



(51) International Patent Classification:

B01J 20/16 (2006.01) C07C 2/08 (2006.01)

B01J 20/06 (2006.01) C07C 2/10 (2006.01)

B01J 20/02 (2006.01) C07C 2/00 (2006.01)

NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(21) International Application Number:

PCT/US2023/021943

(22) International Filing Date:

11 May 2023 (11.05.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/342,560 16 May 2022 (16.05.2022) US

(71) Applicant: **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 FRANKLIN STREET, TWELFTH FLOOR, OAKLAND, California 94607-5200 (US).

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(72) Inventors; and

(71) Applicants: **SEEMALA, Bhogeswararao** [US/US]; c/o Bourns College of Engineering, UCR, 1084 Columbia Ave, Riverside, California 92507 (US). **WYMAN, Charles E.** [US/US]; c/o Bourns College of Engineering, UCR, 1084 Columbia Ave, Riverside, California 92507 (US).

(74) Agent: **CHOI, Anita** et al.; Morrison & Foerster LLP, 425 Market Street, San Francisco, California 94105 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,

(54) Title: ZEOLITE CATALYSTS AND USE IN ETHANOL OLIGOMERIZATION AND PRODUCTION OF FUELS

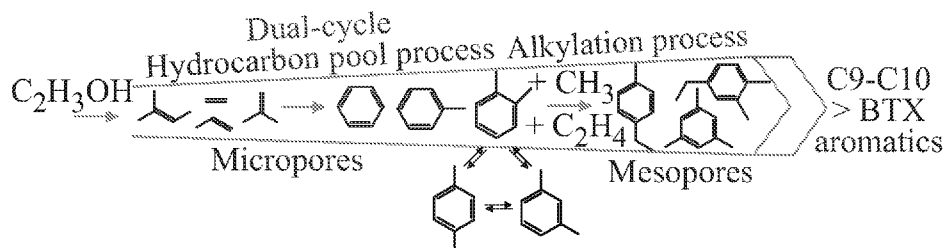


Figure 11

(57) Abstract: Provided here are methods and systems that employ heterogenous catalysis for bioderived ethanol conversion to sustainable aviation fuel blendstocks. Specifically, the methods and systems use Ga or Ru incorporated crystalline-mesoporous zeolite catalysts for ethanol oligomerization and production of fuels, such as jet fuels.



ZEOLITE CATALYSTS AND USE IN ETHANOL OLIGOMERIZATION AND PRODUCTION OF FUELS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 63/342,560 filed on May 16, 2022, which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY-SPONSORED RESEARCH

[0002] This invention was made with government support under Contract/Grant No. 86877 awarded by the Center for Bioenergy Innovations (CBI) and the Department of Energy (DOE). The government has certain rights in the invention.

FIELD

[0003] The present disclosure relates generally to heterogenous catalysis for bioderived ethanol conversion to sustainable aviation fuel blendstocks, and more specifically to the use of Ga incorporated crystalline-mesoporous zeolite catalysts for ethanol oligomerization and production of fuels, such as jet fuels.

BACKGROUND

[0004] Transportation contributes 36% of total US 2020 carbon dioxide emissions, a greater amount than from any other US end use sector, and powering transportation by petroleum derived fuels accounts for 97% of these emissions (EIA report).^{1,2} The primary focus to power light duty vehicles is now to phase in electric batteries and fuel cells, albeit carbon emissions will continue during the considerable time needed to displace current fleets and fuels. However, if aviation is to meet its important carbon emission reduction targets higher mass energy densities are needed than currently possible by electric power.³ On the other hand, biomass conversion to liquid fuels provides the lowest cost option for production of sustainable aviation fuels (SAF) with properties comparable to those for jet fuel derived from petroleum.⁴⁻⁷ The challenge is that conventional jet fuel is a complex mixture that generally consists of 75-85 vol% iso-paraffins and cyclo-paraffins with the rest being aromatics to swell seals and meet other fit-for-purpose requirements. A recent EIA report outlined technologies and projected costs for most sustainable options under current investigation for production of SAF that could replicate key properties needed for jet fuel.⁸

In this study, hydroprocessed esters and fatty acid (HEFA) fuels were shown to currently provide the largest amount of fuel at a reasonable cost, but limited supplies of low-cost plant oils could impede substantial growth. Other options such as catalytic conversion of syngas to SAF could also play a role. A particularly promising route that could facilitate rapid transformation to low carbon emissions by aviation is catalytic conversion of ethanol into SAF that meets energy density and other fit-for-purpose requirements and can build on established US and world ethanol production of about 14 and 26 billion gallons, respectively, by far the largest amount of biofuel in 2020.^{4,9} Many of these alcohol to jet (ATJ) processes being scaled up require 3 to 4 catalytic steps to dehydrate ethanol to C₂ to C₄ olefins, oligomerize these olefins to C₆ to C₈ products, further polymerize the oligomers to higher carbon number compounds, and saturate double bonds by hydrogenation. In addition to entailing multiple steps, these operations require high temperatures and pressures and can suffer from compounding of the yield losses of each step. On the other hand, a new consolidated alcohol deoxygenation and oligomerization (CADO) technology employs zeolite catalysts to combine ethanol dehydration/deoxygenation, oligomerization, and further reaction in a single step without the need to add hydrogen. However, although the high aromatic content and carbon number distribution from CADO are currently suitable for high level blending with gasoline, shifting the product distribution to higher carbon number compounds would increase blend levels for jet fuel. Hence, this study focuses on determining how changes in ZSM-5 zeolite catalyst features can increase the carbon number range of liquid hydrocarbons made from ethanol by CADO technology and thereby allow higher blend levels in aviation fuels.

[0005] Si/Al ratio, crystal size, weight hour space velocity (WHSV), temperature, and reaction pressure have been optimized for ethanol conversion into hydrocarbons using H-ZSM-5 supports.^{10–13} When ethanol is co-fed with inert gases and reaction pressures are maintained above 20 bar for such catalysts, gasoline range paraffins and benzene/toluene/xylene (BTX) are more predominant products while ethylene is the dominant product for reactions at atmospheric pressure without an inert gas carrier.^{14–19} The effect of loading various metals on H-ZSM-5 supports have also been extensively studied for BTX production from ethanol. For example, Inaba et al. reported selectivity for BTX production from ethanol dropped in the order Ga >> Pd > Ir > Au > Ru > Rh > H-ZSM-5 for reaction at 400°C and 0.1589 WHSV for a nitrogen flow rate of 60 cm³/min.²⁰ In another study, Ga doped ZSM-5 catalyst had better stability than Zn doped ZSM-5 for ethanol

conversion to BTX at 360°C and 1h⁻¹ WHSV.²¹ Van der Borgh et al. highlighted the importance of low Ga metal (<1%) loadings onto ZSM-5 to prevent pore blocking and provide maximum access for reactants to interact with acid sites to produce BTX.²² A detailed study by Li et al. demonstrated loading 6.2% gallium oxide on ZSM-5 promoted BTX selectivity while producing $\leq 7\%$ C8+ aromatics at 450°C and 0.4h⁻¹ WHSV.²³ Gas chromatographic analysis of filtrate recovered by washing of post-reaction/used H-ZSM-5 catalyst with dichloromethane solvent showed C9-C14 aromatics had been formed.²⁴ Based on this result, they hypothesized that an ethanol dual-cycle hydrocarbon pool (HCP) mechanism progressively formed C9+ aromatics in addition to BTX. However, because these molecules are larger than the H-ZSM-5 pores, i.e., $4.5 \times 5.2 \text{ \AA}$ for straight pores with an internal pore space of $6.19 \text{ \AA}$, the large substituted aromatic molecules produced had to crack to smaller BTX molecules to escape from the micropores as otherwise they would block ZSM-5 acidic sites in the framework.^{15,24,25} On the other hand, the HCP process was not favored for ethanol conversion over larger micropore zeolites such as H-Beta, USY, and H-mordenite, with the result that BTX production was low and heavy coking resulted.²⁰ The above studies clearly highlighted that H-ZSM-5 supports selectively produce BTX by the ethanol HCP process and Ga addition to H-ZSM-5 further promoted BTX production (C6-C8 aromatics only). However, in these studies, most of the gallium oxide was proven to be on the external zeolite surface due to steric constraints to incorporation inside the pores.^{20-24,26-29} It is still unclear what role gallium oxide inside the zeolite channels plays on ethanol product distributions.

[0006] In view of the above, what is desired in the art are systems and methods that can be tuned to not only promote BTX production (C6-C8 aromatics), but also jet fuel blendstocks.

BRIEF SUMMARY

[0007] The systems and methods provided herein address a need in the art by increasing H-ZSM-5 pore volumes by post synthesis to facilitate greater gallium (Ga) insertion into the zeolite channels. Furthermore, enhanced zeolite pore volumes/size accommodates ethanol reactive intermediates for forming longer hydrocarbon chain lengths (C9+) that are desirable for jet fuel.

[0008] In some aspects, provided is a method for selectively producing C9-C12 aromatics. In some embodiments, the method comprises converting ethanol in the presence of a heterogeneous catalyst at a temperature suitable to produce a product mixture comprising liquid hydrocarbons. In some variations, the heterogeneous catalyst comprises zeolite with one or more of the following properties: (i) a zeolite pore volume of at least 0.05 cm³/g; (ii) a zeolite surface area of 300-450 m²/g; (iii) a crystallinity between 70% and 95% relative to the crystallinity of the zeolite, wherein said crystallinity is determined by powder X-ray diffraction analysis of peaks in the signal area of 22.7° to 24.2° 2 Θ ; (iv) a Ga or Ru loading of 1-10%, 2-8%, or 4-6%; (v) a zeolite surface Si/Ga ratio of 5-30, or 10-20, or 10-15; (v) a total acid site density between 0.5 mmol/g and 1.5 mmol/g; and (vi) a Ga or Ru particle size between 1 nm and 10 nm. In one variation, the heterogeneous catalyst is other than unmodified ZSM-5 zeolite.

[0009] In certain embodiments, the heterogeneous catalyst is prepared by a process comprising desilicating the zeolite and incorporating Ga or Ru. In some variations, the zeolite is desilicated by contacting the zeolite with aqueous hydroxide. In some variations, Ga or Ru is incorporated by wet impregnation. In certain embodiments, the method further comprises protonating the zeolite prior to incorporating Ga or Ru, for example, by contacting the zeolite with an acidic solution. In yet other embodiments, the method further comprises calcining the zeolite to produce the heterogeneous catalyst used in the methods described herein.

[0010] In other aspects, provided is a system, comprising: a catalytic reactor containing a heterogeneous catalyst, and wherein the catalytic reactor comprises an ethanol inlet configured to receive ethanol at an elevated temperature, and a reactor outlet configured to output liquid products produced from the ethanol; and a pump configured to control ethanol flow through the ethanol inlet through the heterogeneous catalyst. The heterogeneous catalyst used in such a system may be as described in any of the embodiments and variations herein.

DESCRIPTION OF THE FIGURES

[0011] The present application can be understood by reference to the following description taken in conjunction with the accompanying figures.

[0012] Figures 1a and 1b show the effect of NaOH treatment concentration on X-ray diffraction spectra and crystallinity of Ga/ZSM-5 catalysts and N₂ adsorption-desorption isotherms for Ga(5 wt. %)/ZSM-5 and Ga(5 wt. %)/modified-ZSM-5 catalysts.

[0013] Figures 2a-f depict the following: (a) STEM images of Ga(5%)/ZSM-5, (b) Ga, and (c) overlaid Ga/Si/Al elemental mapping. STEM images of (d) Ga(5%)/ZSM-5_{0.8M}, (e) Ga, and (f) overlaid Ga/Si/Al elemental mapping.

[0014] Figures 3a and 3b show XPS spectra of Ga(5 wt. %)/ZSM-5 and Ga(5 wt. %)/ZSM-5_{xM} catalysts in the binding energy range for the Ga 2p_{3/2} peak, and H₂-TPR profiles of Ga(5 wt. %)/ZSM-5 and Ga(5 wt. %)/ZSM-5_{xM}.

[0015] Figures 4a-4c show the effect of temperature on liquid product distribution from ethanol reactions on Ga(5 wt. %)/ZSM-5 and Ga(5 wt. %)/ZSM-5_{xM} catalysts at 1.6h⁻¹ WHSV. Product selectivity is calculated based on the total mass of liquid hydrocarbons.

[0016] Figures 5a-5c show the effect of WHSVs on selectivities for formation of C5-C6 paraffins, BTX, and C9-C10 aromatics from reaction of ethanol over Ga(5 wt. %)/ZSM-5 and Ga(5 wt. %)/ZSM-5_{xM} catalysts at 350°C. Product selectivity is calculated based on the total mass of liquid hydrocarbons.

[0017] Figures 6a and 6b show selectivity to C5-C6 paraffins, BTX, and C9-C10 aromatics produced by ethanol oligomerizations at 350°C and 0.4h⁻¹ WHSV over ZSM-5 and ZSM-5_{xM} supports without loading Ga, and selectivity to C5-C6 paraffins, BTX, and C9-C10 aromatics produced by ethanol oligomerizations over Ga(5 wt. %)/ZSM-5 and Ga(5 wt. %)/ZSM-5_{xM} at 350°C and 0.4h⁻¹ WHSV. Product selectivity is based on the total mass of just liquid hydrocarbons.

[0018] Figure 7 depicts the correlation between C9-C10 aromatics selectivity and pore volume and surface Si/Ga ratios (LP: Liquid Product). Product selectivity is based on the total mass of liquid hydrocarbons produced.

[0019] Figures 8a-8b show the effect of (a) catalyst synthesis time and (b) Ga content on liquid hydrocarbon product selectivity following reaction of ethanol on Ga(5%)/ZSM-5_{0.8M} catalysts at 350°C with a 0.4h⁻¹ WHSV. Product selectivity is based on total liquid hydrocarbons.

[0020] Figure 9a depicts product selectivity over time for Ga/ZSM-5_{0.8M} fed ethanol for 32 hours at 350°C and 0.4h⁻¹ WHSV. Figure 9b depicts XPS spectra of used Ga(5%)/ZSM-5_{0.8M} in the binding energy range for the Ga 2p_{3/2} peak (red color: washed catalyst and black color: washed catalyst followed by calcination). Product selectivity is based on total liquid hydrocarbons. Figure 9c shows H₂-TPR profiles of fresh catalyst and used catalysts for ethanol and wet-ethanol stream.

[0021] Figures 10a-10b depict TPO profiles of catalysts following their use for conversion of pure ethanol and wet-ethanol to hydrocarbons.

[0022] Figure 11 depicts a scheme that shows progressive increase in carbon number as ethanol dehydrates, aromatizes, and alkylates to longer chained hydrocarbons and C₉-C₁₀ aromatics along H-ZSM-5 meso-micropores before exiting through large pores through which they can fit. If the hydrocarbon grows to a size that is too large to exit, it must either crack to form smaller molecules that can leave or pyrolyze to form carbon deposits that block access to active sites or restrict hydrocarbons from entering or leaving pores.

[0023] Figure 12 shows BJH pore size distribution curves derived from N₂ adsorption-desorption studies for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/modified-ZSM-5 catalysts.

[0024] Figure 13 shows the effect of Ga loading on ZSM-5_{0.8M} support porosity and surface area.

[0025] Figure 14 shows STEM images for: (a) Ga(5 wt.%)/ZSM-5 (a) support, (b) Ga distribution, and (c) overlaid Ga/Si/Al elemental mapping. STEM images for Ga(5 wt.%)/ZSM-5_{0.8M} (d) support, (e) Ga distribution, and (f) overlaid Ga/Si/Al elemental mapping.

[0026] Figures 15a-15b show Ga average particle diameters in Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{0.8M}.

[0027] Figure 16 shows Ga 2p_{3/2} XPS spectra of 2, 5, and 8% gallium loadings for 4, 16 and 32 hours Ga wet-impregnation synthesis times.

[0028] Figure 17 shows NH₃-TPD profiles of Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} (xM = 0.2, 0.6, 0.8 & 1.0M).

[0029] Figure 18 shows the effect of temperature on ethanol oligomerizations over Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{0.8M} catalysts at 1.6h⁻¹ WHSV.

[0030] Figure 19 X-ray diffraction spectra of fresh Ga/ZSM-5_{0.8M} and used Ga/ZSM-5_{0.8M} after reacting pure ethanol (red color) and 40% wet ethanol (black) to form hydrocarbons.

[0031] Figures 20a-c show: (a) N₂ adsorption-desorption isotherms and (b) surface area (SA), external surface area, and micropore surface area for fresh Ga(5 wt.%)/ZSM-5_{0.8M} and used Ga(5 wt.%)/ZSM-5_{0.8M} catalysts. (c) Pore volumes for fresh Ga(5 wt.%)/ZSM-5_{0.8M} and used Ga(5 wt.%)/ZSM-5_{0.8M} catalysts.

[0032] Figure 21 shows NH₃-TPD profiles of fresh catalyst and used catalysts for pure ethanol and wet ethanol.

[0033] Figure 22 shows ethanol conversions using 5 wt% Ga loaded ZSM-5, beta and Y-zeolites at 350 C and 0.4h⁻¹ SV.

[0034] Figure 23 shows ethanol conversions over Ru(0.5 wt%)/ZSM-5, Ru(2 wt%)/ZSM-5, Ru(2 wt%)/ZSM-5_{0.8M} and Ru(5 wt%)/ZSM-5_{0.8} catalysts.

DETAILED DESCRIPTION

[0035] The following description sets forth exemplary systems, methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

[0036] Jet fuel from petroleum provides energy densities and other attributes vital for aviation but adds to greenhouse gas emissions. Biomass provides an inexpensive resource that is uniquely suited for large-scale conversion into low carbon footprint sustainable aviation fuels (SAF) for the immediate future and likely longer. Through a pool mechanism, novel consolidated alcohol deoxygenation and oligomerization (CADO) zeolite catalysts, including for example ZSM-5, offer low-cost, one-step, complete conversion of biomass ethanol into hydrocarbons without adding hydrogen. However, CADO products mostly contain less than 8 carbon atoms while jet fuel includes up to 16, likely restricting jet fuel blending to 50% or less.

[0037] To overcome this limitation, the effectiveness of reacting zeolites, including for example ZSM-5 with 0.2, 0.6, 0.8, and 1.0M sodium hydroxide concentrations over a range of temperatures and times was evaluated for enhancing the carbon number range. As described in the examples herein, X-ray diffraction, N₂-physisorption, X-ray photoelectron spectroscopy, H₂-TPR, and STEM showed that treating with 0.8M sodium hydroxide at 60°C for 0.5hour increased pore volumes and metal-support interactions more than lower concentrations while retaining crystallinity better than for 1.0M treatment. The larger pores enhanced 5 wt.% gallium oxide migration into ZSM-5_{0.8M} channels and promoted strong interactions between gallium oxide and the support that coupled with retained crystallinity and greater capacity for larger molecules increased liquid hydrocarbon yields (LHYs) from pure ethanol to 46.1% and C9-C10 aromatics selectivity to 45.8%, the first reported direct increase in C9-C10 aromatics selectivity from ethanol. In addition, cofeeding 60% water with ethanol further enhanced LHY and C9-C10 aromatics selectivity to 53.1% and 55.1%, respectively, while extending catalyst stability.

[0038] In some aspects, provided herein is a simple, efficient, and reproducible desilication process that is selective for extracting framework silica without disturbing framework alumina/Bronsted acid sites and for creating new mesopores was adopted for H-ZSM-5. Desilication of ZSM-5 with NaOH concentrations of 0.2, 0.6, 0.8, and 1.0M resulted in continual increases in pore volume/size, but crystallinity dropped significantly for 1.0M NaOH as determined by XRD and N₂-physisorption studies. In addition, STEM and XPS studies revealed greater Ga migration into the channels of ZSM-5 that had been treated with 0.8 and 1.0M NaOH than for parent ZSM-5 catalyst. The ability of ZSM-5 catalysts treated with 0.8M NaOH but without gallium oxide to accommodate larger hydrocarbon molecules in enhanced pore sizes combined with retained crystallinity and greater Ga penetration into zeolite pores increased liquid hydrocarbon yields (LHYs) yields by nearly five times to 27.1% compared to 5.3% from the parent support. Loading ZSM-5_{0.8M} with 5% Ga further increased LHYs and C9-C10 hydrocarbon selectivity to 46.1% and 45.8%, respectively, from 35.1% and 17.2%, respectively, for the parent catalyst for reactions at 350°C and 0.4h⁻¹ WHSV. Furthermore, feeding 40% ethanol in water vapor increased LHYs to ≥50% and C9-C10 aromatic selectivity to 55.1% while maintaining catalyst stability over 32 hours.

Methods for Selective Production of Aromatics from Alcohol

[0039] In one aspect, provided is a method for selectively producing C9-C10 aromatics, comprising converting ethanol in the presence of a heterogeneous catalyst at a temperature suitable to produce a product mixture comprising liquid hydrocarbons. In some variations, the method further comprises isolating the liquid hydrocarbons from water produced.

Ethanol

[0040] The ethanol may be sourced from any commercially available sources or produced according to any known methods in the art. In some embodiments, the ethanol used in the methods provided is delivered in vapor form, such as wet-ethanol vapor.

Heterogeneous Catalyst

[0041] In some variations, the heterogeneous catalyst comprises Ga or Ru loaded onto zeolite, wherein the heterogeneous catalyst has one or more of the following properties: (i) a zeolite pore volume of at least 0.05 cm³/g, or between 0.05-0.5 cm³/g; (ii) a zeolite surface area of 300-450 m²/g; (iii) a crystallinity between 70% and 95% relative to the crystallinity of the zeolite, wherein said crystallinity is determined by powder X-ray diffraction analysis of peaks in the signal area of 22.7° to 24.2° 2 θ ; (iv) a Ga or Ru loading of 1-10%, 2-8%, or 4-6%; (v) a zeolite surface Si/Ga ratio of 5-30, or 10-20, or 10-15; (vi) a total acid site density between 0.5 mmol/g and 1.5 mmol, or between 0.8 mmol/g and 1.2 mmol; and (vii) a Ga or Ru particle size between 1 nm and 10 nm. In certain variations, the heterogeneous catalyst comprises zeolite with two, three, four or all five properties.

[0042] In some variations, the heterogeneous catalyst comprises Ga loaded onto zeolite. In other variations, the heterogeneous catalyst comprises Ru loaded onto zeolite. In one variation, the heterogeneous catalyst is other than unmodified ZSM-5 zeolite.

[0043] In some variations, the heterogeneous catalyst has a catalyst stability of greater than 30 hours.

Reaction Conditions

[0044] Reaction conditions suitable to produce a product mixture comprising liquid hydrocarbons from the ethanol provided may be employed. For example, in one variation, the temperature is between 350°C and 500°C.

Product Mixture

[0045] In some embodiments, the methods provided yield a product mixture that has: (a) less than 50% for C5-C6 paraffins; (b) less than 80% for benzene, toluene and xylene (BTX); and/or (c) at least 10% for C9-10 aromatics. In one variation, the product mixture has all three properties (a)-(c) above.

[0046] In certain embodiments, the methods provided yield a product mixture that has: (a) less than 30% for C5-C6 paraffins; (b) less than 60% for benzene, toluene and xylene (BTX); and (c) at least 20% for C9-10 aromatics. In one variation, the product mixture has all three properties (a)-(c) above. In some variations of the foregoing, the produce mixture has at least 50% for C9-10 aromatics.

[0047] In other embodiments, the liquid hydrocarbon yield is at least 25%, at least 30%, at least 35%, at least 40%, at least 45%, at least 50%.

[0048] In some variations, the product mixture comprises C9-C10 aromatics such as trimethyl benzene, ethyl methyl benzene, or ethyl dimethyl benzene, or any combination thereof. In some embodiments, the product mixture further comprises gaseous hydrocarbons (C2-C4). In one variation, the product mixture further comprises C2-C5 olefins.

Methods for Preparing Heterogeneous Catalyst

[0049] In some embodiments, provided is a method for preparing the heterogeneous catalyst, comprising desilicating the zeolite and incorporating Ga or Ru. In some variations, the zeolite is desilicated by contacting the zeolite with aqueous hydroxide. Suitable hydroxides include, for example, sodium hydroxide. In some variations, the hydroxide concentration is between 0.2 M and 1.0 M. In some variations, Ga or Ru is incorporated by wet impregnation.

[0050] In some embodiments, the method for preparing the heterogeneous catalyst further comprises protonating the zeolite prior to incorporating Ga or Ru. In some variations, the zeolite is protonated by contacting the zeolite with an acidic solution. Suitable acidic solutions include aqueous ammonium nitrate.

[0051] In some embodiments, the method for preparing the heterogeneous catalyst further comprises calcining the zeolite. Any suitable temperatures may be used for calcining.

For example, in some variations, the calcining is performed at a temperature of at least 400°C, at least 450 °C, or at least 500 °C.

[0052] In some embodiments, the heterogeneous catalyst produced according to the methods herein has a zeolite pore volume between 0.4-0.5 cm³/g; a zeolite surface area between 375-400 m²/g; a zeolite crystallinity between 80-85% relative to ZSM-5; and/or a zeolite surface Si/Ga ratio 5 to 30, 10 to 20, or 10 to 15.

[0053] In some embodiments, the heterogeneous catalyst produced according to the methods herein has a zeolite pore volume between 0.4-0.5 cm³/g; a crystallinity between 80-85% relative to the crystallinity of the zeolite; a Ga or Ru loading between 3-7%; a zeolite surface Si/Ga ratio or Si/Ru ratio between 10-15; a total acid site density between 0.85 mmol/g and 0.95 mmol/g; and a Ga or Ru particle size between 3.5 nm and 4.5 nm.

Systems

[0054] In certain aspects, provided is a system, comprising: a catalytic reactor containing a heterogeneous catalyst, and wherein the catalytic reactor comprises an ethanol inlet configured to receive ethanol at an elevated temperature, and a reactor outlet configured to output liquid products produced from the ethanol; and a pump configured to control ethanol flow through the ethanol inlet through the heterogeneous catalyst.

[0055] In some variations, any of the heterogeneous catalysts described herein, including any of the heterogeneous catalysts produced according to the methods described herein, may be employed in the system.

[0056] In some variations, any of the reaction conditions provided for the methods to selectively producing C9-C10 aromatics may be employed in the system.

EXAMPLES

[0057] The presently disclosed subject matter will be better understood by reference to the following Examples, which are provided as exemplary of the invention, and not by way of limitation.

Example 1

Relationship between ZSM-5 pore modifications and gallium proximity and liquid hydrocarbon number distribution from ethanol oligomerization

[0058] This example explores increasing H-ZSM-5 pore volumes by post synthesis to facilitate greater gallium insertion into the zeolite channels. Furthermore, it was reasoned that enhanced zeolite pore volumes inside zeolite pores would accommodate longer hydrocarbon chain lengths that are desirable for jet fuel. To test this concept, a simple, efficient, and reproducible desilication process that is selective for extracting framework silica without disturbing framework alumina/Bronsted acid sites and for creating new mesopores was adopted for H-ZSM-5 (Si/Al – 23).^{30–34} In particular, H-ZSM-5 (Si/Al-23) supports were desilicated by treatment with NaOH to produce mesopore-crystalline H-ZSM-5. Then, Ga was loaded onto parent and modified ZSM-5 supports by following incipient wet-impregnation procedures, and the resulting catalysts were used to catalyze ethanol conversions at different temperatures and WHSVs. The effects of Ga proximity on the zeolite external surface and inside the channels on ethanol product distributions were then determined.

[0059] This example demonstrates how pore modification, crystallinity, and Ga proximity in zeolite channels affect yields and carbon number distribution of hydrocarbons formed by single step reaction of ethanol on ZSM-5 catalysts. ZSM-5 pore modification with 0.8M NaOH showed significant influence on ethanol liquid hydrocarbon (LHYs) and raised nearly 5x higher in case of ZSM-5_{0.8M} (27.1%) compared to parent ZSM-5 (LHYs- 5.3%), without adding gallium oxide. Gallium addition to ZSM-5_{0.8M} further promoted the LHYs and C9-C10 aromatics selectivity to 46.1% and 45.8%, respectively, at 350 °C reaction temperatures and 0.4h⁻¹ WHSV. Presence of water in the ethanol feed further increased the product selectivity of C9-C10 aromatic to 55.1%.

MATERIALS:

[0060] ZSM-5, NaOH (99.99%), ammonium nitrate (99.99%), and ethyl alcohol (99.5%) were employed for these studies.

CATALYST SYNTHESIS:

[0061] *Desilication of H-ZSM-5:* Framework silica was extracted/removed from H-ZSM-5 supports by treatment with 0.2M, 0.6M, 0.8M, and 1.0M NaOH solutions to synthesize ZSM-5_{0.2M}, ZSM-5_{0.6M}, ZSM-5_{0.8M} and ZSM-5_{1.0M}, respectively. These modified supports are hereafter referred to as ZSM-5_{xM}, in which x indicates the Molarity. First, the appropriate amount of ZSM-5 was mixed with aqueous NaOH solution at 60°C by magnetic stirring for 0.5 hours. The reaction mixture was quickly quenched in an ice water bath and centrifuged to separate and wash the solids with deionized-water until the filtrate pH reached 7. The desilicated solids were then dried in an oven at 105°C for 6 hours.

[0062] *Ammonium nitrate treatment:* To regenerate the protonic form of zeolites from each Na- ZSM-5_{xM}, 2g of the desilicated solids were added to 120ml of deionized water containing 3.298g of aqueous ammonium nitrate, and the resulting mixture was heated at 80°C while magnetically stirring for 24 hours. During this time, decomposition of the ammonium nitrate released ammonia and protons, with the latter replacing Na⁺ ions in Na-ZSM-5. Next, the solids were separated from the liquid by centrifugation and dried at 105°C for 6 hours, followed by calcining at 500°C for 5 hours.

[0063] *Ga/ZSM-5 catalysts synthesis:* For this study, 2, 5 and 8% Ga was loaded onto ZSM-5 and each ZSM-5_{xM} by following the incipient wet-impregnation procedure. In a typical synthesis, the appropriate amount of gallium nitrate precursor was dissolved in water and then added to H-ZSM-5 or ZSM-5_{xM} at a water/ZSM-5 mass ratio of 50:1. This combination was then mixed on a magnetic hot-plate that also kept the temperature at 80°C for 16 hours for most samples. However, a few samples were wet-impregnated for 4 hours and 32 hours. The solid material was separated from the liquid using a rotary evaporator. The solid obtained was dried at 105°C for 6 hours and calcined at 500°C for 5 hours by a muffle furnace at a ramp rate of 10°C/min from 25°C. A similar procedure was followed for 2 wt.% and 8 wt.% Ga impregnations on the ZSM-5_{0.8M} support. Without any further pretreatment, as synthesized materials were used for catalytic conversion of ethanol at 350°C, 400°C, 450°C, and 500 °C and space velocities of 1.6, 1.2, 0.8, and 0.4h⁻¹, unless otherwise noted.

CATALYST CHARACTERIZATION:

[0064] *X-ray diffraction (XRD)*: XRD spectra of all gallium loaded catalysts were recorded in the 2θ range of 20 to 90° using an X'pert Pro PANalytical diffractometer, equipped with a Nickel filtered Cu-K α radiation source.

[0065] *Surface Area*: The total accessible surface area (S_{BET}) and pore volume of the catalysts were measured by N₂ physisorption using a Micromeritics instrument. The mesopore volume and size distribution were estimated from the desorption branch of the isotherm by applying the Barrett–Joyner–Halenda (BJH) model.

[0066] *Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)*: Metal concentrations in the solids were measured by ICP-OES analysis using a Perkin-Elmer Optima ICP-OES apparatus that combines an SCD detector and an echelle optical system.

[0067] *Scanning Transmission Electron Microscopy (STEM)*: STEM imaging was at 300 kV accelerating voltage on a FEI/Philips Titan Themis 300 instrument fitted with an X-FEG electron source, a three-lens condenser system, and an S-Twin objective lens. STEM images were recorded with a M3000 High Angle Annular Dark Field (HAADF) Detector at a probe current of 0.2 nA, frame size of 2048 × 2048, dwell time of 15 μs /pixel, camera length of 195 mm, and convergence angle of 10 mrad. Elemental X-ray microanalysis and mapping utilized a FEI Super-X EDS system with four symmetrically positioned SDD detectors of 30 mm² each, resulting in an effective collection angle of 0.7 srad. Elemental maps were collected in STEM mode with a beam current of 0.4 to 0.25 nA, a 512 × 512-pixel frame, 30 μs dwell time, and up to 10 min acquisition time. Specimens prepared from suspensions in distilled water were deposited on copper grids coated with lacey carbon. Average metal particle sizes were measured based on the diameter of 100 particles from corresponding TEM images of each catalyst.

[0068] *X-ray photoelectron spectroscopy (XPS)*: XPS characterization was by a Kratos XPS system equipped with an Al K α monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. Vacuum pressure was kept below 3×10^{-9} torr during analysis. Binding energy calibrations were with reference to the carbon 1s peak by adjusting spectra to 284.8 eV. Surface composition of gallium was calculated using sensitivity factors of 5.581.

[0069] *H₂-Temperature Program Reduction and Oxidation studies:* H₂-Temperature program reduction (TPR) and temperature program oxidation (TPO) experiments were conducted with a Hiden Analytical CATLAB instrument (2375 Maxwell Lane, Sedona, AZ 86336). For H₂-TPR experiments, a 100mg sample was dried in a 2% O₂/He stream for 1 h at 450°C and then cooled to 150 °C prior to analysis. Then the sample was reduced in a 10% H₂/He (50 mL/min) stream at a heating rate of 10°C/min to 950°C. TPO characterization techniques were applied in the same system to about 100mg of catalysts that had been used for ethanol and wet-ethanol streams. Prior to analysis, the samples were dried in a 2% O₂/He stream (30 mL/min) at 150°C for 1 h, followed by heating at a ramp up rate of 10°C/min to 950°C. Peaks for CO₂ (m/z = 44), CO (m/z = 28), and H₂O (m/z = 18) were recorded with a mass spectrometer (Hiden Quadrupole, 2375 Maxwell Lane, Sedona, AZ 86336).

REACTIVITY EXPERIMENTS:

[0070] *Liquid product analysis:* Organic liquid products were analyzed using a gas chromatograph equipped with a 30 m long × 0.320 mm internal diameter × 20 micron HP-PLOT/Q-column and an FID detector. The GC program held the column at 50°C for 3 min followed by ramping from 50 to 250°C at 15°C min⁻¹ and then holding at 250°C for 50 min. Product concentrations were quantified based on calibration curves of standard samples measured following the same protocol on the same equipment. Ethanol conversion, theoretical liquid hydrocarbon yields (THY), liquid hydrocarbon yields (LHY), and product selectivity were calculated as follows:

$$\text{Equation 1: Ethanol conversion} = 1 - \frac{\text{Moles of unreacted ethanol}}{\text{Moles of ethanol before reaction}}$$

Percent liquid product selectivity (LPS) to form hydrocarbons of chain length C:

$$\text{LS} = \frac{\text{Mass of C compound collected}}{\text{Total mass of organic liquid collected}} \times 100$$

$$\text{Liquid hydrocarbon yields (LHYs)} = \frac{\text{Mass of liquid HC in product (g)}}{\text{Theoretical HC yield from ethanol (g)}}$$

$$\text{Theoretical liquid HC yield} = \text{Mass of ethanol feed (g)} \times 0.564$$

[0071] *Catalyst performance evaluations:* Ethanol catalytic reactions were run with a custom-made stainless steel fixed-bed reactor (1/4" diameter by 6.5" inch long stainless steel tube) fed ethanol through a heated line into the catalytic reactor. Temperatures in

the preheating line and reactor bed were monitored by a PID controller, and liquid hydrocarbon products from the reactor were condensed for collection by cooling the outlet line to below 5°C. For each reactor run, a high-precision peristaltic pump (DRIVE MFLEX L/S 100RPM 115/230 Cole-Parmer, IL) controlled ethanol inlet flows at desired rates through 0.6 g of as-synthesized Ga-ZSM-5 or Ga-ZSM-5_{xM} catalyst powder. The catalyst was preheated to 500°C for 1 hour at an ethanol space time velocity of 1.6 h⁻¹ prior to heating up to 350, 400, 450, or 500 °C for the catalyst performance evaluations. After running at steady-state for 3 hours, liquid products were collected every two hours from the reactor outlet. The products usually contained liquid and gaseous hydrocarbons plus a significant amount of water (theoretically 39.07 g of water from 100 g of ethanol) with little ethanol left. Because water would quickly damage the gas chromatograph (GC) packing, liquid hydrocarbons were extracted from the water with dichloromethane before injecting into the GC for liquid hydrocarbon analysis. Hydrocarbon gases were not analyzed to avoid GC column damage by vaporized water. Reported catalyst performance data were based on analyses of the organic liquid product collected after at least 4 hours of reactor operation. Catalyst performance and stability were determined for feeding either pure ethanol or 40% ethanol in water for 32 hours. Used catalyst recovered after reaction was washed with dichloromethane to remove organic deposits and then calcined prior to characterization by XRD, N₂-physisorption, and XPS.

RESULTS AND DISCUSSION

[0072] *Effect of NaOH treatment on catalyst characteristics:* To understand what caused differences in ethanol oligomerization and product distribution from ethanol reactions on the different treated ZSM-5 supports, crystallinity, pore volume, gallium oxide particle size, binding energy, and surface Si/Ga ratio of all synthesized catalysts were determined by XRD, S_{BET}, STEM, and XPS techniques.

[0073] Figure 1a pictures X-ray diffraction (XRD) patterns of H-ZSM-5 and alkali treated H-ZSM-5_{xM} catalysts. As shown, typical ZSM-5 diffraction peaks identified in the 2θ range of 22.8 to 25.0 are consistent with those for reference ZSM-5 (PDF#44-0003). However, the shape and intensity of diffraction peaks for alkali treated ZSM-5_{xM} catalysts were altered due to extraction of framework silica. Minimal losses in the intensity of ZSM-5 characteristic reflections were observed after treating ZSM-5 with 0.2, 0.6 and 0.8M

NaOH, but 1.0M NaOH treatment resulted in significant loss of both diffraction peak shape and intensity. As shown in Table 1, the larger amount of NaOH could damage framework silica and potentially hurt ZSM-5 crystallinity. The relative crystallinity of these materials calculated from the signal area in the 22.7° to 24.2° range decreased in the following order: ZSM-5(100%) > ZSM-5_{0.2M} (94.7%) > ZSM-5_{0.6M} (90.3%) > ZSM-5_{0.8M} (82.4%) > ZSM-5_{1.0M} (72.9%). As shown in Table 2, removing framework silica as measured from ICP-OES experiments resulted in a gradual loss in crystallinity. Thus, treating ZSM-5 with 1.0M NaOH suddenly increased both silica and alumina losses to nearly 40% of the total material (Table 2). X-rays did not show any gallium oxide peaks, suggesting gallium oxide was amorphous. But the shift in XRD peaks to higher angles for the alkali treated H-ZSM-5 might increase ZSM-5 unit-cell dimensions.

Table 1: Physicochemical properties of Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/modified-ZSM-5 catalysts.

Catalyst	XRD, Relative crystallinity of support	N ₂ -adsorption-desorption			XPS, External Surface ratio of Si/Ga
		Total Surface Area (SA; m ² /g)	External Surface Area (ESA; m ² /g)	Meso and Macro Pore Volume (cm ³ /g)	
Ga(5%)/ZSM-5	100	338	60.1	0.064	5.4
Ga(5%)/ZSM-5 _{0.2M}	94.7	334	64.6	0.092	6
Ga(5%)/ZSM-5 _{0.6M}	90.3	366	106.7	0.156	14
Ga(5%)/ZSM-5 _{0.8M}	82.4	393	134.2	0.238	13.5
Ga(5%)/ZSM-5 _{1.0M}	72.9	421	170.6	0.457	12.5

Table 2: ICP-OES analysis for the liquid fraction collected after treating ZSM-5 with 0.2, 0.6, 0.8, & 1.0M NaOH

Modified-ZSM-5 Catalyst	ICP-OES				Material loss (%)
	Loss of SiO ₂ (g)	Loss of Al ₂ O ₃ (g)	Combined loss (g)	Loss of Si/Al	
0.2M	0.216	0.009	0.226	24	11.3±0.9
0.6M	0.665	0.051	0.716	13.0	20.6±1.1
0.8M	0.749	0.070	0.819	10.7	26.4±1.2
1.0M	0.788	0.103	0.891	7.7	38.6±3.1

[0074] Figure 1b shows N₂ adsorption-desorption isotherms for Ga(5 wt%)/ZSM-5 and Ga(5 wt%)/ZSM-5_{xM} catalysts, and the corresponding BET total surface areas (SA), external surface areas, and mesopore volumes are reported in Table 1. As shown, Ga/ZSM-

5 exhibited a type-I isotherm and no distinct hysteresis loop, indicating a typical microporous structure even after Ga incorporation. Upon alkali treatment with NaOH, all Ga/ZSM-5_{xM} catalysts except Ga/ZSM-5_{0.2M} took up more N₂ and displayed a type-4 isotherm with a H4-hysteresis loop, indicating enhanced total surface area and mesopores formation (Table 1 & Figure 12). Furthermore, the enhanced total and external surface areas in modified-ZSM-5 supports was due to newly formed pore walls and more outer surface area of microcrystallites.³⁵ However, 0.2M alkali treatment of ZSM-5 had little effect on both total SA and mesopore volume, suggesting minimal removal of framework silica, removed framework silica on the external framework, or blocking of micropores. On the other hand, Table 1 shows mesopore volumes increased by 1.5, 2.6, and 4 times when ZSM-5 was treated with 0.6M, 0.8M, and 1.0M NaOH, respectively. Although 1.0M NaOH treatment of ZSM-5 resulted in significant improvements in mesopore volume, excessive silica removal from the framework significantly damaged ZSM-5_{1.0M} crystallinity, as shown by XRD results. The BJH pore size distribution curves in Figure 12 showed H-ZSM-5 mesopore size consistently increased with increasing NaOH concentration.

[0075] STEM images of Ga(5 wt%)/ZSM-5 and Ga(5 wt%)/ZSM-5_{0.8M} catalysts in Figures 2 and 14 show both contained large needle shaped gallium oxide particles with sizes of 0.5-1.5 μm and 0.25-0.8 μm, respectively. Figures 15a and 15b also indicate gallium oxide nanoparticles had an average diameter of 4.1 ± 1.3 nm and 3.8 ± 1.8 nm on parent-ZSM-5 and ZSM-5_{0.8M} supports, respectively, consistent with a previous report.³⁶ Alkali treatment of ZSM-5 marginally increased the number of gallium oxide nanoparticles and gallium oxide dispersion by reducing the size of micro size gallium oxide particles on the external ZSM-5_{0.8M} support. STEM images of the ZSM-5_{0.8M} support in Figures 2 and 14 clearly suggest that NaOH treatment selectively extracted silica from the zeolite crystals and facilitated mesopores formation. Generally, the negatively charged framework tetrahedral alumina zeolite species as determined by ICP-OES and recorded in Tables 2 and 3 are inert under NaOH treatment.³⁴

[0076] XPS spectra were collected for Ga(5%)/ZSM-5 and Ga(5%)/ZSM-5_{xM} catalysts to determine Ga binding energy (B.E) and surface Si/Ga ratios. Figure 3 shows Ga 2p_{3/2} XPS spectra of as-synthesized catalysts, and Tables 1 and 4 list surface Si/Ga ratios. Generally, the higher Ga 2p_{3/2} peak B.E for supported Ga₂O₃ catalysts in the 1117.8 to 1118.5 eV range than for bare Ga₂O₃ particles could result in either strong metal-support

interactions or Ga^{+3} bounded to neighboring oxygen or strong interactions of gallium (GaO^+) with zeolite framework.³⁷⁻⁴¹ But in the present study, the Ga 2p_{3/2} peak B.E observed at 1118.8eV for all catalyst cases indicated Ga to be in as native oxide that formed a thin oxide layer on the outer surface.⁴²

[0077] Figure 16 shows that applying 2 and 8% gallium loadings for 4 hours and 32 hours Ga wet-impregnation synthesis times had no effect on the B.E of Ga 2p_{3/2} peak, thereby indicating similar Ga electronic structures for all cases. The surface Si/Ga ratio for all catalysts were calculated from Ga, Si, Al and O metal XPS peak areas and normalized by their relative sensitivity factors. Interestingly, surface Si/Ga ratios nearly doubled for Ga/ZSM-5_{0.6,0.8&1.0M} catalysts compared to Ga/ZSM-5 and Ga/ZSM-5_{0.2M} due to reduced Ga on the surface. In other words, enhancing pore volume of modified-ZSM-5 supports by treating with higher NaOH concentrations promoted greater Ga migration into the zeolite channels³⁸. Reducing the Ga loading to 2% on ZSM-5_{0.8M} increased the surface Si/Ga ratio to 29, while increasing the Ga loading to 8% resulted in a Si/Ga ratio 13, nearly the same as when 5% Ga was loaded onto ZSM-5_{0.8M}.

[0078] *H₂-Temperature Program Reduction:* H₂-TPR was applied to determine gallium oxide reduction temperature, nature of the gallium oxide and metal-support interactions. The H₂-TPR profiles for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} catalysts show broad reduction peaks starting from 500°C to 950°C, suggesting that gallium oxide is in the form of nanoparticles (nano-Ga₂O₃), gallium oxide ions (GaO^+) and segregated large Ga₂O₃ clusters (extra framework (EF)-Ga₂O₃; 200nm to 1500 nm) consistent with STEM data and previous reports.^{43,44,45,46} Generally, gallium oxide nanoparticles are known to be reduced at 500°C to 600°C, whereas the GaO^+ ions and surface segregated large gallium oxide clusters are reported to be reduced at above 650°C and 800°C, respectively.⁴⁶ In the present case of Ga (5 wt.%)/ZSM-5, gallium oxide reduction started at 504°C, whereas the gallium oxide reduction started at higher temperatures for modified support cases that increased in the following order: Ga(5 wt.%)/ZSM-5_{0.2M} (543°C) < Ga(5 wt.%)/ZSM-5_{0.6M} (550°C) < Ga(5 wt.%)/ZSM-5_{0.8M} (560°C). These results clearly suggested that more severe zeolite modifications enhanced metal-support interactions between gallium oxide and the ZSM-5 support.

[0079] As the nature of the gallium oxide plays an important role in ethanol oligomerization/aromatization, TPR profiles of 2, 5, and 8 wt% Ga loadings on ZSM-5,

modified-ZSM-5 catalysts and Ga loaded beta and Y-zeolite catalysts were deconvoluted and then compared the data. Peak deconvolution of H_2 -TPR profiles revealed the presence of nano- Ga_2O_3 , GaO^+ , and EF- Ga_2O_3 on ZSM-5, modified-ZSM-5, and beta and Y-zeolite supports. The composition of each gallium oxide species (nano- Ga_2O_3 , GaO^+ , and EF- Ga_2O_3) was quantified by considering their corresponding peak area. Particularly, the GaO^+ peak composition for modified-ZSM-5 catalysts increased with increasing ZSM-5 modification severity, except for the Ga/ZSM-5_{1.0M} case. The percentage of GaO^+ peak is higher in case of Ga(5%)/ZSM-5_{0.8M} case compared to other catalysts, could be the cause of more gallium migrated into the modified-ZSM-5 channels and interacted strongly with support hydroxyl groups. Whereas no GaO^+ peak observed for Ga/ZSM-5 catalyst suggesting gallium migration into zeolite channels and interaction with hydroxyl groups inside the zeolite pores are negligible. Thus, enhancing the mesopore volume of ZSM-5_{xM} supports promoted gallium oxide penetration into the pores and facilitated gallium oxide cationic species formation by strong interactions with the support hydroxyl groups and the increase in reduction of cationic species at higher temperature.^{27,44,45} Whereas in case of Ga(5 wt.%)/ZSM-5_{1.0M}, the loss in support crystallinity and disturbed pore structure might cause a drop in metal-support interactions, with the result that the GaO^+ peak percentage decreased than Ga(5 wt.%)/ZSM-5_{0.8M} catalyst.

[0080] Similarly, three gallium oxide reduction peaks corresponding to nano- Ga_2O_3 , GaO^+ , and EF- Ga_2O_3 were observed for 2, 5, and 8 wt% Ga loadings on ZSM-5_{0.8M} catalysts. The nano- Ga_2O_3 peak composition is nearly same (~10 %) for 5 and 8 wt% Ga loadings and higher (18%) for 2 wt% Ga loading on ZSM-5_{0.8M} suggesting lower Ga loading facilitated enhanced Ga dispersion on external ZSM-5_{0.8M} support. Interestingly, GaO^+ peak percentage increased from 37% to 54% by increasing the Ga loading from 2 to 5 wt% on ZSM-5_{0.8M} support and then decreased to 33% with further increase in Ga loading to 8 wt% for the ZSM-5_{0.8M} case. In addition, GaO^+ peak position was shifted to higher temperature for 5 wt% Ga/ZSM-5_{0.8M} case compared to other cases, indicating more gallium oxide migrated into modified zeolite channels and interacted strong with hydroxyl groups presented inside the pores. The peak percentage of gallium oxide clusters (EF- Ga_2O_3) is higher for 8 wt% Ga catalyst case compared to lower loadings (2 and 5 wt%) of Ga on ZSM-5_{0.8M} cases. It clearly demonstrated that 5 wt% Ga loading is

optimal for generating Ga₂O₃ nanoparticles and GaO⁺ species and further increasing the Ga loading led formation of gallium oxide clusters as EF-Ga₂O₃ particles.

[0081] *NH₃-Temperature Program Desorption (TPD) experiments:* NH₃-TPD experiments were conducted with a Micrometrics AutoChem II 2090 chemisorption analyzer equipped with a Pfeiffer OmniStar quadrupole mass spectrometer. In a typical experiment, 0.4 g of the sample sample was taken in a U-shaped, flow-through, quartz sample tube. Prior analysis, sample was pretreated in He (50 ml/min; ramp rate 5°C/min) at 550 °C for 1 h. After cooling to 110°C, the catalyst was flushed with 50 ml/min Ar flow for one hour and then exposed to a flow of 100 ml/min 1%NH₃ in Ar for 1.5 hour. After purging with 50 ml/min Ar flow for 3.5 hour, TPD measurements were carried out in the range 110–800 °C at a heating rate of 10 °C/min. The amount of desorbed ammonia was determined based on the area under the peak. Figure 17 shows NH₃-temperature program desorption (TPD) data for Ga(5 wt.%)/ZSM-5 and Ga(5 wt.%)/ZSM-5_{xM} catalysts, with densities of acid sites calculated based on peak areas. Ga(5 wt.%)/ZSM-5 catalyst resulted two NH₃ desorption peaks that were centered at 200 °C and 373°C. The low temperature peak corresponds to weak acid sites that allowed NH₃ to desorb from extra framework silanol/alumina species, while the high temperature peak is attributed to strong acid sites that require more energy for NH₃ desorption from framework bridged hydroxyl groups (Si-OH-Al). Alkali treatment of ZSM-5 with 0.2M NaOH resulted in significant loss in intensity of the high temperature strong acid site peak while further increasing NaOH concentrations from 0.6M to 1.0M for ZSM-5 treatment exhibited a gradual loss of strong acid site peak intensities. A minimal loss in intensities of low temperature weak acid peaks (200 °C) were observed for modified Ga(5 wt.%)/ZSM-5_{xM} catalysts. The total density of acid sites dropped in the order of Ga(5 wt.%)/ZSM-5 (1.11 mmol/g) > Ga(5 wt.%)/ZSM-5_{0.2M} (0.953 mmol/g) > Ga(5 wt.%)/ZSM-5_{0.6M} (0.916 mmol/g) > Ga(5 wt.%)/ZSM-5_{0.8M} (0.904 mmol/g) > Ga(5 wt.%)/ZSM-5_{1.0M} (0.886 mmol/g). The loss of total acidity for used Ga/ZSM-5_{xM} catalysts could be due to loss of framework acid species (Si-OH-Al) and partial replacement of Bronsted acid sites (proton H⁺ in hydroxyl group) by gallium cations.

[0082] *Effect of catalyst modification on ethanol product distributions:* Ethanol conversion to liquid, i.e., C₅⁺, hydrocarbons is reported to occur via a dual-cycle hydrocarbon pool involving ethanol dehydration followed by aromatization. According

to this mechanism, the ethanol hydrocarbon pool (HCP) reaction starts by producing ethylene that the inherent H-ZSM-5 pore structure converts to BTX.^{14,24} During the ethanol HCP process, only a limited quantity of C9-C10 aromatic hydrocarbons can be formed due to their large size relative to the pore volume capacity.²⁴ Thus, desilicating parent ZSM-5 (Si/Al = 23) by treating with different concentrations of NaOH removes framework silica to create mesopores that should be able to accommodate larger hydrocarbon molecules. As a result, the pore volume should be sufficient to accommodate more intermediate olefins and aromatics (BTX) for single stage conversion into C9-C10 aromatics. The larger pores in modified ZSM-5 supports should also increase LHYS by allowing a much greater fraction of active metals to impregnate inside the zeolite pores.

[0083] Alkali treatment of H-ZSM-5 is very selective for hydrolyzing the framework silica without disturbing framework alumina or Bronsted acid sites much.^{30,33,43} But zeolite crystallinity can be damaged if alkali treatment extracts too much framework silica. Hence, ZSM-5 crystallinity and pore volume were characterized to determine how the concentration of NaOH impacted these properties and their relationship to carbon number distribution of product hydrocarbons. It was found that increasing NaOH concentration consistently increased support pore volume. However, treatment with 0.8M NaOH was optimum for generating mesopores in ZSM-5_{0.8M} without compromising crystallinity as further increasing the alkali concentration to 1.0M NaOH resulted in excessive extraction of framework silica. The ICP-OES data in Table 2 shows this detrimental influence of 1.0M NaOH on ZSM-5_{1.0M} crystallinity as measured by XRD. J. C. Groen et al found that alkali treatment of ZSM-35 that had a Si/Al ratio of 40 produced a high density of Si-O-Si bonds that are more easily hydrolyzed by NaOH, such that treatment with 0.2M NaOH at 60 °C for 30 minutes led to the maximum mesopore volume without disturbing zeolite crystallinity or Bronsted acidity. However, for the present study with a Si/Al ratio of 23 for parent ZSM-5, the greater proportion of more recalcitrant Si-O-Al bonds makes it necessary to apply higher concentrations of NaOH for hydrolysis than needed for less recalcitrant Si-O-Si bonds in the earlier report. Therefore, 0.8M NaOH treatment at 60°C for 30 minutes was required to dissolve framework silica and to create mesopores without significantly disturbing crystallinity. Generally, because solvated Ga⁺³ ions for wet-impregnation are too large to enter ZSM-5 pores or exchange with Bronsted acid sites, they deposit as clusters on the external surface of the zeolite.^{28,29,44,45} In line with

this expectation, STEM showed large needle shape gallium oxide particles on the external surface of the parent H-ZSM-5 support in the present study. Interestingly, because the enhanced pore volume of H-ZSM-5_{0.6,0.8&1.0M} supports facilitated gallium oxide migration into zeolite channels, less gallium oxide was left on the external surface with the result that smaller gallium oxide particles were formed compared to parent ZSM-5. Calculating the Si/Ga ratio on the external surface based on XPS measurements reinforced that larger pores resulted in less Ga on the external surface of Ga(5 wt. %)/ZSM-5_{0.6,0.8&1.0M} compared to Ga(5 wt. %)/ZSM-5. Further, employing H₂-TPR revealed that enhancing pore volume resulted in more gallium migrating into the zeolite channels, thereby increasing interactions between gallium oxide and the modified-ZSM-5_{xM} supports.

[0084] The goal of this study was to maximize liquid product yields from ethanol through ZSM-5 modifications coupled with optimizing reaction temperature and WHSVs. Previous reports show that complete ethanol dehydration to form gas products (C1-C4 hydrocarbons) occurs at 200°C-300°C,¹⁰⁻¹⁸ and ethanol aromatization to liquid products takes place above 350°C.^{19-22,46,49} Hence, to increase liquid hydrocarbon formation, ethanol oligomerizations were conducted from 350°C to 500°C at different space velocities of 1.6, 0.8, and 0.4h⁻¹.

[0085] Figure 4 shows the effect of temperature on ethanol conversion and product distribution using Ga(5%)/ZSM-5 and Ga(5%)/ZSM-5_{xM} catalysts. All catalysts completely converted ethanol over a temperature range of 350°C to 500°C. The liquid hydrocarbon composition as analyzed by GC after separating the organic liquid from the aqueous phase was divided into C5-C6 paraffins, BTX, and C9-C10 aromatics [trimethyl benzene, ethyl methyl benzene and ethyl dimethylbenzene]. As shown in Figure 4 at 350°C, BTX selectivity in the liquid products dropped in the order of Ga-ZSM-5 (69.3%) > Ga/ZSM-5_{0.2M} (57.8%) > Ga/ZSM-5_{0.6M} (49.1%) > Ga/ZSM-5_{0.8M} (44%) > Ga/ZSM-5_{1.0M} (30.1%). On the other hand, this data show that C5-C6 paraffins selectivity in the liquid products followed the opposite trend, with Ga/ZSM-5_{1.0M} in particular realizing the highest C5-C6 paraffins selectivity compared to other catalysts.

[0086] The C9-C10 aromatics selectivity at 350°C dropped in the order Ga/ZSM-5_{0.8M} (24.3%) > Ga/ZSM-5_{0.6M} (21.1%) > Ga/ZSM-5_{1.0M} (15.6%) > Ga/ZSM-5_{0.2M}

(13.4%) > Ga/ZSM-5 (8.1%). Thus, Ga/ZSM-5_{0.8M} realized higher C9-C10 aromatics selectivity than the other catalysts and nearly three times as much as for the parent Ga/ZSM-5. This increase appears to be due to alkali treatment increasing pore volumes while preserving crystallinity as evidenced by lower C9-C10 aromatics and higher C5-C6 paraffins selectivities for ZSM-5_{1.0M} with even greater pore volume but lower crystallinity.

[0087] Because the highest selectivity to C9-C10 chain lengths in liquid products was at 350°C, further experiments were conducted at this temperature for WHSVs of 0.4h⁻¹ and from 0.8h⁻¹ to 1.6h⁻¹. Figure 5 shows that these changes in WHSVs did not have much influence on C5-C6 paraffin selectivity for all catalysts and that Ga/ZSM-5_{1.0M} catalyst still produced the highest selectivity to C5-C6 paraffins of nearly 50% for all WHSVs. However, BTX and C9-C10 aromatic selectivities changed with WHSVs. Interestingly, the lower 0.4 and 0.8h⁻¹ WHSVs favored C9-C10 aromatics production at the expense of BTX. The selectivity of C9-C10 aromatics in liquid products increased nearly 3 times when the WHSV was dropped from 1.6h⁻¹ (17.2% selectivity) to 0.4h⁻¹ (6.3% selectivity) for the parent Ga/ZSM-5 catalyst. A minimal drop in C9-C10 aromatics selectivity resulted from increasing WHSVs from 0.4 to 0.8h⁻¹ for all catalysts. Among the modified catalysts, Ga/ZSM-5_{0.8M} had the highest selectivity to C9-C10 aromatics at 1.6h⁻¹ (24.3%) and 0.4h⁻¹ (45.8%) WHSVs.

[0088] To understand the effect of Ga loading coupled with alkali treatment on ethanol LHYs and product carbon number distribution, ethanol was reacted using bare ZSM-5 and ZSM-5_{xM} supports without loading gallium oxide at the previously optimized conditions of 350°C and 0.4h⁻¹ WHSV. As shown in Figure 6a, the extent of pore modification significantly increased LHYs with ZSM-5_{0.8M} reaching 27.1% and ZSM-5_{1.0M} increasing yields to 30.3%, the latter being nearly six times that from the 5.3% LHY from operation of the parent ZSM-5 support. As shown by comparing Table 1 and Figure 6a, LHYs increased with increased newly generated pore volume of modified ZSM-5_{xM} supports. These results indicate that the enhanced pore volume accommodated more ethanol reactive intermediates inside the pores and promoted tandem dehydration-aromatization reactions. The 27.1% LHYs with 73.1% selectivity to aromatics (46.1% of BTX and 27% of C9-C10 aromatics) can be attributed to the combined contributions of enhanced pore volume and crystallinity for ZSM-5_{0.8M}. Although the

LHYs achieved were greater from ZSM-5_{1.0M} than from ZSM-5_{0.8M}, C5-C6 paraffins (selectivity 48.4%) were more prominent than BTX (15.4%) and C9-C10 aromatics (31.6%) in the liquid products. These results clearly suggest that ZSM-5 crystallinity is vital to producing higher molecular weight hydrocarbons, i.e., BTX and C9-C10 aromatics.

[0089] Comparing Figure 6a to Figure 6b shows that loading Ga onto ZSM-5 and modified-ZSM-5_{xM} significantly affected ethanol LHYs and C9-C10 aromatics selectivity by promoting the dual-cycle hydrocarbon pool path. In particular, loading 5% Ga onto ZSM-5, ZSM-5_{0.6M}, and ZSM-5_{0.8M} resulted in 7, 2.6, and 1.7 times higher LHYs, respectively, compared to corresponding supports that were not loaded with Ga. Figure 7 shows that the incremental increase in C9-C10 aromatics selectivity correlated well with enhanced pore volume/size and increased surface Si/Ga ratios. The consistent increase in pore volume with increasing NaOH concentrations for treatment of ZSM-5 supports promoted more Ga migration into the modified-zeolite channels. Hence, the XPS measured surface Si/Ga ratios for both Ga(5%)/ZSM-5_{0.8M} and Ga(5%)/ZSM-5_{1.0M} catalysts are higher, suggesting that more Ga migrated into the larger modified-zeolite channels. Enhancing Ga migration while retaining crystallinity in modified ZSM-5_{xM} supports enabled strong interactions between gallium oxide and the hydroxyl groups in ZSM-5_{xM} support, as shown by H₂-TPR. Specifically, increasing the presence of gallium oxide inside zeolite pores promoted alkylation, and hence, increased C9-C10 aromatics selectivity at the expense of BTX. On the other hand, the location of most of the Ga on the external surface of ZSM-5 only promoted dehydration and aromatization with the result that BTX was the major product. Combining greater gallium migration inside zeolite pores with enhanced metal-support interactions for Ga(5 wt.%)/ZSM-5_{0.8M} catalyst promoted the tandem reactions of ethanol dehydration, aromatization, and alkylation to thereby increase LHYs and C9-C10 aromatics formation. Although the pore volume was greater for Ga(5 wt.%)/ZSM-5_{1.0M}, loss of support crystallinity and weak metal-support interactions led to a drop in C9-C10 aromatic selectivity. Thus, the results shown in Figure 7 strongly suggest that the ability of greater ZSM-5_{0.8M} pore volumes to accommodate longer chain lengths and greater Ga penetration into the pores for Ga/ZSM-5_{0.8M} catalyst combined with retained crystallinity and greater metal-support interactions significantly enhanced C9-C10 aromatics selectivity.

[0090] In order to evaluate the effect of catalyst synthesis time on Ga migration into ZSM-5_{0.8M} channels, Ga wet-impregnation times of 4 hours and 32 hours were applied for production of two additional batches of Ga(5%)/ZSM-5_{0.8M} catalysts. As XPS measurements show in Figure 16 and Table 4, the surface Si/Ga ratio for the 4 hours batch of Ga/ZSM-5_{0.8M} catalyst was 9 while that for the 16 hours batch was measured to be about two thirds of that value. These results indicate that more Ga was deposited on the external surface of the zeolite that had been synthesized for 4 hours while impregnating for 16 hours allowed more Ga to migrate into the pores, a conclusion that is also supported by the bulk elemental analysis reported in Table 3.

Table 3: ICP-OES analysis for Ga (5 wt.%)/ZSM-5_{0.8M} catalysts synthesized at different times.

Catalyst	Ga impregnation time	ICP-OES data of Ga nominal loading in wt. %
Ga (5 wt.%)/ZSM-5 _{0.8M}	4	4.8
Ga (5 wt.%)/ZSM-5 _{0.8M}	16	4.9
Ga (5 wt.%)/ZSM-5 _{0.8M}	32	4.8

Table 4: XPS derived Si/Ga surface ratios of as-synthesized samples.

Sample	External surface Si/Ga ratio
^a Ga(5 wt.%)/ZSM-5 _{0.8M}	9
^b Ga(5 wt.%)/ZSM-5 _{0.8M}	13.5
^c Ga(5 wt.%)/ZSM-5 _{0.8M}	13.5
Ga(8 wt.%)/ZSM-5 _{0.8M}	13
Ga(2 wt.%)/ZSM-5 _{0.8M}	29

^aCatalyst synthesis time of 4 hours, ^bcatalyst synthesis time of 16 hours, and ^ccatalyst synthesis time of 32 hours. External Si/Ga surface ratios were measured based on relative surface concentration of Ga, Na, Si, Al, and O atoms.

[0091] Furthermore, because the surface Si/Ga ratio was the same for catalysts that were synthesized for 16 and 32 hours, a 16 hours impregnation was adequate to maximize Ga insertion into ZSM-5_{0.8M} channels. When Ga(5%)/ZSM-5_{0.8M} catalysts that had been impregnated for 4 hours, 16 hours and 32 hours were employed for ethanol conversion to hydrocarbons at 350°C and 0.4h⁻¹ WHSV, Figure 8(a) shows that C9-C10 aromatics selectivity in the liquid products increased from 20.1% for the 4 hours synthesis time to 45.6% for a 16 hours synthesis and then changed little to 43.9% for a 32 hour time. These results clearly reveal that the high fraction of Ga inside the zeolite channels not only facilitated ethanol dehydration and aromatization but also promoted alkylation to higher C9-C10 aromatics selectivity while alkylation was impeded when less Ga was inside the pores.

[0092] The effect of Ga on hydrocarbon product distribution was evaluated by loading 2 wt.% and 8 wt.% Ga on ZSM-5_{0.8M} while keeping the catalyst synthesis time at 16 hours. Figure 8(b) shows that compared to results for 5 wt.% Ga, 2 wt.% and 8 wt.% Ga loadings produced more C5-C6 paraffins and BTX, respectively, while suppressing C9-C10 aromatics formation. In the case of 2 wt.% Ga/ZSM-5_{0.8M}, the lower loading of gallium oxide suppressed aromatization and resulted in more C5-C6 paraffins. On the other hand, the 8 wt.% Ga loading might have blocked zeolite pores and interfered with escape of C9-C10 aromatics from the pores due to steric constraints, as supported by the N₂-physisorption results shown in Figure 13. The result that the surface Si/Ga ratios of 5 wt.% Ga/ZSM-5_{0.8M} and 8 wt.% Ga/ZSM-5_{0.8M} catalysts as measured by XPS had about the same values suggests that migration of more gallium oxide into zeolite channels for the latter case reduced formation of larger chains by blocking pores. Although the surface Si/Ga ratio of 29 for 2 wt.% Ga/ZSM-5_{0.8M} meant a high fraction of Ga was in the pores, the lower amount of Ga left to enter the zeolite channel than for 5% loadings would be expected to reduce C9-C10 aromatics yields.

[0093] Figure 9a shows that ethanol LHYs and >45% C9-C10 aromatics selectivities were maintained for 32 hours for the Ga(5 wt.%)/ZSM-5_{0.8M} catalyst. Thus, it appears that enhanced zeolite pore volume and Ga metal insertion into ZSM-5_{0.8M} channels maintained catalyst activity over these time periods without loss of C9-C10 aromatics selectivity. Ga(5 wt.%)/ZSM-5_{0.8M} stability was also evaluated when fed wet-ethanol vapor (40% vol), about the concentration that would be produced by vaporizing fermentation broth at the feed tray to an ethanol recovery distillation train.⁴ As shown in Figure 9b, LHYs and C9-C10 aromatics selectivity were both higher when Ga(5 wt.%)/ZSM-5_{0.8M} was fed wet ethanol at 350°C with a 0.4h⁻¹ WHSV than when just pure ethanol was the feed at the same conditions. Furthermore, the C9-C10 aromatics selectivity drifted upward to 55.1% at 20 hours reaction time for wet ethanol and then remained about the same after that. Previous reports that steam treatment of ZSM-5 can increase catalyst stability and affect final product distributions by facilitating new mesopores formation could account for greater C9-C10 aromatics selectivity in the present case.⁴⁶

[0094] Hence, to determine the change in physical and chemical properties of catalysts used to convert pure ethanol and wet ethanol to hydrocarbons and the influence of water on

C9-C10 aromatic selectivity, used catalysts were extensively characterized by XRD, N₂-physisorption, H₂-TPR, and TPO. As shown in Figure 19, XRD revealed that the support crystallinity did not change after several hours of reactions with pure wet ethanol, indicating the zeolite framework was not damaged at longer times. However, the top layer of used catalysts turned dark black while the gray color of the middle and lower portions suggested carbon formation progressed slowly through the catalyst.

[0095] Figures 20a-c indicates a marginal loss in total surface area for used catalysts due to partial damage to the micropore surface area of the ZSM-5_{0.8M} support. A marginal loss in mesopore volume was observed for used catalysts compared to fresh catalyst and the pore volume dropped in order of Ga/ZSM-50.8M (0.2483 cm³/g; fresh catalyst) > used Ga/ZSM-50.8M for wet-ethanol feed (0.2279 cm³/g) > used Ga/ZSM-50.8M for ethanol feed (0.2164 cm³/g). The loss in pore volume for used Ga/ZSM-50.8M catalysts cause either pore blocking by extra framework alumina (EFAl) species which are leached out from zeolite framework or migration of more gallium from the surface into the mesopores for ethanol conversion at 350 °C.

[0096] Interestingly, the shift of the H₂-TPR profiles of gallium oxide reduction peaks to higher temperatures shown in Figure 9c for used catalysts compared to fresh Ga/ZSM-50.8M catalyst suggests enhanced interactions between gallium oxide and support hydroxyl groups that occurred during ethanol and wet-ethanol conversions. In particular, catalyst used with wet-ethanol showed gallium oxide reduction starting from 601°C, a higher temperature than for catalyst used with pure ethanol (576°C) and fresh catalyst (560°C). These results suggest that more gallium migrated into the zeolite pores and enabled strong metal-support interactions, resulting in higher C9-C10 aromatic selectivity. TPO experiments were conducted to determine the extent of formation of soft carbon (hydrogen rich hydrocarbons) versus hard carbon (hydrogen lean polyaromatics or graphite type carbon) on used catalysts.

[0097] Figure 10 shows desorption peaks for carbon dioxide, carbon monoxide, and water produced by burning off the carbon from used catalysts. The high coke combustion temperatures suggest that a substantial amount of hard carbon had been formed on the catalysts, likely via polymerization of aromatic compounds during conversion of both pure and wet ethanol. However, the amount of carbon produced was lower from used catalyst that had been used with wet (4.8 wt.%) than with pure ethanol (7.1 wt.%).

[0098] Previous studies showed less than 5% C₉+ aromatics formation in addition to light weight hydrocarbons and BTX from an ethanol feed.^{23,24} The high molecular weight C₉+ hydrocarbon may occur either on the external ZSM-5 surface or inside its pores by alkylation of C₇/C₈ aromatics with C₁/C₂ paraffin. Any chains too long to escape through the pore mouth would need to either crack to smaller molecules that could leave through zeolite micropores or breakdown to deposit carbon on the walls that would interfere with adsorption or block micropores. However, this study showed the catalyst could maintain stable production of C₉-C₁₀ aromatics, mostly as ethyl methyl benzene, trimethyl benzene (mesitylene), and ethyl dimethyl benzene (C₁₀). As illustrated in Scheme 1, the combination of micro and mesopores in modified-ZSM-5 supports could accommodate sequential ethanol dehydration, aromatization, and alkylation and reduce trapping of bulky C₉-C₁₀ aromatics that would otherwise either crack to smaller molecules that could escape or pyrolyze to coke that would interfere with catalytic activity inside the pores.

[0099] The present study provides insights into the roles of zeolite pore volume, crystallinity, and gallium penetration into channels and metal-support interactions on the distribution of hydrocarbon chain lengths produced by reaction of ethanol to liquid hydrocarbons on ZSM-5 catalysts. Although ZSM-5 alone produced aromatic hydrocarbons, LHYs were very low due to the small support microporosity. Treatment of ZSM-5 with 1.0M NaOH increased pore volume, but selectivity to liquid hydrocarbons containing more than 5 carbon atoms (C₆+) dropped significantly due to loss of support crystallinity and metal-support interaction. However, by maintaining crystallinity while also increasing pore volume, treatment of ZSM-5 with 0.8M NaOH increased both LHYs and selectivity to C₆+ hydrocarbons. Furthermore, enlarging pores by treatment with NaOH increased C₉-C₁₀ selectivity by nearly 50% from ethanol dehydration, aromatization, and alkylation through promoting gallium migration into ZSM-5_{0.8M} channels and enabling strong metal-support interactions. Finally, the ZSM-5 inherent pore structure played a key role in controlling LHYs compared to other large pore zeolites (Figure 22).

CONCLUSIONS:

[0100] This study reveals how pore modification, crystallinity, Ga proximity, and metal-support interactions in zeolite channels affect yields and carbon number distributions of hydrocarbons formed by single step reaction of ethanol on ZSM-5 catalysts. Treatment of

ZSM-5 with of 0.2, 0.6, 0.8, and 1.0M NaOH progressively increased pore volume/size, but crystallinity dropped significantly for 1.0M NaOH as determined by XRD and N₂-physisorption studies. In addition, STEM and XPS studies revealed greater Ga migration into the channels of ZSM-5 that had been treated with 0.8 and 1.0M NaOH than for parent ZSM-5 catalyst. H₂-TPR studies revealed that enhanced gallium migration into the mesopores further promoted strong metal-support interactions. The ability of ZSM-5 catalysts treated with 0.8M NaOH but without gallium oxide to accommodate larger hydrocarbon molecules in the larger pores combined with retained crystallinity and greater Ga penetration into zeolite pores increased LHYS yields by nearly five times to 27.1% compared to 5.3% from the parent support. Loading ZSM-5_{0.8M} with 5% Ga further increased LHYS and C9-C10 hydrocarbon selectivity to 46.1% and 45.8%, respectively, from 35.1% and 17.2%, respectively, for the parent catalyst for reactions at 350°C and 0.4h⁻¹ WHSV. Furthermore, feeding 40% ethanol in water vapor increased LHYS to ≥50% and C9-C10 aromatic selectivity to 55.1% while maintaining catalyst stability over 32 hours.

Example 2

Metal Screen

[0101] This example explores the use of various metals loaded on ZSM-5. The zeolite was modified generally in accordance with the procedure set forth in Example 1, and the modified zeolite was used in ethanol conversion experiments in generally in accordance with the procedure set forth in Example 1.

[0102] Ru (2 and 5 wt%) on ZSM-5_{0.8M} catalysts showed similar performance as Ga(5 wt%)/ZSM-5_{0.8M} catalyst. At 350 °C and 0.4h⁻¹ WHSV, complete ethanol converted into 45% liquid hydrocarbons in single stage reaction. Maximum selectivity of 45% C9-C10 aromatics was obtained using Ru(5 wt%)/ZSM-5_{0.8M} catalyst at above conditions. Ru loadings from 0.5 to 10% on ZSM-5_{0.8M} catalyst can result similar liquid hydrocarbons and C9-C10 aromatics from ethanol conversions.

[0103] Cobalt, Nickel, Vanadium and Indium metals were each incorporated on to ZSM-5_{0.8M} support; however, these catalysts did not result any liquid hydrocarbon products from ethanol conversions.

REFERENCES:

- 1 U.S. Energy Information Administration (EIA),
https://www.eia.gov/environment/emissions/carbon/pdf/2019_co2analysis.pdf.
- 2 EPA, *Invent. U.S. Greenh. Gas Emiss. Sink.*, 2019, **EPA430-R-2**, 2–99.
- 3 C. Yang and S. Yeh, *AIP Conf. Proc.*, 2011, **1401**, 259–270.
- 4 J. R. Hannon, L. R. Lynd, O. Andrade, P. T. Benavides, G. T. Beckham, M. J. Bidy, N. Brown, M. F. Chagas, B. H. Davison, T. Foust, T. L. Junqueira, M. S. Laser, Z. Li, T. Richard, L. Tao, G. A. Tuskan, M. Wang, J. Woods and C. E. Wyman, *Proc. Natl. Acad. Sci. U. S. A.*, 2020, **117**, 12576–12583.
- 5 J. Holladay, Z. Abdullah and J. Heyne, *Rev. Tech. Pathways*, 2020, 1–81.
- 6 C. Gutiérrez-Antonio, F. I. Gómez-Castro, J. A. de Lira-Flores and S. Hernández, *Renew. Sustain. Energy Rev.*, 2017, **79**, 709–729.
- 7 S. S. Doliente, A. Narayan, J. F. D. Tapia, N. J. Samsatli, Y. Zhao and S. Samsatli, *Front. Energy Res.*, 2020, **8**, 1–38.
- 8 J. Teter, P. Le Feuvre, P. Bains and L. Lo Re, *IEA, Paris*, 2020, <https://www.iea.org/reports/aviation-2>.
- 9 O. Rosales-Calderon and V. Arantes, *Biotechnol. Biofuels*, 2019, **12**, 2–58.
- 10 J. Bi, X. Guo, M. Liu and X. Wang, *Catal. Today*, 2010, **149**, 143–147.
- 11 N. Zhan, Y. Hu, H. Li, D. Yu, Y. Han and H. Huang, *Catal. Commun.*, 2010, **11**, 633–637.
- 12 Q. Sheng, K. Ling, Z. Li and L. Zhao, *Fuel Process. Technol.*, 2013, **110**, 73–78.
- 13 R. Barthos, A. Sze and F. Solymosi, *J. Phys. Chem. B*, 2006, **110**, 21816–21825.
- 14 K. K. Ramasamy and Y. Wang, *Catal. Today*, 2014, **237**, 89–99.
- 15 J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo and G. W. Huber, *J. Catal.*, 2011, **279**, 257–268.
- 16 N. Viswanadham, S. K. Saxena, J. Kumar, P. Sreenivasulu and D. Nandan, *Fuel*, 2012, **95**, 298–304.
- 17 K. Murata, M. Inaba and I. Takahara, *J. Japan Pet. Inst.*, 2008, **51**, 234–239.
- 18 S. Moon, H. J. Chae and M. B. Park, *Catalysts*, 2019, **9**, 1–12.
- 19 Z. Wang, L. A. O'Dell, X. Zeng, C. Liu, S. Zhao, W. Zhang, M. Gaborieau, Y. Jiang and J. Huang, *Angew. Chemie*, 2019, **131**, 18229–18236.
- 20 M. Inaba, K. Murata, M. Saito and I. Takahara, *React. Kinet. Catal. Lett.*, 2006,

- 88**, 135–142.
- 21 S. K. Saha and S. Sivasanker, *Catal. Letters*, 1992, **15**, 413–418.
- 22 K. Van Der Borcht, V. V. Galvita and G. B. Marin, *Appl. Catal. A Gen.*, 2015, **504**, 621–630.
- 23 Z. Li, A. W. Lepore, M. F. Salazar, G. S. Foo, B. H. Davison, Z. Wu and C. K. Narula, *Green Chem.*, 2017, **19**, 4344–4352.
- 24 R. Johansson, S. L. Hruby, J. Rass-Hansen and C. H. Christensen, *Catal. Letters*, 2009, **127**, 1–6.
- 25 P. Gallezot, C. Leclercq, M. Guisnet and P. Magnoux, *J. Catal.*, 1988, **114**, 100–111.
- 26 R. A. Van Santen and W. M. H. Sachtler, *J. Phys. Chem. B*, 1999, **103**, 4611–4622.
- 27 K. M. Dooley, C. Chang and G. L. Price, *Appl. Catal. A Gen.*, 1992, **84**, 17–30.
- 28 G. L. Price and V. Kanazirev, *J. Catal.*, 1990, **278**, 267–278.
- 29 A. Biscardi and E. Iglesia, *Catal. Today*, 1996, **31**, 207–231.
- 30 J. C. Groen, J. A. Moulijn and J. Pérez-Ramírez, *J. Mater. Chem.*, 2006, **16**, 2121–2131.
- 31 A. Čižmek, B. Subotić, I. Šmit, A. Tonejc, R. Aiello, F. Crea and A. Nastro, *Microporous Mater.*, 1997, **8**, 159–169.
- 32 K. Sadowska, K. Góra-Marek, M. Drozdek, P. Kuśtrowski, J. Datka, J. Martinez Triguero and F. Rey, *Microporous Mesoporous Mater.*, 2013, **168**, 195–205.
- 33 A. Aloise, A. Marino, F. Dalena, G. Giorgianni, M. Migliori, L. Frusteri, C. Cannilla, G. Bonura, F. Frusteri and G. Giordano, *Microporous Mesoporous Mater.*, 2020, **302**, 110198 (1–8).
- 34 R. M. Dessau, E. W. Valyocsik and N. H. Goeke, *ZEOLITES*, 1992, **12**, 776–779.
- 35 T. Suzuki and T. Okuhara, *Microporous Mesoporous Mater.*, 2001, **43**, 83–89.
- 36 R. Fricke, H. Kosslick and M. Richter, *Chem. Rev.*, 2000, **100**, 2303–2405.
- 37 L. I. U. Ru-ling, Z. H. U. Hua-qing, W. U. Zhi-wei, Q. I. N. Zhang-feng, F. Wei-bin and W. Jian-guo, *J. Fuel Chem. Technol.*, 2015, **43**, 961–969.
- 38 I. Nowak, J. Quartararo, E. G. Derouane and J. C. Védrine, *Appl. Catal. A Gen.*, 2003, **251**, 107–120.
- 39 H. Xiao, J. Zhang, X. Wang, Q. Zhang, H. Xie, Y. Han and Y. Tan, *Catal. Sci. Technol.*, 2015, **5**, 4081–4090.

- 40 E. S. Shpiro, D. P. Shevchenko, O. P. Tkachenko and R. V. Dmitriev, *Appl. Catal. A, Gen.*, 1994, **107**, 147–164.
- 41 A. Wang, D. Austin, H. Qian, H. Zeng and H. Song, *ACS Sustain. Chem. Eng.*, 2018, **6**, 8891–8903.
- 42 A. Wang, D. Austin, A. Karmakar, G. M. Bernard, V. K. Michaelis, M. M. Yung, H. Zeng and H. Song, *ACS Catal.*, 2017, **7**, 3681–3692.
- 43 J. Li, M. Liu, X. Guo, S. Zeng, S. Xu, Y. Wei, Z. Liu and C. Song, *Ind. Eng. Chem. Res.*, 2018, **57**, 15375–15384.
- 44 R. Fricke, H. Kosslick, G. Lischke and M. Richter, *Chem. Rev.*, 2000, **100**, 2303–2405.
- 45 K. M. Dooley, G. L. Price, V. I. Kanazirev and V. I. Hart, *Catal. Today*, 1996, **31**, 305–315.
- 46 Q. Sheng, K. Ling, Z. Li and L. Zhao, *Fuel Process. Technol.*, 2013, **110**, 73–78.

CLAIMS

What is claimed is:

1. A method for selectively producing C9-C12 aromatics, comprising:

converting ethanol in the presence of a heterogeneous catalyst at a temperature suitable to produce a product mixture comprising liquid hydrocarbons,

wherein the heterogeneous catalyst comprises Ga or Ru metal loaded onto zeolite, wherein the heterogeneous catalyst has one or more of the following properties:
 - (i) a zeolite pore volume of at least 0.05 cm³/g;
 - (ii) a Ga or Ru loading between 1% and 10%;
 - (iii) a zeolite surface Si/Ga ratio between 5 and 30;
 - (iv) a total acid site density between 0.5 mmol/g and 1.5 mmol/g; and
 - (v) a Ga or Ru particle size between 1 nm and 10 nm.
2. The method of claim 1, wherein the heterogeneous catalyst has all five properties (i)-(v).
3. The method of claim 2, wherein the heterogeneous catalyst is prepared by a process comprising desilicating the zeolite and incorporating Ga.
4. The method of claim 3, wherein desilicating the zeolite is performed by contacting the zeolite with aqueous hydroxide.
5. The method of claim 4, wherein the hydroxide source is NaOH.
6. The method of claims 4 or 5, wherein the hydroxide concentration is between 0.2 M and 1.0 M.
7. The method of any one of claims 3 to 6, wherein incorporating Ga is performed by wet impregnation.
8. The method of any one of claims 3 to 7, further comprising protonating the zeolite prior to incorporating Ga.

9. The method of claim 8, wherein protonating the zeolite is performed by contacting the zeolite with an acidic solution.
10. The method of claim 9, wherein the acidic solution comprises aqueous ammonium nitrate.
11. The method of any one of claims 8 to 10, further comprising calcining the zeolite.
12. The method of claim 11, wherein the calcining is performed at a temperature of at least 450 °C.
13. The method of any one of claims 1 to 12, wherein the zeolite pore volume is between 0.4-0.5 cm³/g; the Ga or Ru loading is 3-7%; the zeolite surface Si/Ga ratio or Si/Ru ratio is 10-15; the total acid site density is between 0.85 mmol/g and 0.95 mmol/g; and the Ga or Ru particle size is between 3.5 nm and 4.5 nm.
14. The method of any one of claims 1 to 13, wherein the product selectivity is:
 - (a) less than 50% for C5-C6 paraffins;
 - (b) less than 80% for benzene, toluene and xylene (BTX); and
 - (c) at least 10% for C9-10 aromatics.
15. The method of any one of claims 1 to 14, wherein the product selectivity is:
 - (a) less than 30% for C5-C6 paraffins;
 - (b) less than 60% for benzene, toluene and xylene (BTX); and
 - (c) at least 20% for C9-10 aromatics.
16. The method of any one of claims 1 to 15, wherein the product selectivity is at least 50% for C9-10 aromatics.
17. The method of any one of claims 1 to 16, wherein the liquid hydrocarbon yield is at least 25%.
18. The method of any one of claims 1 to 16, wherein the liquid hydrocarbon yield is at least 50%.

19. The method of any one of claims 14 to 16, wherein the C9-C10 aromatics comprise trimethyl benzene, ethyl methyl benzene, or ethyl dimethyl benzene, or any combination thereof.
20. The method of any one of claims 1 to 19, wherein the heterogeneous catalyst has a catalyst stability of greater than 30 hours.
21. The method of any one of claims 1 to 20, wherein the product mixture further comprises gaseous hydrocarbons.
22. The method of any one of claims 1 to 21, wherein the ethanol is delivered in vapor form.
23. The method of claim 22, wherein the ethanol is delivered as wet-ethanol vapor.
24. The method of any one of claims 1 to 23, wherein the product mixture further comprises water.
25. The method of claim 24, further comprising isolating the liquid hydrocarbons produced from water.
26. The method of any one of claims 1 to 25, wherein the temperature is between 350°C and 500°C.
27. The method of any one of claims 1 to 26, wherein the heterogeneous catalyst further comprises a zeolite surface area between 300 m²/g and 450 m²/g, and a crystallinity between 70% and 95% relative to the crystallinity of the zeolite, wherein said crystallinity is determined by powder X-ray diffraction analysis of peaks in the signal area of 22.7° to 24.2° 2 θ .
28. The method of any one of claims 1 to 27, wherein the heterogeneous catalyst comprises Ga metal loaded onto zeolite.
29. The method of any one of claims 1 to 27, wherein the heterogeneous catalyst comprises Ru metal loaded onto zeolite.
30. A composition comprising C9-C12 aromatics, produced according the method of any one of claims 1-29.

31. A system, comprising:
a catalytic reactor containing a heterogeneous catalyst,
wherein the catalytic reactor comprises:
an ethanol inlet configured to receive ethanol at an elevated temperature,
and
a reactor outlet configured to output a product mixture comprising liquid hydrocarbons produced from the ethanol, wherein the liquid hydrocarbons comprise C9-C10 aromatics,
wherein the heterogeneous catalyst comprises Ga or Ru metal loaded onto zeolite,
wherein the heterogeneous catalyst has one or more of the following properties:
- (i) a zeolite pore volume of at least 0.05 cm³/g;
 - (ii) a Ga or Ru loading between 1% and 10%;
 - (iii) a zeolite surface Si/Ga ratio between 5 and 30;
 - (iv) a total acid site density between 0.5 mmol/g and 1.5 mmol/g; and
 - (v) a Ga or Ru particle size between 1 nm and 10 nm; and
- a pump configured to control ethanol flow through the ethanol inlet through the heterogeneous catalyst.
32. The system of claim 31, wherein the heterogeneous catalyst has all five properties (i)-(v).
33. The system of claim 31 or 32, wherein the zeolite pore volume is between 0.4-0.5 cm³/g; the Ga or Ru loading is 3-7%; the zeolite surface Si/Ga ratio or Si/Ru ratio is 10-15; the total acid site density is between 0.85 mmol/g and 0.95 mmol/g; and the Ga or Ru particle size is between 3.5 nm and 4.5 nm.
34. The system of any one of claims 31 to 33, wherein the system is configured to output liquid products having:
- (a) less than 50% for C5-C6 paraffins;
 - (b) less than 80% for benzene, toluene and xylene (BTX); and
 - (c) at least 10% for C9-10 aromatics.

35. The system of any one of claims 31 to 34, wherein the system is configured to output liquid products having:

- (a) less than 30% for C5-C6 paraffins;
- (b) less than 60% for benzene, toluene and xylene (BTX); and
- (c) at least 20% for C9-10 aromatics.

36. The system of any one of claims 31 to 35, wherein the system is configured to output liquid products having at least 50% for C9-10 aromatics.

37. The system of any one of claims 31 to 36, wherein the system is configured to output liquid products at a liquid hydrocarbon yield of at least 25%.

38. The system of any one of claims 31 to 37, wherein the C9-C10 aromatics comprise trimethyl benzene, ethyl methyl benzene, or ethyl dimethyl benzene, or any combination thereof.

39. The system of any one of claims 31 to 38, wherein the heterogeneous catalyst has a catalyst stability of greater than 30 hours.

40. The system of any one of claims 31 to 39, wherein the product mixture further comprises gaseous hydrocarbons.

41. The system of any one of claims 31 to 40, wherein the ethanol is delivered in vapor form.

42. The system of claim 41, wherein the ethanol is delivered as wet-ethanol vapor.

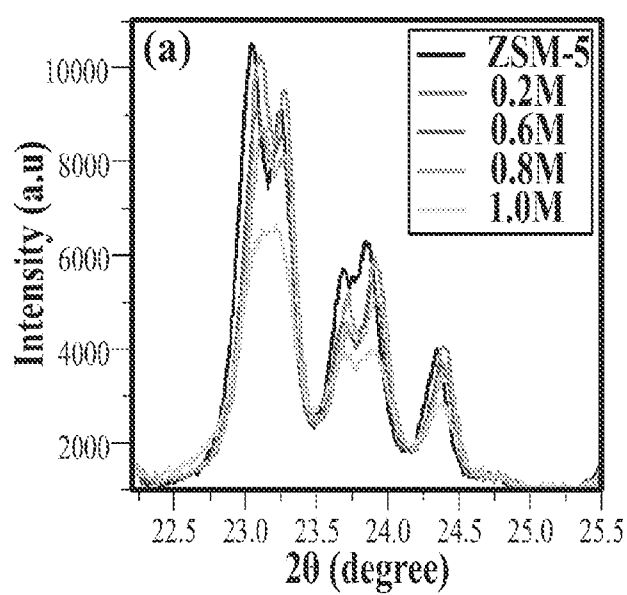
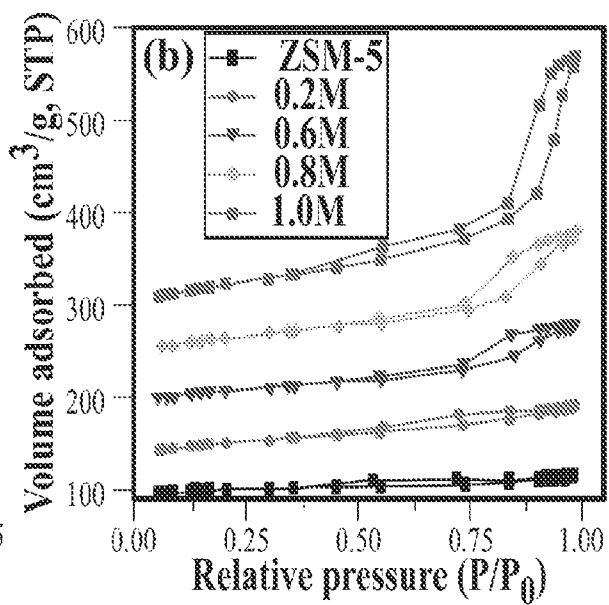
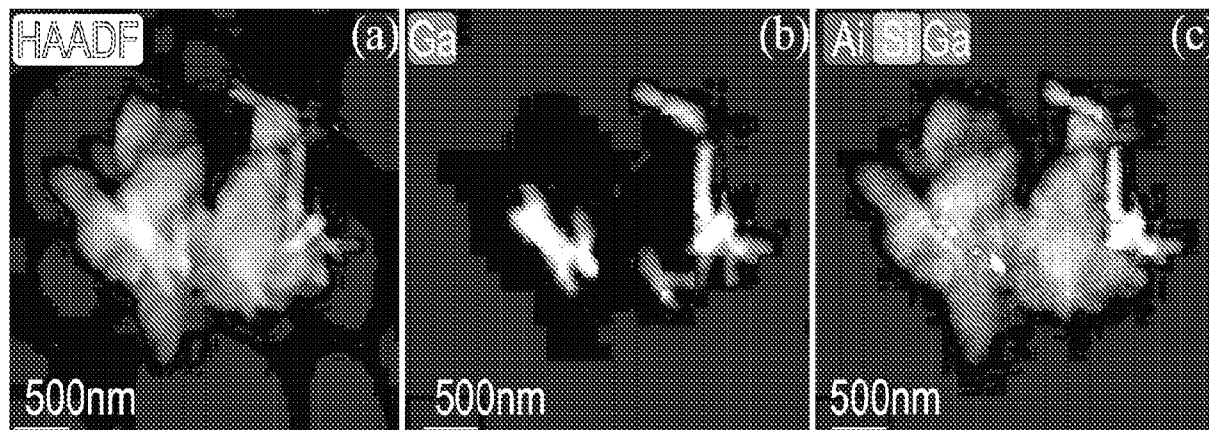
43. The system of any one of claims 31 to 42, wherein the catalytic reactor is configured to operate at a temperature is between 350°C and 500°C.

44. The system of any one of claims 31 to 43, wherein the heterogeneous catalyst further comprises a zeolite surface area between 300 m²/g and 450 m²/g, and a crystallinity between 70% and 95% relative to the crystallinity of the zeolite, wherein said crystallinity is determined by powder X-ray diffraction analysis of peaks in the signal area of 22.7° to 24.2° 2 θ .

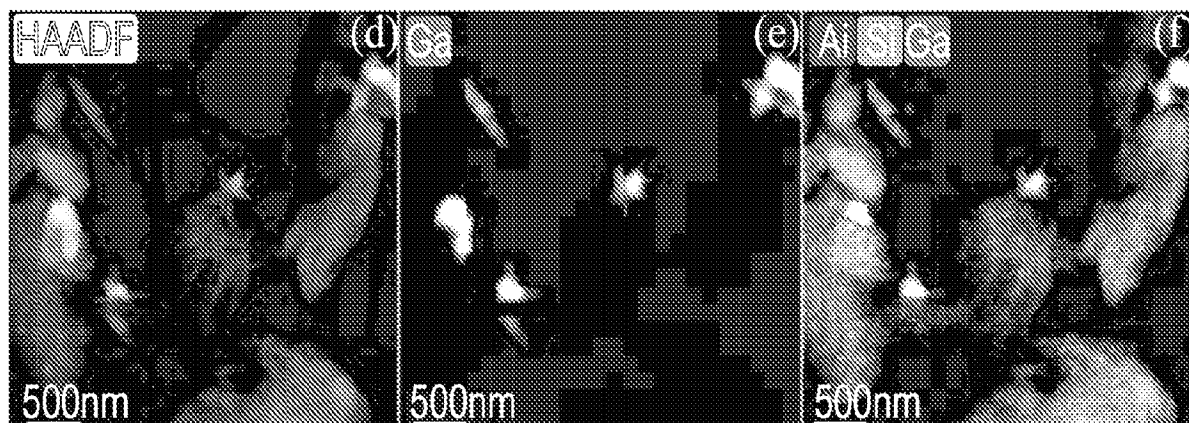
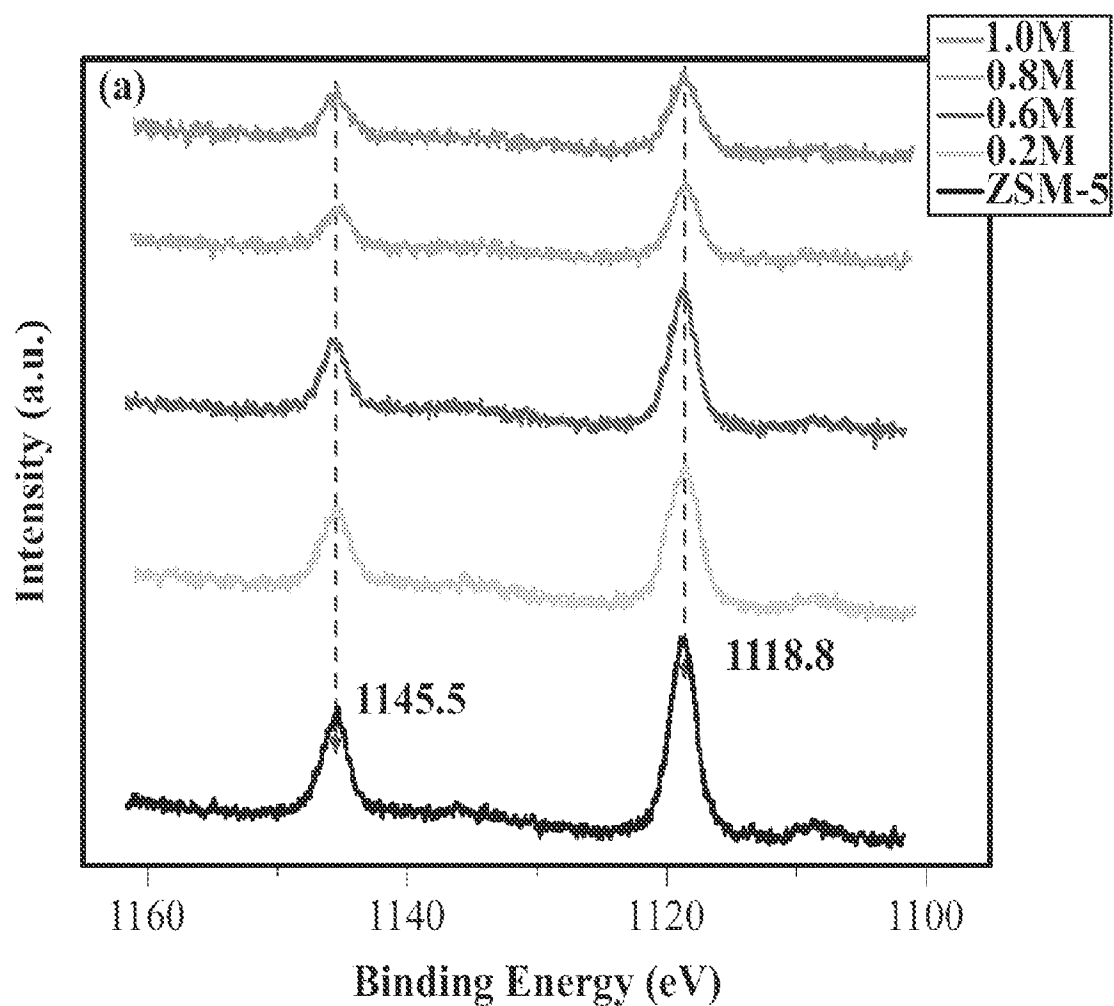
45. The method of any one of claims 31 to 44, wherein the heterogeneous catalyst comprises Ga metal loaded onto zeolite.

46. The method of any one of claims 1 to 44, wherein the heterogeneous catalyst comprises Ru metal loaded onto zeolite.
47. A composition, comprising:
C9-C12 aromatics;
C5-C6 paraffins;
C2-C5 olefins; and
benzene, toluene and xylene (BTX).
48. The composition of claim 47, comprising at least 10% C9-10 aromatics, and less than 5% C11 and C12 aromatics.
49. The composition of claim 48, comprising at least 20% or at least 50% C9-10 aromatics.
50. The composition of any one of claims 47 to 49, wherein C11 and C12 aromatics are present in trace amounts.
51. The composition of any one of claims 47 to 50, wherein no metal is detectable in the composition.

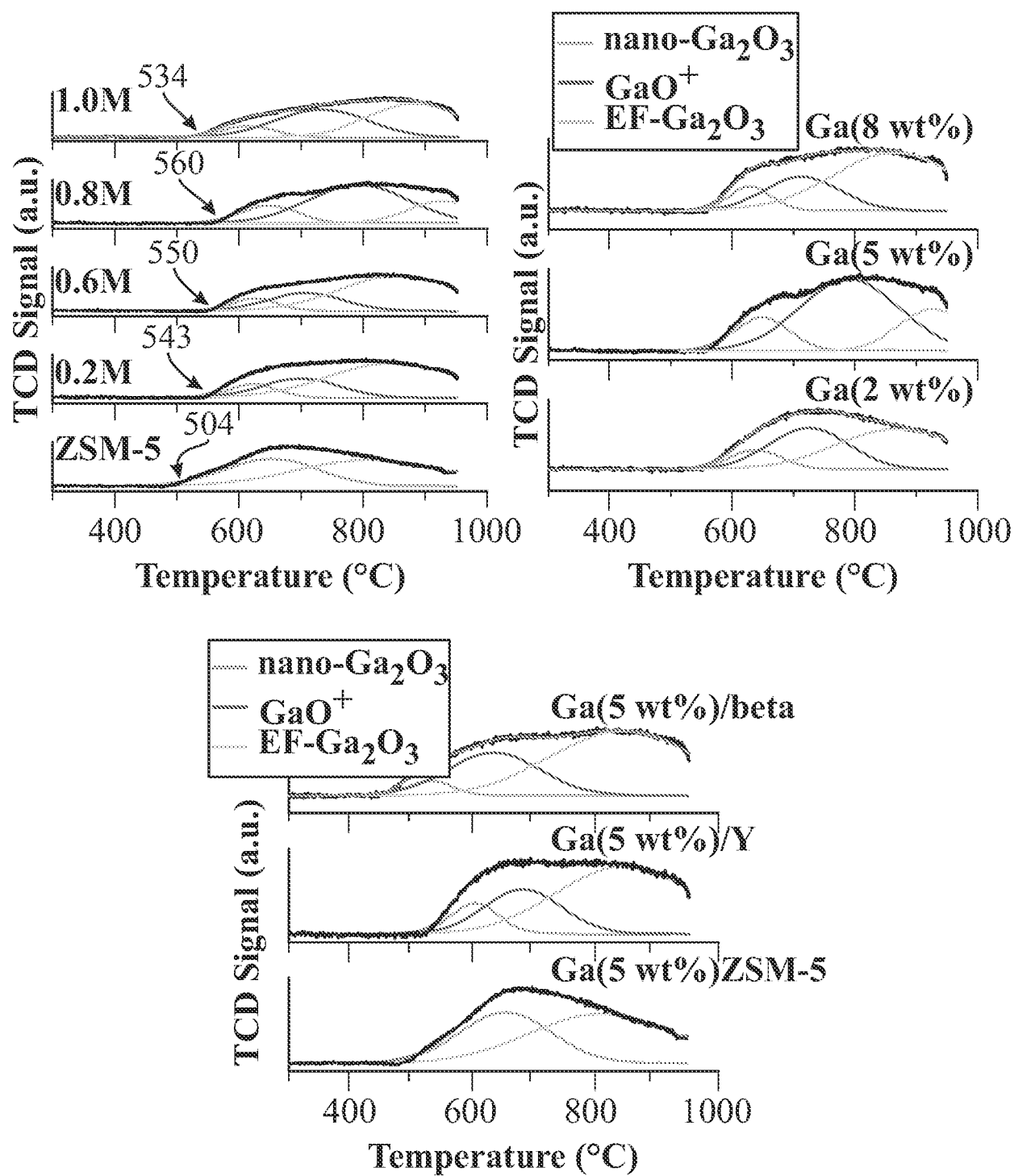
1/18

*Figure 1a**Figure 1b**Figure 2a**Figure 2b**Figure 2c*

2/18

*Figure 2d**Figure 2e**Figure 2f**Figure 3a*

3/18

*Figure 3b*

4/18

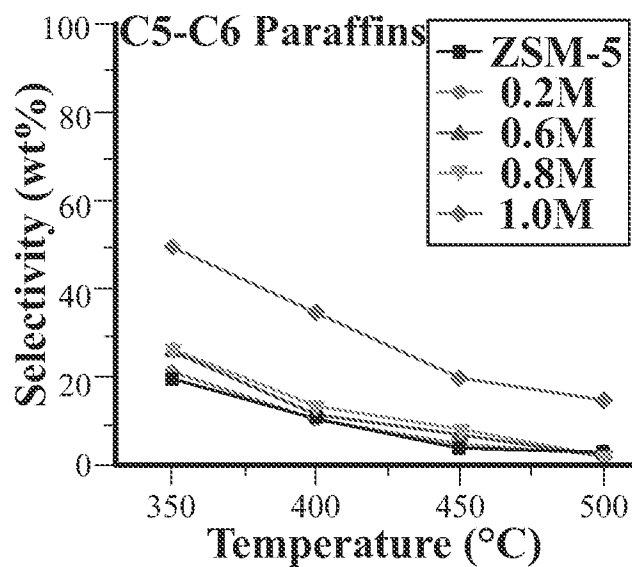


Figure 4a

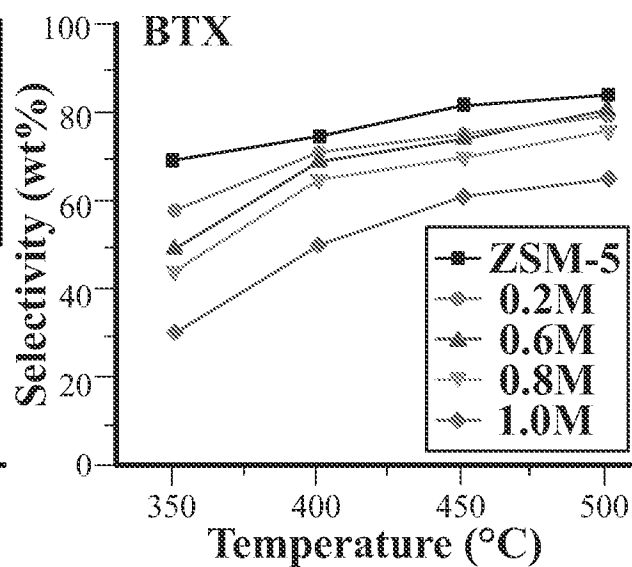


Figure 4b

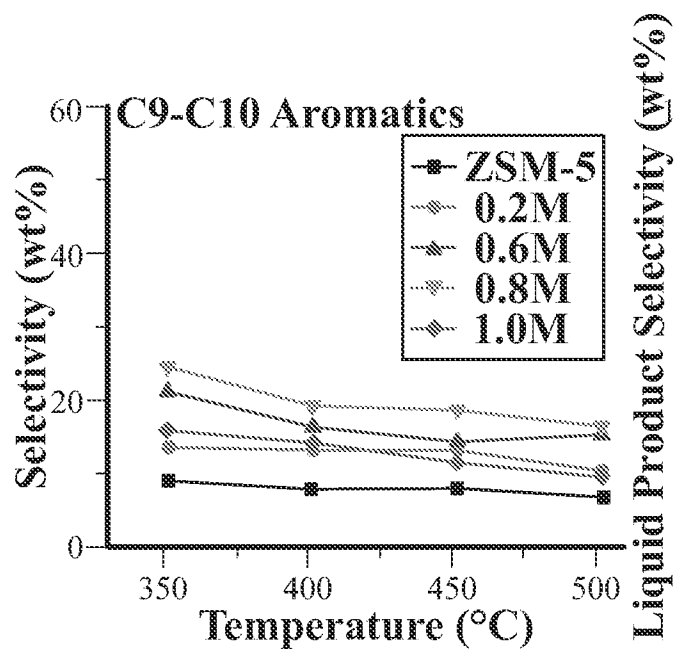


Figure 4c

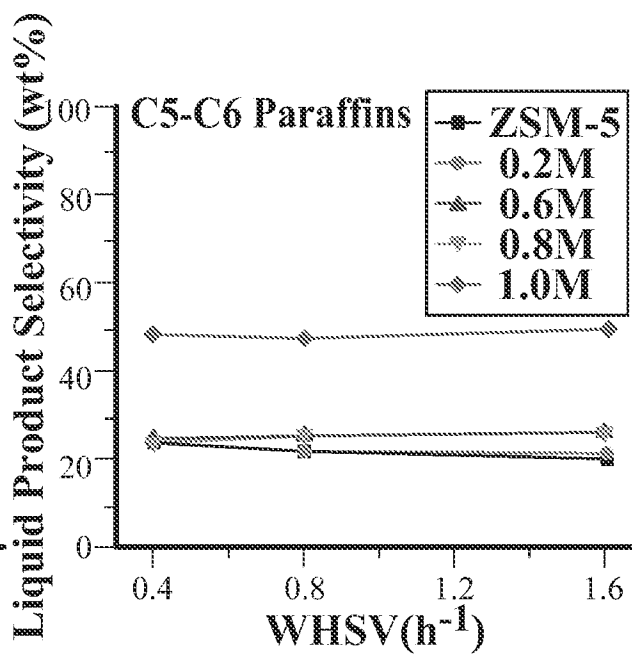


Figure 5a

5/18

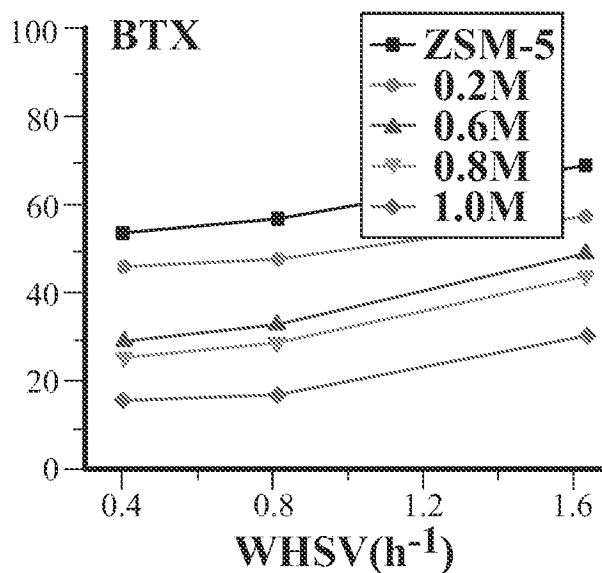


Figure 5b

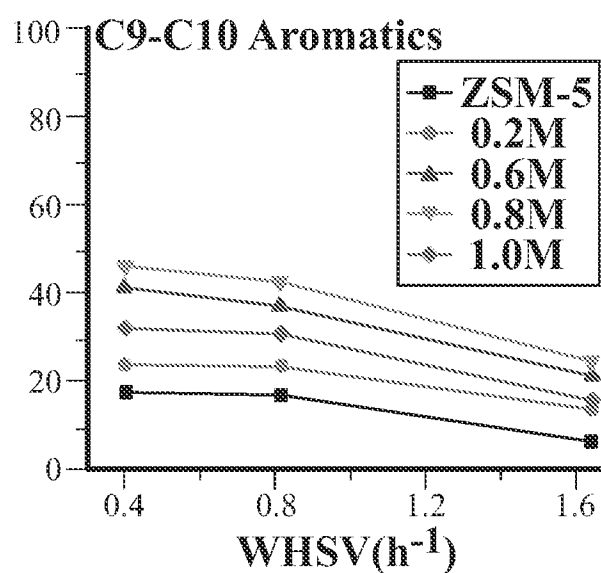


Figure 5c

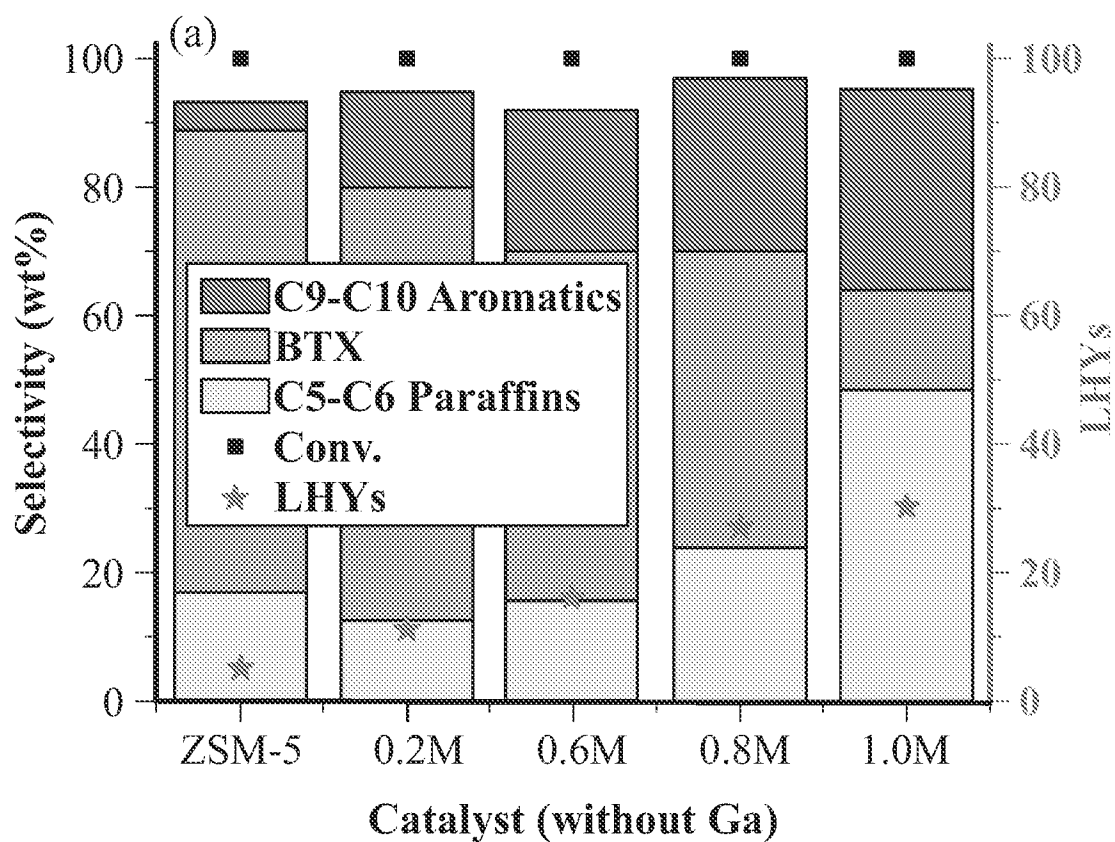
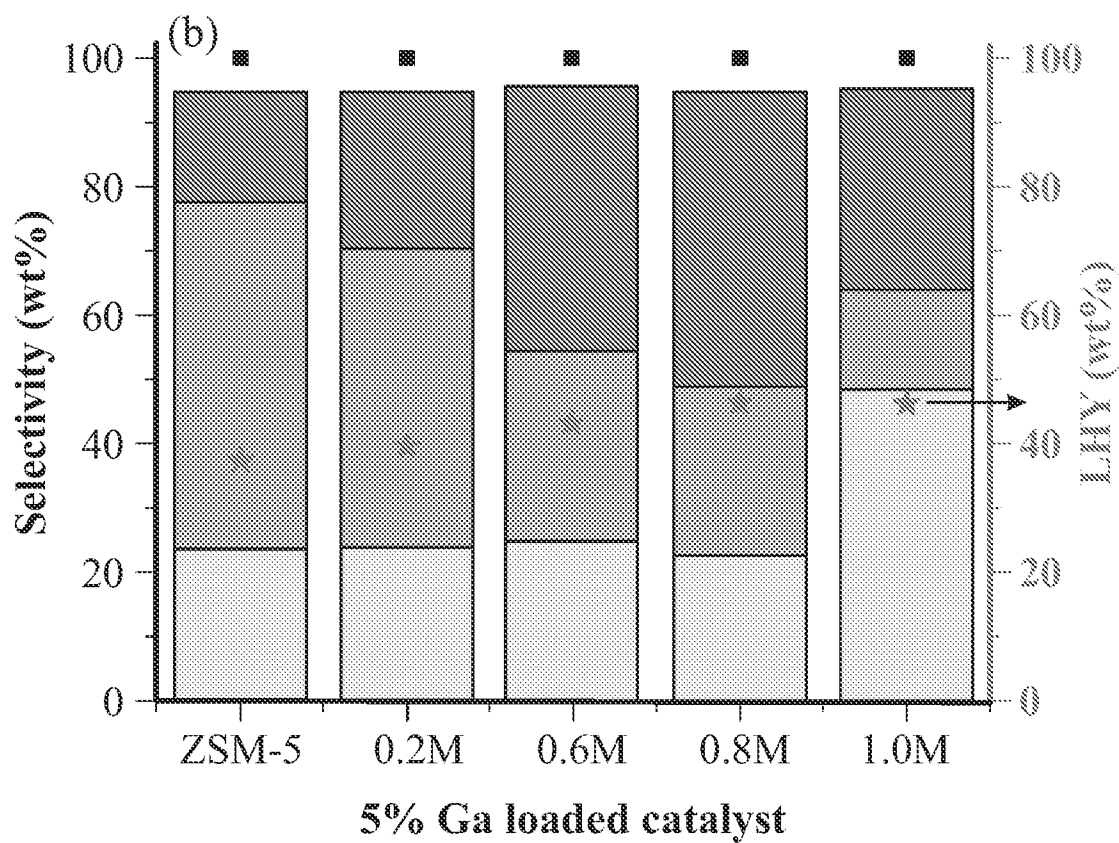
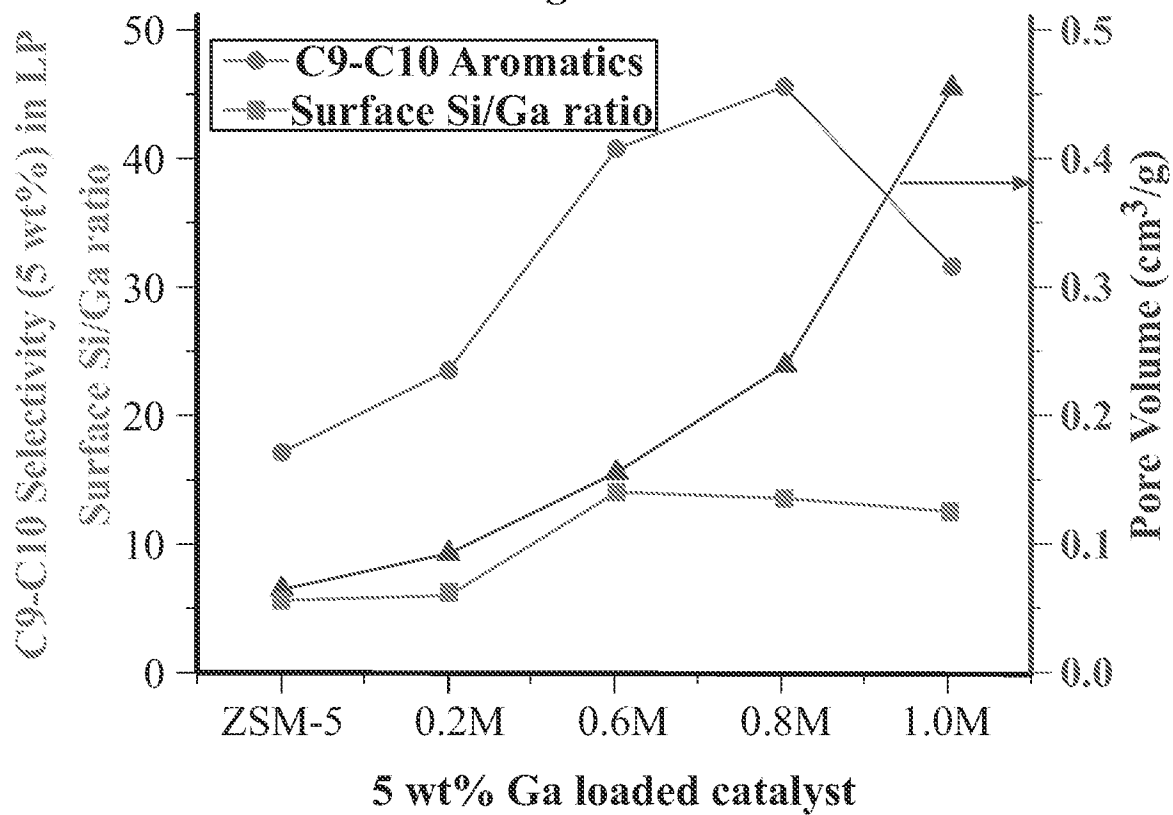


Figure 6a

6/18

*Figure 6b**Figure 7*

7/18

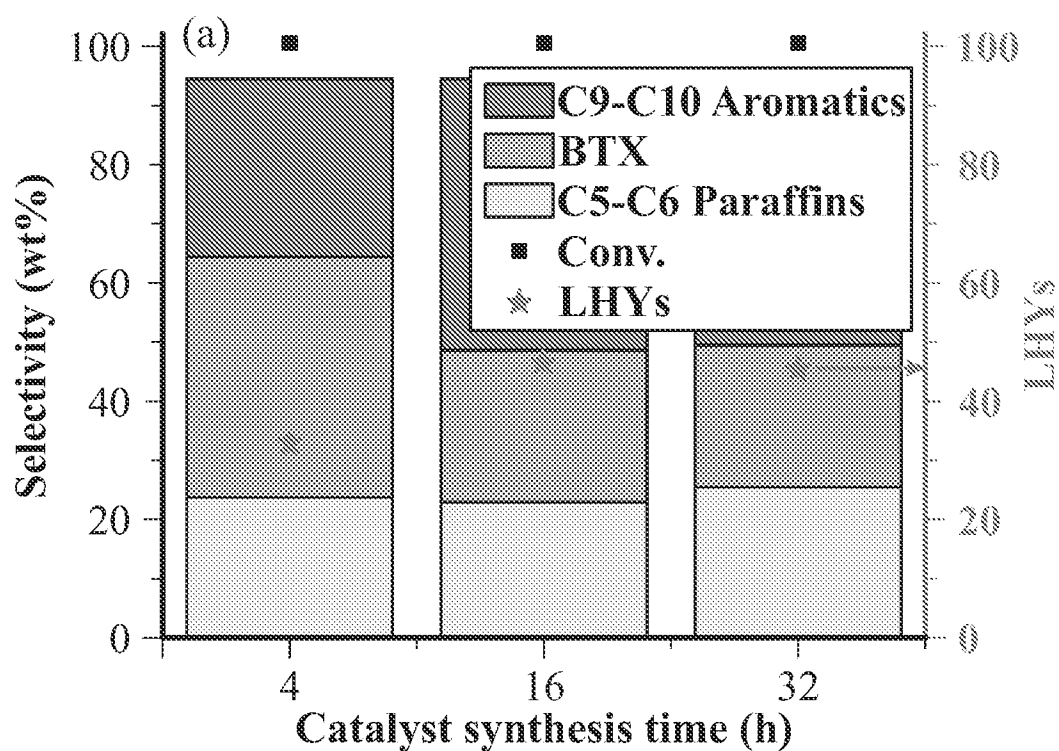


Figure 8a

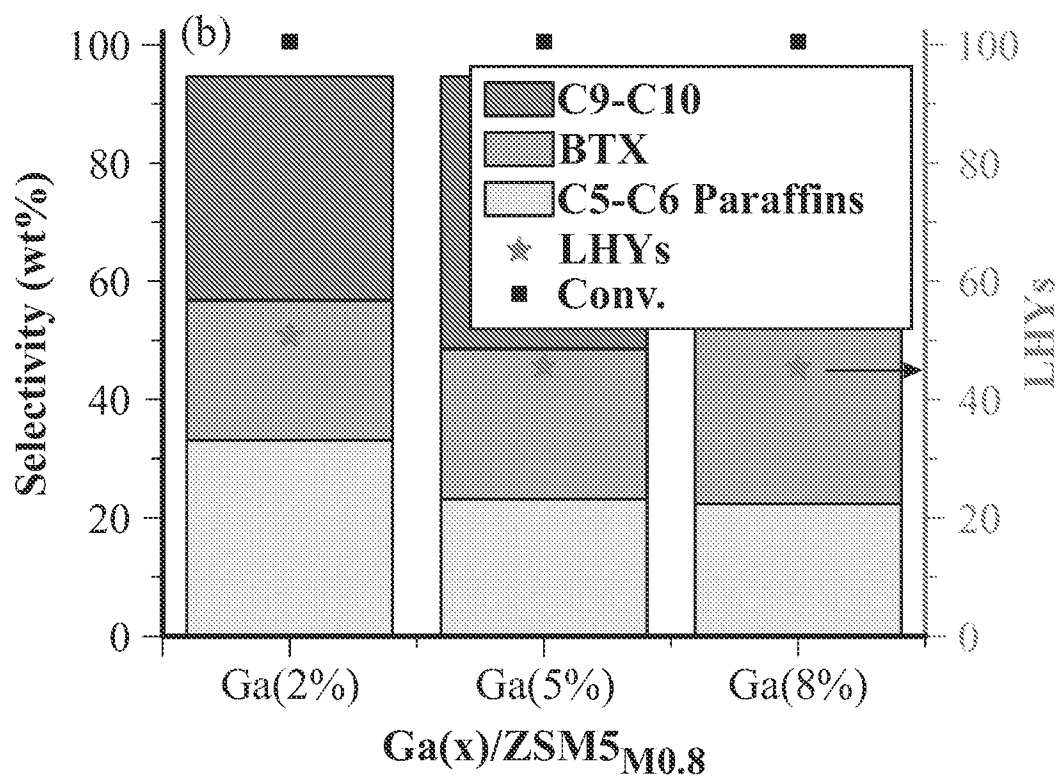
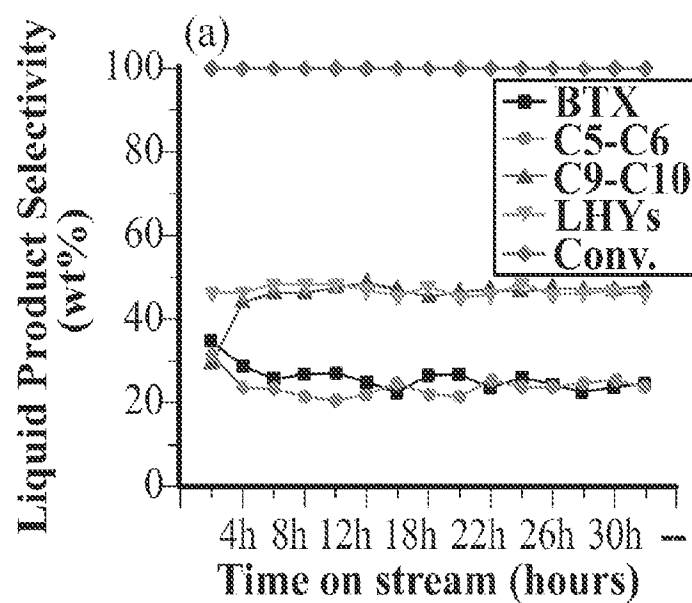
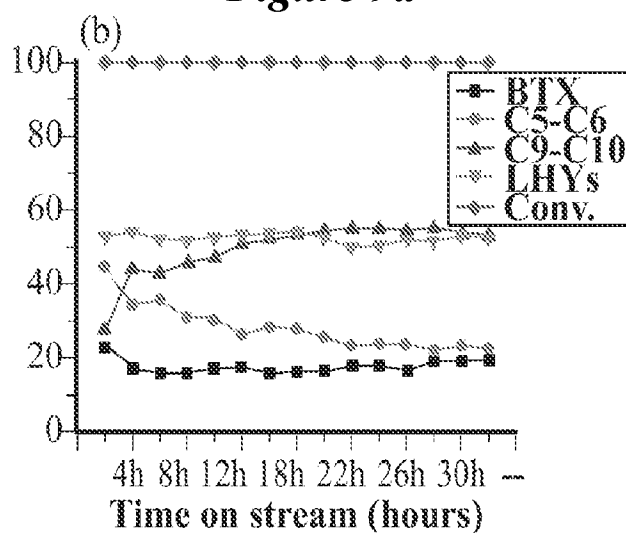
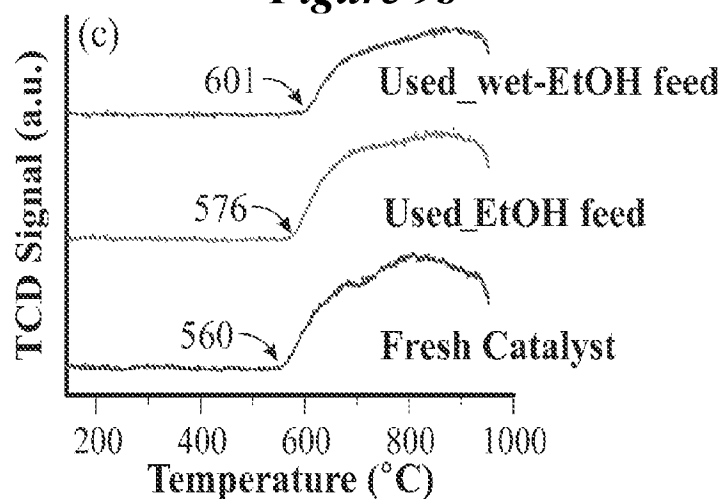


Figure 8b

8/18

**Figure 9a****Figure 9b****Figure 9c**

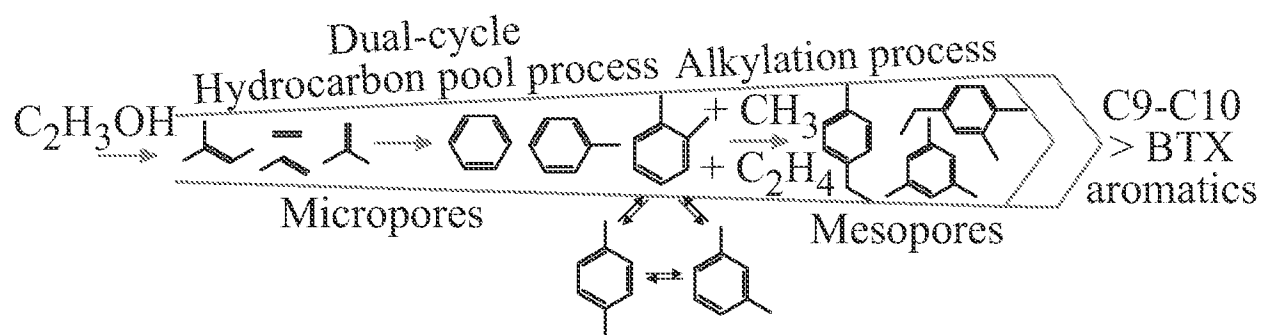
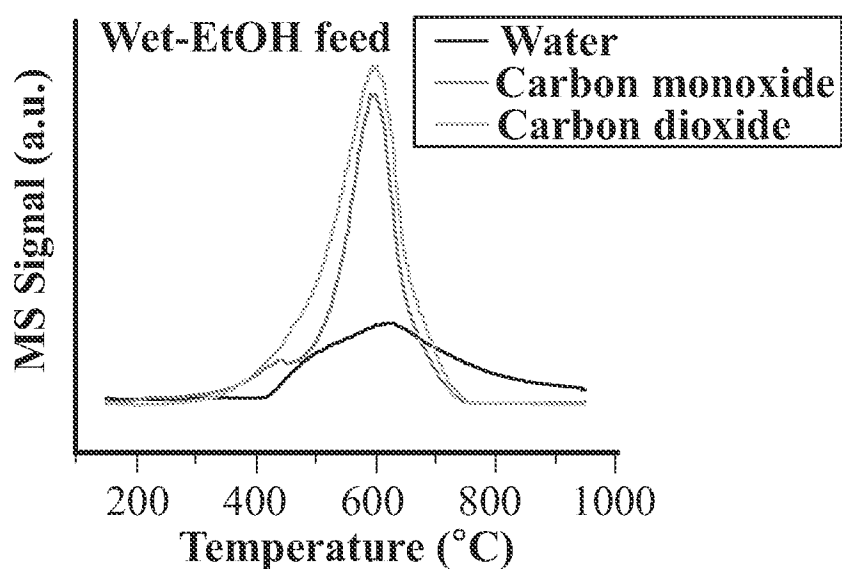
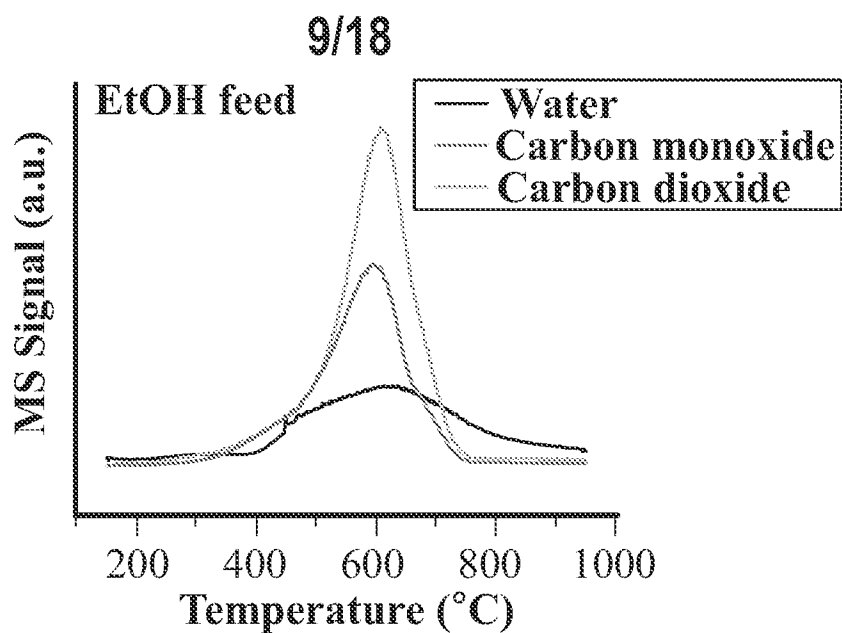


Figure 11

10/18

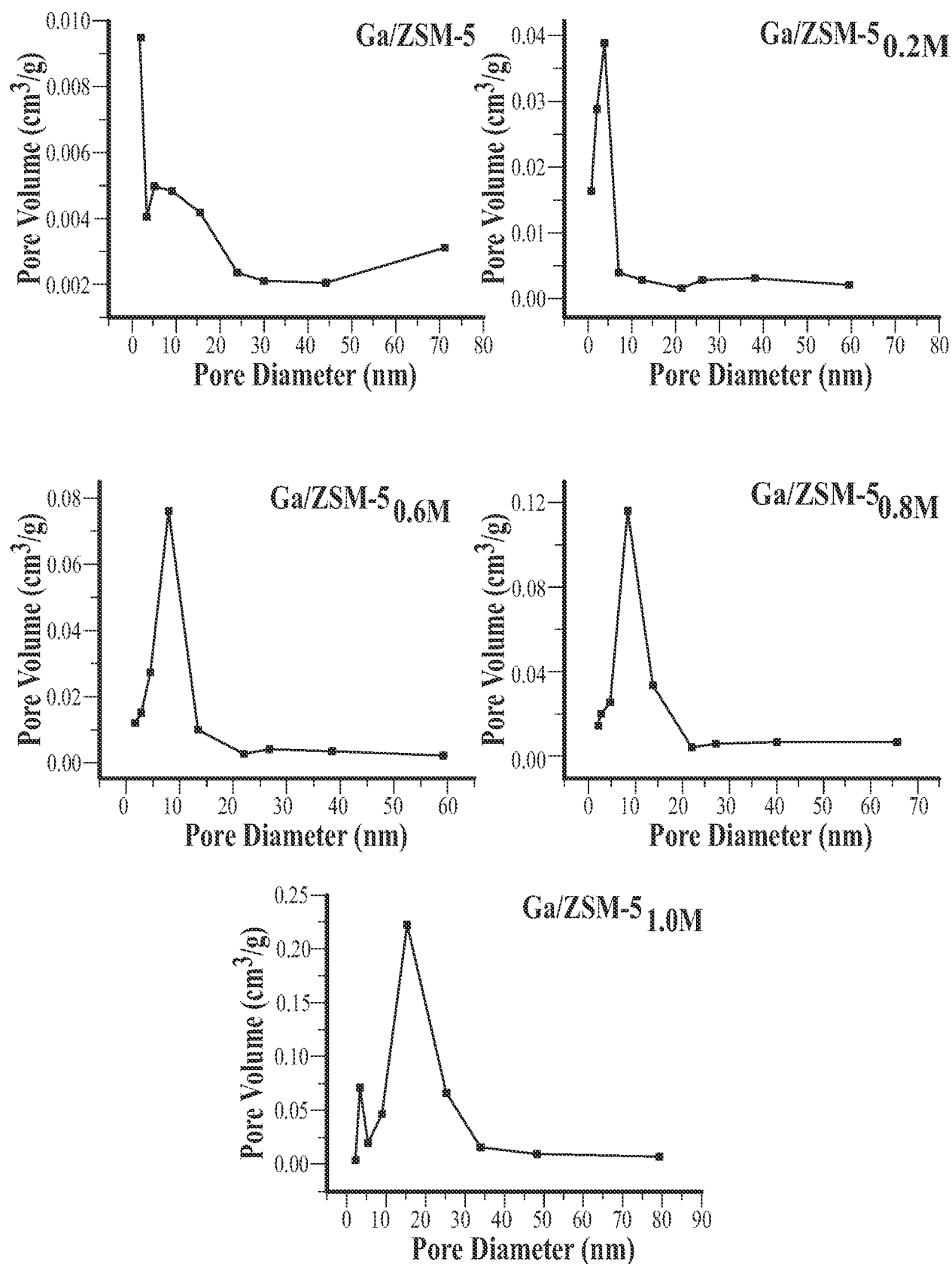
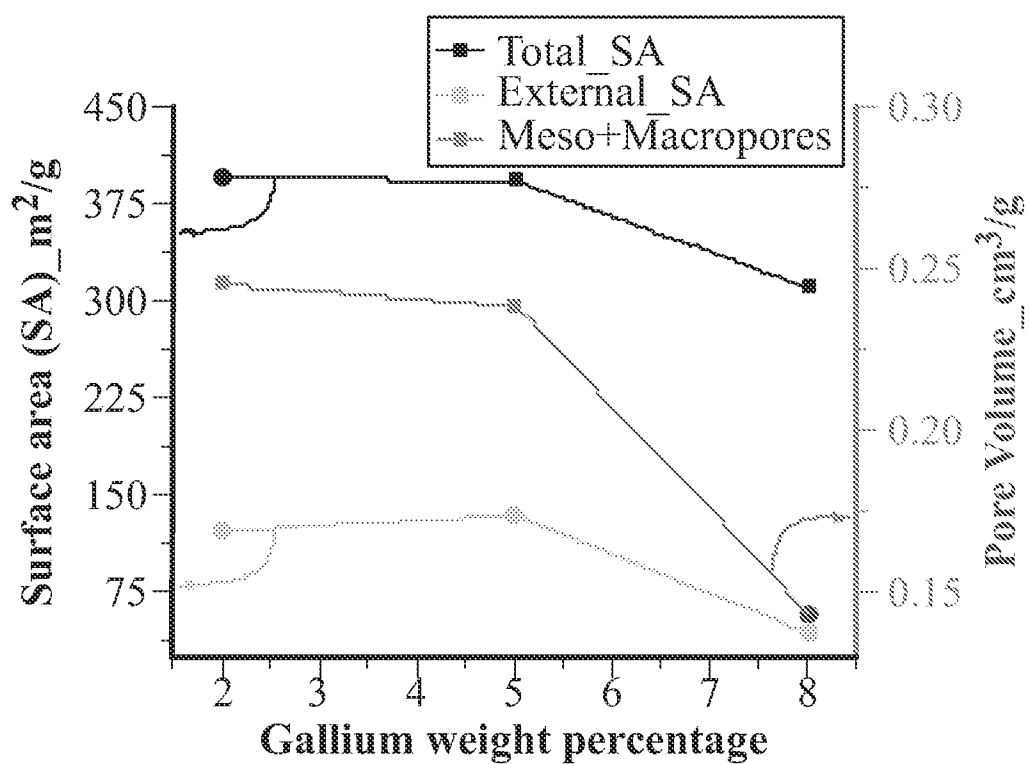
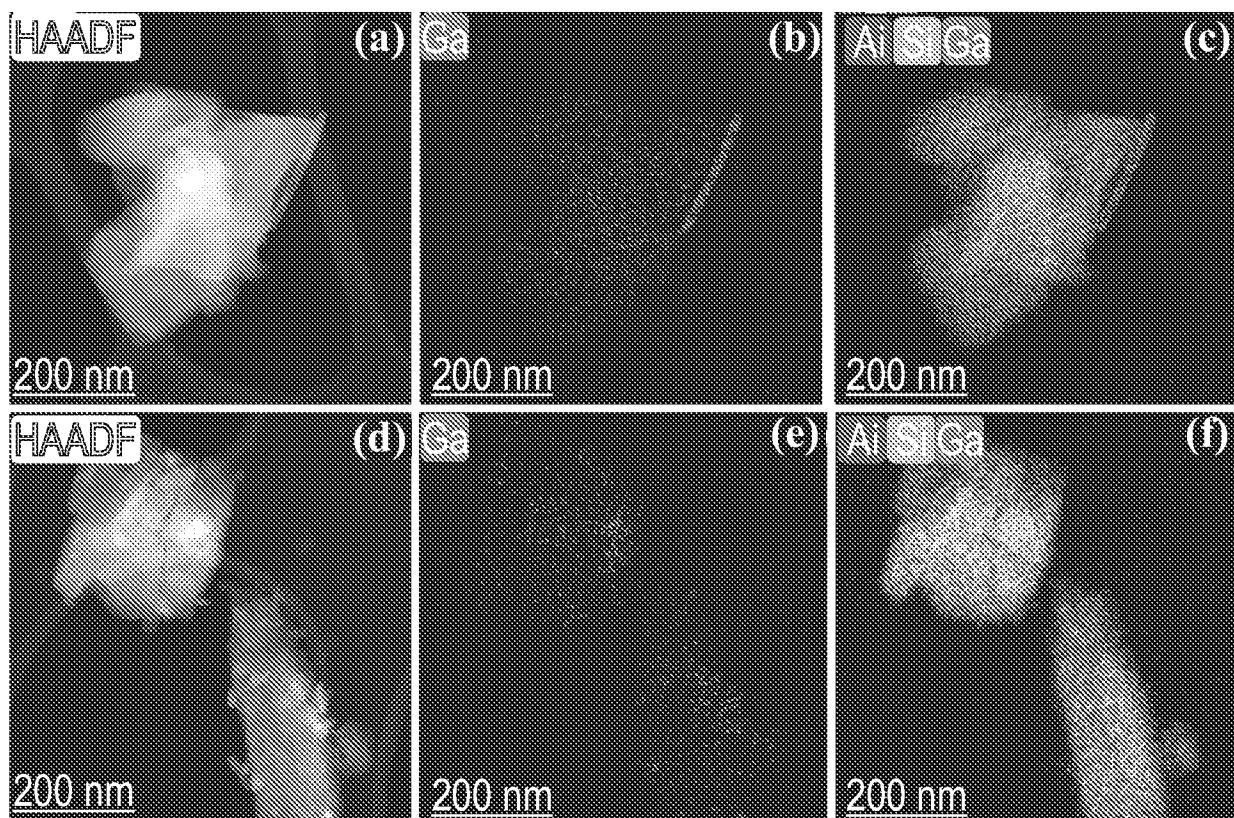
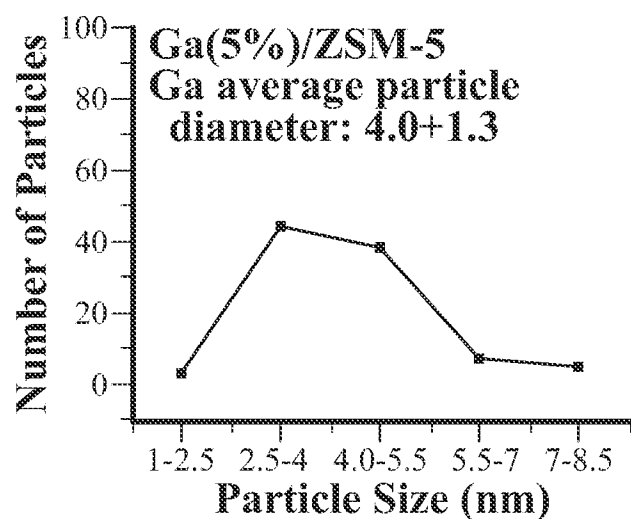
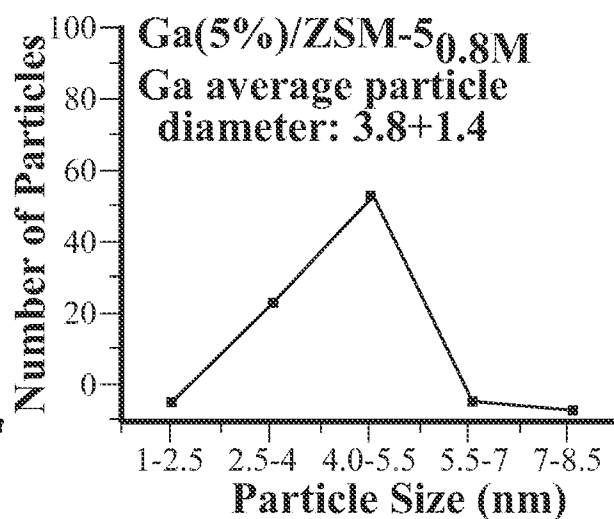
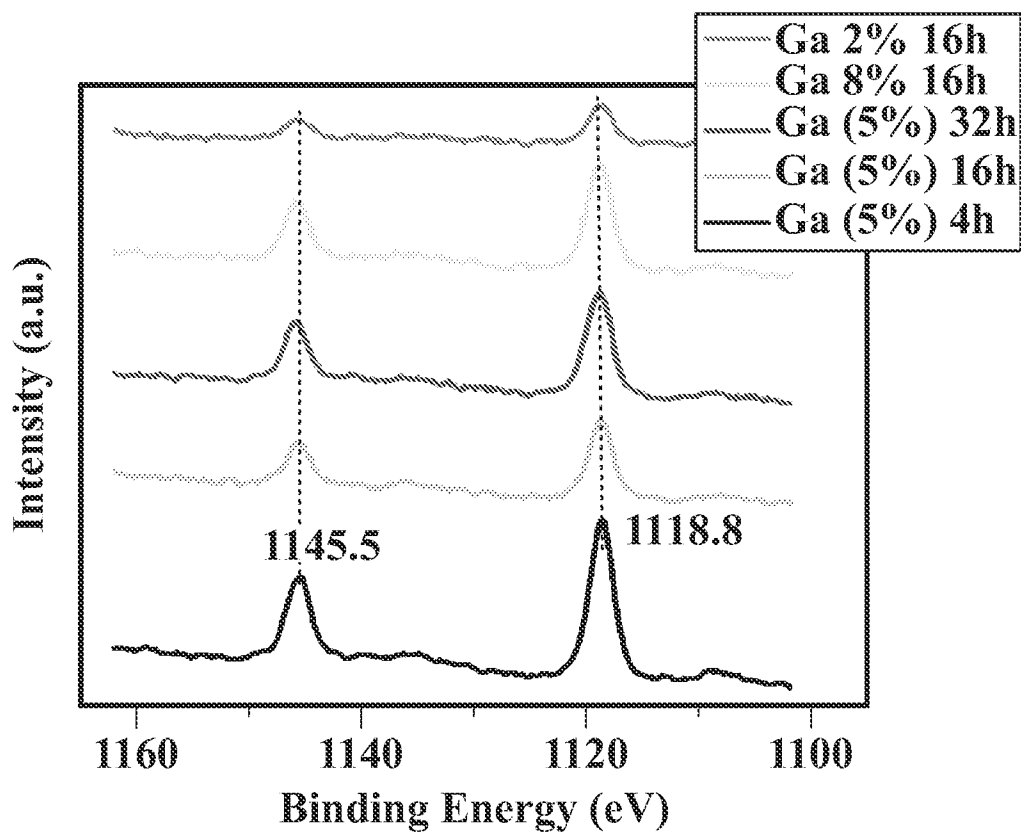


Figure 12

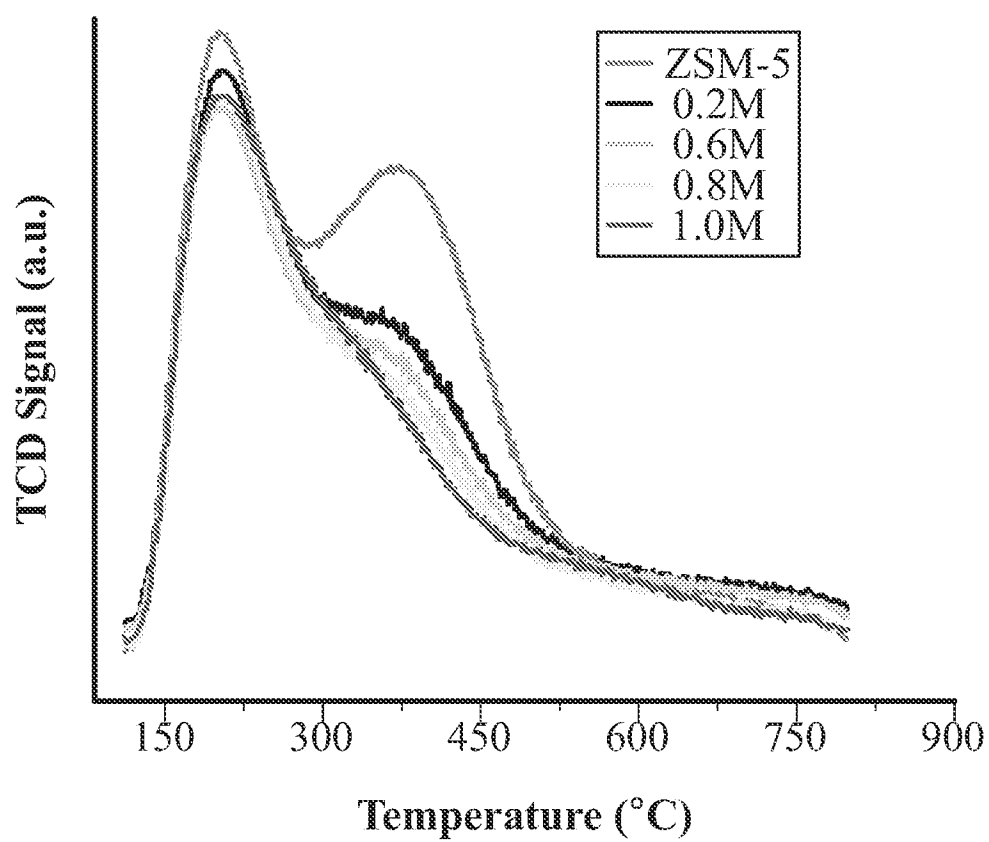
11/18

*Figure 13**Figure 14*

12/18

*Figure 15a**Figure 15b**Figure 16*

13/18

*Figure 17*

14/18

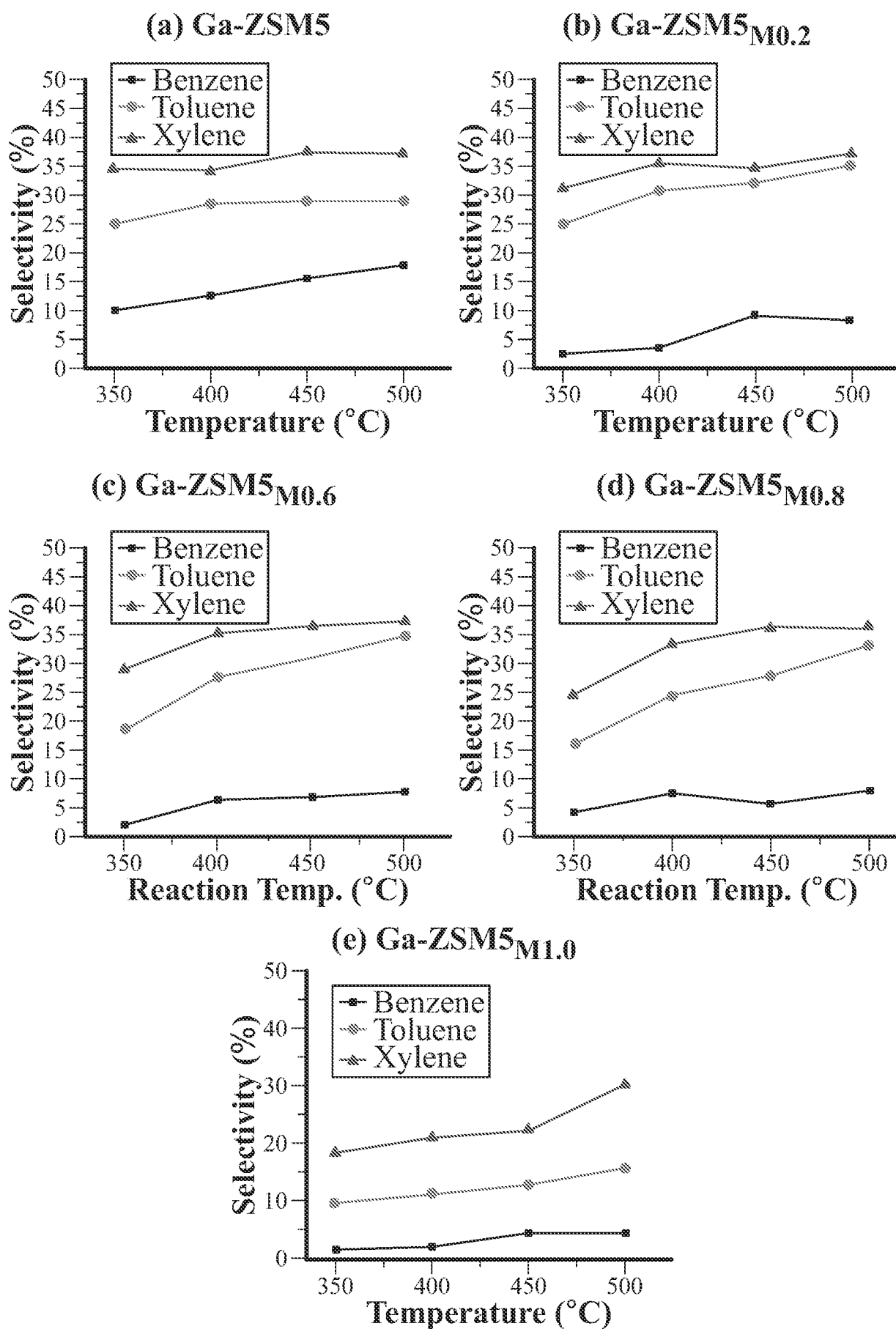
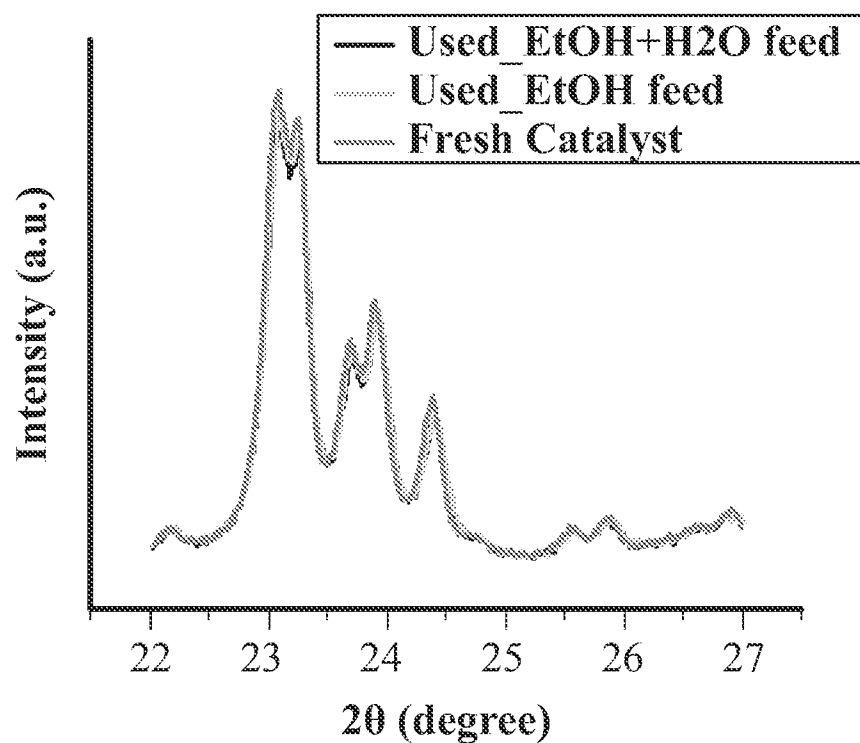
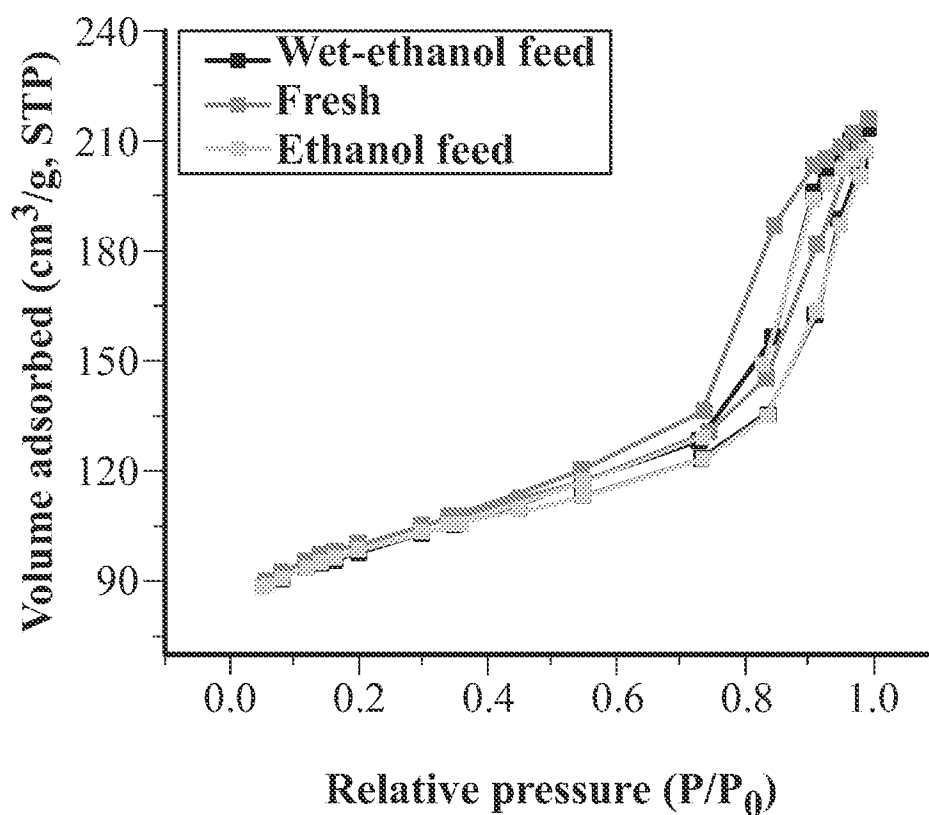
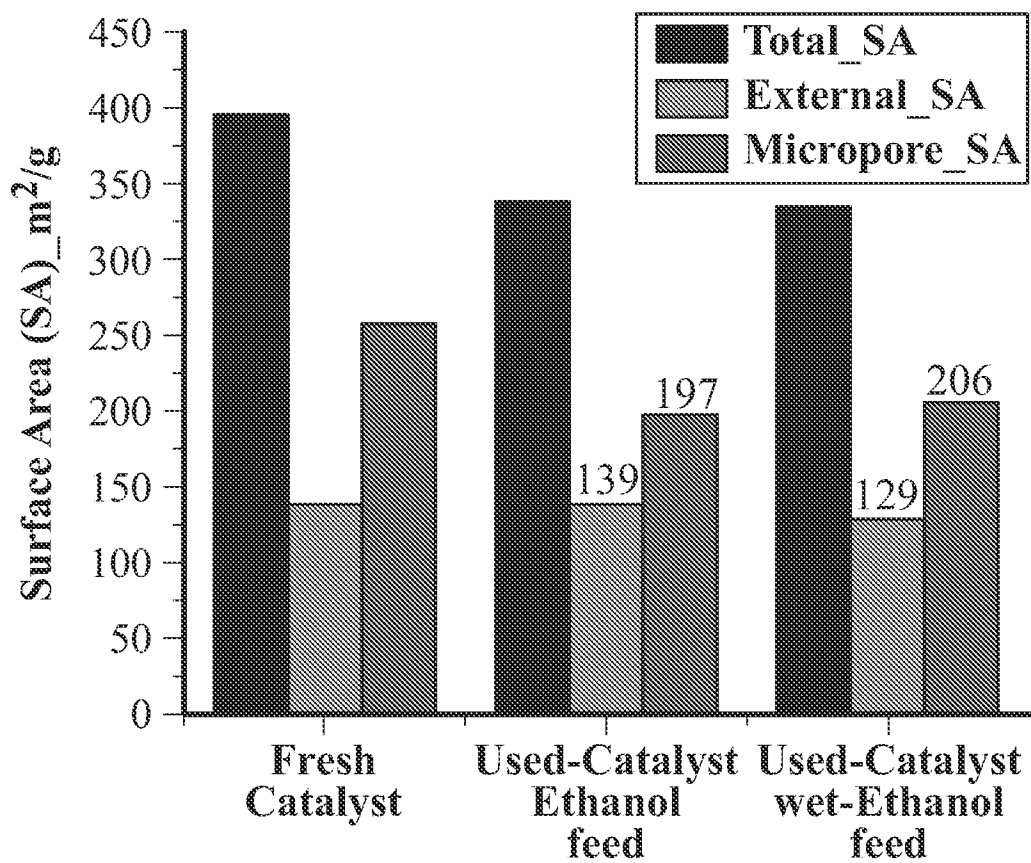
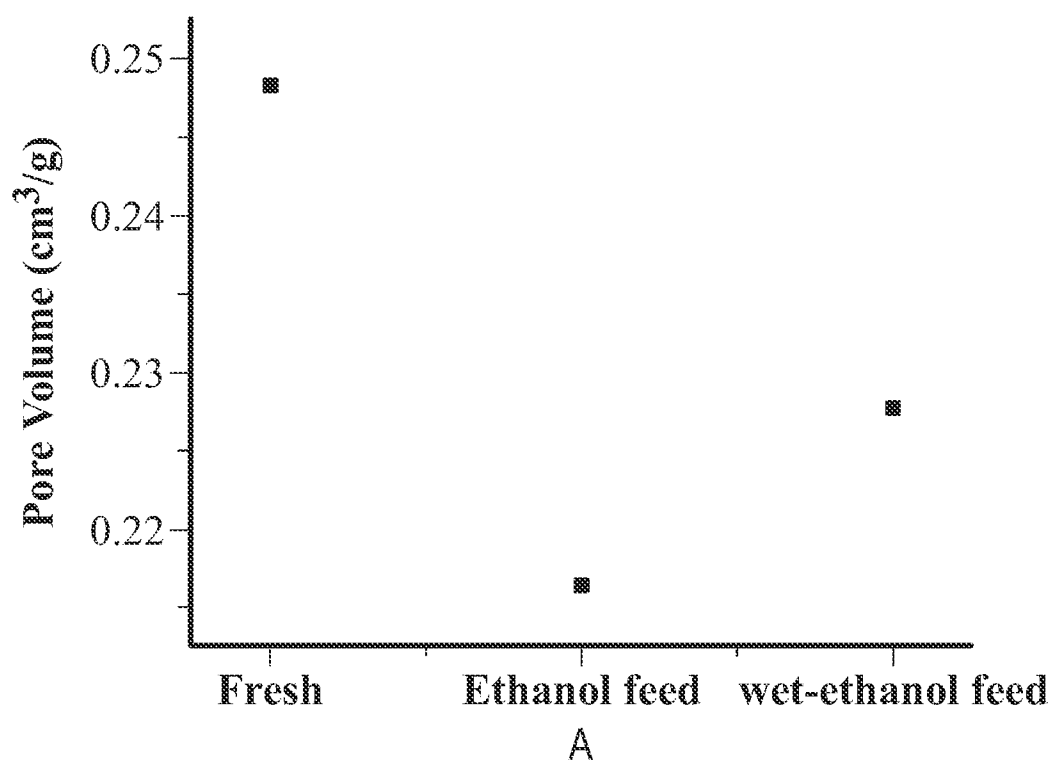


Figure 18

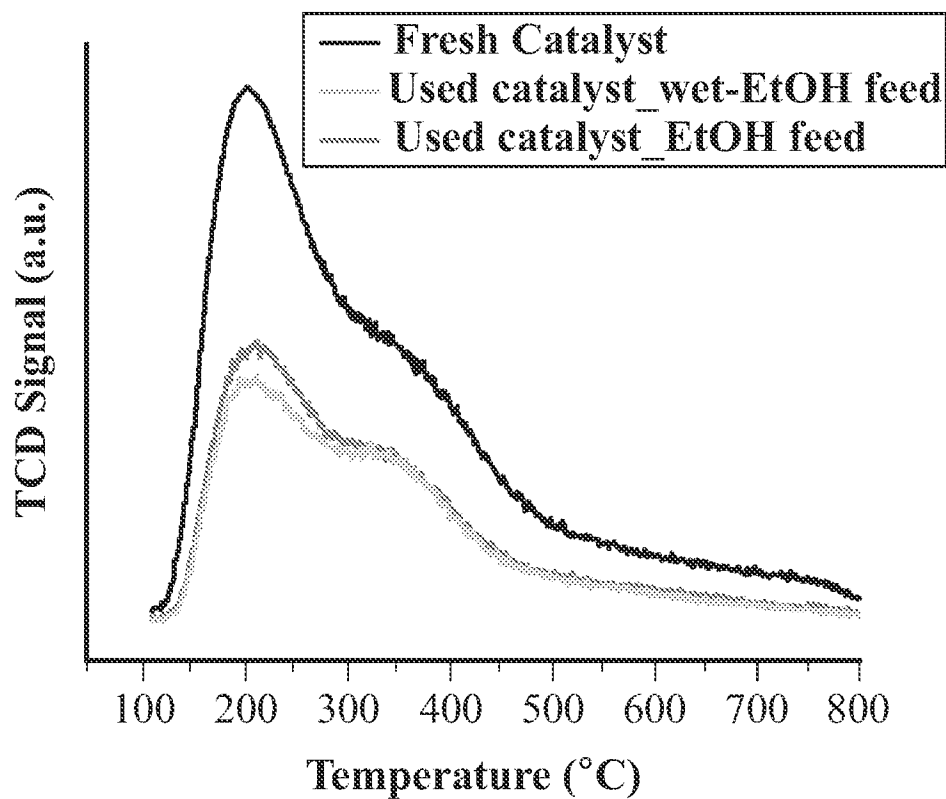
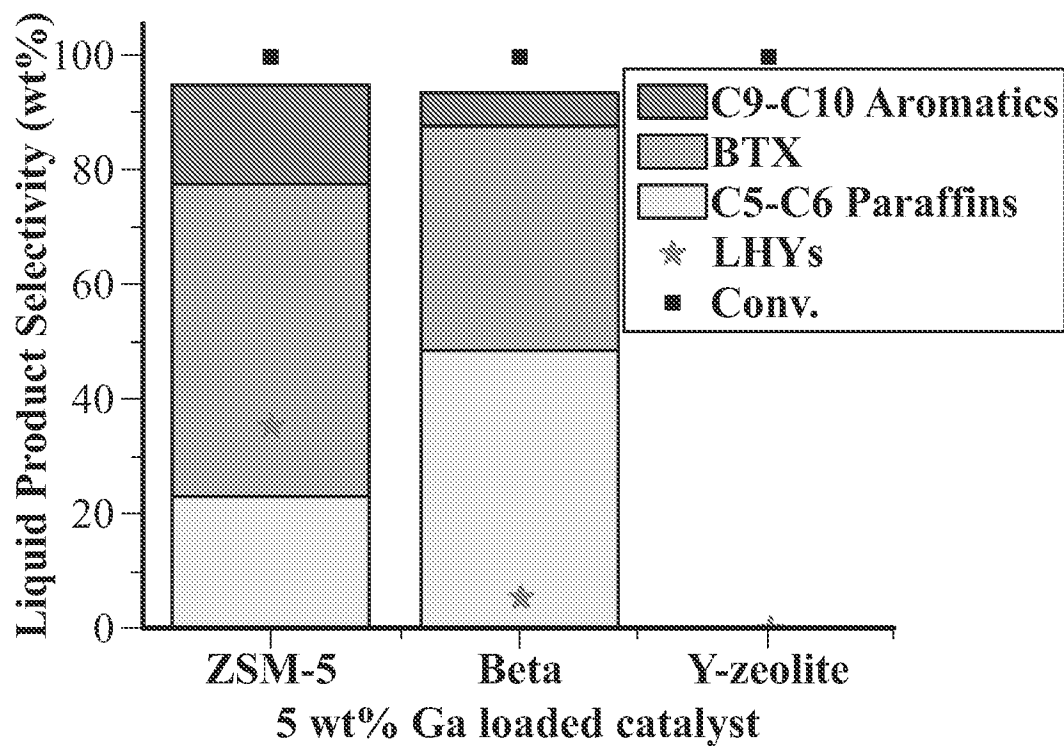
15/18

*Figure 19**Figure 20a*

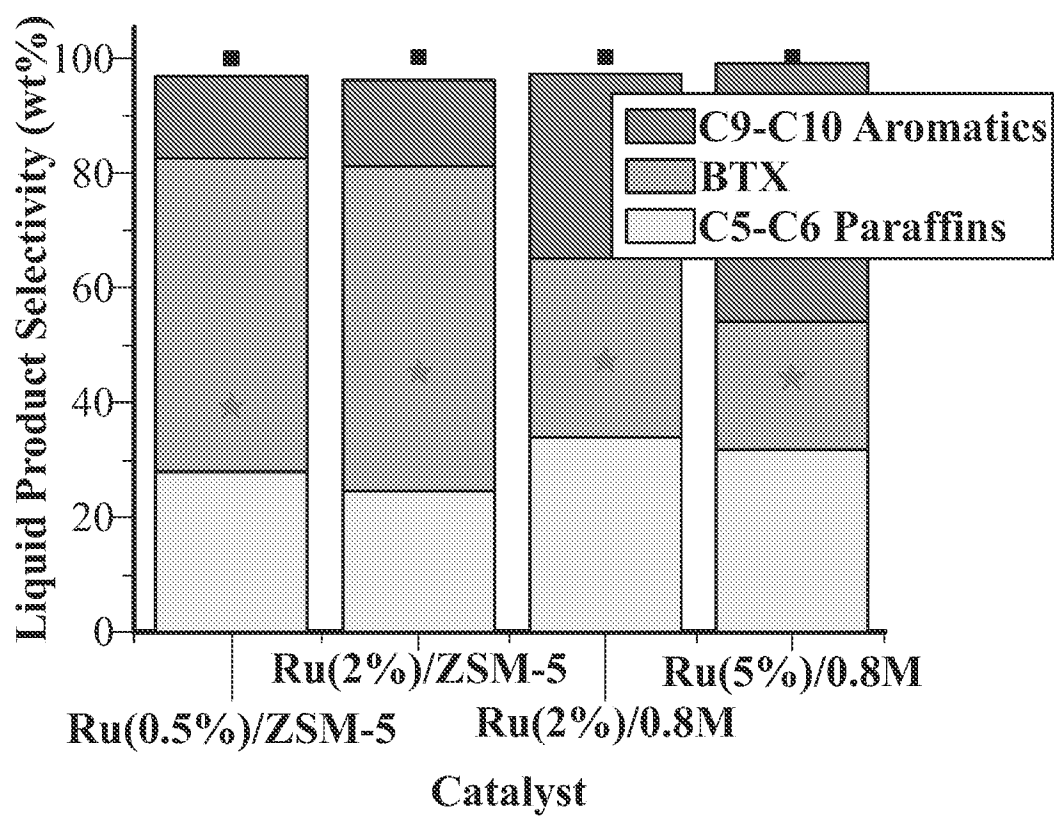
16/18

*Figure 20b**Figure 20c*

17/18

*Figure 21**Figure 22*

18/18

*Figure 23*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/21943

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. B01J 20/16, B01J 20/06, B01J 20/02, C07C 2/08, C07C 2/10 (2023.01)

ADD. C07C 2/00 (2023.01)

CPC - INV. B01J 20/165, B01J 20/06, B01J 20/02, C07C 2/08, C07C 2/10

ADD. C07C 2/00

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 3016923 B1 (NARULA ET AL.) 18 December 2019 (18.12.2019)- entire document especially para [0001], [0011]-[0012], [0019], [0024], [0026], [0035]-[0037], [0030]	1-6
A	US 2019/0127292 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 2 May 2019 (02.05.2019)- entire document	1-6
A	US 2022/0098498 A1 (IFP ENERGIES NOUVELLES) 31 March 2022 (31.03.2022)- entire document	1-6
A	WO 2022/015971 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 20 January 2022 (20.01.2022)- entire document	1-6
A	US 2015/0183694 A1 (VIRENT, INC.) 2 July 2015 (02.07.2015)- entire document	1-6

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"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

13 July 2023 (13.07.2023)

Date of mailing of the international search report

SEP 19 2023

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Kari Rodriguez

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/21943

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 7-30, 34-46, 51
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Continuation of Box No. III (Observations where unity of invention is lacking)

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-6 are directed towards a method for selectively producing C9-C12 aromatics, comprising: converting ethanol in the presence of a heterogeneous catalyst at a temperature suitable to produce a product mixture comprising liquid hydrocarbons, wherein the heterogeneous catalyst comprises Ga or Ru metal loaded onto zeolite, wherein the heterogeneous catalyst has one or more of the following properties: (i) a zeolite pore volume of at least 0.05 cm³/g; (ii) a Ga or Ru loading between 1% and 10%; (iii) a zeolite surface Si/Ga ratio between 5 and 30; (iv) a total acid site density between 0.5 mmol/g and 1.5 mmol/g; and (v) a Ga or Ru particle size between 1 nm and 10 nm.

Group II: Claims 31-33 are directed towards a system, comprising: a catalytic reactor containing a heterogeneous catalyst, wherein the catalytic reactor comprises: an ethanol inlet configured to receive ethanol at an elevated temperature, and a reactor outlet configured to output a product mixture comprising liquid hydrocarbons produced from the ethanol, wherein the liquid hydrocarbons comprise C9-C10 aromatics, wherein the heterogeneous catalyst comprises Ga or Ru metal loaded onto zeolite, wherein the heterogeneous catalyst has one or more of the following properties: (i) a zeolite pore volume of at least 0.05 cm³/g; (ii) a Ga or Ru loading between 1% and 10%; (iii) a zeolite surface Si/Ga ratio between 5 and 30; (iv) a total acid site density between 0.5 mmol/g and 1.5 mmol/g; and (v) a Ga or Ru particle size between 1 nm and 10 nm; and a pump configured to control ethanol flow through the ethanol inlet through the heterogeneous catalyst.

Group III: Claims 47-50 are directed towards a composition, comprising: C9-C12 aromatics; C5-C6 paraffins; C2-05 olefins; and benzene, toluene and xylene (BTX).

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires a method for selectively producing C9-C12 aromatics, comprising: converting ethanol in the presence of a heterogeneous catalyst at a temperature suitable to produce a product mixture comprising liquid hydrocarbons, not required by Group II or III.

Group II requires a system, comprising: a catalytic reactor containing a heterogeneous catalyst, wherein the catalytic reactor comprises: an ethanol inlet configured to receive ethanol at an elevated temperature, and a reactor outlet; and a pump configured to control ethanol flow through the ethanol inlet through the heterogeneous catalyst, not required by Group I or III.

Group III requires a composition, comprising: C5-C6 paraffins; C2-05 olefins; and benzene, toluene and xylene (BTX), not required by Group I or II.

Shared Technical Features:

Group I-II share the common technical features of producing C9-C12 aromatics, comprising: converting ethanol in the presence of a heterogeneous catalyst at a temperature to produce a product mixture comprising liquid hydrocarbons, wherein the heterogeneous catalyst comprises Ga or Ru metal loaded onto zeolite, wherein the heterogeneous catalyst has one or more of the following properties: (i) a zeolite pore volume of at least 0.05 cm³/g; (ii) a Ga or Ru loading between 1% and 10%; (iii) a zeolite surface Si/Ga ratio between 5 and 30; (iv) a total acid site density between 0.5 mmol/g and 1.5 mmol/g; and (v) a Ga or Ru particle size between 1 nm and 10 nm. However, these shared technical features do not represent a contribution over prior art because the shared technical features are being anticipated by EP 3016923 B1 to Narula et al. (hereinafter "Narula"). Narula teaches producing C9-C12 aromatics (para [0001], the present invention relates to the catalytic conversion of alcohols to hydrocarbons and more particularly, to zeolite-based catalytic methods for such conversion; para [0011]-[0012], the disclosure is directed to an alcohol-hydrocarbon catalytic conversion method that advantageously produces a hydrocarbon blendstock having greater relative amount of higher hydrocarbons, particularly those hydrocarbons having least 6, 7, 8, 9, or 10 carbon atoms, the resulting hydrocarbon blendstock preferably contains at least 75 vol% of hydrocarbon compounds containing at least six, seven, eight, nine, or ten carbon atoms; para [0019], the mixture of hydrocarbon compounds produced herein can be exclusively composed of aromatics), comprising: converting ethanol in the presence of a heterogeneous catalyst at a temperature to produce a product mixture comprising liquid hydrocarbons (para [0001], the present invention relates to the catalytic conversion of alcohols to hydrocarbons and more particularly, to zeolite-based catalytic methods for such conversion; para [0011], the alcohol includes a mixture of at least one C3+ alcohol and ethanol; para [0024], a suitable reaction temperature is employed during contact of the alcohol with the catalyst, the reaction temperature is at least 100 degrees C and up to 550 degrees C; para [0026], the catalyst and reactor can have any of the designs known in the art for catalytically treating a fluid or gas at elevated temperatures; para [0036], the zeolite described above is loaded with a catalytic metal in a catalytically effective concentration, the metal is a catalytically active main group metal, such as gallium. Hence, the fluid/liquid ethanol-containing alcohol mixture is converted into fluid aromatics (liquid hydrocarbons) at 100-550 degrees C in the presence of the Ga-loaded zeolite catalyst (heterogeneous catalyst); see instant specification para [0042], the heterogeneous catalyst comprises Ga loaded onto zeolite; see instant specification para [0044], reaction conditions suitable to produce a product mixture comprising liquid hydrocarbons from the ethanol provided may be employed, the temperature is between 350 degrees C and 500 degrees C), wherein the heterogeneous catalyst comprises Ga or Ru metal loaded onto zeolite (para [0030], the conversion catalyst used herein includes a zeolite portion and a metal loaded into the zeolite; para [0035]-[0036], the zeolite contains an amount of cationic species, some examples of cationic species include main group metal ions, some examples of main group metal ions that may be included in the zeolite include gallium (Ga³⁺), the zeolite described above is loaded with a catalytic metal in a catalytically effective concentration, the metal loaded into the zeolite is selected such that the resulting metal-loaded zeolite is catalytically active for converting an alcohol to a hydrocarbon, the metal is a catalytically active main group metal such as gallium), wherein the heterogeneous catalyst has one or more of the following properties: (ii) a Ga or Ru loading between 1% and 10% (para [0036]-[0037], the zeolite described above is loaded with a catalytic metal in a catalytically effective concentration, the metal is a catalytically active main group metal such as gallium, the metal loading can be any suitable amount, but is generally no more than about 2.5%, wherein the loading is expressed as the amount of metal by weight of the zeolite, the metal loading is precisely, at least, less than, or up to, for example, 2.5%).

--see next page--

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/21943

Continuation of Box No. III (Observations where unity of invention is lacking)

Group I-III share the common technical features of C9-C12 aromatics. However, these shared technical features do not represent a contribution over prior art because the shared technical features are being anticipated by Narula. Narula teaches C9-C12 aromatics (para [0011]-[0012], the disclosure is directed to an alcohol-hydrocarbon catalytic conversion method that advantageously produces a hydrocarbon blendstock having greater relative amount of higher hydrocarbons, particularly those hydrocarbons having least 6, 7, 8, 9, or 10 carbon atoms, the resulting hydrocarbon blendstock preferably contains at least 75 vol% of hydrocarbon compounds containing at least six, seven, eight, nine, or ten carbon atoms; para [0019], the mixture of hydrocarbon compounds produced herein can be exclusively composed of aromatics).

Group II-III share the common technical features of C9-C12 aromatics. However, these shared technical features do not represent a contribution over prior art because the shared technical features are being anticipated by Narula. Narula teaches C9-C12 aromatics (para [0011]-[0012], the disclosure is directed to an alcohol-hydrocarbon catalytic conversion method that advantageously produces a hydrocarbon blendstock having greater relative amount of higher hydrocarbons, particularly those hydrocarbons having least 6, 7, 8, 9, or 10 carbon atoms, the resulting hydrocarbon blendstock preferably contains at least 75 vol% of hydrocarbon compounds containing at least six, seven, eight, nine, or ten carbon atoms; para [0019], the mixture of hydrocarbon compounds produced herein can be exclusively composed of aromatics).

As the shared technical features were known in the art at the time of the invention, they cannot be considered special technical features that would otherwise unify the groups. Therefore, Groups I-III lack unity under PCT Rule 13.

Note: Claims 7-30, 34-46, and 51 are determined unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).