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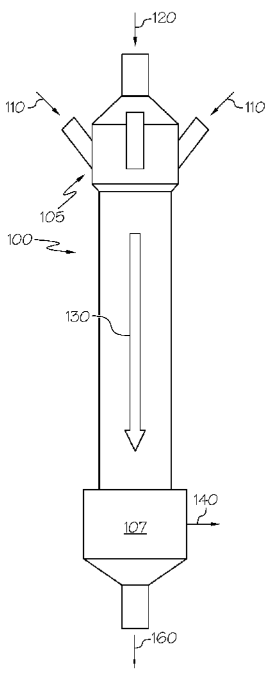

FIG. 1

(57) **Abstract:** Embodiments of methods for converting gas condensate into a product stream comprising propylene comprise feeding gas condensate at a top region of a downflow high severity fluidized catalytic cracking reactor (HSFCC), where the gas condensate comprises: at least 50% by weight paraffins, and less than 0.1 % by weight olefins. The method further comprises feeding catalyst to the top region of the downflow HSFCC reactor in an amount characterized by a catalyst to gas condensate weight ratio of about 5:1 to about 40:1, where the catalyst comprises nano-ZSM-5 zeolite catalyst having an average particle diameter from 0.01 to 0.2 µm, a Si/Al molar ratio from 20 to 40, and a surface area of at least 20 cm^2/g. The method further comprises cracking the gas condensate in the presence of the catalyst at a reaction temperature of about 500° C to about 700° C to produce the product stream comprising propylene.

[Continued on next page]

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PROCESSES FOR HIGH SEVERITY FLUID CATALYTIC CRACKING SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

TECHNICAL FIELD

[0001] This application claims priority to U.S. Patent Application 15/190,327 filed June 23, 2016, which is incorporated by reference in its entirety.

[0002] Embodiments of the present disclosure generally relate to fluid catalytic cracking processes, and more specifically relate to cracking catalysts used in high severity fluid catalytic cracking (HSFCC) systems, where the cracking catalyst comprises nano-ZSM-5 zeolites.

BACKGROUND

[0003] The worldwide increasing demand for light olefins remains a major challenge for many integrated refineries. In particular, the production of some valuable light olefins such as ethylene, propylene, and butylenes has attracted increased attention as pure olefin streams are considered the building blocks for polymer synthesis. The production of light olefins depends on several process variables like the feed type, operating conditions, and the type of catalyst. Despite the options available for producing a higher yield of propylene and light olefins, intense research activity in this field is still being conducted. These options include the use of HSFCC systems, developing more selective catalysts for the process, and enhancing the configuration of the process in favor of more advantageous setting.

[0004] The HSFCC process is capable of producing yields of propylene up to four times higher than the traditional fluid catalytic cracking unit and higher conversion levels for a range of petroleum steams. That being said, achieving maximum propylene and conversion from a wide range of feed qualities offers considerable challenges to the catalyst design for the HSFCC.

[0005] Moreover, the conventional FCC feedstocks range from hydrocracked bottoms to heavy feed fractions such as vacuum gas oil and atmospheric residue. However, these feedstocks are limited, obtained through costly and energy intensive refining steps, and thus are not expected to fulfill the ever growing market demands.

[0006] The addition of zeolites to an HSFCC catalyst is utilized for improving the yield of light olefins due to its shape selectivity, special pore structure and large specific surface area. However, when the crystal size of the zeolites is close to the molecular diameter of light hydrocarbons, the diffusion of the reactant/product molecules within the micropores is usually the rate-limiting step of the reaction. Furthermore, the crystal surface of the zeolites are susceptible to coke formation, which obstructs the accessibility of the micropores and thus deactivates the catalyst.

SUMMARY

[0007] Embodiments of the present disclosure are directed to improved HSFCC cracking systems, which convert gas condensate into light olefins using catalysts with nano-ZSM-5 catalysts, while reducing coke formation and pore diffusion on the nano-ZSM-5 zeolites.

[0008] In one embodiment, a method of converting gas condensate into a product stream comprising propylene is provided. The method comprises feeding gas condensate at a top region of a downflow high severity fluidized catalytic cracking reactor (HSFCC), where the gas condensate comprises at least 50% by weight paraffins, and, in some embodiments, less than 0.1% by weight olefins. The method further comprises feeding catalyst to the top region of the downflow HSFCC reactor in an amount characterized by a catalyst to gas condensate weight ratio of about 5:1 to about 40:1, where the catalyst comprises a nano-ZSM-5 zeolite catalyst having an average particle diameter from 0.01 to 0.2 μm, a Si/Al atomic ratio from 20 to 40, and a surface area of at least 20 cm^2/g. The method further comprises cracking the gas condensate in the presence of the catalyst at a reaction temperature of about 500° C to about 700° C to produce the product stream comprising propylene.

[0009] Additional features and advantages of the described embodiments will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the described embodiments, including the detailed description which follows, the claims, as well as the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is a schematic depiction of a downflow HS-FCC reactor according to one or more embodiments of the present disclosure.

[0011] FIG. 2A is an X-ray Diffraction (XRD) pattern of the nano-ZSM-5 based catalyst embodiments at various of sodium hydroxide.

[0012] FIG. 2B is an enlarged segment of the XRD pattern of FIG. 2A.

[0013] FIG. 3 is a graphical illustration of the phase selectivity of catalyst synthesis solutions based on the Al/Si and Na/Si ratios in the synthesis solution.

[0014] FIG. 4A is an environmental scanning electron microscopy (ESEM) micrograph of micron-size ZSM-5 zeolite embodiments.

[0015] FIG. 4B is an ESEM micrograph of nano-ZSM-5 zeolite embodiments.

[0016] FIG. 5A is a graphical plot of Weight Fraction vs. Temperature which depicts the results of thermogravimetric analysis (TGA) conducted on ZSM-5 zeolite embodiments synthesized with different Na and Al concentrations.

[0017] FIG. 5B is a graphical plot of Differential Gravimetric Analysis vs. Temperature which depicts further results of the TGA analysis of FIG. 5A conducted on ZSM-5 zeolite embodiments synthesized with different Na and Al concentrations.

[0018] FIG. 6A is a Thermal Desorption Spectroscopy (TPD) curve depicting a high silica MFI-type zeolite embodiments prepared at Si/Al=100 at multiple mass to charge (m/z) ratios.

[0019] FIG. 6B is a TPD curve depicting a low silica MFI-type zeolite embodiments prepared at Si/Al=20 at multiple m/z ratios.

[0020] FIG. 7A is an ESEM image of a Y zeolite embodiment.

[0021] FIG. 7B is Energy Dispersive Spectrum (EDS) of the Y zeolite embodiment which corresponds to the ESEM of FIG. 7A.

[0022] FIG. 8A is an ESEM image of a lanthanum-impregnated Y zeolite embodiment.

[0023] FIG. 8B is an EDS of the lanthanum-impregnated Y zeolite embodiment which corresponds to the ESEM of FIG. 8A.

[0024] FIG. 9 is an XRD pattern of a parent Y zeolite embodiment versus its lanthanum impregnated Y zeolite form.

[0025] The embodiments set forth in the drawings are illustrative in nature and not intended to be limiting to the claims. Moreover, individual features of the drawings will be more fully apparent and understood in view of the detailed description.

DETAILED DESCRIPTION

[0026] Embodiments of the present disclosure are directed of systems and methods of converting gas condensate into a product stream comprising propylene in a downflow high severity fluidized catalytic cracking (HSFCC) reactor in the presence of catalyst slurry comprising a nano-ZSM-5 zeolite catalyst.

[0027] Referring to FIG. 1, the system and methods utilize a downflow HSFCC reactor **100,** where the gas condensate **110** may be fed at a top region **105** of the FCC reactor **100**. Similarly, the catalyst **120** may be fed at the top region **105** of the HSFCC reactor **100** in an amount characterized by a catalyst **120** to gas condensate **110** weight ratio of about 5:1 to about 40:1. As shown in FIG. 1, the catalyst **120** and gas condensate **110** may be fed via different inlet ports at the top region **105** of the downflow HSFCC reactor **100.** After being fed, the gas condensate **110** is cracked in the presence of the catalyst **120** at a reaction temperature of about 500° C to about 700° C to produce the product stream **140** comprising propylene. In some embodiments, a catalyst bed may be fixed at the bottom of the HSFCC reactor 100. While not shown, steam may be injected into the downflow HSFCC to achieve the requisite high operating temperatures. Referring to FIG. 1, the gas condensate **110** is cracked as it travels a downward path as indicated by arrow **130**. As shown, the catalyst **120** and the product stream **140** may be separated through a separator region **107** at the bottom of the HSFCC reactor **100**, and are then passed out of the downflow HSFCC reactor **100** separately. The gas condensate **110** and the product stream **140** comprising propylene may be separated in the separator region **107**. In some embodiments, the liquid products may be collected in a liquid receiver and the gaseous products may be collected in a gas burette by water displacement.

[0028] Without being bound by theory, the present embodiments may provide a greater propylene yield in the product stream **140** as compared to conventional HSFCC reactors. In specific embodiments, the product stream **140** comprises at least a 20 wt% yield of propylene. In further embodiments, the product stream **140** may comprise at least a 10 wt% yield of ethylene. Moreover, the product stream **140** may comprise at least a 30 wt% yield of ethylene and propylene. The product stream may comprise less than a 3 wt% yield of coke, or less than 1 wt% yield of coke.

[0029] The present downflow HSFCC reactor **100** is characterized by high temperature, shorter residence times, and a high catalyst to oil ratio. In one or more embodiments, the reaction temperature is from 500 °C to 700 °C, or from 550 °C to 630 °C. Regarding residence time, the gas condensate may have a residence time of 0.7 seconds to 10 seconds, or from 1 second to 5 seconds, or from 1 second to 2 seconds. Moreover, the catalyst to gas condensate ratio may be from 5:1 to 40:1, or from 5:1 to 25:1, or from 5:1 to about 15:1, or from 5:1 to about 10:1.

[0030] The gas condensate **110** is a heavily paraffinic composition including at least 50% by weight paraffins and less than 0.1 % by weight olefins. Additionally, the gas condensate **110** may comprise naphthenes and aromatics. From a property standpoint, the gas condensate **110** may have an initial boiling point of at least 0 °C and a final boiling point of at least 450 °C when measured according to a true boiling point analysis. The gas condensate may have a research octane number (RON) of 70 to 75 according to ASTM 2699 or ASTM 2700.

[0031] In specific embodiments, the gas condensate may comprise Khuff Gas Condensate (KGC) which comprises 65 wt% paraffins, 0 wt% olefins, 21 wt% naphthenes, and 15 wt% aromatics. Feeds like KGC have attractive feedstock properties in terms of low sulfur, nitrogen, metals and Conradson Carbon Residue (CCR). That being said, the highly paraffinic nature of gas condensate, for example, KGC, makes it quite challenging for cracking into light olefins, such as propylene. Without being limited to application, the present downflow HSFCC system overcomes these challenges and produces excellent propylene yield using KGC, while being complementary to the current refinery FCC reactors

[0032] As stated previously, the catalyst **120**, which may be in slurry form, comprises nano-ZSM-5 zeolites having an average particle diameter from 0.01 to 0.2 μm, a Si/Al molar ratio from 20 to 40, and a surface area of at least 20 cm^2/g. In further embodiments, the Si/Al molar ratio is from 25 to 35, and the nano ZSM-5 has a surface area of at least 30 cm^2/g. Said another way, the nano ZSM-5 has a surface area of from 30 cm^2/g to 60 cm^2/g, or from 40 cm^2/g to 50 cm^2/g. The nano-ZSM-5 zeolites solve the diffusional limitations encountered during the cracking reactions, thereby enhancing the rate of the cracking reactions to produce more olefins. Moreover, the nano-ZSM-5 zeolites reduces coke formation on the surface of the catalyst, thereby prolonging the life of the nano-ZSM-5 zeolite catalyst.

[0033] For increased catalytic cracking activity, it is contemplated that the nano-ZSM-5 zeolite catalyst may be impregnated with additional components. In one embodiment, the nano ZSM-5 catalyst is impregnated with phosphorus. In specific embodiments, the nano ZSM-5 catalyst comprises 1 to 20 wt% of phosphorus, or from 2 to 10 wt% of phosphorus. Alternatively, the nano ZSM-5 catalyst is impregnated with rare earth oxides.

[0034] Various amounts of nano-ZSM-5 zeolite are contemplated with the catalyst. For example, the catalyst may comprise from 10 to 50 wt% of nano ZSM-5 catalyst, or from 15 to 40 wt% of nano ZSM-5 catalyst, or from 15 to 25 wt% of nano ZSM-5 catalyst.

[0035] Moreover, the catalyst may also comprise USY (Ultrastable Y zeolite). For increased catalytic cracking activity, it is contemplated that the USY catalyst may also be impregnated with additional components. In specific embodiments, the USY catalyst may be impregnated with lanthanum. Various amounts of the USY catalyst are contemplated within the catalyst. For example, the catalyst may comprise 10 to 50 wt% of USY catalyst, or from 15 to 40 wt% of USY catalyst, or from 15 to 25 wt% of USY catalyst.

[0036] USY zeolite impregnation with lanthanum impacts the selectivity towards light olefins. The impregnation with rare earth can also work as an enhancer to the stability and activity of the catalyst. Lanthanum impregnation in the USY zeolite (also called Y zeolites) is used to improve both the activity and hydrothermal stability, since it acts as a dealumination inhibitor in the zeolite structure.

[0037] Various amounts of alumina are also contemplated within the catalyst. In one or more embodiments, the catalyst comprises 2 to 20 wt% of alumina, or from 5 to 15 wt% of alumina. The catalyst may also comprise silica. In one or more embodiments, the catalyst comprises 0.1 to 10 wt% of silica, or from 1 to 5 wt% of silica. Without being bound by theory, the alumina may act as a binder for the catalyst.

[0038] For example and not by way of limitation, the clay comprises one or more components selected from kaolin, montmorilonite, halloysite, and bentonite. In specific embodiments, the clay comprises kaolin. In one or more embodiments, the catalyst may comprise 30 to 70 wt% of clay, or 40 to 60 wt% of clay.

[0039] In one or more embodiments, the catalyst may comprise the nano ZSM-5 catalyst, USY catalyst, alumina, clay, and silica. In further embodiments, the catalyst comprises from 10 to 50 wt% of nano ZSM-5 catalyst, 10 to 50 wt% of USY catalyst, 2 to 20 wt% of alumina, 30 to 70 wt % of clay, and 0.1 to 10 wt % of silica. Moreover, the catalyst may comprise from 15 to 25 wt% of nano ZSM-5 catalyst, 15 to 25 wt% of USY catalyst, 5 to 15 wt% of alumina, 40 to 60 wt % of clay, and 1 to 5 wt % of silica.

[0040] EXAMPLES

[0041] The following examples illustrate one or more additional features of the present disclosure described previously.

[0042] All chemicals and solvents used in the studies are shown in Table 1.

Table 1: Chemicals and Solvents

Chemical	**Supplier**
Ludox TM40 colloidal silica (SiO_2)	DuPont
Tetrapropylammonium hydroxide (TPAOH, $C_{12}H_{28}NOH$), 40% w/w	Alfa Aesar
Sodium hydroxide (NaOH)	Sigma Aldrich
Aluminum isopropoxide ($Al(O\text{-}I\text{-}Pr)_3$)	Sigma Aldrich
Y zeolite (CBV-780)	Zeolyst International
Formic acid	Sigma Aldrich
Clay	Petrobras
Alumina, Pural SB Grade	Petrobras
Diammonium hydrogen phosphate	Sigma Aldrich
Lanthanum Nitrate (III) hydrate	Fluka

[0043] The main properties of Khuff Gas Condensate (KGC) utilized in the examples are shown in Table 2 as follows.

[0044] Table 2: KGC Properties

Property	**Petroleum Condensate-1**
Density @15°C, gm/cc	0.7695
Carbon residue (MCR), wt%	0.03
Sulfur, ppm	271
Hydrogen content, wt%	14.1
Metals, ppb	
V	< 20
Ni	< 20
Fe	< 20
Na	50
PONA Analysis, wt%	
Paraffins	63.9
Olefins	0
Naphthenes	21.3
Aromatics	14.8
TBP analysis, wt% /°C	
5 / 10 / 30 /	24 / 57 / 112 /
50 / 80 / FBP	163 / 273 / 478

[0045] Catalyst Preparation Procedure

[0046] *ZSM-5 Zeolite Synthesis*

[0047] The details for the synthesis of a micron size ZSM-5 zeolites with Si-to-Al molar ratio of 100 are shown in Table 3 as follows. The details for the synthesis of nano ZSM-5 zeolites having Si-to-Al ratios of 20 and 33 are shown in Table 4 and Table 5, respectively. The precursor synthesis solutions were prepared by mixing all components and reagents together and stirring them for one day at room temperature. The mixture was then transferred into Teflon lined stainless steel autoclaves and heated to 140 °C for 4 days. After that, the solutions were centrifuged and the solid products were collected. The solid products were then dispersed in deionized water, centrifuged to obtain the final products which were then dried in the oven at 80 °C. The products were calcined using the following program. Using a heating rate of 3 °C/min the products were maintained at 200 °C for two hours and at 550 °C for 8 hours. The micron sized ZSM-5 were produced with a particle diameter of 1.1 µm, while the nano-ZSM-5 zeolites were produced with a particle size of 0.07 µm for a Si-to-Al molar ratio of 20 in one example, and a particle size of 0.084 µm for a Si-to-Al molar ratio of 33 in a second example.

[0048] Table 3: Completed synthesis solution compositions, synthesis details, yield, and phase selectivity for nano-ZSM-5 zeolites having Si-to-Al molar ratio of 100.

Sample	Synthesis Conditions				Synthesis Sol. Composition (mole/mole)					Yield	Product
	Heating Time (h)	Heating Temp. (°C)	Synthesis Solution Mass (g)	Rotation	H_2O	Ludox TM40	NaOH	TPAOH	Al(O-I-Pr)$_3$		
SAZ-10	120	140	40	static	20	1	0	0.250	0.01	4.82	MFI
SAZ-11										4.78	
SAZ-12										4.78	

[0049] Table 4: Completed synthesis solution compositions, synthesis details, yield, and phase selectivity for nano ZSM-5 zeolites having Si-to-Al molar ratio of 20.

Sample	Synthesis Conditions				Synthesis Sol. Composition (mole/mole)					Yield	Product
	Heating Time (h)	Heating Temp. (°C)	Synthesis Solution Mass (g)	Rotation	H_2O	Ludox TM40	NaOH	TPAOH	Al(O-I-Pr)$_3$		
SAZ-25	120	140	40	dynamic	20	1	0.2	0	0.050	4.54	MFI
SAZ-26										4.53	
SAZ-27										4.51	
SAZ-28										4.31	

[0050] Table 5: Completed synthesis solution compositions, synthesis details, yield, and phase selectivity for nano ZSM-5 zeolites having Si-to-Al molar ratio of 33.

Sample	Synthesis Conditions				Synthesis Sol. Composition (mole/mole)					Yield	Product
	Heating Time (h)	Heating Temp. (°C)	Synthesis Solution Mass (g)	Rotation	H_2O	Ludox TM40	NaOH	TPAOH	Al(O-I-Pr)$_3$		
SAZ-21	96	140	40	dynamic	20	1	0.1	0.250	0.030	2.14	MFI
SAZ-22										4.44	
SAZ-23										4.61	
SAZ-24										4.61	

[0051] ***Modification of Nano-ZSM-5 Zeolites and the Production of the Final Catalyst Formulation***

[0052] The following procedure was aimed at producing a catalyst formulation with the compositions reported in Table 6 as follows.

[0053] Table 6: Catalyst composition for in-house made HSFCC catalyst.

Component	Weight %	Notes
ZSM-5	20	Phosphorus impregnated at 7.5 wt% P_2O_5 on zeolite
USY	21	Lanthanum impregnated at 2.5 wt% La_2O_3 on zeolite
Alumina	8	Pural SB from Sasol
Clay	49	Kaolin
Silica	2	Added as colloidal silica Ludox TM-40

ZSM-5 zeolites were impregnated with phosphorous and Y zeolites were impregnated with lanthanum. The impregnated zeolites were mixed with alumina binder, silica and clay and were stirred for 1 hour. The obtained slurry was placed in temperature programmed oven for drying and calcination as per the following program: (rate(°C/min):Temperature(°C):time(hrs))

$$7{:}125{:}7 \rightarrow 3{:}200{:}1 \rightarrow 2{:}320{:}1 \rightarrow 2{:}440{:}7 \rightarrow 1{:}500{:}1 \rightarrow 7{:}100{:}1$$

[0054] The calcined catalyst was grounded to a fine powder by means of a mortar and a pestle. Then, the grounded catalyst was sieved for a fraction between 40-120 μm and used for characterization and evaluation.

[0055] The reactions were conducted in a Sakuragi Rikagaku (Japan) Micro Activity Test (MAT) instrument using a quartz tubular reactor. The synthesized catalysts were evaluated for cracking Khuff gas condensate according to ASTM D-3907 method. All catalysts were steamed at 750 ºC for 3 h prior to the reaction. The experiments were conducted in the MAT unit at 30 s time-on-stream (TOS). After each reaction, catalysts were stripped using 30 mL/min N_2 flow. The liquid product was collected in the liquid receiver and the gaseous products were collected in a gas burette by water displacement and sent to the gas chromatograph (GC) for analysis. The spent catalysts were used to measure the amount of generated coke from the reaction.

[0056] The MAT results from the micro and nano-ZSM-5 based catalysts are shown in Table 7. As can be seen, high propylene yields of greater than 18 wt% were obtained for the three catalysts. The nano-ZSM-5 having Si-to-Al molar ratio of 33 achieved the highest propylene yield of 21.12 wt% compared to 20.07 wt% propylene yield obtained with the nano-ZSM-5 having Si-to-Al molar ratio of 20. The micron sized ZSM-5 achieved the lowest propylene yield of 18.78 wt% which signifies the role of the higher surface area provided by the nano ZSM-5 zeolites for the selective production of light olefins.

[0057] Table 7: Highlight from MAT results of in-house prepared nano-ZSM-5 based catalyst

Catalyst	**Micro-ZSM-5 (Si-to-Al=100)**	**Nano-ZSM-5 (Si-to-Al=33)**	**Nano-ZSM-5 (Si-to-Al=20)**
Temp. (°C)	650	650	650
T.O.S.(s)	30	30	30
Steaming	750C, 3h	750C, 3h	750, 3h
Feed	KGC	KGC	KGC
Catalyst/KGC	8.14	8.21	8.39
Yield (mass%)			
C2=	8.95	10.97	9.39
C3=	18.78	21.12	20.07
Total Gas	56.96	58.66	59.50
Gasoline	36.83	36.51	33.06
Light Cycle Oil (LCO)	2.01	2.01	2.78
Heavy Cycle Oil (HCO)	0.91	0.64	0.71

Catalyst	**Micro-ZSM-5 (Si-to-Al=100)**	**Nano-ZSM-5 (Si-to-Al=33)**	**Nano-ZSM-5 (Si-to-Al=20)**
Coke	3.29	2.17	3.95
Total	100	100.00	100.00

[0058] *Characterization of nano-ZSM-5 zeolites*

[0059] The synthesized MFI-type zeolites with organic and organic-inorganic structure directing agents were examined by X-ray Diffraction (XRD) technique and the acquired data revealed an exact match with the diffraction pattern of MFI type zeolite structure as shown in FIGS. 2A and 2B.

[0060] Moreover, the XRD was also used to develop a phase envelope where $[AlO_2/4]/[SiO_2/4]$ was plotted along the ordinate while $NaOH/[SiO_2/4]$ was plotted along the abscissa as presented in FIG. 3. The diagram determined that the MFI-type zeolite is only formed in a small region in the phase space. Solutions with relatively low concentrations of the sodium hydroxide (i.e., Si / Na ~ 5) and aluminum (i.e., Si / Al ~ 25) were found to lead to pure MFI-type products. Lower concentrations of the sodium hydroxide and alumina were observed to give some mixed phase products that included unknowns and relatively important concentrations of amorphous phases as shown in FIG. 3.

[0061] The obtained ESEM micrographs in FIGS. 4A and 4B were used to measure the particle size and to determine the surface morphologies of the synthesized samples. Selected samples were analyzed to indicate whether the produced MFI zeolites were nano-sized particles or micro-sized particles as shown in FIGS 4A and 4B. The average particles size measurements for the selected samples are listed in Table 8.

[0062] Table 8: BET measurement of ZSM-5 zeolite.

Sample	**Zeolite**	**Size Characteristic**	**Surface Area (cm^2/g)**	**Particle Diameter (μm)**
SAZ-11	MFI	Micronsized Particles	3	1.1
SAZ-21	MFI	Nanoparticles	40	0.084
SAZ-24	MFI	Nanoparticles	40	0.084
SAZ-28	MFI	Nanoparticles	48	0.07

[0063] The thermogravimetric (TGA) analysis of any newly synthesized zeolites is an important characterization as the catalysts have to withstand a temperature range of 500-750 °C typical for the HSFCC process. The water and tetrapropylammonium (TPA+) content of the synthesized zeolites were calculated from the weight loss upon heating. The weight loss between 25-200 °C was attributed to water content desorbing from the zeolite. It was observed that the water desorbed between 25-200 °C was proportional to sodium content in the zeolite. In contrast, the more TPA+ in the sample, the less water desorbed from the sample in the heating process. This is due to the fact that the TPA+ is relatively large as compared to sodium ions. The TPA+ has hydrophobic properties that prevent the water molecules from adsorbing inside the zeolite samples. Moreover, the TPA+ fills the majority of the microspores leaving no space for water to attach to the zeolites (*See* Table 9).

[0064] At higher temperatures, between 200-550 °C, the TPA+ converts to tripropylammonia and releases a propylene molecule. This gives rise to the weight loss, which is presented in FIGS. 5A and 5B. From TGA traces, the number of TPA atoms per unit cell can be calculated assuming no defect in the unit cell structure. An ideal MFI-type zeolite that is defect-free has the following molecular formula ($|TPAn|[Al_nSi_{96}\text{-}nO_{182}]$). Therefore, the number of TPA+ can be calculated using weight loss fraction and the molecular formula of MFI-type type zeolite as shown in Table 9.

[0065] Table 9: TGA analysis of ZSM-5 zeolites synthesized with different Na and Al concentrations.

Sample content		Weight fraction Loss Between 0 and 200 °C	Weight Loss Between 200 and 550 °C	Total Wight loss	Number of TPA^+ Molecules Per 96 TO_2
Al	Na				
0.01	0	0.01	0.126	0.142	4.45
0.03	0.1	0.1074	0.1029	0.2129	3.54
0.05	0.2	0.1163	0.0952	0.2148	3.255

[0066] Referring to FIGS. 6A and 6B, temperature programmed desorption curves of high silicate sample and low silicate sample (high alumina) were collected. The mass to charge curves of 16, 17, and 18 corresponds to NH_2+, NH_3+, H_2O+ ions, respectively. The high silica sample exhibited two peaks with different energies. The low energy peak occurred at 109 °C and was attributed to weakly bonded ammonia. This low energy (low temperature) peak suggests the presence of silanol groups to which the ammonia was physisorbed. The peak at 350 °C was a high energy peak which represented strongly bonded ammonia into the strong Brønsted acid sites. A signal was observed between 200-500 °C that was split into two peaks at 225 °C and 400 °C for the high alumina samples. These peaks were higher in energy than the peaks detected for the high silica sample. They were assigned to Brønsted active sites present in the catalyst, which may give better cracking as more active sites are present. In conclusion, the presence of more alumina in the sample gave rise to peaks at higher temperature which were assigned to more Brønsted acid sites and less silanol groups bound to ammonia.

[0067] ***Characterization of Y zeolites***

[0068] As stated previously, USY zeolite impregnation with lanthanum impacts the selectivity towards light olefins. That being said, the ESEM analysis of both parent and impregnated Y zeolites, shown in FIGS 7A and 8A, respectively, revealed no changes in the topographical features of the parent zeolites. On the other hand, the elemental analysis using EDS detector integrated within the ESEM indicated that the zeolite samples were mainly composed of silicon, aluminum, and oxygen in addition to lanthanum for the impregnated Y zeolite shown in FIG. 8B.

[0069] As shown in FIG. 9, an XRD analysis was used to investigate the effects of lanthanum impregnation on the crystallography structure of the parent Y zeolite. The produced diffractograms of both parent and impregnated forms of zeolites were identical, thus indicating no effect on crystal structure as shown in FIG. 9. Moreover, the surface area and pore volume analysis (See Table 10) revealed there was negligible difference between the Y zeolite and its impregnated form.

[0070] Table 10: BET measurements of Y zeolite.

	Surface area	**Pore volume**
Y zeolite	774	0.486
La-impregnated Y zeolite	774	0.482

[0071] It should be apparent to those skilled in the art that various modifications and variations can be made to the described embodiments without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various described embodiments provided such modification and variations come within the scope of the appended claims and their equivalents.

CLAIMS

1. A method of converting gas condensate into a product stream comprising propylene, the method comprising:

feeding gas condensate at a top region of a downflow high severity fluidized catalytic cracking reactor (HSFCC), the gas condensate comprising at least 50% by weight paraffins;

feeding catalyst to the top region of the downflow HSFCC reactor in an amount characterized by a catalyst to gas condensate weight ratio of about 5:1 to about 40:1, where the catalyst comprises nano ZSM-5 zeolite catalyst having an average particle diameter from 0.01 to 0.2 µm, a Si/Al molar ratio from 20 to 40, and a surface area of at least 20 cm^2/g; and

cracking the gas condensate in the presence of the catalyst at a reaction temperature of about 500° C to about 700° C to produce the product stream comprising propylene.

2. The method of claim 1 further comprising adding steam to the top region of the downflow HSFCC reactor.

3. The method of any preceding claim, where the cracking occurs at a pressure of about 1 to 2 atm to produce the product stream comprising propylene.

4. The method of any preceding claim, where the gas condensate comprises less than 0.1% by weight olefins.

5. The method of any preceding claim, where the Si/Al atomic ratio is from 25 to 35.

6. The method of any preceding claim, where the product stream comprises at least a 20 wt% yield of propylene.

7. The method of any preceding claim, where the product stream comprises at least a 10 wt% yield of ethylene.

8. The method of any preceding claim, where the nano ZSM-5 catalyst is impregnated with phosphorus.

9. The method of any preceding claim, where the catalyst comprises 10 to 50 wt% of nano ZSM-5 catalyst.

10. The method of any preceding claim, where the catalyst comprises USY (Ultrastable Y zeolite).

11. The method of claim 10, where the USY catalyst is impregnated with lanthanum.

12. The method of any preceding claim, where the catalyst comprises 10 to 50 wt% of USY catalyst.

13. The method of any preceding claim, where the catalyst comprises one or more of alumina, clay, and silica.

14. The method of claim 13, where the clay comprises one or more components selected from kaolin, montmorilonite, halloysite, and bentonite.

15. The method of any preceding claim, where the catalyst comprises 30 to 70 wt% of clay.

16. The method of any preceding claim, where the catalyst comprises 2 to 20 wt% of alumina.

17. The method of any preceding claim, where the catalyst comprises 0.1 to 10 wt% of silica.

18. The method of any preceding claim, where the reaction temperature is about 550° C. to about 630° C.

19. The method of any preceding claim, where the gas condensate has a residence time in the downflow fluidized catalytic cracking reactor of 0.7 seconds to 10 seconds.

20. The method of any preceding claim, where the catalyst to gas condensate ratio is 5:1 to about 10:1.

21. The method of any preceding claim, where the catalyst comprises the nano ZSM-5 catalyst, USY catalyst, alumina, clay, and silica.

22. The method of any preceding claim, where the catalyst comprises from 10 to 50 wt% of nano ZSM-5 catalyst, 10 to 50 wt% of USY catalyst, 2 to 20 wt% of alumina, 30 to 70 wt % of clay, and 0.1 to 10 wt % of silica.

23. The method of any preceding claim, where the gas condensate comprises naphthenes and aromatics.

24. The method of any preceding claim, where the gas condensate comprises 65 wt% paraffins, 0 wt% olefins, 21 wt% naphthenes, and 15 wt% aromatics.

25. The method of any preceding claim, where the gas condensate has an initial boiling point of at least 0 °C and a final boiling point of at least 450 °C when measured according to a true boiling point analysis.

26. The method of any preceding claim, where the nano ZSM-5 zeolites has a surface area of at least 30 cm^2/g.

27. The method of any preceding claim, where the gas condensate has a research octane number (RON) of 70 to 75 according to ASTM 2699 or ASTM 2700.

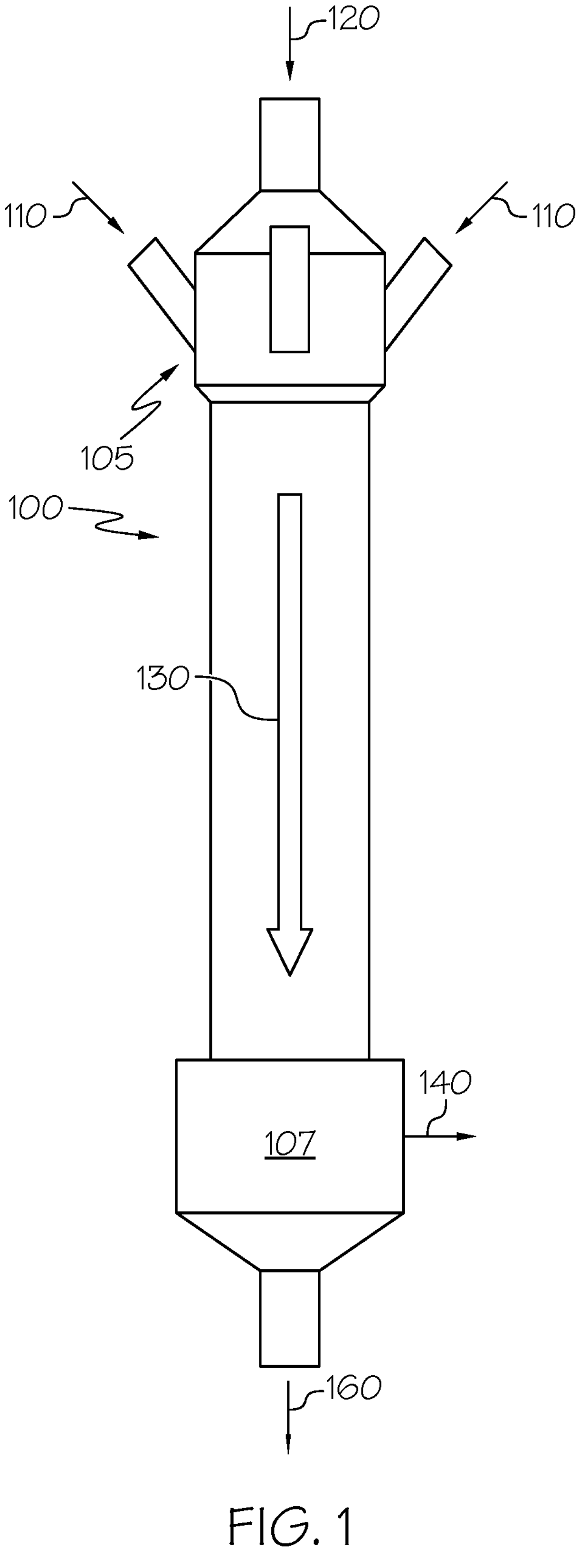

FIG. 1

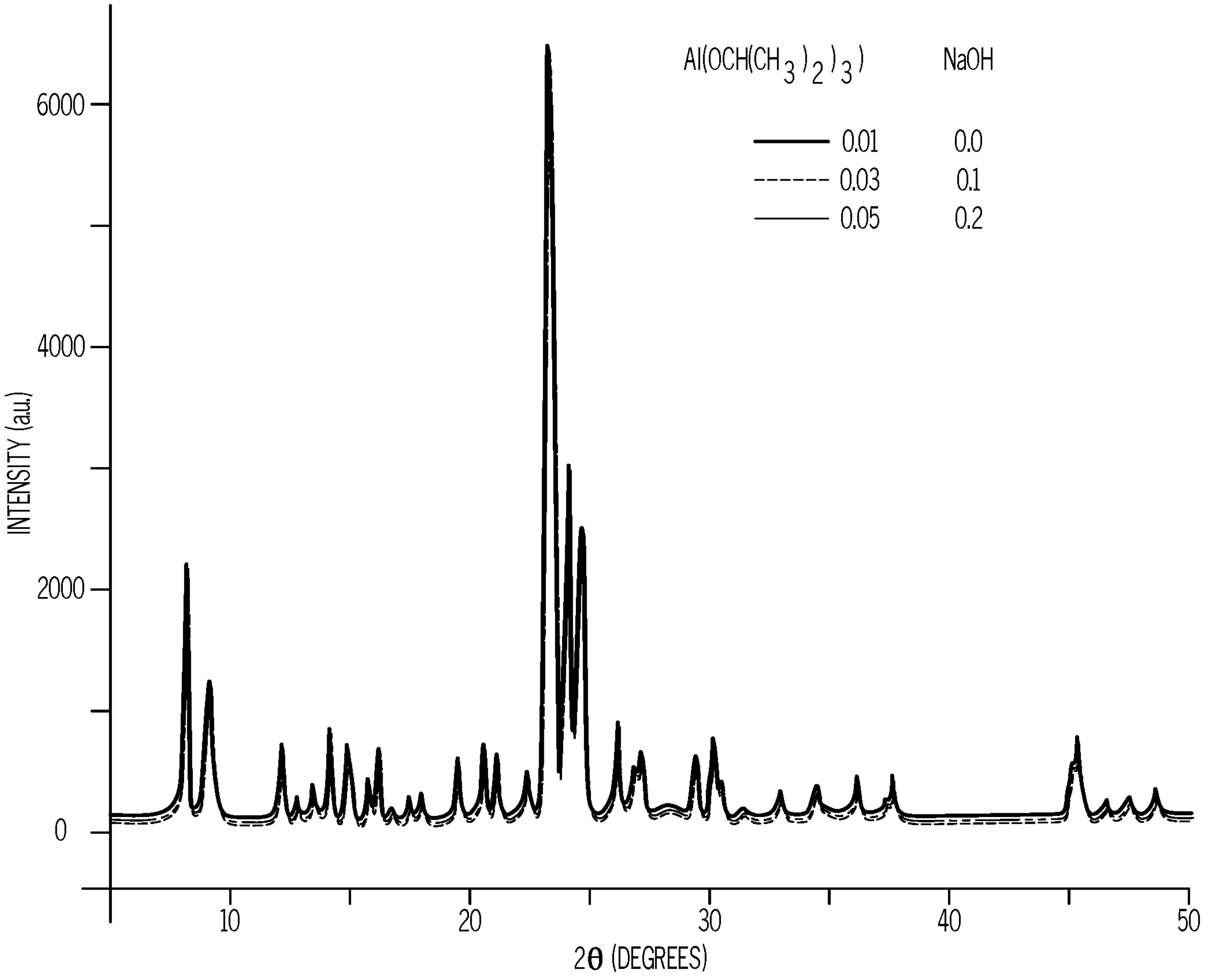
Al(OCH(CH$_3$)$_2$)$_3$)
NaOH
0.01
0.0
0.03
0.1
0.05
0.2
INTENSITY (a.u.)
6000
4000
2000
0
10
20
30
40
50
2θ (DEGREES)

FIG. 2A

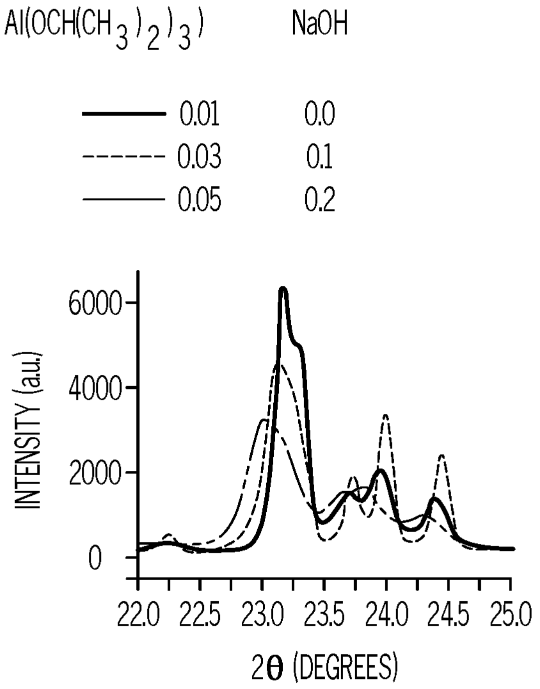
Al(OCH(CH$_3$)$_2$)$_3$)
NaOH
0.01
0.0
0.03
0.1
0.05
0.2
INTENSITY (a.u.)
6000
4000
2000
0
22.0
22.5
23.0
23.5
24.0
24.5
25.0
2θ (DEGREES)

FIG. 2B

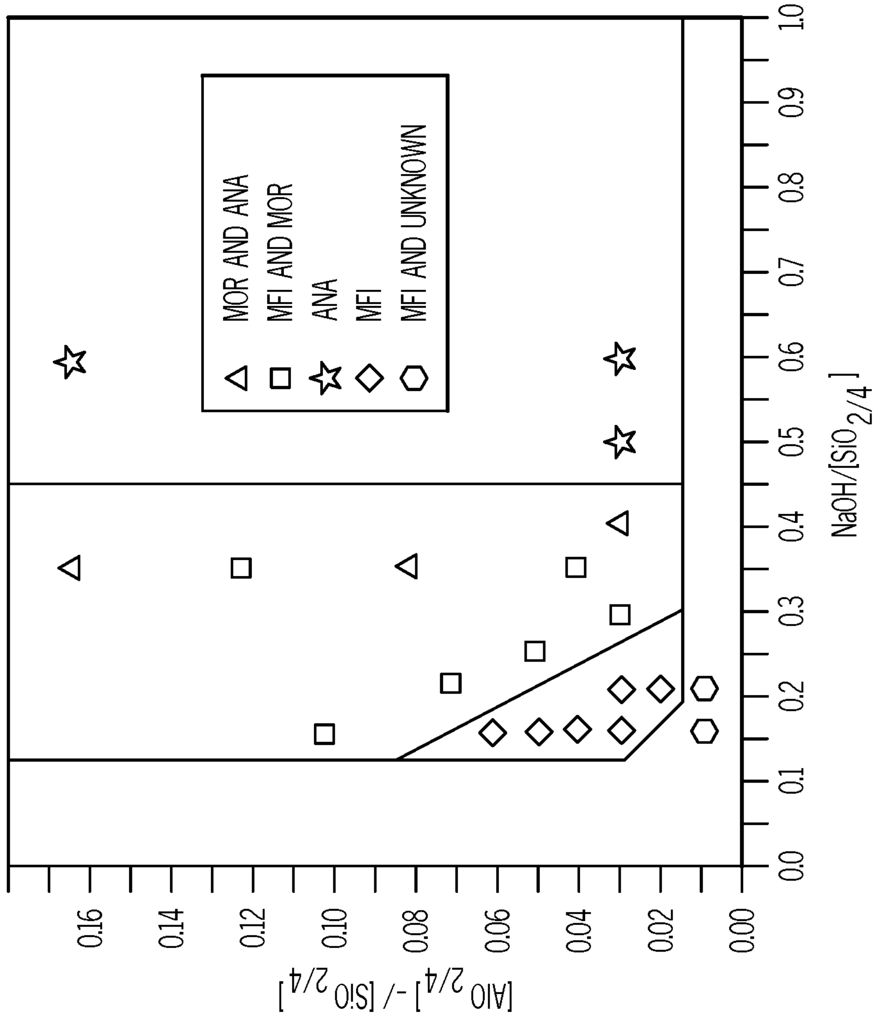
[AlO 2/4] -/ [SiO 2/4]
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
NaOH/[SiO$_{2/4}$]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
△ MOR AND ANA
□ MFI AND MOR
☆ ANA
◇ MFI
⬡ MFI AND UNKNOWN

FIG. 3

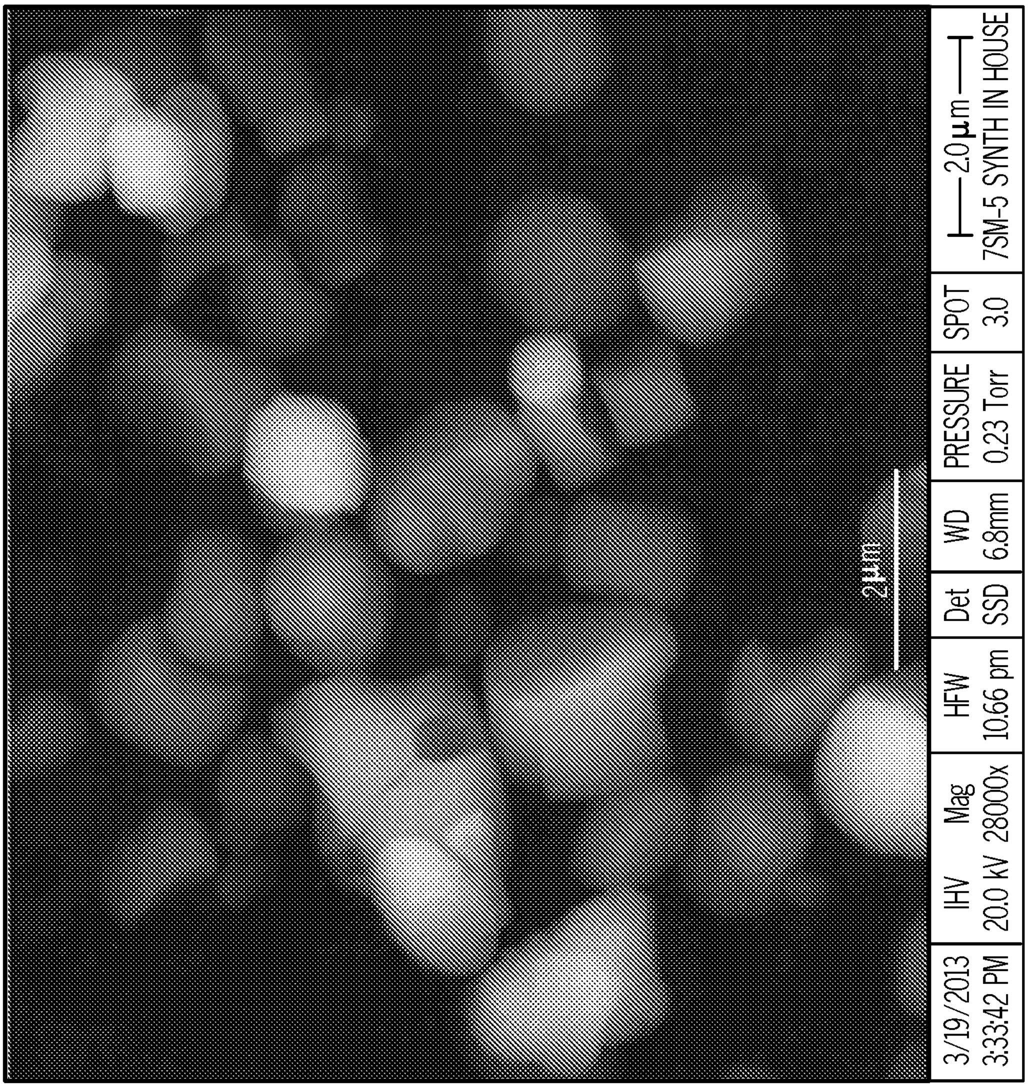
2μm
3/19/2013
3:33:42 PM
IHV
20.0 kV
Mag
28000x
HFW
10.66 pm
Det
SSD
WD
6.8mm
PRESSURE
0.23 Torr
SPOT
3.0
2.0 μm
7SM-5 SYNTH IN HOUSE

FIG. 4A

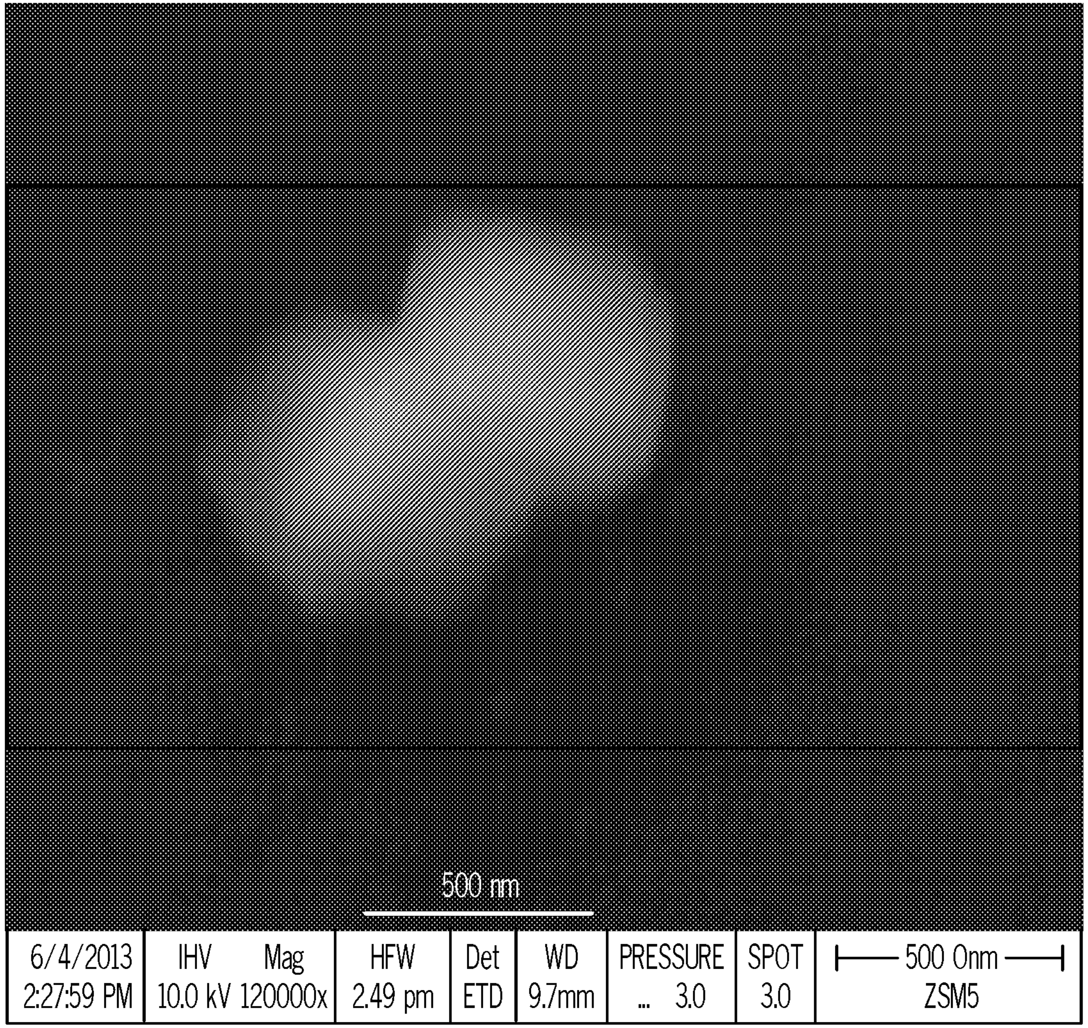
500 nm
6/4/2013
2:27:59 PM
IHV
10.0 kV
Mag
120000x
HFW
2.49 pm
Det
ETD
WD
9.7mm
PRESSURE
... 3.0
SPOT
3.0
500 0nm
ZSM5

FIG. 4B

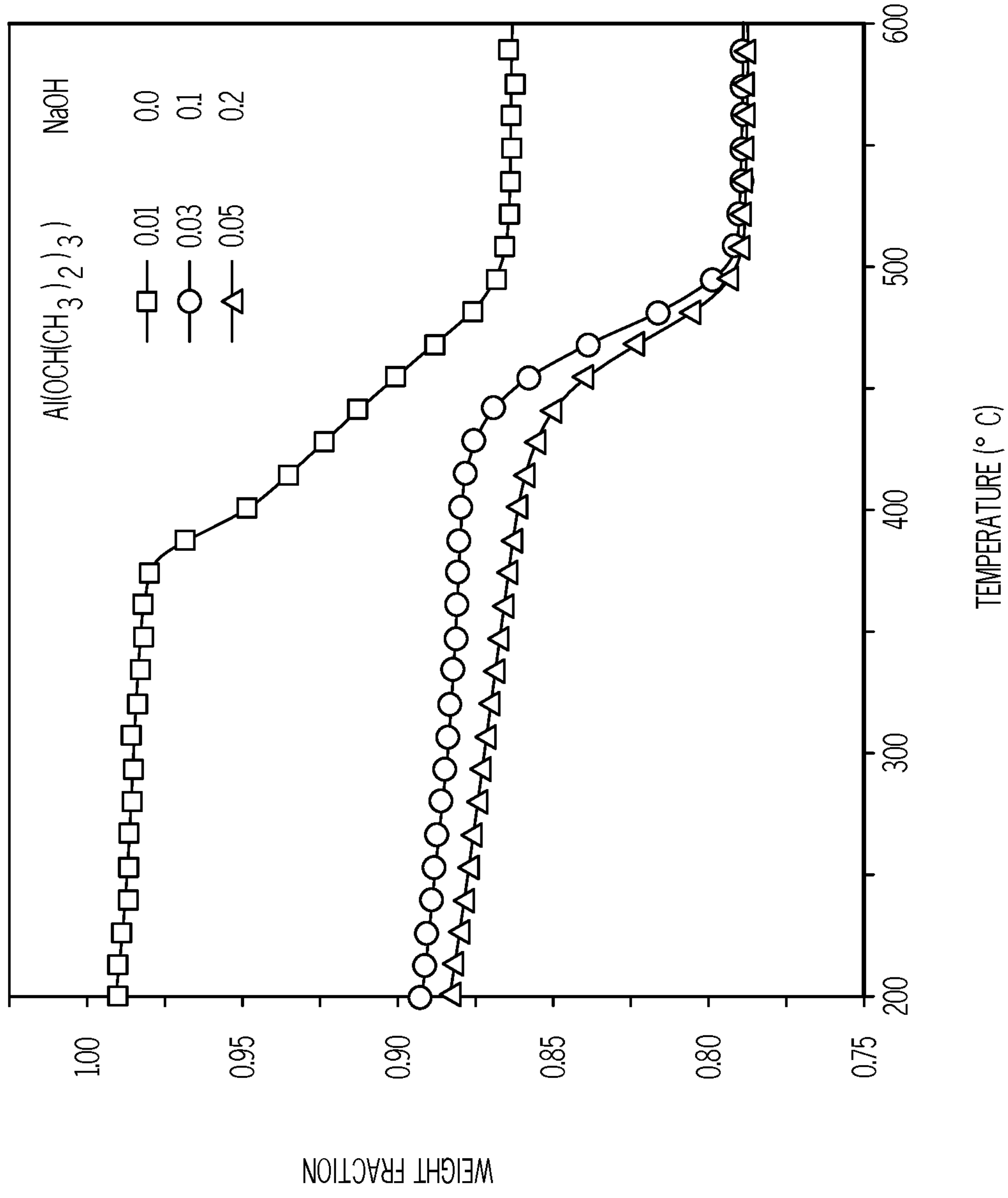
WEIGHT FRACTION
1.00
0.95
0.90
0.85
0.80
0.75
TEMPERATURE (° C)
200
300
400
500
600
Al(OCH(CH$_3$)$_2$)$_3$)
NaOH
0.01
0.03
0.05
0.0
0.1
0.2

FIG. 5A

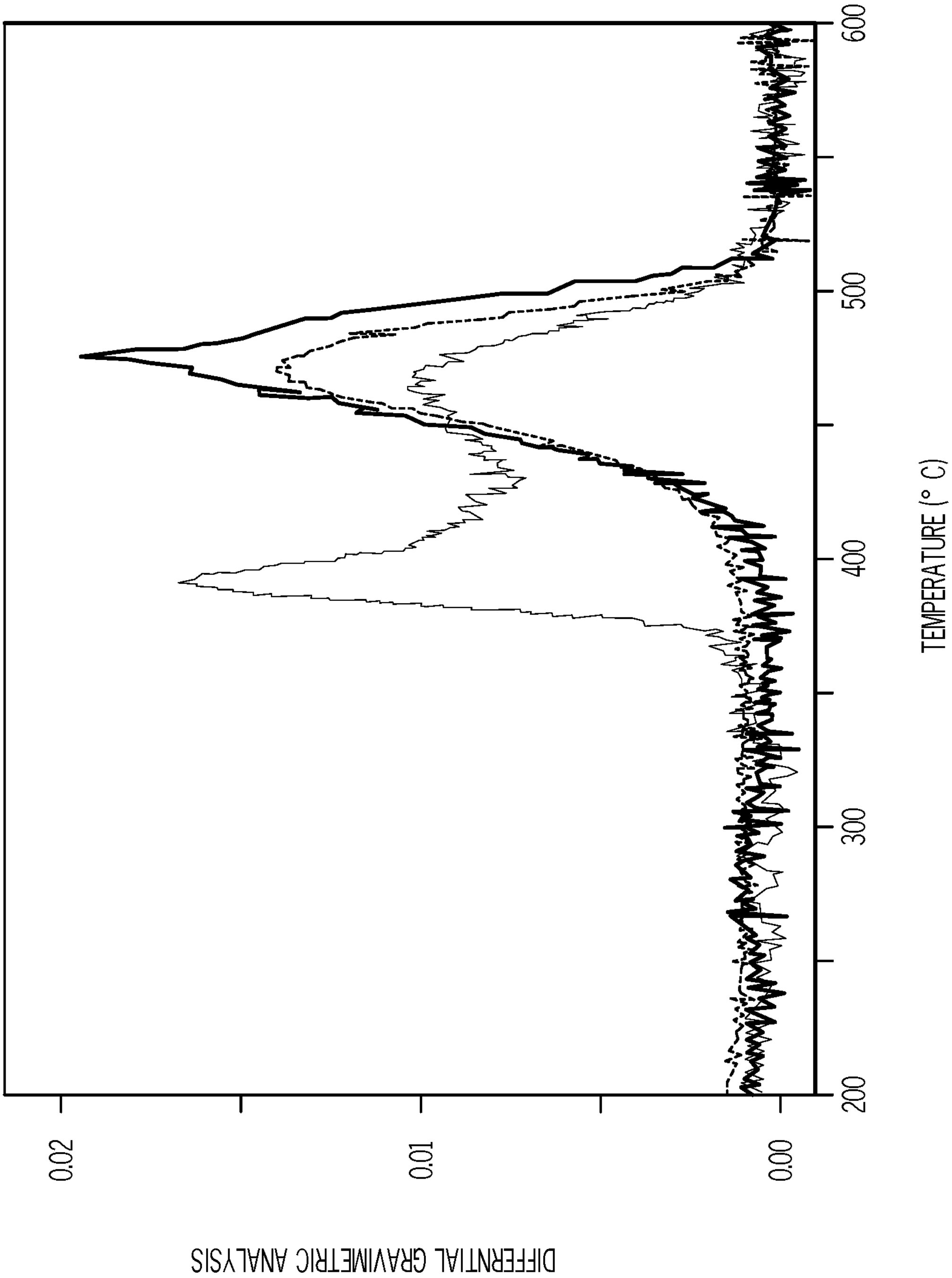
DIFFERNTIAL GRAVIMETRIC ANALYSIS
0.02
0.01
0.00
TEMPERATURE (° C)
200
300
400
500
600

FIG. 5B

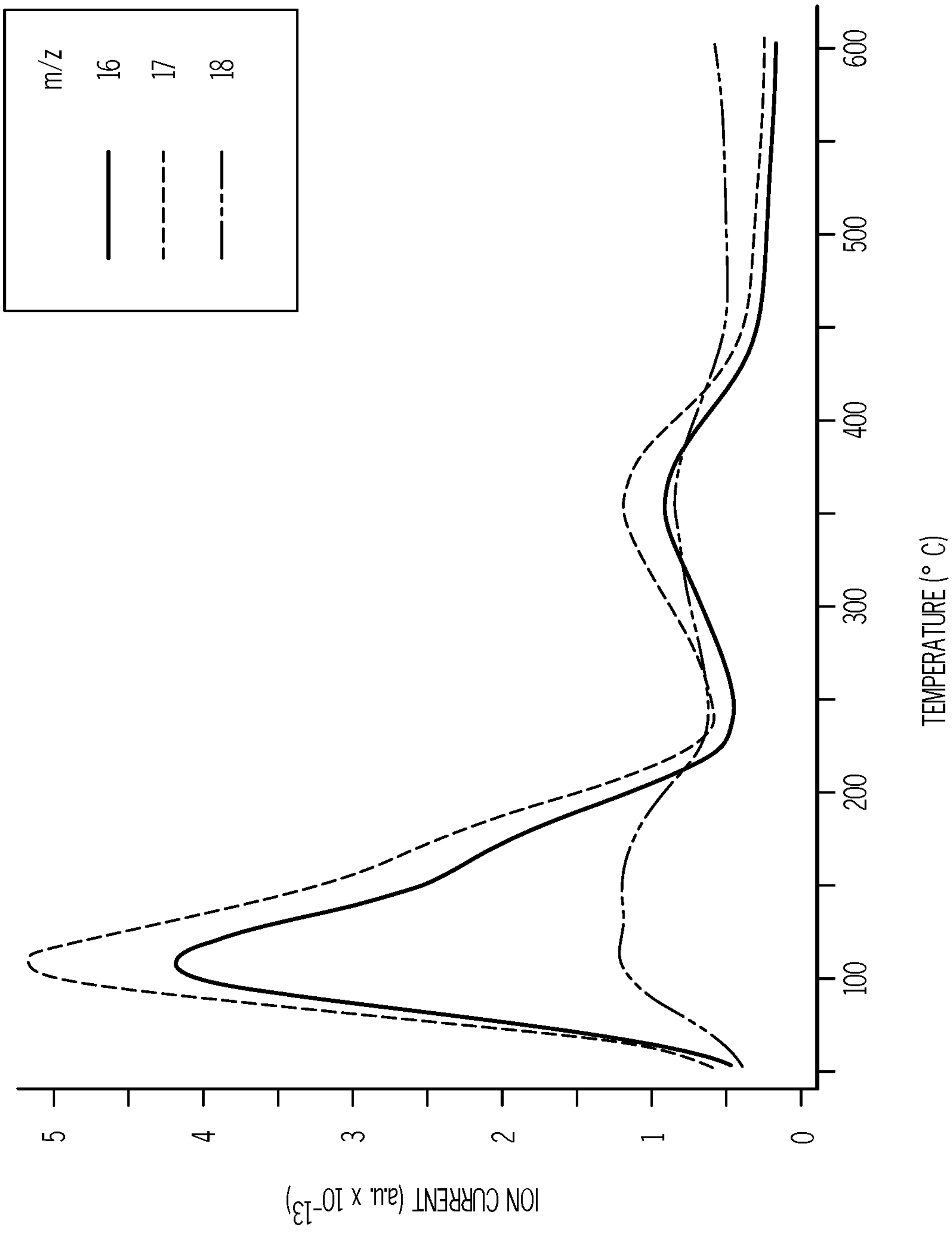
ION CURRENT (a.u. x 10^{-13})
0
1
2
3
4
5
TEMPERATURE (° C)
100
200
300
400
500
600
m/z
16
17
18

FIG. 6A

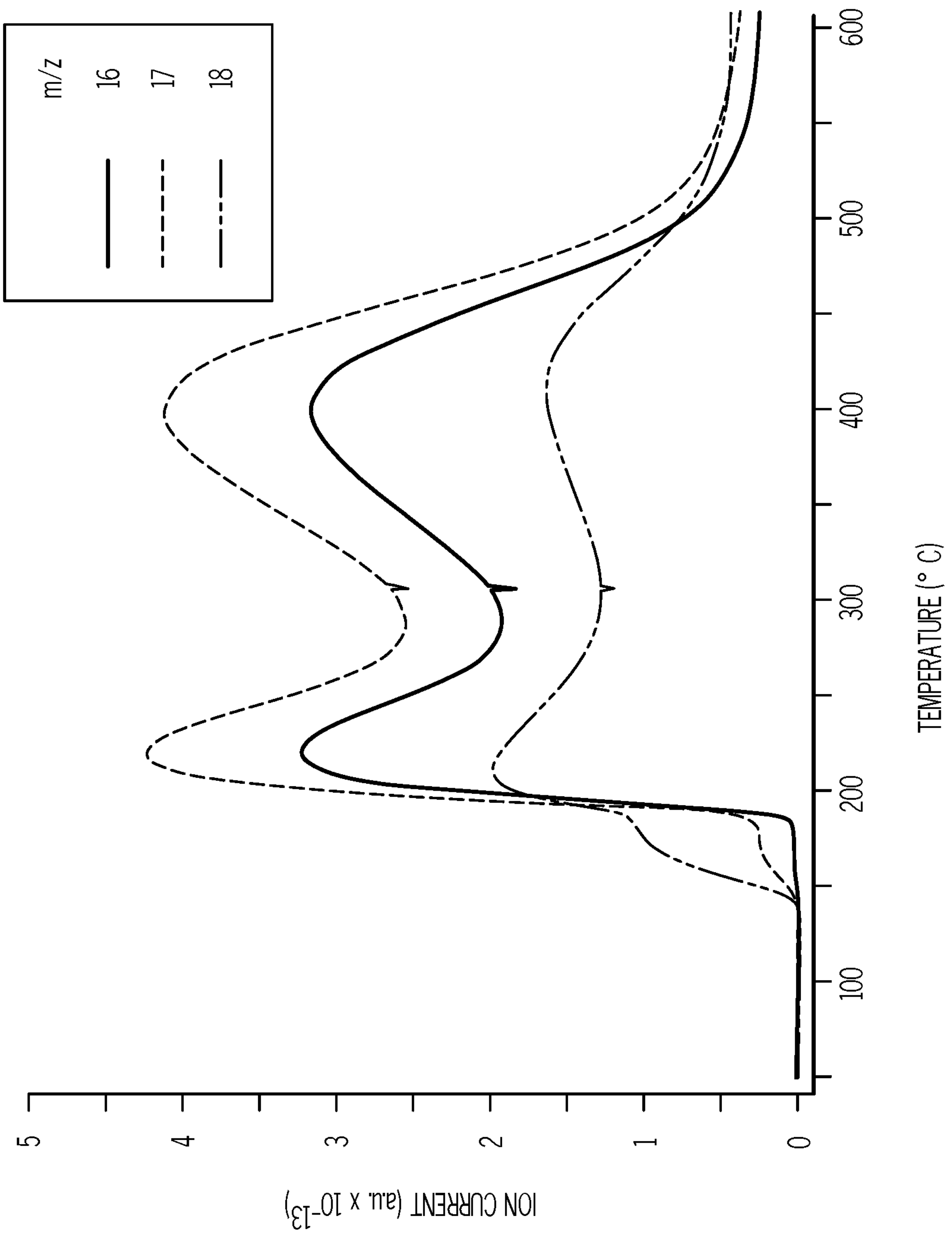
ION CURRENT (a.u. x 10^{-13})
0
1
2
3
4
5
TEMPERATURE (° C)
100
200
300
400
500
600
m/z
16
17
18

FIG. 6B

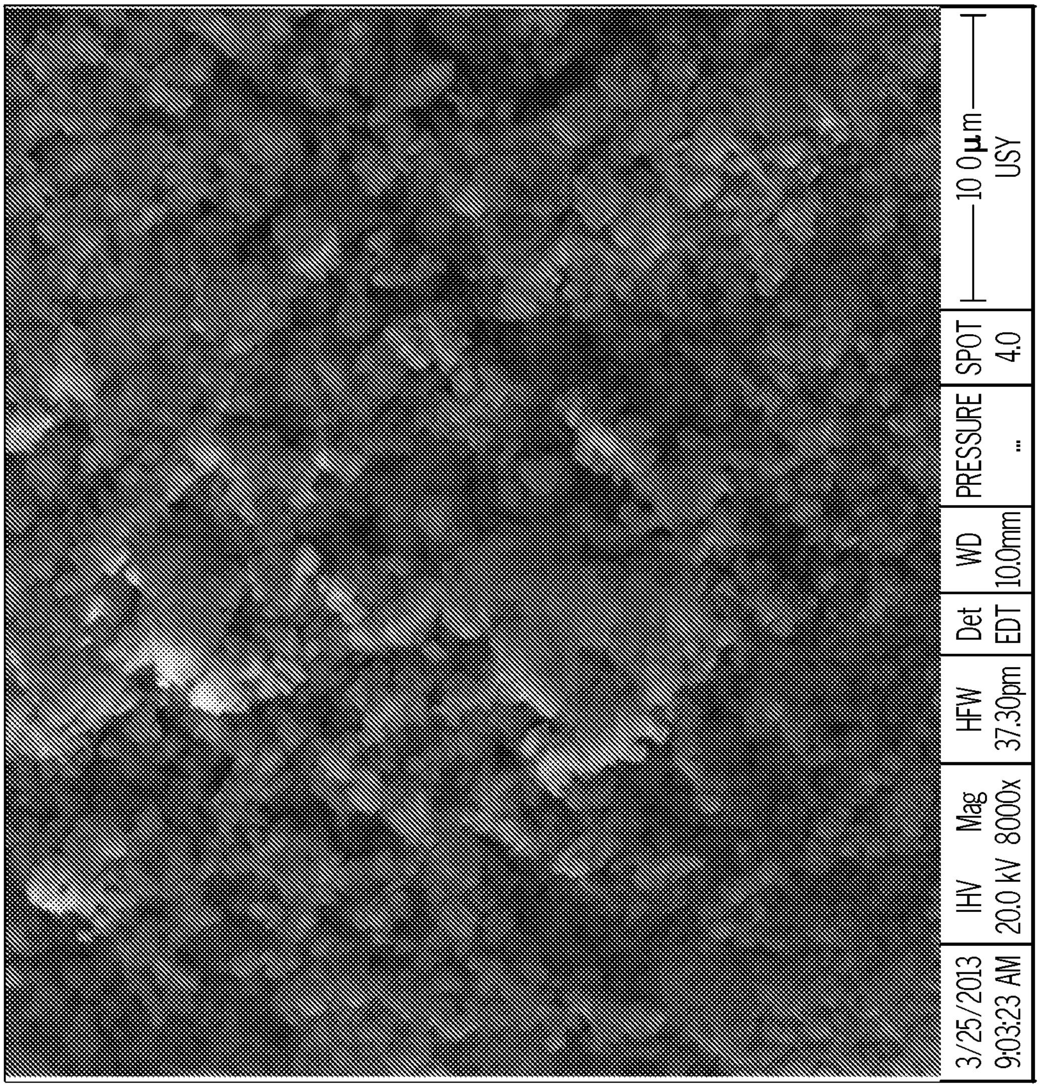
3/25/2013
9:03:23 AM
IHV
20.0 kV
Mag
8000x
HFW
37.30pm
Det
EDT
WD
10.0mm
PRESSURE
...
SPOT
4.0
10 0µm
USY

FIG. 7A

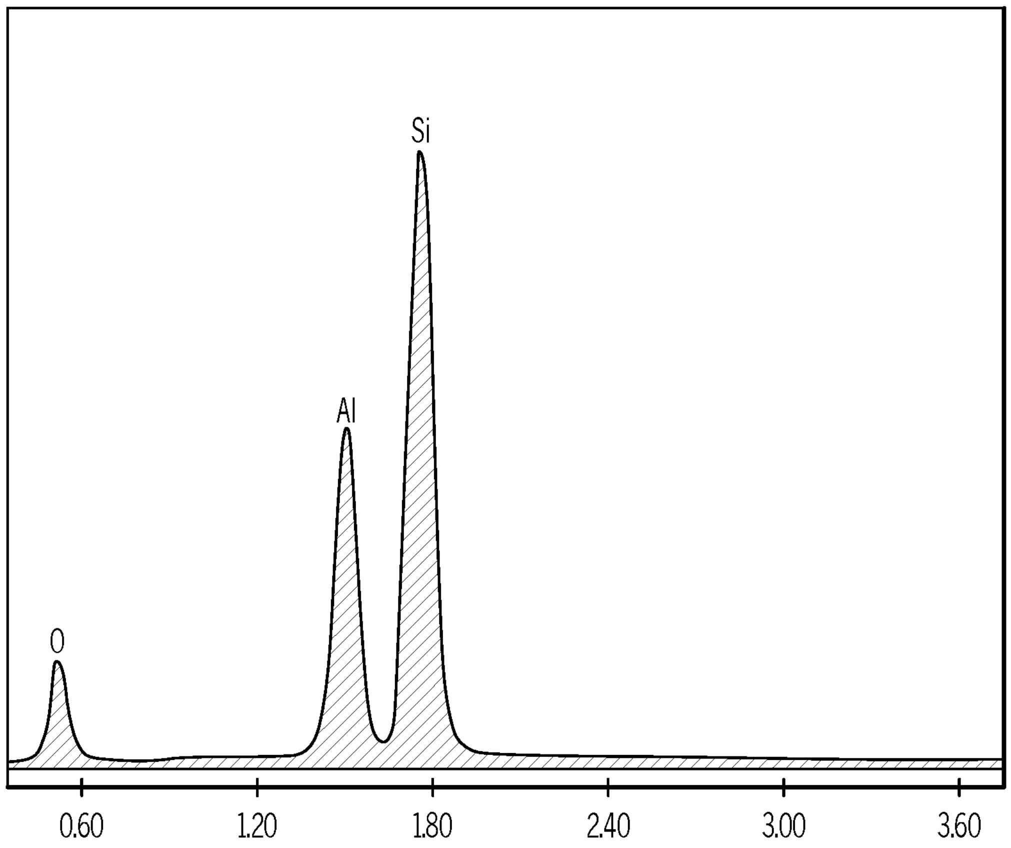

FIG. 7B

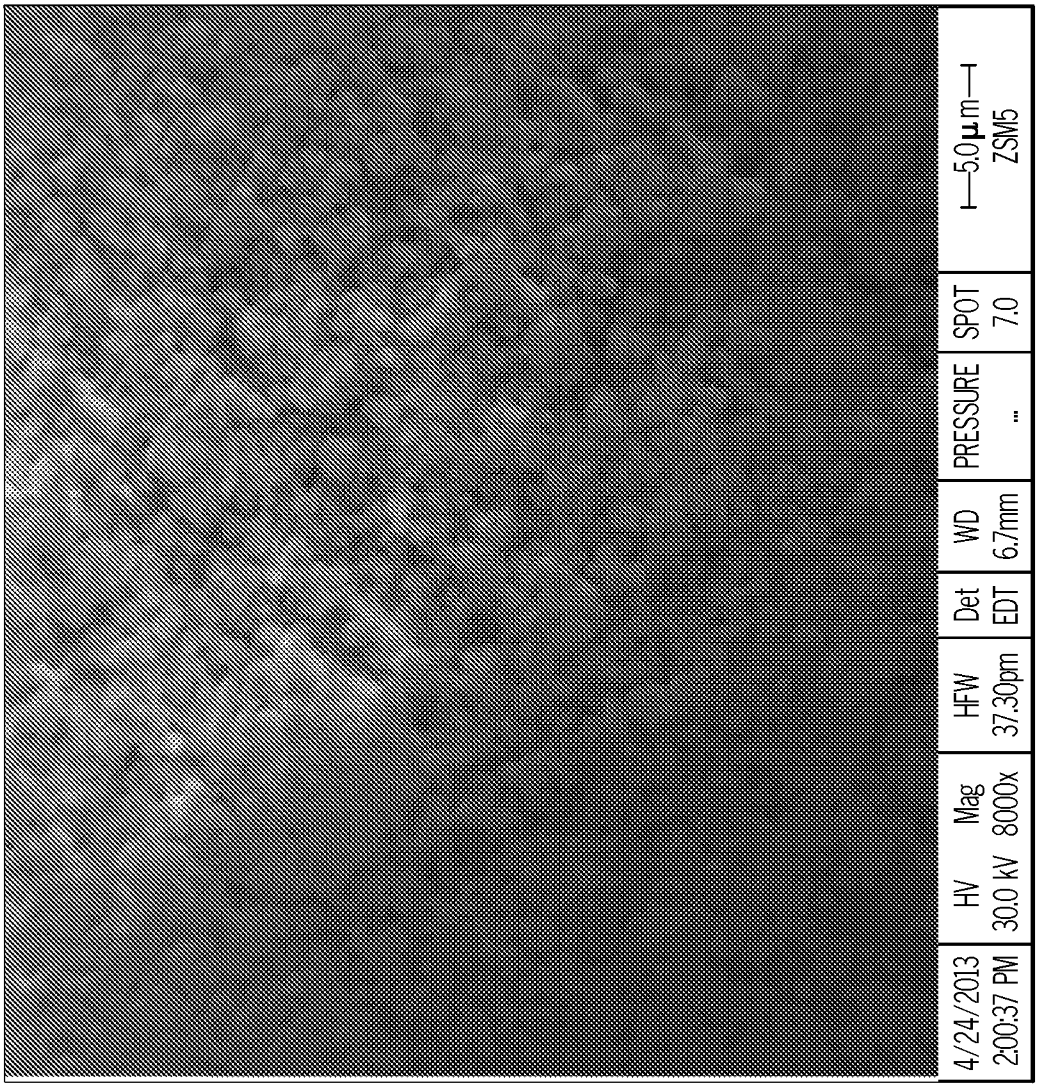
4/24/2013
2:00:37 PM
HV
30.0 kV
Mag
8000x
HFW
37.30pm
Det
EDT
WD
6.7mm
PRESSURE
...
SPOT
7.0
5.0μm
ZSM5

FIG. 8A

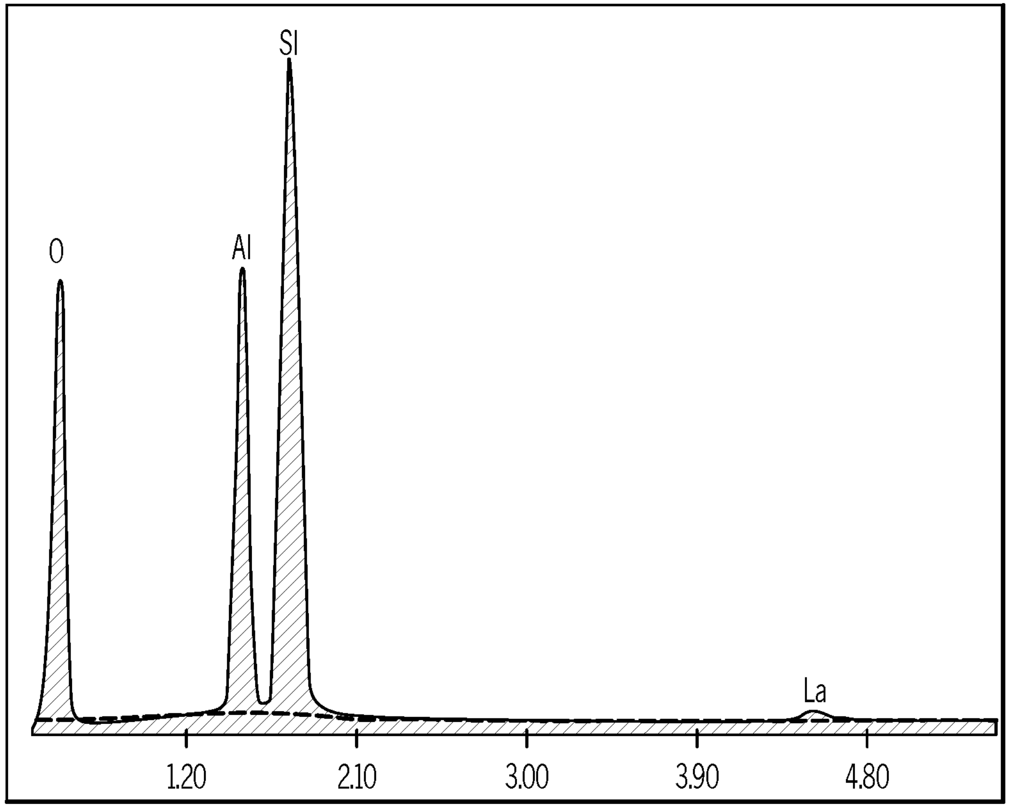

FIG. 8B

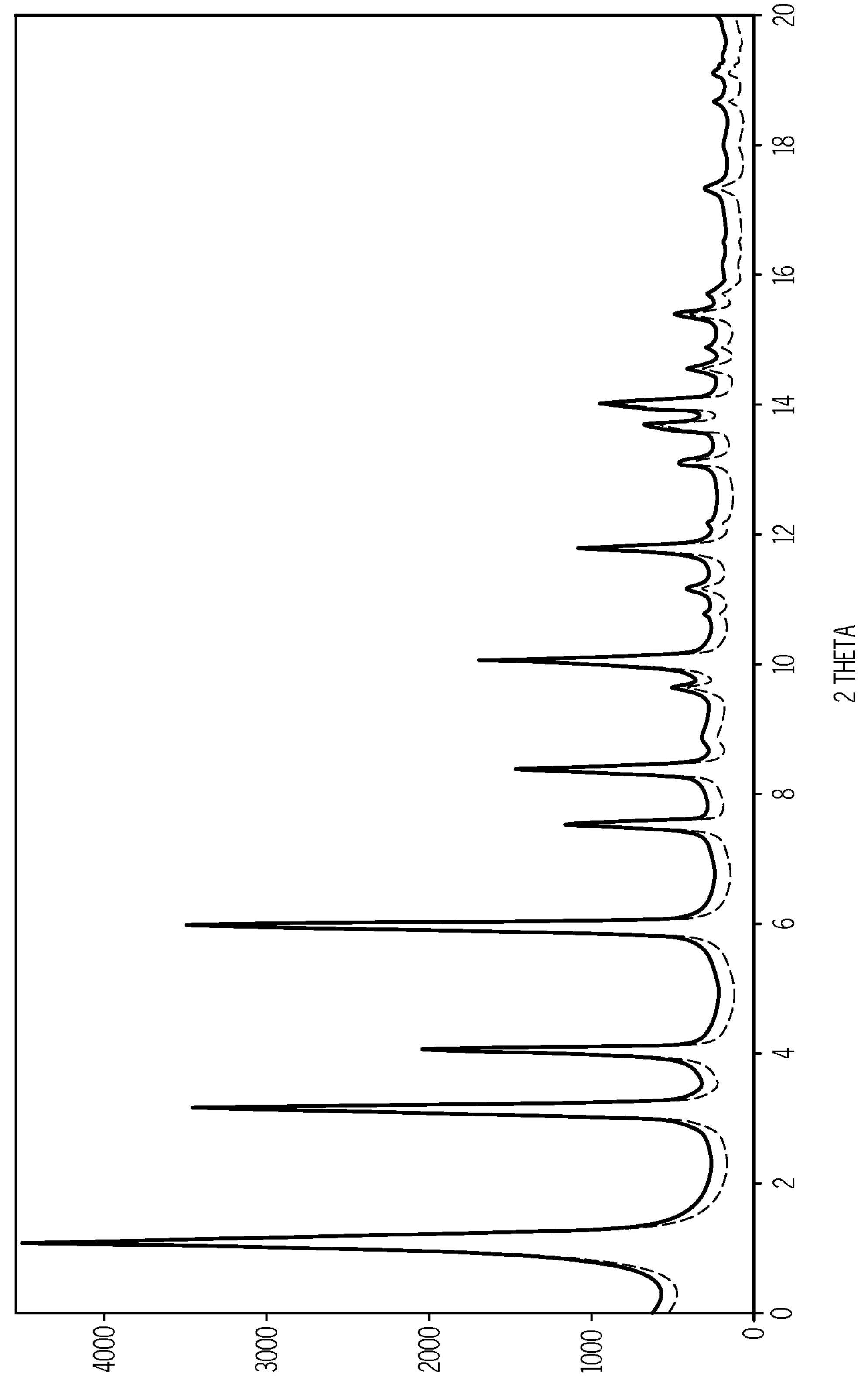

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/038740

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G11/05 C10G11/18 B01J29/40
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/288990 A1 (XIE ZAIKU [CN] ET AL) 26 November 2009 (2009-11-26) claims 1-11 paragraphs [0014], [0015], [0019], [0024] -----	1-27
A	TERUOKI TAGO ET AL: "Size-Controlled Synthesis of Nano-Zeolites and Their Application to Light Olefin Synthesis", CATALYSIS SURVEYS FROM ASIA, KLUWER ACADEMIC PUBLISHERS, DO, vol. 16, no. 3, 15 July 2012 (2012-07-15), pages 148-163, XP035090924, ISSN: 1574-9266, DOI: 10.1007/S10563-012-9141-4 pages 157-159 -----	1-27
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 11 September 2017	Date of mailing of the international search report 22/09/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pardo Torre, J

2

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/038740

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HIROSHI MOCHIZUKI ET AL: "Facile control of crystallite size of ZSM-5 catalyst for cracking of hexane", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER, AMSTERDAM, NL, vol. 145, no. 1, 10 May 2011 (2011-05-10), pages 165-171, XP028261880, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2011.05.011 [retrieved on 2011-05-14] pages 168-169 -----	1-27

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/038740

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009288990 A1	26-11-2009	CN 1915516 A	21-02-2007
		KR 20080035701 A	23-04-2008
		SG 10201506253U A	29-09-2015
		US 2009288990 A1	26-11-2009
		WO 2007019797 A1	22-02-2007