowly added dropwise into solution A with vigorous stirring, followed by transferring the obtained initial gel into a hydrothermal autoclave and maintained at 160° C for 48 hours for crystallization followed by centrifugation and several times washing of the product with deionized water until become neutral. The obtained filter cake was then dried at 120°C for 12 hours and calcined at 500°C for 5h to remove the template, and the obtained product was isolated core and washed with deionized water until neutral, the filter cake was dried for 5-18 hours at a temperature of 120 °C, with a calcination temperature of 200-600°C for 1-6 hours obtain the Na type nanosized HZSM-5 molecular sieve.

The obtained Na type HZSM-5 was then treated cation exchange process through ammonium form by dispersing it into 1M NH_4Cl solution in vigorous stirring for 5 h, followed by the centrifugation and several (4) times washing with deionized water to remove residual chloride ions. The described ions exchange was completed after the repetition of several (usually 3-4) times, and finally the obtained NH_4-HZSM-5 was dried for 24 hours at 120 °C followed by calcining it at 600 °C for 6 h to obtain nanoscale HZSM-5.

The pore volume of nanosized HZSM-5 molecular sieve was 0.340cm^3/g, BET specific surface area was 289m^2/g, and average aperture was 4.71nm, the ratio of silicon to aluminium is between 50.

The metal oxide prepared in the first step of 2g and the nanosized HZSM-5 molecular sieve prepared in the second step of 2g, respectively were pressed and pelletized into tablets of 20-40 mesh, and uniformly mixed in physical way to obtain the composite catalyst.

Example 2. Manufacturing value added aromatics from synthesis gas with the catalyst of the invention

The composite catalyst of above-mentioned 4g was loaded in a fixed-bed tubular reactor for the direct manufacturing of value-added aromatics from synthesis gas. The catalyst bed was heated gradually by purging N_2 flow for 2 hours, followed by the catalyst reduction process using hydrogen at 400°C for 6 hours. Then the H_2 was replaced by reaction gas mixture of H_2/CO and (or) CO_2 at the desired reaction conditions of taking the H_2/CO gas volume ratio of 2, at the temperature of 350°C, pressure 4MPa, and space velocity 2000.gcat^{-1}.h^{-1}, for the reaction time of 24h. The raw material gas (CO: H_2: N_2 = 10:20:20) was pre-heated to 200°C by the preheater and enters the fixed bed reactor.

Unless defined otherwise, the mentioned reaction conditions were kept the same for the overall different catalytic materials, except for exploring the effect of the different parameters such as at different temperatures 280 ° C, 290° C, 300° C, 310° C, 320° C, 330° C, 340 ° C and 350° C, pressure 10 bar, 15 bar, 20 bar, 25 bar, 30 bar, 35 bar, 40 bar, space velocity of 1000mL·h^{-1}·gcat^{-1}, 1500mL·h^{-1}·gcat^{-1} ,2000mL·h^{-1}·gcat^{-1}, 2500mL·h^{-1}·gcat^{-1}, 3000mL·h^{-1}·gcat^{-1}, 3500mL·h^{-1}·gcat^{-1}, 4000mL·h^{-1}·gcat^{-1}, and syngas (H_2/CO) ratio of 1, 2, and 3 (or) with different CO_2 composition of 10%, 20%, 30%, 40%, 50%.

The Table 1 includes a chart showing the effect of temperature on CO conversion and CO_2 and hydrocarbon selectivity with 3 g of an embodiment of the present catalysts at 30 bar, gas hourly space velocity (GHSV) of 2000 h^{-1}, and time on stream of 12-48 hours with syngas (20.0% H_2, 10.0% CO, 5.0% CO_2, and balance N_2). The Table 1 shows the variation of CO conversion and C_1-$C_5{}^+$ selectivity at various temperatures and with the other variables remaining constant. The Table 1 also shows that temperature influenced CO conversion that increased from 84% at 290° C. to 97% at 340° C.

Table 1 also shows that the hydrocarbon distribution changed with temperature, where the higher hydrocarbons were relatively more sensitive to temperature, while the light hydrocarbons being favored at higher temperatures.

Table 1. CO conversion and product selectivity obtained over the NaFeCu-HZSM-5 (Si/Al=50) bifunctional catalyst system at varied reaction conditions in the synthesis of aromatic hydrocarbons.

Reaction conditions						Hydrocarbon distribution (C%)						
T°C	P(bar)	GHSV (mL $g^{-1}h^{-1}$)	H_2/CO ratio	CO conv. (%)	CO_2 Sel. C%	CH_4	C_2-C_4	n-C_2^o-C_4^o	i-C_4^o	i-C_{5+}^d		Aromatic content in C_{5+} liquid phase ^{e} C%
										i-C_{5+}^c	Aro-matics	
280	30	2000	2	84.1	22.3	9.3	8.4	13.7	9.5	11.4	47.7	87.5
300^a	30	2000	2	96.6	26.5	10.5	0.5	11.8	6.2	3.5	67.5	96.4
320	30	2000	2	97.4	29.4	18.5	0.2	16.4	6.91	3.1	54.89	98.5
340	30	2000	2	98.8	33.1	25.4	1.4	21.2	9.2	2.4	40.4	98.7
300^b	30	2000	2	97.1	25.8	11.1	40.4	15.2	11.3	22	0	0

[a] Conducted over Na-FeCu/HZSM-5 catalyst at optimal reaction conditions.

[b] Conducted over FeCu catalyst only.

[c] Confirmed to be mainly olefins

[d] fractions of *i*-C_{5+} and aromatics in the final collected liquid hydrocarbon phase.

[e] fractions of aromatics in the final collected liquid hydrocarbon phase.

The stability of the composite catalyst prepared in Example 1 of the present invention is significantly better than that of the other molecular sieves, with it has excellent long-range life and commercial application potential.

The Figure 1 shows the effect of time on stream (TOS) on the performance of the catalyst was observed with that of the exemplary best suitable catalyst for 500 h by carrying out the reaction in the same manner as that of Example 1 for optimal test, giving a constant yield of benzene as 75.5 % and 97% CO conversion for a stability test of 50-500 h. The TOS results showed that the activity of the catalyst reached the steady state under the overall reaction period, thus giving a stable catalytic activity with a constant CO conversion over 95% for the overall reaction stream of 50-500 h.

Example 3. Effect of the pressure

Effect of pressure on CO conversion, CO_2 and hydrocarbon selectivity, hydrocarbon distribution, and liquid hydrocarbon distribution was observed at different reaction pressure. The reaction was carried out in the same manner as in Example 2 for the optimal case, except the pressure was changed to different values of 10, 15, 20, 25, 30, and 40 bar, thus giving a maximum yield of 67.5 % aromatics and 97% CO conversion at 30 bar. The higher total pressure could shift the equilibrium towards forward direction that can eventually enhance the CO conversion and change the product distribution as well. The results in Table 2 indicate that the increased pressure has a significant impact on both CO conversion and process selectivity, increasing the CO conversion up to a certain level of 99.1 % at 40 bar from the lower CO conversion level of only 46.5 % at 5 bar. Similarly, the product distribution has also observed an obvious change for decreasing the CO_2 and CH_4 selectivity from 42 % and 28% at 5 bars to 26 % and 10 % at 30 bars, respectively, while accelerating the overall aromatics contents to 67 % at 30 bars from that lower fraction of only 26 % at 5 bars.

Table 2. CO conversion and product selectivity obtained over the NaFeCu-HZSM-5 (Si/Al =50) bifunctional catalyst system at varied reaction conditions in the synthesis of aromatic hydrocarbons.

Reaction conditions						Hydrocarbon distribution (C%)						
T°C	P(bar)	GHSV (mL $g^{-1}h^{-1}$)	H_2/CO ratio	CO conv. (%)	CO_2 Sel. C%	CH_4	C_2-C_4[b]	n-C_2^o-C_4	i-C_4^o	i-C_{5+}[d]		Aromatic content in C_{5+} liquid phase [e] C%
										i-C_{5+}[c]	Aromatics	
300	5	2000	2	46.7	42.5	28.5	15.4	14.1	6.4	9.4	26.2	98.5
300	10	2000	2	55.3	37.3	23.4	13.8	15.2	6.5	10.3	30.8	97.1
300	15	2000	2	68.2	32.6	16.9	11.1	15.9	9.4	11.5	35.2	92
300	20	2000	2	82.4	29.1	16.4	8.4	14.8	8.5	9.4	42.5	85
300	25	2000	2	90.4	27.7	14.5	3.5	13.5	6.3	6.4	55.8	86.4
300[a]	30	2000	2	96.6	26.5	10.5	0.5	11.8	6.2	3.5	67.5	96.4
300	35	2000	2	98.1	25.2	13.5	0.5	10.2	8.1	8.6	59.1	70.2
300	40	2000	2	99.7	29.4	11.1	0.9	13.2	5.1	18.5	51.2	51.8

[a] Conducted over Na-FeCu/HZSM-5 catalyst at optimal reaction conditions.

[b] Conducted over FeCu catalyst only.

[c] Confirmed to be mainly olefins

[d] fractions of *i*-C_{5+} and aromatics in the final collected liquid hydrocarbon phase.

[e] fractions of aromatics in the final collected liquid hydrocarbon phase.

Example 4. Effect of different space velocity

The effect of different space velocity on CO conversion, CO_2 and hydrocarbon selectivity, hydrocarbon distribution, and liquid hydrocarbon distribution was observed at different gas flow rates. The reaction was carried out in the same manner as in Example 1 for optimal test, except at different space velocity of $1000mL\cdot h^{-1}\cdot gcat^{-1}$, $1500mL\cdot h^{-1}\cdot gcat^{-1}$, $2000mL\cdot h^{-1}\cdot gcat^{-1}$, $2500mL\cdot h^{-1}\cdot gcat^{-1}$, $3000mL\cdot h^{-1}\cdot gcat^{-1}1$, $3500mL\cdot h^{-1}\cdot gcat^{-1}$, 4000mL·h^{-1}·gcat^{-1}. It was observed that enhancing the gas flow rate could increase the CO conversion rate while giving a maximum yield of aromatics as 67.5 % and 97% CO conversion at 2000mL·h^{-1}·gcat^{-1}. (Table 3). However, an extensive high space time while decreasing the overall contact time of reactant molecules, could also influence the product distribution in decreasing the gasoline range fraction (C_5+) while affecting the overall aromatics content in the final product.

Table 3. CO conversion and product selectivity obtained over the NaFeCu-HZSM-5 (Si/Al =50) bifunctional catalyst system at varied reaction conditions in the synthesis of aromatic hydrocarbons.

Reaction conditions						Hydrocarbon distribution (C%)						
T°C	P(bar)	GHSV (mL $g^{-1}h^{-1}$)	H_2/CO ratio	CO conv. (%)	CO_2 Sel. C%	CH_4	C_2-C_4[b]	n-C_2^o-C_4^o	i-C_4^o	i-C_{5+}[d]		Aromatic content in C_{5+} liquid phase [e] C%
										i-C_{5+}[c]	Aro-matics	
300	30	1000	2	85.2	38.9	19.8	12.4	21.4	8.4	14.2	23.8	84
300	30	1500	2	90.7	32.1	16.2	8.2	9.7	8.1	9.6	48.2	94.6
300[a]	30	2000	2	96.6	26.5	10.5	0.5	11.8	6.2	3.5	67.5	96.4
300	30	2500	2	91.2	27.2	11.4	0.9	11.2	10.7	9.7	56.1	95
300	30	3000	2	81.2	28.7	14.7	1.8	13.9	14	11.8	43.8	98.2

[a] Conducted over Na-FeCu/HZSM-5 catalyst at optimal reaction conditions.

[b] Conducted over FeCu catalyst only.

[c] Confirmed to be mainly olefins

[d] fractions of *i*-C_{5+} and aromatics in the final collected liquid hydrocarbon phase.

[e] fractions of aromatics in the final collected liquid hydrocarbon phase.

Example 5. Effect of different syngas composition

The effect of different syngas composition on CO conversion, CO_2 and hydrocarbon selectivity, hydrocarbon distribution, and liquid hydrocarbon distribution was carried at different reaction gas mixture. The reaction was carried out in the same manner as in Example 1 for optimal test, except at different syngas composition with (H_2/CO) ratio of 1, 2, and 3 (or) with different CO_2 composition of 10%, 20%, 30%, 40%, 50%. It was deduced that the synthesis gas composition can, in some instances, affect both reaction rates and activity giving a maximum yield of aromatics as 67.5 % and 97% CO conversion at contacting a gaseous mixture comprising 20.0% H_2, 10% CO, 5% CO_2, and balanced N_2.

Table 4. CO conversion and product selectivity obtained over the NaFeCu-HZSM-5 (Si/Al =50) bifunctional catalyst system at varied reaction conditions in the synthesis of aromatic hydrocarbons.

Reaction conditions						Hydrocarbon distribution (C%)						
T°C	P(bar)	GHSV (mL $g^{-1}h^{-1}$)	H_2/CO ratio	CO conv. (%)	CO_2 Sel. C%	CH_4	C_2-C_4[b]	n-C_2^o-C_4^o	i-C_4^o	i-C_{5+}[d]		Aromatic content in C_{5+} liquid phase [e] C%
										i-C_{5+}[c]	Aro-matics	
300	30	2000	0.5	76.9	41.2	19.7	8.4	19.4	9.5	5.4	37.6	97.4
300	30	2000	1	87.5	36.1	15.4	5.3	16.4	6.4	3.8	52.7	98.1
300[a]	30	2000	2	96.6	26.5	10.5	0.5	11.8	6.2	3.5	67.5	96.4
300	30	2000	3	96.7	26.5	28.7	2.4	18.2	9.4	5.2	36.1	99.3

[a] Conducted over Na-FeCu/HZSM-5 catalyst at optimal reaction conditions.

[b] Conducted over FeCu catalyst only.

[c] Confirmed to be mainly olefins

[d] fractions of *i*-C_{5+} and aromatics in the final collected liquid hydrocarbon phase.

[e] fractions of aromatics in the final collected liquid hydrocarbon phase.

CLAIMS

1. A process to obtain aromatic hydrocarbons, from a syngas, characterized by comprising the steps of:
    a) preheating a composite catalyst to a temperature lower than a reaction temperature;
    b) reducing the composite material;
    c) reacting in a fixed bed the gas at the reaction temperature from 150ºC to 350ºC, at a pressure from $1\cdot10^5$ Pa to $5\cdot10^6$ Pa and at a gas hour space velocity (GHSV) is in a range from 1000 $mLg^{-1}h^{-1}$ to 5000 $mLg^{-1}h^{-}1$ in the presence of the composite catalyst;

wherein the composite catalyst comprising:
an alkali-Fe- transition metal oxide wherein the Fe is from 50% to 90% by weight relative to the total weight of the alkali-Fe- transition metal oxide and
a nano molecular sieve zeolite;
and wherein the mass ratio of the metal oxide to the nanosized molecular sieve zeolite is (0.1-10):1.

2. The process according to the claim 1 characterized by the aromatic hydrocarbon obtained in the process is benzene, toluene and/or xylene.

3. The process according to any of the claims 1 to 2 characterized by the metal oxide are irregular particles with a particle size of from 800μm to 400 μm, the pore volume of the metal oxide in the catalyst is from 0.03 cm^3/g to 35 cm^3/g, and the BET (Brenauer Emmett Teller) specific surface area is from 20 m^2/g to 300 m^2/g.

4. The process according to any of the claims 1 to 3 characterized by the pore volume of the nano molecular sieve zeolite is from 0.04 cm^3/g to 120 cm^3/g, the BET specific surface area is from 50 m^2/g to 500 m^2/g, and the average pore diameter, measured as a ratio of total pore volume is in a range from 1nm to 10nm.

5. The process according to any of the claims 1 to 4 characterized by the molar ratio of alkali metal to iron atoms is (0.03-0.20):1.

6. The process according to any of the claims 1 to 5 characterized by the step a) is carried out the temperature range is from 150ºC to 280ºC; the reduction step b) is carried out at a temperature between 350ºC to 450ºC; the temperature of step c) is from 280ºC to 340ºC,

7. The process according to any of the claims 1 to 6 characterized by the syngas comprises CO_2 from the 10% to 50 % weight CO_2/weight syngas and H_2 and CO in a ratio from 1:1 to 1:3.

8. The process according to any of the claims 1 to 7 characterized by the nano molecular sieve zeolite is a metal modified nano molecular sieves.

9. The process according to any of the claims 1 to 8 characterized by the nano molecular sieve zeolite is obtained by hydrothermal method.

ABSTRACT

The present invention relates to an improved process of efficiently synthesizing value-added chemicals, i.e. aromatic hydrocarbons, from syngas in one pot process by metal-based/zeolite composite catalyst. The invention especially relates the manufacturing of lower aromatic hydrocarbons such as benzene, toluene, xylenes (BTX) from syngas fractions ($CO/CO_2/H_2$) via catalytic treatment.

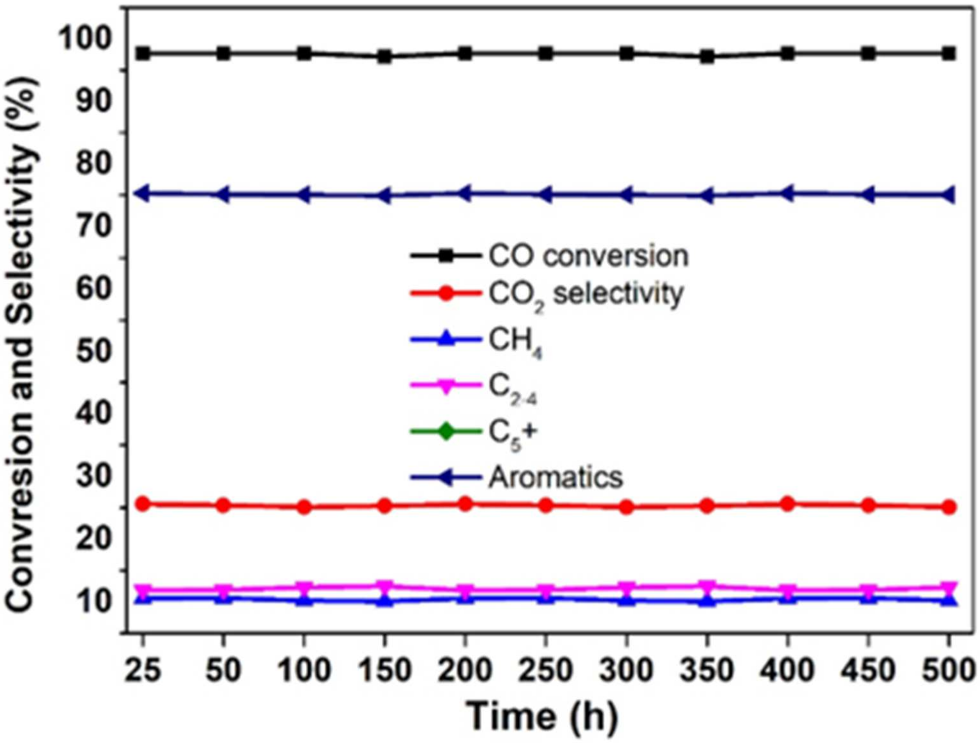
Convresion and Selectivity (%)
100
90
80
70
60
50
40
30
20
10
25
50
100
150
200
250
300
350
400
450
500
Time (h)
CO conversion
CO_2 selectivity
CH_4
C_{2-4}
C_5+
Aromatics

FIG. 1

Otros méritos e impacto

Los resultados del proyecto NICER-BIOFUELS han permitido al equipo del profesor Tomás Ramírez establecer una línea de investigación sólida en el desarrollo de tecnologías catalíticas avanzadas para la producción de biocombustibles y la conversión de CO2 impulsando el papel central la catálisis para la economía circular. Los resultados de NICER han sido claves para asugurar proyectos de máximo prestigio como la ERC-Consolidator condecida recientemente a Tomás en marco del diseño innovador de catalizadores para nuevas rutas de producción de biocombustibles (CLEVER-FUEL). Además han permitido armar consorcios académicos-industriales como FLEXBY donde se está diseñando una planta piloto producción de biocumbustibles que se instalará en la Universidad de Sevilla y que cuenta con socios industriales relavantes en el sector energético como GALP.

Estas actividades en el área de los biocombustibles y más allá del proyecto NICER-BIOFUELS están actualmente en ebullición en el grupo de investigación del profesor Ramírez y han atráido la atención de medios de comunicación nacionales e internacionales permitiendo su divulgación al público general.

Ejemplos son medios como:

El Páis (https://elpais.com/noticias/biocombustibles/)

Canal Sur (https://www.canalsur.es/multimedia.html?id=2152572)

Onda Cero (https://www.ondacero.es/emisoras/andalucia/sevilla/audios-podcast/andalucia-onda/andalucia-verde-13032025_2025031467d3c8cdde9a6f0001ab0132.html)

Europa Press (https://www.europapress.es/andalucia/sevilla-00357/noticia-investigador-us-sevilla-recibe-dos-millones-financiacion-europea-estudio-biocombustibles-20241203141051.html)

Esta labor de divulgación que destaca el impacto del proyecto permite además cumplir cumpliendo con una visión de **ciencia abierta para todos y al servicio del progreso social**.