

Understanding green-hydrocarbon production through the strategy of biomass ketalization reaction

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Supplementary Section 1 – Figures

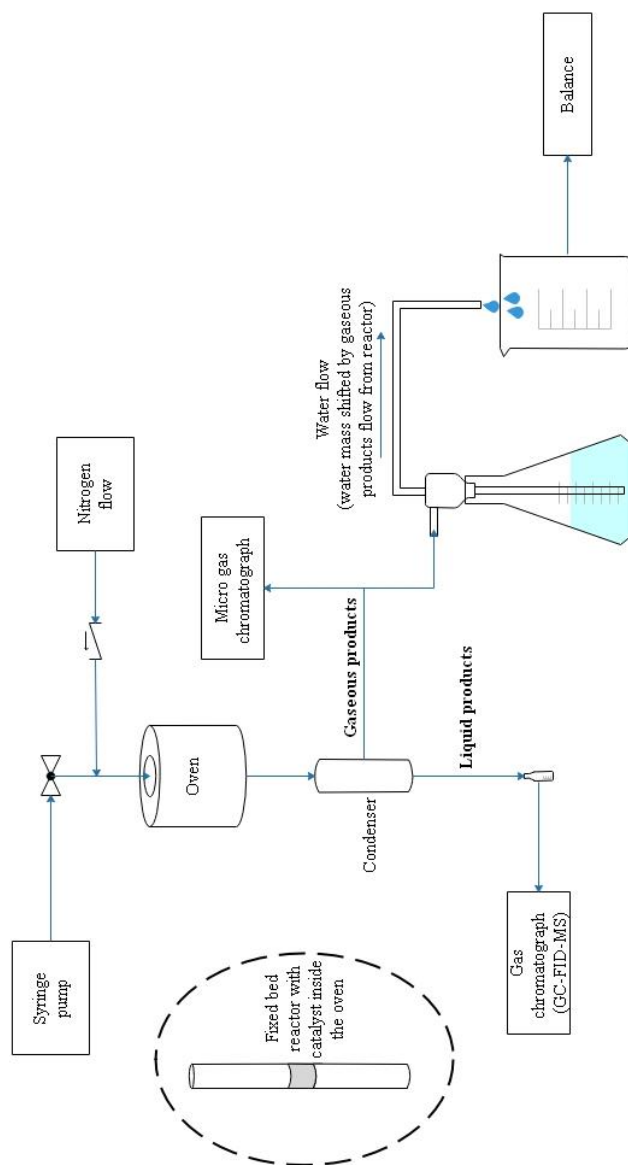


Figure S1. Diagram of fixed bed reactor unit for catalytic cracking.

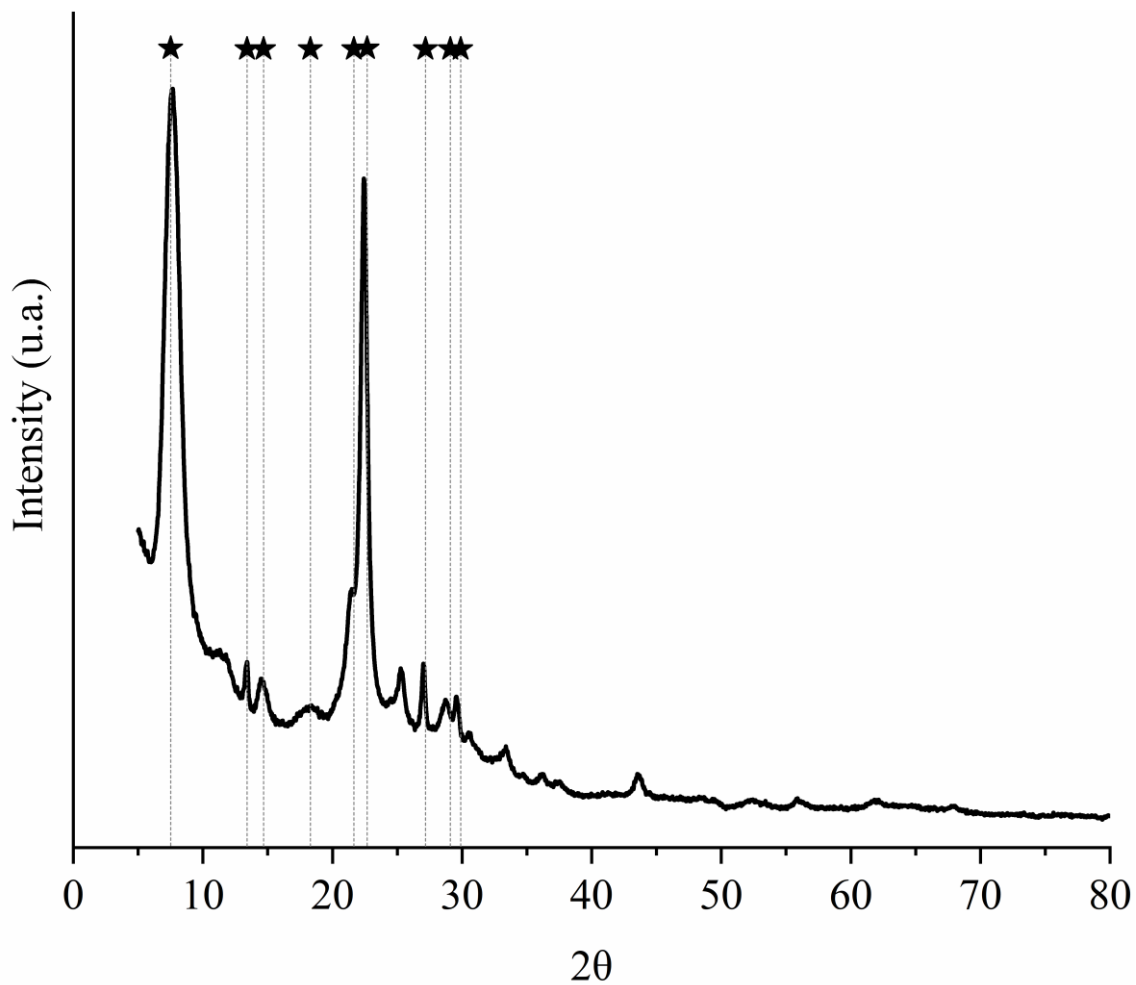


Figure S2. X-ray diffraction characterization of Beta zeolite (BEA) (ICDD 048-0038).

The position and intensity of the reflections were compared with data supplied by JCPDS (Joint Committee on Powder Diffraction Standards) reference cards through the International Center for Diffraction Data (ICDD) library.

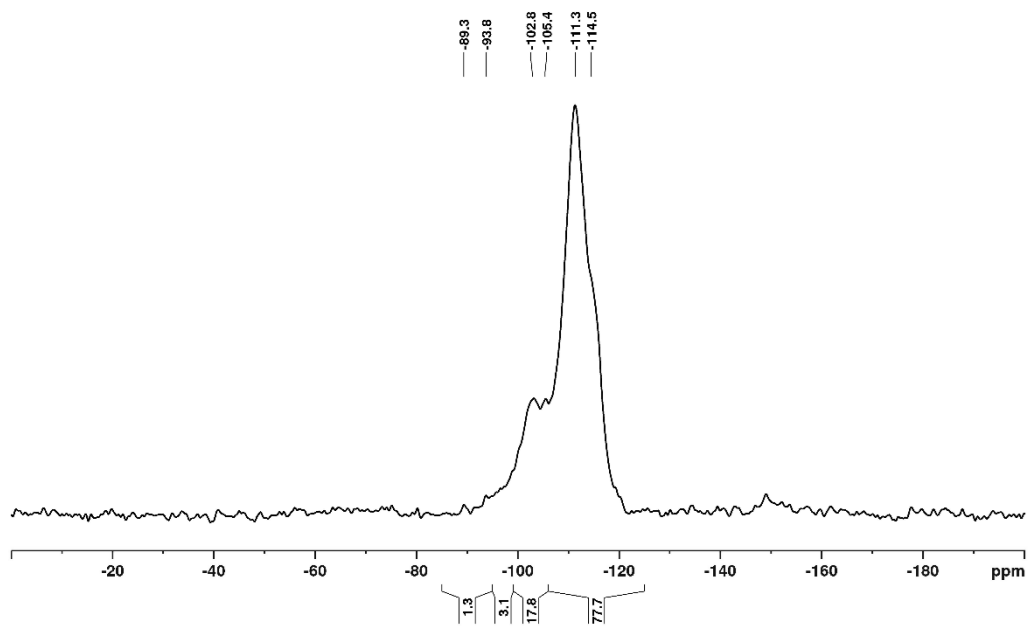


Figure S3. ^{29}Si MAS-NMR of Beta zeolite.

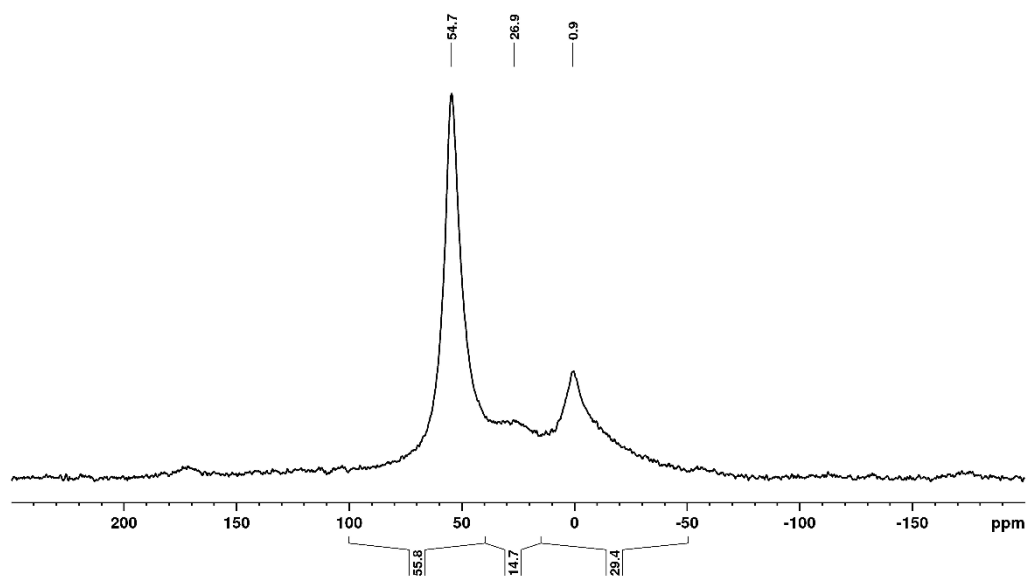


Figure S4. ^{27}Al MAS-NMR of Beta zeolite.

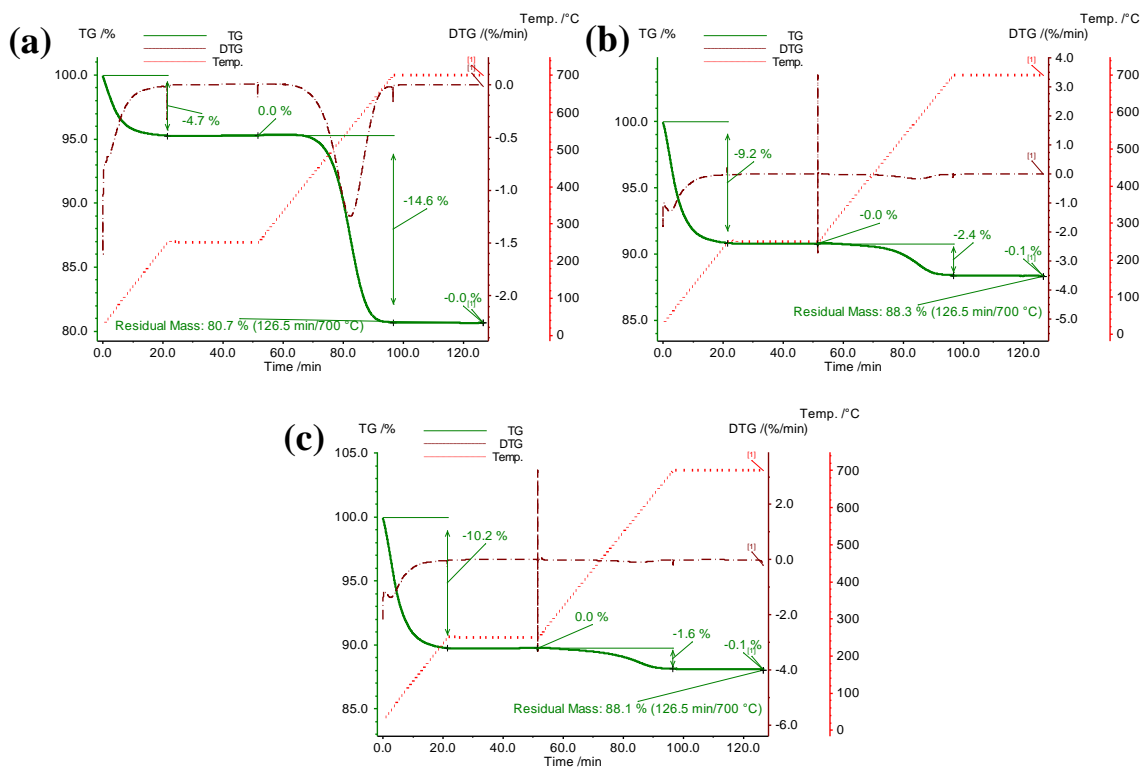


Figure S5. Thermogravimetric analysis - differential thermal analysis (TGA-DTA) of Beta catalysts after reaction for the following systems: (a) 10%DX/n-Hexane; (b) n-Hexane; (c) n-Hexane*.

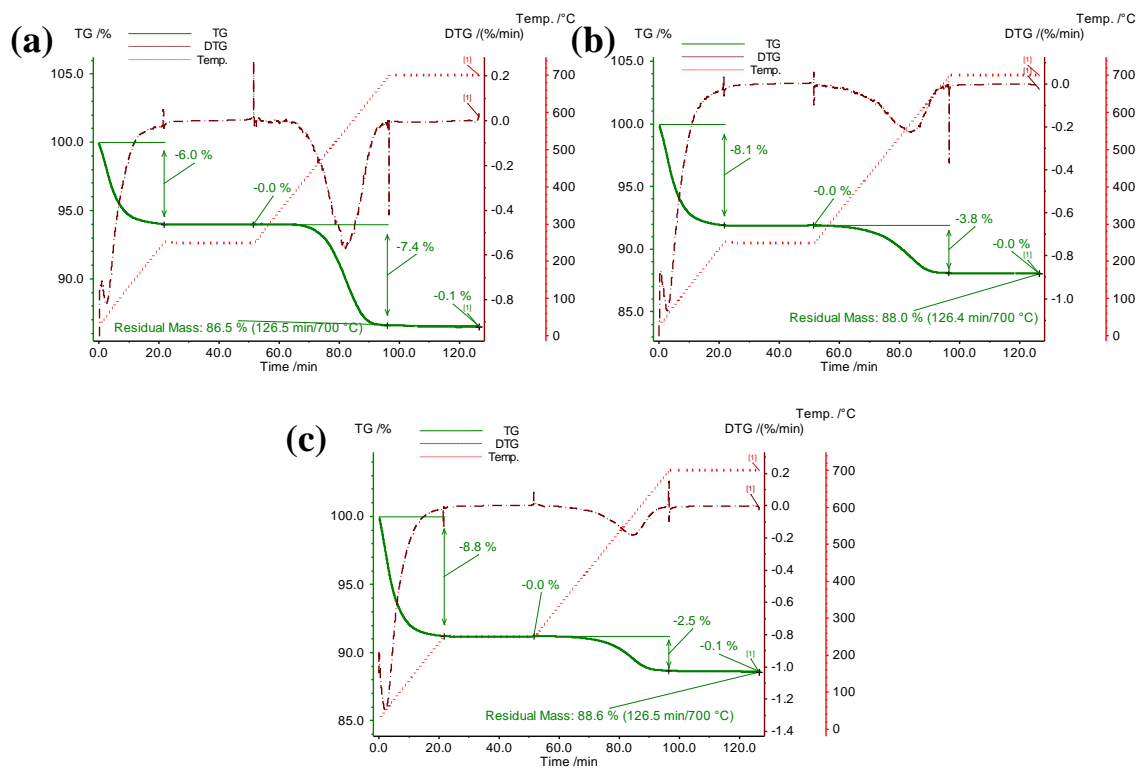


Figure S6. Thermogravimetric analysis - differential thermal analysis (TGA-DTA) of Beta catalysts after reaction for the following systems: (a) 10%DX/Cyclohexane; (b) Cyclohexane; (c) Cyclohexane*.

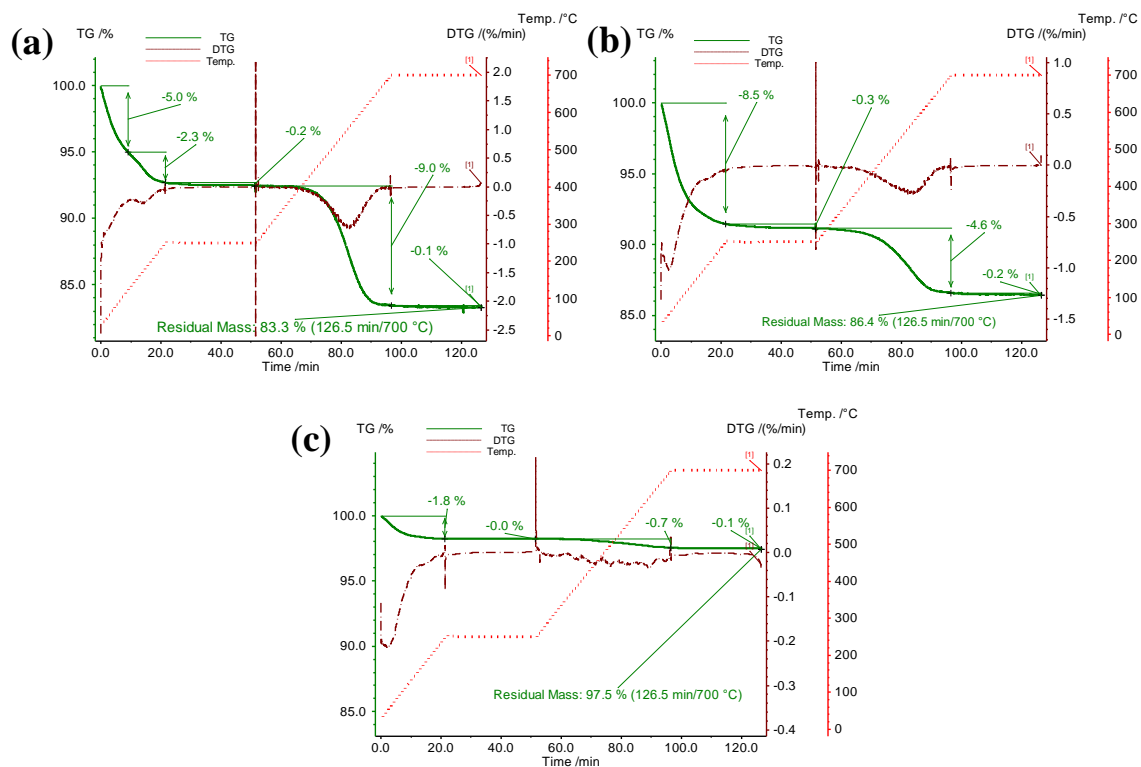


Figure S7. Thermogravimetric analysis - differential thermal analysis (TGA-DTA) of Beta catalysts after reaction for the following systems: (a) 10%DX/Methylcyclohexane; (b) Methylcyclohexane; (c) Methylcyclohexane*.

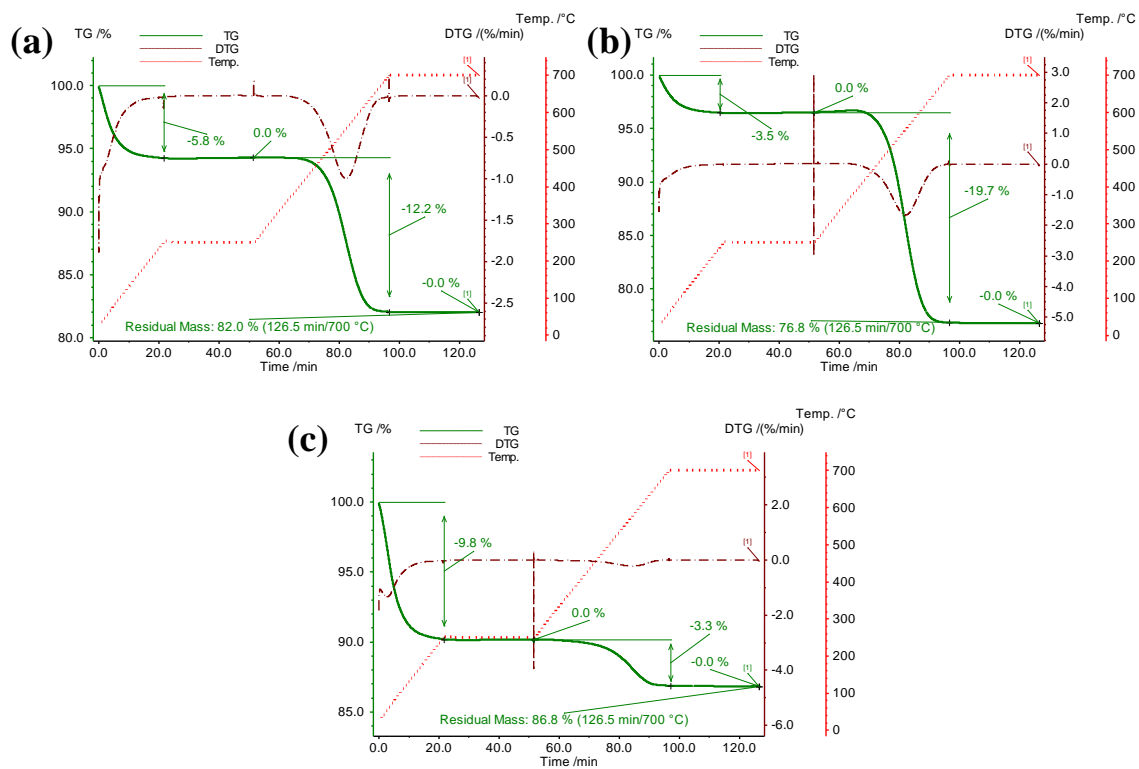


Figure S8. Thermogravimetric analysis - differential thermal analysis (TGA-DTA) of Beta catalysts after reaction for the following systems: (a) 10%DX/Toluene; (b) 20%DX/Toluene; (c) Toluene*.

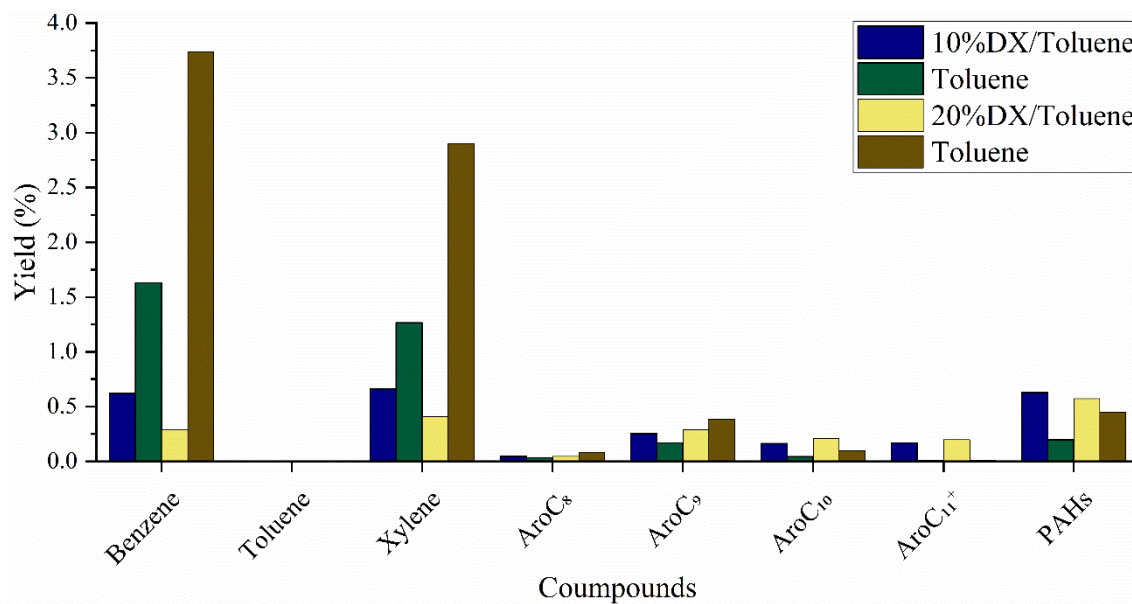


Figure S9. Liquid fraction yield (%) for aromatics C₆-C₁₁⁺ and polyaromatics in the catalytic cracking of the toluene and 10%DX/toluene, and toluene and 20%DX/toluene.

Both reactions had similar hydrocarbon conversion at the reaction temperature of 500°C, according to the reaction conditions in Table 1.

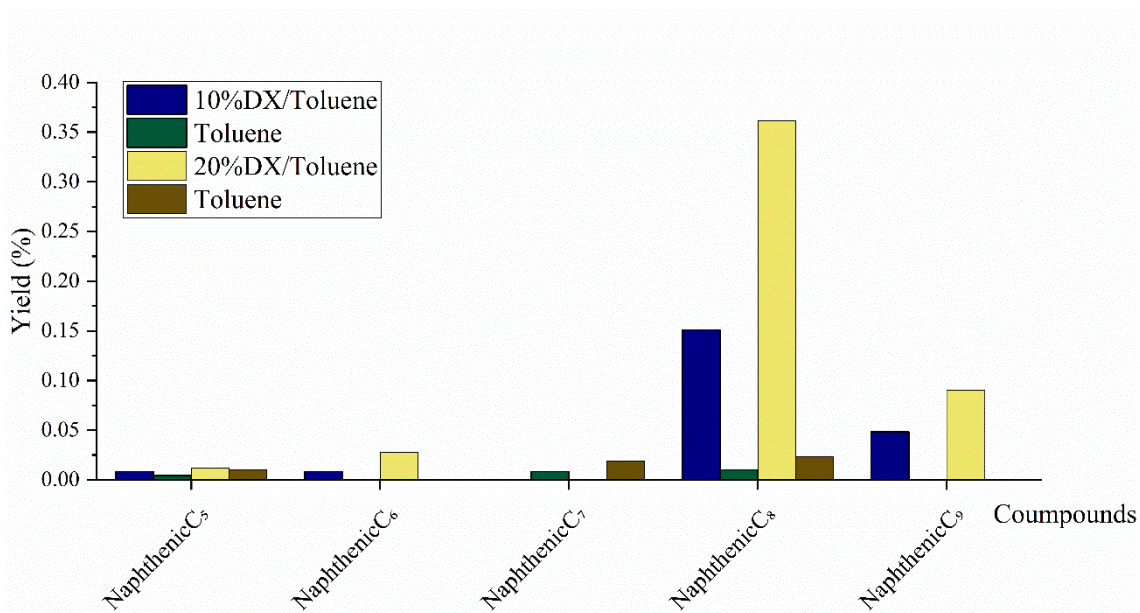


Figure S10. Liquid fraction yield (%) for naphthenics C₅-C₈ in the catalytic cracking of the toluene and 10%DX/toluene, and toluene and 20%DX/toluene. Both reactions had similar hydrocarbon conversion at the reaction temperature of 500°C, according to the reaction conditions in Table 1.

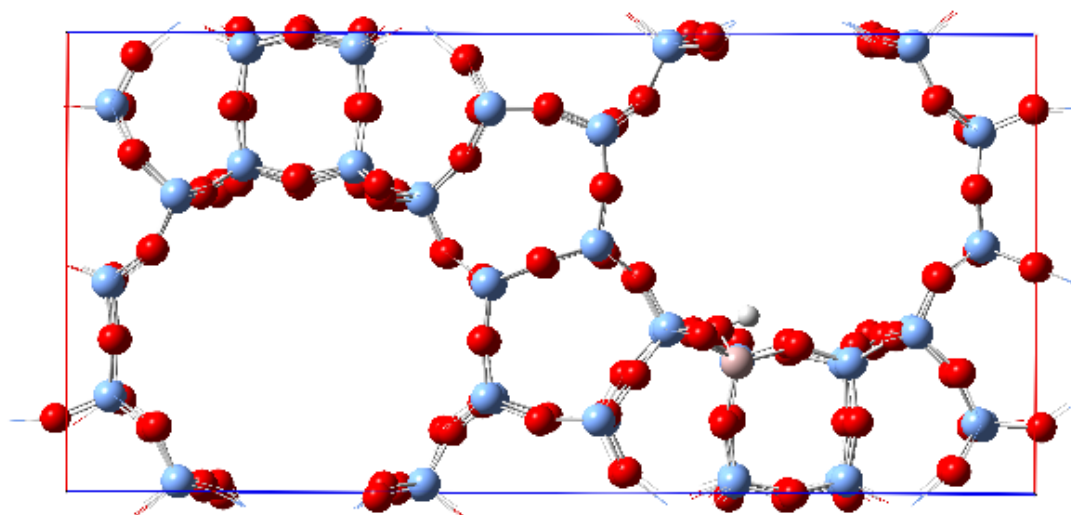


Figure S11. Primitive unit cell of HBEA zeolite. The atom colors are blue = silicon; pink = aluminum, red = oxygen and hydrogen = white.

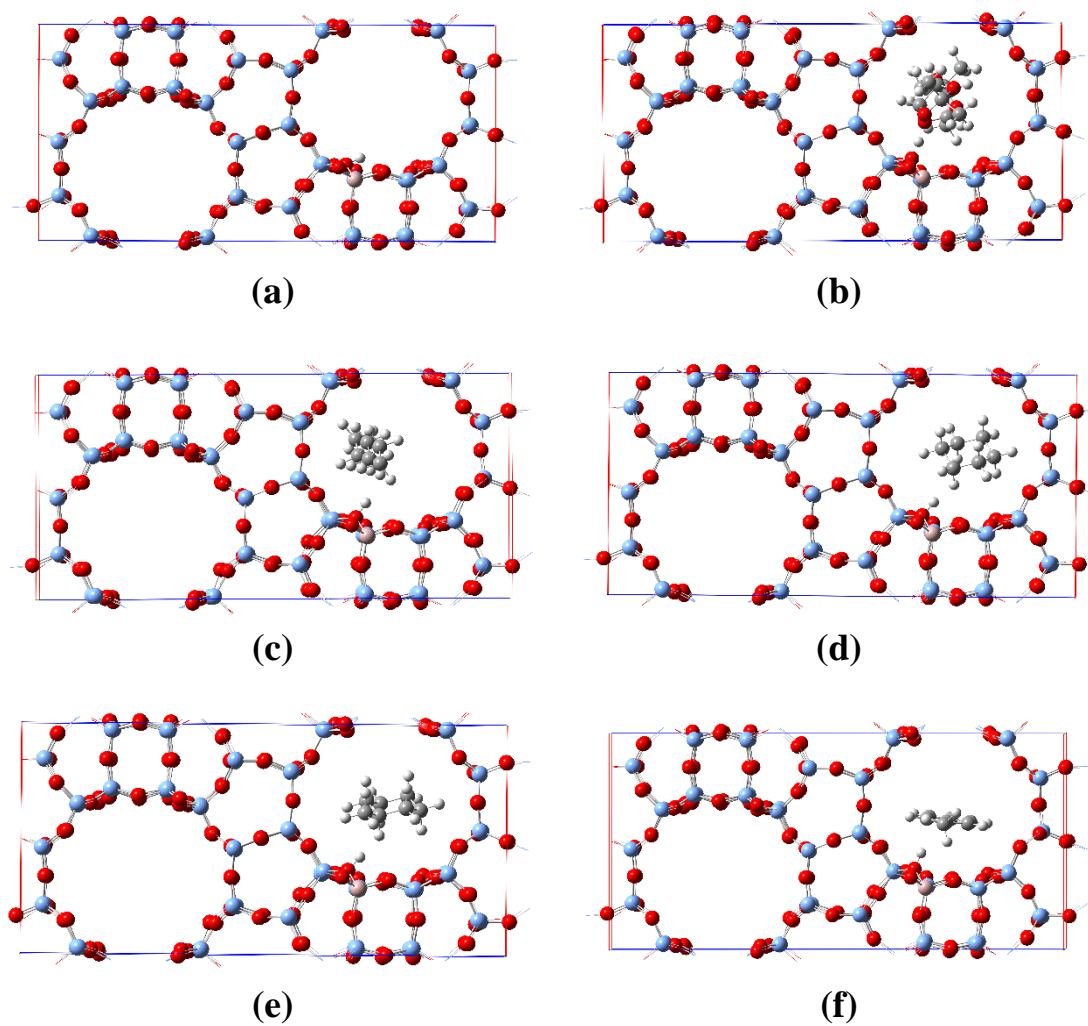


Figure S12. (a) HBEA primitive unit cell and the adsorption complexes of (b) DX, (c) n-Hexane, (d) Cyclohexane, (e) Methylcyclohexane and (f) Toluene under the acid site of zeolite.

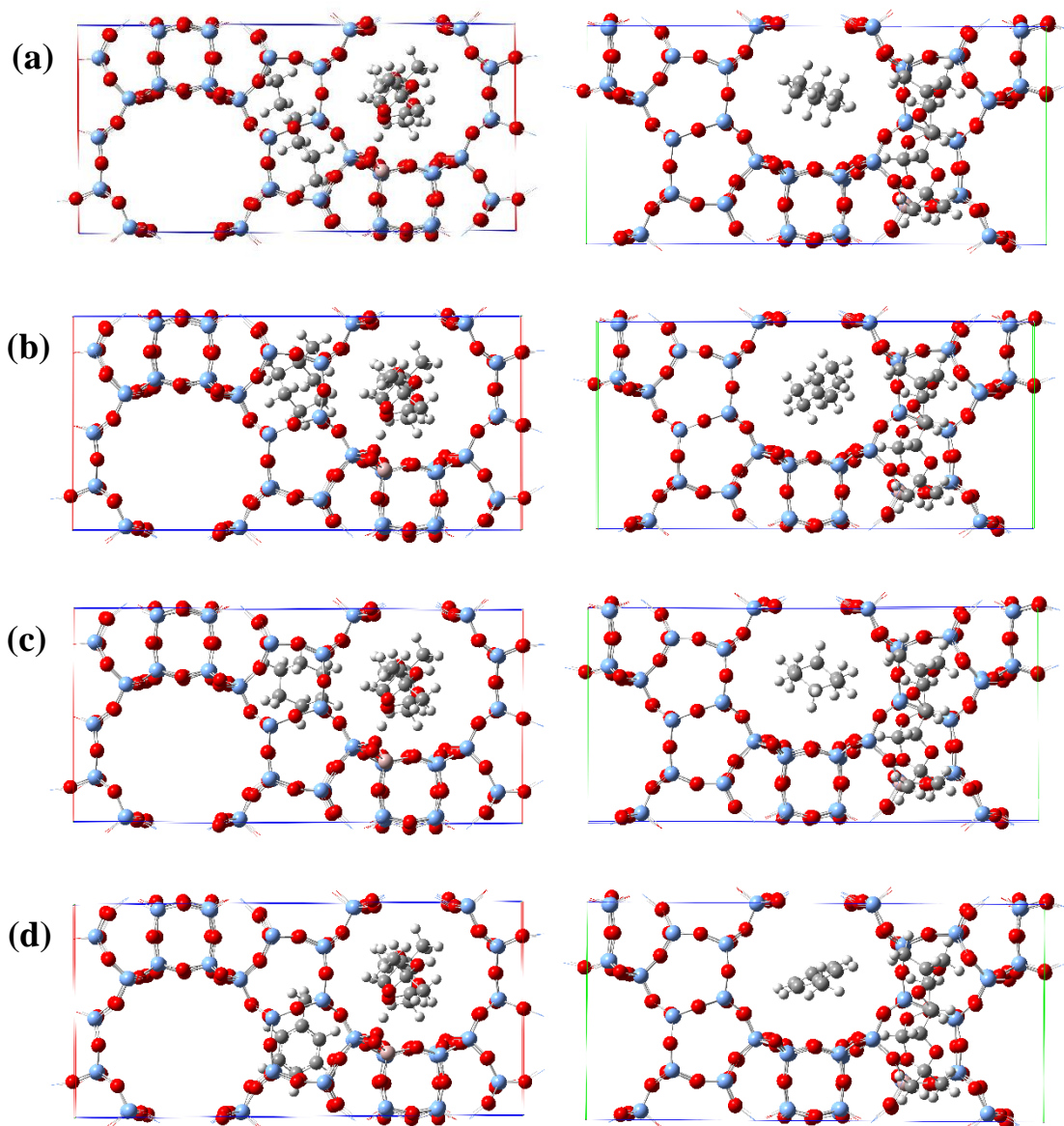


Figure S13. Front and top view of DX near the acid site and the hydrocarbons (a) n-Hexane, (b) Cyclohexane, (c) Methylcyclohexane and (d) Toluene adsorbed in the pores of HBEA zeolite.

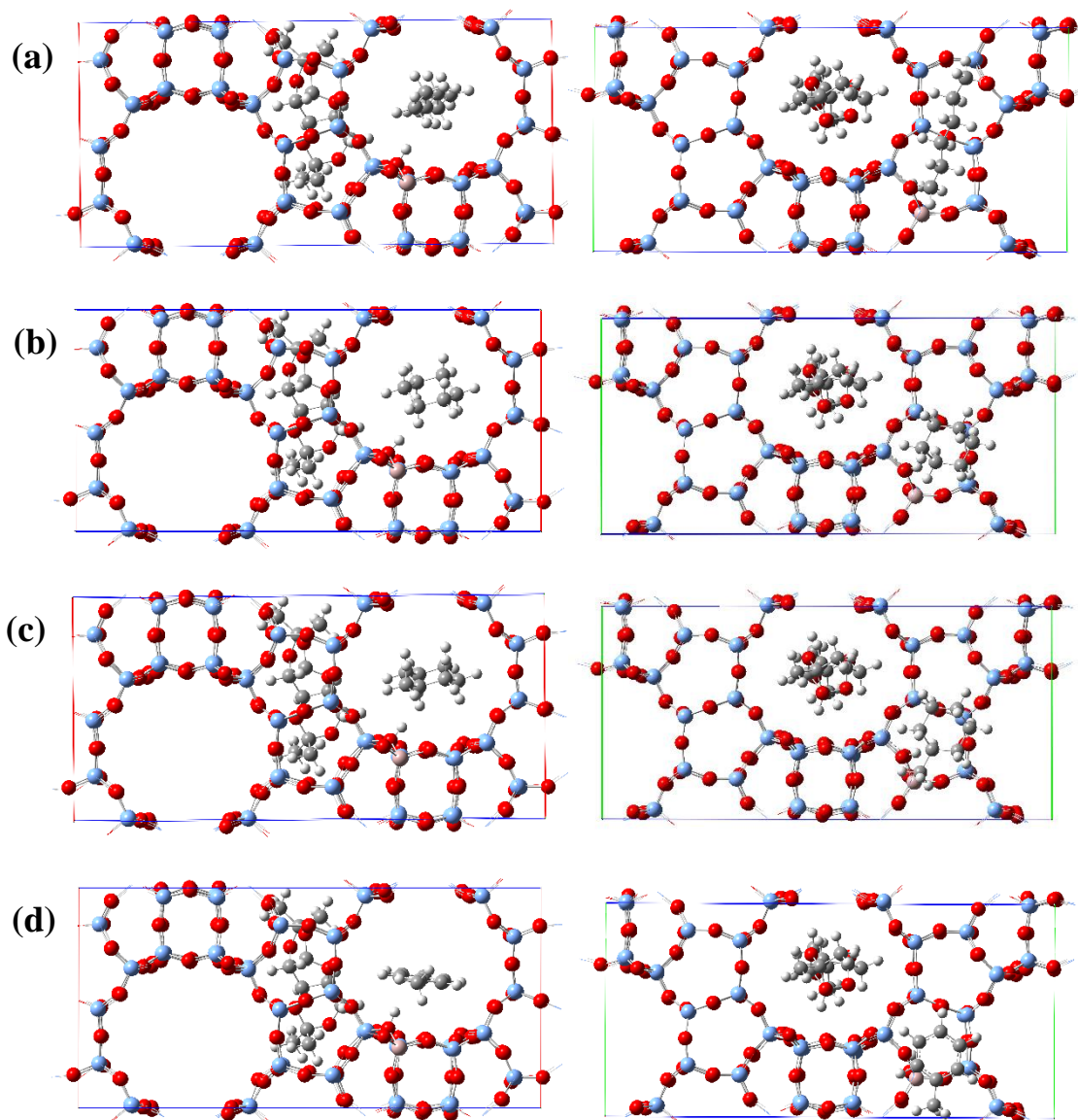


Figure S14. Front and top view of the hydrocarbons (a) n-Hexane, (b) Cyclohexane, (c) Methylcyclohexane and (d) Toluene near the acid site and DX in the pores of HBEA zeolite.

Supplementary Section 2 – Tables

Table S1. Chemical shifts and areas of ^{29}Si MAS-NMR. Topspin program calculations.

Sample	Q ⁴ (3Al)		Q ⁴ (2Al)		Q ⁴ (1Al)		Q ⁴ (0Al)		Ratio Si/Al
	δ , ppm	Area (%)	δ , ppm	Area (%)	δ , ppm	Area (%)	δ , ppm	Area (%)	(SAR)
HBEA	-89 to -94	1.3	-94 to -99	3.1	-99 to -106	17.8	-106 to -116	77.7	14.1 (28.2)

Table S2. Chemical shift and area of ^{27}Al MAS-NMR. Topspin program calculations.

Sample	Máx. signal (δ , ppm)	Area (%)	Assignment suggested
	54.7	55.8	Al ^{IV} framework
HBEA	~26.9	14.7	Al ^{IV} and/or Al ^V extra-framework
	0.9	29.4	Al ^{VI} extra-framework

Table S3. Standard deviation for hydrocarbons and DX conversion of catalytic cracking of DX/hydrocarbons and pure hydrocarbons reactions at 500 °C. The experimental conditions were presented in Table 1.

System	Standard deviation hydrocarbons conversion (%)	Standard deviation DX conversion (%)
10%DX/n-Hexane	0.66	0.03
n-Hexane	2.30	-
10%DX/Cyclohexane	0.13	0.46
Cyclohexane	1.47	-
10%DX/Methylcyclohexane	0.84	0.26
Methylcyclohexane	3.22	-
10%DX/Toluene	0.38	0.55
20%DX/Toluene	-	-
Toluene*	0.87	-

* Hydrocarbons conversion similar to the conversion of hydrocarbon in the corresponding DX/hydrocarbon system.

Table S4. Contribution of the DX compound in the formation of aromatics C₆-C₁₁⁺, polyaromatics and naphthenics C₅-C₈ in the catalytic cracking, if the hydrocarbon behaves in the same way in both tests (hydrocarbon and DX/hydrocarbon). The calculation is based on subtracting the yield of products (%) DX/hydrocarbons minus the yield of products (%) hydrocarbons, if negative or zero values do not present DX contribution.

Compound	10%DX/ nC ₆	10%DX/ CycloC ₆	10%DX/ MethylCycloC ₆	10%DX/ Toluene	20%DX/ Toluene
Benzene	0.08	-0.08	0.15	-1.01	-3.44
Toluene	0.31	0.27	0.88	0	0
Xylene	0.19	0.16	0.49	-0.60	-2.49
AroC₈	0.05	0.05	0.09	0.01	-0.03
AroC₉	0.30	0.51	0.69	0.09	-0.10
AroC₁₀	0.20	0.25	0.40	0.12	0.11
AroC₁₁⁺	0.19	0.20	0.32	0.16	0.19
PAHs	0.53	0.32	0.58	0.43	0.12
Naphthenic C₅	0.01	-0.01	0.04	0	0
Naphthenic C₆	0.05	-0.54	0.23	0.01	0.03
Naphthenic C₇	0.09	0.28	0.32	-0.01	-0.02
Naphthenic C₈	0.07	0.10	0.04	0.14	0.34
Naphthenic C₉	0.05	0.10	-0.02	0.05	0.09

Table S5. Estimation of carbon and hydrogen efficiency in the five DX systems in the presence of hydrocarbons.

System	C+H efficiency (%)
10%DX/n-Hexane	65
10%DX/Cyclohexane	101
10%DX/Methylcyclohexane	105
10%DX/Toluene	36
20%DX/Toluene	43

Experimental Section

Catalyst characterization

The measurements of X-ray diffraction (XRD) were performed in a Rigaku Ultima IV diffractometer with copper $K\alpha$ x-ray (1.54 Å) and geometry $\theta - \theta$ with radius of 185 mm. The values of the diffractograms were recorded increasing Bragg angles (2θ) from an angle of 5° to 80° with a pitch of 0.02° and a velocity of $10^\circ/\text{s}$. The crystallographic records were obtained using the Rigaku PDXL program.

Solid state NMR spectra were acquired at magnetic field of 9.4T (Bruker Avance III400WB spectrometer) at Larmor frequencies of 79.46 Mz ($\nu_{\text{Larmor}}^{29\text{Si}}$) and 104.23 MHz ($\nu_{\text{Larmor}}^{27\text{Al}}$). Setup and pulse calibrations were established with solid kaolinite ($^{29\text{Si}}$ signal at -91.5 ppm) and liquid 1M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ($^{27\text{Al}}$ signal at 0.0 ppm). Solid AlCl_3 was used for calibration of the central transition excitation, using a factor less than $90/(I + 1/2)$. Acquisition details were: $^{29\text{Si}}$ – Bruker 7 mm HX MAS probe, spinning frequency of 3kHz, one $\pi/2$ (8.38 μs) pulse sequence, recycle delay of 60 s and 256 scans; and $^{27\text{Al}}$ – Bruker HXY triple channel 4 mm MAS probe, spinning frequency of 12 kHz, one $\pi/12$ (1.29 μs) pulse sequence, recycle delay of 0.5 s and 8192 scans. Quantification of framework and extra-framework Al was performed by $^{27\text{Al}}$ solid state MAS NMR spectra, through the measurement of relative areas (Topspin program) in the following regions: 100 to 40 ppm, framework Al; 40 to 10 ppm, distorted Al^{IV} and/or Al^{V} extra-framework Al; and 10 to -50 ppm, Al^{VI} extra-framework Al. The spectra were also simulated by employing central transition MAS model with DMfit program, and the results showed the same trend of the integrals measured with Topspin Program.

The determination of the textural properties of the catalyst was carried out by means of nitrogen physisorption in the Quantachrome Nova e-4200 instrument. First, the catalyst was pre-treated by heating from room temperature to 220 °C and then kept at 220 °C under vacuum for 16 h. After pre-treatment, the adsorption-desorption isotherms were determined at 77 K. The specific surface area (S_{BET}) and the specific external area (S_{ext}) were calculated using Brunauer-Emmett-Teller (BET) and t-plot, respectively. The total pore volume was determined from the BJH fit and the micropore volume was determined from the t-plot.

The chemical compositions were determined in a Supermini 200 X-ray (Rigaku) fluorescence spectrometer (XRF). Detection was performed by PC and SC detectors with an element detection range from F to U. The X-ray source consisted of a Pd lamp set at 50 kV and 4.0mA. The powder samples were dispersed evenly in the sample holder and then analyzed in the equipment.

Quantitative and qualitative analyses of gaseous products

As described on manuscript, the quantitative analysis of gaseous products used standard compound molar response factors (MRF) and their respective retention times together with the water displacement mass. A scheme of this apparatus is illustrated on Figure S4. It was assumed that gas inside Erlenmeyer flask was in ideal conditions. Retention times along with molar response factors (MRF) of standard compounds were used to identify and quantitate, respectively, different compounds on gaseous products. Gaseous product masses were calculated using the equations S1, S2, S3 and S4.

Gaseous product moles were calculated following Equation S1.

$$n_{\text{mols}} = \text{Area}_{\text{gas}} \times \text{MRF}_{\text{gas}} \quad (\text{Equation S1})$$

Where,

n_{mols} = Total of gaseous product moles collected into Erlenmeyer flask;

Area_{gas} = Gas area;

MRF_{gas} = Molar response factor gas.

Molar fraction (% molar) of gaseous product on gas collected into Erlenmeyer flask were calculated from Equation S2.

$$\% \text{molar} = \frac{n_{\text{mols}}}{n_{\text{mols total}}} \quad (\text{Equation S2})$$

Mass of gas was obtained from Equation S3.

$$\text{Mass of gas (g)} = \frac{\text{total gas volume} \times \text{MM} \times \% \text{molar}}{\text{NTP gas volume}} \quad (\text{Equation S3})$$

Where,

Total gas volume (mL) = Eater volume shifted by gaseous products;

MM (g mol^{-1}) = Molecular mass of gas;

NTP gas volume = 22400 mL.

Finally, gas yield (%) was obtained from Equation S4.

$$\text{Gas yield (\%)} = \% \text{molar} \times \left(\frac{\text{mass of gas}}{\text{injected mass}} \times 100 \right) \quad (\text{Equation S4})$$

Where,

Injected mass = Reaction reactant mass (g) (DX+hydrocarbon or hydrocarbon mass).

Qualitative and quantitative analyses of liquid products

Some liquid samples produced from reactions could contain up to 300 different compounds. Considering this, the quantification of the formed products was based on the method proposed by ASTM D5769. A certified reference material (ASTM Method D5769 Aromatics in Finished Gasoline, Calibration Level 1 without internal standard) was purchased from Dr. Ehrenstorfer (LGC Standards). This multicomponent solution presents 23 standard compounds (Benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, isopropylbenzene, n-propylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,4-diethylbenzene, n-butylbenzene, indane, 1,2-diethylbenzene, 1,2,4,5-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene. In addition to this standard, n-heptane, cyclohexane, 2-pentanone and 2,5-dimethylfuran were added to the solution. ASTM/EPA Aromatics Internal Standard Mix was purchased from Supelco and used as internal standard, being composed of Benzene-d₆, Ethylbenzene-d₁₀ and Naphthalene-d₈. Moreover, these compounds were assigned to different classes (paraffins, aromatics, polyaromatics, naphthenics and oxygenates compounds) in order to facilitated data treatment and understanding of work. In this sense, standard compounds retention times along with compound identification provided by NIST library mass spectra database were used to perform the qualitative analysis. Quantitative analysis was performed through external standard calibration using standard compound response factors obtained from flame ionization detector. For example,

concentration of benzene was calculated from benzene area and benzene calibration curve. Paraffins were quantitated through heptane's curve. Naphthenic were quantitated through cyclohexane's curve. Oxygenated compounds (ketones, alcohols, etc.) on liquid fraction were quantitated through calibration curve produced by 3- pentanone as standard compound. Table S6 describes which analytical calibration curves were used to quantify certain products and/or product classes. The calibration curve of the standard compounds was obtained by dissolving the standard compounds in n-hexane at the concentrations described in Table S6. A dilution of the internal standard solution was made in n-hexane, in order to obtain concentrations of 19.4 mg mL^{-1} for benzene-d6 and ethylbenzene-d10, and 9.7 mg mL^{-1} for naphthalene-d8. Analytical calibration curves were performed with five points in duplicate. Sample preparation consisted of dilution of $25 \text{ }\mu\text{L}$ of internal standard into $500 \text{ }\mu\text{L}$ of liquid product fraction. With this last dilution, the analytes concentration of the internal standard was 0.8 mg mL^{-1} for benzene-d6 and ethylbenzene-d10, and 0.4 mg mL^{-1} for naphthalene-d8.

Table S6. Analytical calibration curves used with the concentration (mg mL⁻¹) ranges of the standards and the respective products quantified in each curve.

Standard compound analytical calibration curve	Standard concentration range (mg mL⁻¹)	Products or products classes quantified
Benzene	0.08-6.29	Benzene
Cyclohexane	0.08-0.92	Naphthenic C ₅ -C ₉
Heptane	0.05-0.85	Paraffins C ₅ ⁻ , C ₆ , C ₇ ⁺
Toluene	0.33-23.92	Toluene
Ethylbenzene	0.08-6.29	Ethylbenzene
m-xylene, p-xylene	0.10-7.55	m-xylene, p-xylene
o-xylene	0.10-7.55	o-xylene
Isopropylbenzene	0.05-3.78	Isopropylbenzene (Aromatic C ₉)
N-propylbenzene	0.05-3.78	N-propylbenzene (Aromatic C ₉)
3-ethyltoluene	0.05-3.78	3-ethyltoluene (Aromatic C ₉)
4-ethyltoluene	0.05-3.78	4-ethyltoluene (Aromatic C ₉)
1,3,5-trimethylbenzene	0.05-3.78	1,3,5-trimethylbenzene (Aromatic C ₉)
2-ethyltoluene	0.05-3.78	2-ethyltoluene (Aromatic C ₉)
1,2,4-trimethylbenzene	0.08-6.28	1,2,4-trimethylbenzene (Aromatic C ₉)
1,2,3-trimethylbenzene	0.05-3.78	1,2,3-trimethylbenzene (Aromatic C ₉)
Indane	0.05-3.83	Indane
1,4-diethylbenzene	0.05-3.78	Aromatic C ₁₀ -C ₁₁ ⁺
Naphthalene	0.03-2.50	All naphthalenes
2-Pentanone	0.06-0.88	Oxygenated compounds (ketones, alcohols, etc.)
2,5-Dimethylfuran	0,08-0.84	Furanic derivatives
1,2:3,5-di-O-isopropylidene- α-D-xylofuranose (DX)	6.25-34.03	DX, DX-derived carbohydrates

The concentration (mg mL^{-1}) of a compound was calculated through the analytical calibration curves obtained. From this, the product mass was calculated according to Equation S5.

$$m_{\text{product}} = \frac{\left(\text{Product conc.} \times \frac{\text{liquid product mass}}{\text{liquid density}} \right)}{1000} \quad (\text{Equation S5})$$

Where,

m_{product} = Product mass;

Product conc. (mg mL^{-1}) = Liquid product concentration;

Liquid product mass = Liquid product obtained at the end of the reaction;

Liquid density = The density of the hydrocarbon used as co-feed was considered as the density of the liquid product, so for reactions with n-hexane the density of the liquid considered was 0.655 g mL^{-1} . Thus, for the reactions with the other hydrocarbons as co-feed, it was 0.779 mg mL^{-1} , 0.77 mg mL^{-1} and 0.867 mg mL^{-1} for cyclohexane, methylcyclohexane and toluene, respectively.

The liquid product yield (%) was calculated according to Equation S6.

$$\text{Product yield (\%)} = \left(\frac{\text{product mass}}{\text{injected mass}} \right) \times 100 \quad (\text{Equation S6})$$

Where,

Injected mass = Reaction reactant mass (g) (DX+hydrocarbon or hydrocarbon mass).

For determination of n-hexane, cyclohexane, methylcyclohexane and toluene conversion, calibration curves was obtained through dissolution of n-hexane, cyclohexane, methylcyclohexane and toluene (standard compound) and n-hexadecane (internal standard) into acetone. Concentration of n-hexadecane was equal to 60 mg mL^{-1} and concentration of each hydrocarbon varies from 20 mg mL^{-1} to 80 mg mL^{-1} . For sample preparation, $100 \text{ }\mu\text{L}$ of n-hexadecane along with $50 \text{ }\mu\text{L}$ of liquid product fraction were dissolved into $950 \text{ }\mu\text{L}$ of acetone.