Supporting Information

Controlling reactive pathways in complex one-pot using novel shape-selective catalyst with multifunctional active-sites

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Methods

Catalyst preparation. Na-form ZSM-5 zeolite with a Si/Al ratio of 26 was synthesized according to the reported procedure.[1] After the above ZSM-5 zeolite was transformed into the NH$_4$-form by ion-exchange with NH$_4$NO$_3$ solution, it was changed into an H-form by calcination in air at 793 K. In the SiO$_2$ modification of ZSM-5, the as-synthesized ZSM-5 was impregnated with the hexane solution of polyphenylmethylsiloxane (Dow Chemicals; CH$_3$-(Si(CH$_3$)ph-O)$_n$-CH$_3$, MW 2000~3000) at 20 wt % polysiloxane to ZSM-5. The above impregnated ZSM-5 was calcined in a flow of mixed air and N$_2$ (V/V=1:2) by heating it to 793 K at a rate of 3 K/min and holding at this temperature for 2 h. As a result, after the above procedure of silica deposition was repeated, the SiO$_2$ modified ZSM-5 by the two-cycle silica deposition was obtained for preparing the composite catalyst. Na-form Beta zeolite with a Si/Al ratio of 32 was purchased from Fuxu Company of Shanghai. After it was transformed into an H-form according to the same method used above for ZSM-5, the La$_2$O$_3$ modification of Beta was performed by the impregnating treatment of La(NO$_3$)$_3$ solution and the following calcination at 773 K. The composite of ZSM-5/Beta zeolites were typed with the mixture of 54 wt% modified ZSM-5 and 26 wt% modified Beta using 20% silicon dioxide as an adhesive. Then the obtained ZSM-5/Beta composite was impregnated with Pd(NO$_3$)$_2$ solution at 0.4 wt % Pd loading. Finally, the composite ZSM-5/Beta catalyst was reduced by the treatment at 773 K in hydrogen flow and for 4 h, for

use in the one-pot reactions of mixed C_8 aromatics conversion. For the one-pot reactions for dewaxing & deolefin of gas oil fraction, the composite catalyst was fine-tuned as following: the as-prepared H-form ZSM-5 was modified by first Pd-loading and subsequent silica deposition; Na-form Beta was modified by Ni-loading; Then it was extruded with the mixture of 54 wt% modified ZSM-5 and 26 wt% modified Beta using 20% silicon dioxide as an adhesive; Finally, the new multi-functional & shape-selective catalyst was obtained after reduction at 773 K in the hydrogen flow and for 3 h.

Catalyst characterization and analysis. The particle morphology of the parent zeolite was observed by means of a scanning electron microscope (SEM, S-4800, Hitachi). The X-ray diffraction patterns were collected using a Bruker D8 ADVANCE instrument with Cu Kα radiation. The specific surface area and pore volume were measured by N_2 adsorption-desorption at 77 K (NOVA 2200e, Quantachrome). NH_3-TPD experiment was performed on a conventional instrument equipped with a TCD (CHEMBET 3000). The strength and number of the acidic sites was determined according to the temperature and the area of NH_3 desorption peaks.[2] Infrared spectroscopy with pyridine adsorption (Py-IR) was obtained respectively at 473 K and 673 K, with Perkin-Elmer 2000 FT-IR spectrometry and a self-supported wafer of sample. Infrared spectroscopy with 2,6-di-*tert*-butylpyridine adsorption (DTBPy-IR) was obtained at 473 K, with Pekin-Elmer 2000 FT-IR spectrometry and a self-supported wafer of samples. The probe reactions, cracking of cumen/1,3,5-triisopropylbenzene, were carried out in the fixed-bed reactor at 1.0 h^{-1} WHSV, 663 K and atmospheric pressure with a 40 ml/min N_2 flow. The constraint index

(CI) was determined with a fixed-bed micro-reactor and hexane/3-methylpetane of 1/1 as the mixed reactants, 1.0 h^{-1} WHSV under total conversion 10 ~ 60 %, in the helium flow at atmosphere pressure. The products were analyzed using on-line gas chromatography (HP5890) with a 50 m HP-PLOT/Al$_2$O$_3$ capillary column and FID, and the constraint index (CI) was calculated according to the reported method.[3] Adsorption of aromatic components mentioned in the one-pot reactions was respectively measured in an Intelligent Gravimetric Analyser (IGA-002, Hiden Analytical Ltd.) at 298 K. The samples (10 mg) were outgassed at 593 K for 4 h prior to measurement. Their saturated adsorption were measured in the flow of He with about 60% saturated vapour pressure of each aromatic hydrocarbon (for example, 23 mbar for toluene adsorption, because the saturated vapour pressure of toluene is 38 mbar at 298 K). The Bromine Number was measured by using a Bromine Number/Bromine Index Analyzer (ZH6866, Beijing Zhongyitiancheng).

Catalytic reaction. The one-pot reactions for isomerization of o-X & m-X, dealkylation of EB in the mixed C$_8$ aromatics and hydrogenation of the immediate ethylene were carried out in a single fixed-bed reactor. Before the reaction, the catalyst is activated in situ in a pure H$_2$ flow at 773 K for 1 h. The reaction conditions are as follows: temperature (T) = 673 K, pressure (P) = 0.5 MPa, weight hourly space velocity (WHSV) = 4.0 h^{-1}, molar ratio of hydrogen to aromatics (H$_2$/C$_8$) = 3.0. The industrial feedstock is composed of 12.31% EB, 61.09% m-X and 25.11% o-X with impurity of 0.26% p-X and 1.23% toluene. Analysis of effluent gas and effluent liquid was performed on two gas

chromatograms (GC, HP5890) equipped with a HP&PLOT/Al_2O_3 capillary column and a PEG-20M capillary column respectively. Besides, the one-pot reactions for dewaxing & deolefin of gas oil fraction (obtained from Shanghai Huayi Company) were performed at WHSV = 1.0 h^{-1}, T= 653 K, P =1.5 MPa and H_2/C = 4.0 (mol/mol), after catalyst was pretreated (H_2 flow at 773 K for 1 h) in a fixed-bed reactor. Analysis of reaction products were similar to that was used for the one-pot reactions of mixed C_8 aromatics.
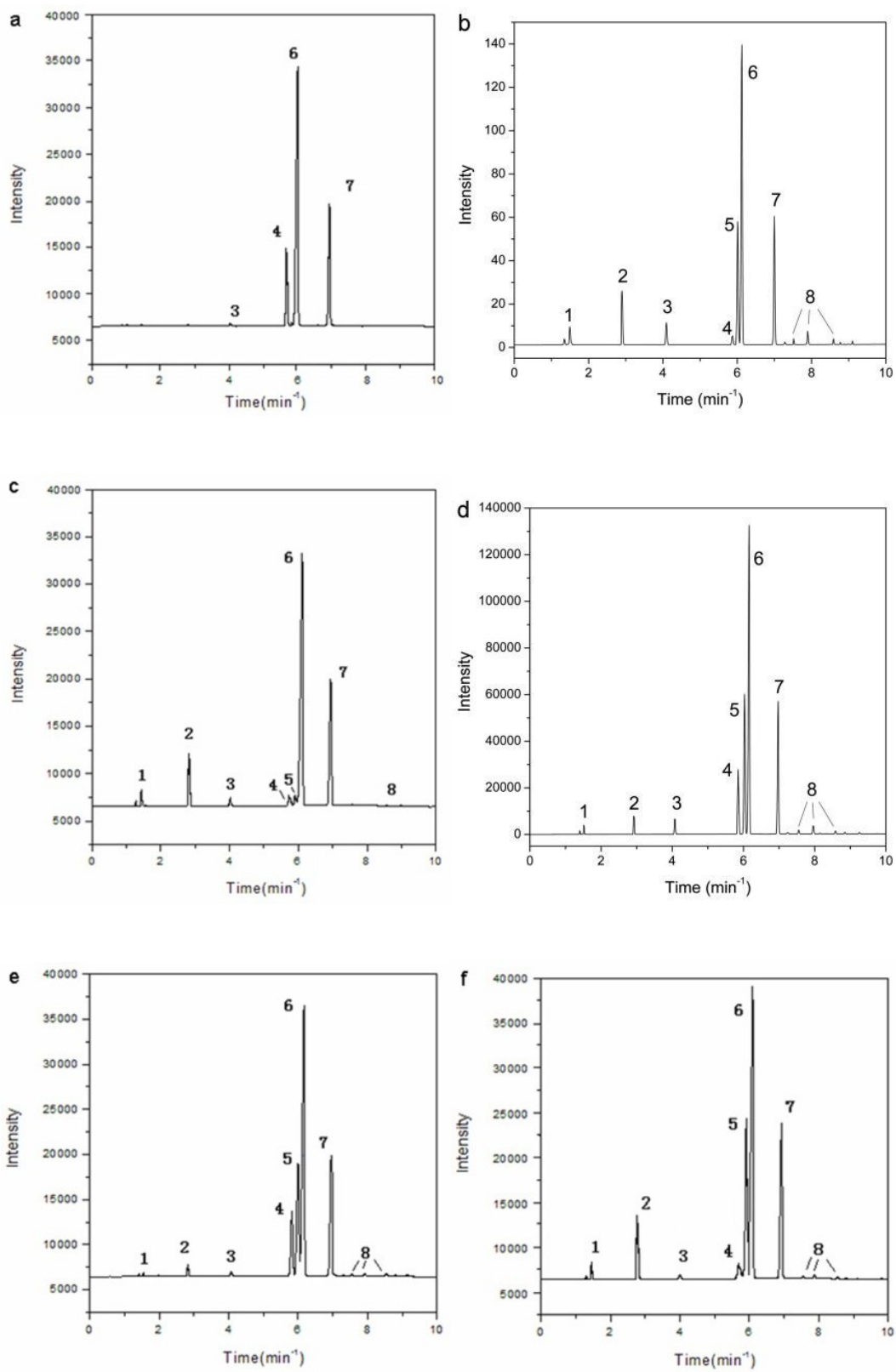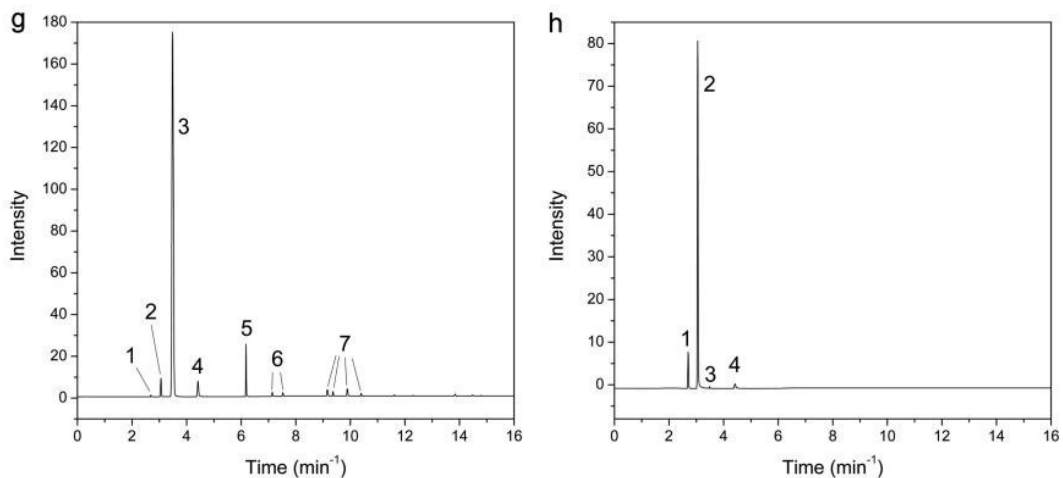
Figure S1. The chromatography of the effluent liquid and the effluent gas for the mixed C_8 aromarics (industrial feedstock) conversion. a: feedstock aromatics; b: effluent liquid over HZSM-5; c: effluent liquid over SiO_2-ZSM-5; d: effluent liquid over Beta; e: effluent liquid over La_2O_3-Beta; f: effluent liquid over ZSM-5/Beta composite; 1: aliphatics, 2: benzene, 3: toluene, 4: ethylbenzene, 5: *p*-X, 6: *m*-X, 7: *o*-X; 8: trimethylbenzene. g: effluent gas over SiO_2-ZSM-5; h: effluent gas over ZSM-5/Beta composite; 1: methane; 2: ethane; 3: ethylene; 4: propane; 5: propylene; 6: butane; 7: butylene.
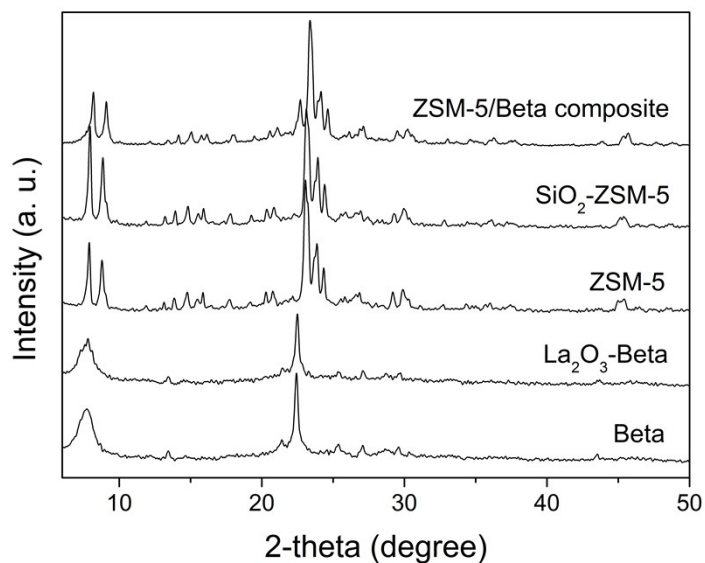
Figure S2. XRD patterns of ZSM-5, 8.9 wt % SiO_2 modified ZSM-5, Beta, 4.0 wt % La_2O_3 modified Beta and ZSM-5/Beta composite catalyst.

As shown in Figure S2, the modified zeolites showed very similar peaks to the parent zeolites and no new diffraction peak appeared, this suggests that the zeolite structure was not destroyed and no new phase was produced during modification. Besides, it's understandable that the composite catalyst showed the characteristic peaks for both ZSM-5 and Beta.
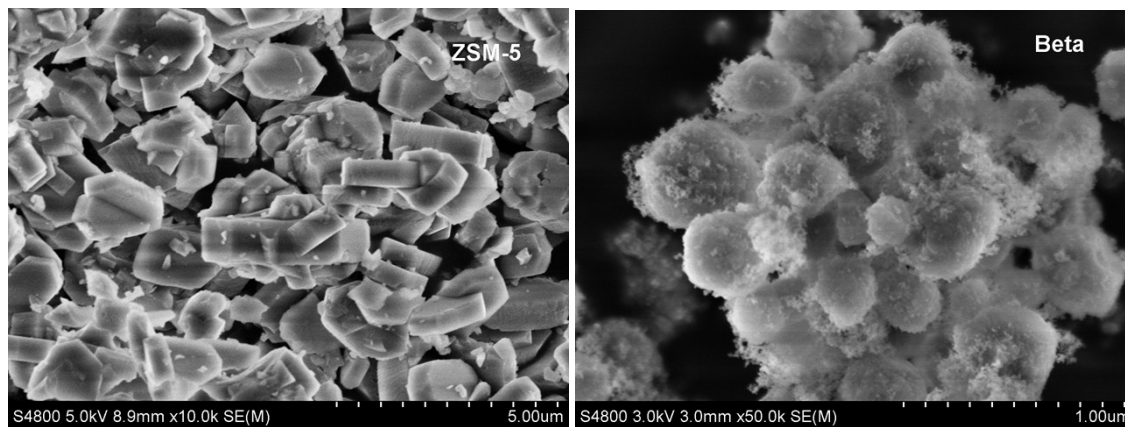
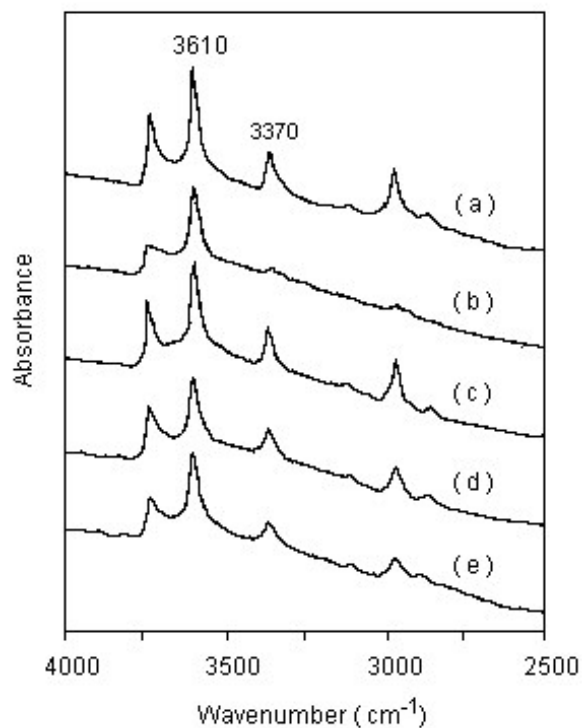**Figure S3**. SEM image of the parent ZSM-5 and Beta zeolites.

Figure S4. Spectra of DTBPy-IR characterization: (a) ZSM-5, (b) 8.9 wt % SiO_2 modified ZSM-5, (c) Beta, (d) 4.0 wt % La_2O_3 modified Beta, (e) ZSM-5/Beta composite catalyst

The adsorption of 2,6-di-*tert*-butylpyridine (DTBPy) was used to quantitatively distinguish the external and internal acid sites of parent and SiO_2-modified ZSM-5. In contrast to adsorption of pyridine both on external surface and in pores, the adsorption of DTBPy occurs only on the external surface of ZSM-5 (10 member ring pore) due to its large molecular size.[4,5] Thus, it can monitor the number of external acidic sites of ZSM-5 according to IR absorbance at 3370 cm^{-1} (corresponding to the $\equiv$N-H$^+$ stretching of protonated DTBPy).[6,7,8] Comparatively, the band at 3610 cm^{-1} is associated with the internal acidic OH, which doesn't interact with DTBPy molecule.[8] As can be seen in

Figure S4, the band at 3370 cm^{-1} for SiO_2-ZSM-5 disappears compared to ZSM-5, this suggests that the external Brønsted acidic sites of ZSM-5 were effectively passivated by SiO_2 modification.

Table S1. The results of Py-IR for these zeolite catalysts.

Catalyst	B acid sites		L acid sites		B/L ratio
	473 K	673 K	473 K	673 K	
ZSM-5	4.12	2.26	1.01	0.5	4.08
8.9 wt % SiO_2- ZSM-5	3.46	1.91	0.84	0.42	4.12
Beta	3.56	1.2	0.84	0.28	4.24
4.0 wt % La_2O_3- Beta	2.83	0.52	0.65	0.14	4.35
Composite sample without Pd	2.77	1.19	0.65	0.27	4.26
ZSM-5/Beta composite	2.75	1.18	0.64	0.26	4.30

The number of acid sites is a relative value of Brønsted (B) acid sites to Lewis (L) acid sites, estimated by the corresponding calibrated peak area. Composite sample without Pd: the extruded composite sample without Pd loading (the precursor of the ZSM-5/Beta composite catalyst).

As listed in Table S1, the trend of acidic density reflected by the Py-IR results is in accord with that for NH_3-TPD showed in Figure 2a. Besides, no significant change of the ratio of Brønsted/Lewis acid sites was observed for the modified ZSM-5 or Beta. Especially, compared with parent ZSM-5, the density of both Brønsted (B) and Lewis (L) acid site decreased for the SiO_2-ZSM-5, and these two zeolites showed the very close ratio of B/L acid sites. Combing with the results for the spectra of DTBPy-IR (Figure S4), it's confirmed that not only B acid sites but also L acid site on the external surface of ZSM-5 was effectively passivated during silica deposition. This ensures that SiO_2-ZSM-5 does not show any catalytic activity on its external surface. Because for example, L acid site can also catalyze xylene isomerization through its interaction with B acid site[9,10]. In

addition, the loading of 0.4 wt% Pd showed the very slight effect on the acidity of the extruded composite. As can be seen in Table S1, compared with its extruded precursor, ZSM-5/Beta composite catalyst exhibited the very slight decrease in acidic density. This may prove that Pd was loading on the surface of zeolites.

Table S2. The results of N$_2$ adsorption and the CI value for these zeolites

Sample	Specific surface area (BET) m^2/g	Micropore volume cm^3/g	Mesopore volume cm^3/g	CI value
ZSM-5	420	0.14	0.043	6.2
8.9 wt % SiO$_2$- ZSM-5	385	0.13	0.020	9.8
Beta	459	0.18	0.049	1.5
4.0 wt % La$_2$O$_3$- Beta	441	0.16	0.040	2.4
Composite sample without Pd	391	0.11	0.056	4.7
ZSM-5/Beta composite	390	0.11	0.056	4.7

CI value: Constraint Index Value

The results of nitrogen adsorption are listed in Table S2. As can be seen, the external surface area and mesopore volume greatly decreased for SiO$_2$-HZSM-5, while the internal surface area and micropore volume almost kept constant. This implies that silica deposition occurred only on the external surface. However, La$_2$O$_3$-modification resulted in the decrease of external surface, internal surface, mesopore volume and micropore volume of Beta, indicating that La$_2$O$_3$ species was not only loaded on the external surface but also into the Beta pores. Besides, owing to the introducing of silicon dioxide (inactive adhesive), the ZSM-5/Beta composite catalyst shows the increased mesopore volume. Constraint index (CI) is an effective method to determinate the porous shape-selectivity of zeolite, based on cracking reaction of probe molecules.[7] As shown in Table S2, the much increased CI value for SiO$_2$-HZSM-5 indicates its stronger porous shape-selectivity due to the finely narrowing of pore-opening during silica deposition. In addition, 0.4 wt% Pd loading hardly affects the surface area and pore volume of extruded composite.

Table S3. The results of cracking reactions of cumene/1,3,5-triisopropylbenzene over the zeolites.

Catalyst	Cumene conversion %	1,3,5-Triisopropylbenzene conversion %
ZSM-5	93.2	59.1
8.9 wt % SiO_2- ZSM-5	82.9	0.7
Beta	25.5	19.2
4.0 wt % La_2O_3- Beta	6.5	3.0
ZSM-5/Beta composite	74.6	1.3

Cumene can diffuse into the pores and on the external surface of these zeolites, while 1,3,5-triisopropylbenzene stays only on the external surface.[11] Therefore, cracking reactions of cumene/1,3,5-triisopropylbenzene was used to evaluate the change of the internal and external surface acidity of modified zeolites here. As shown in Table S3, 1,3,5-triisopropylbenzene cracking almost could not take place over SiO_2-HZSM-5, while the conversion of cumene still remained at the very high level. These suggest that silica deposition effectively passivated the external acid sites of HZSM-5 without obvious influence on the internal acidity. Nevertheless, the conversion of both cumene and 1,3,5-triisopropylbenzene significantly decreased for La_2O_3-Beta, indicating that basic La_2O_3 covered the stronger acid sites on both external and internal surface.

Table S4. The results of one-pot reactions for the dewaxing & deolefin of gas oil fraction over the fine-tuned ZSM-5/Beta composite catalyst.

	Content of normal alkanes (%)											Bromine Number
	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	$>C_{21}$	(gBr/100g)
Gas oil fraction	1.42	1.80	2.04	2.26	2.17	2.01	1.83	1.59	1.35	1.02	3.09	17.5
Reaction product	0.15	0.22	0.20	0.30	0.26	0.23	0.20	0.25	0.19	0.18	0.39	1.9

Normal alkanes: $C_{12} \sim C_{24}$; The one-pot reactions for dewaxing & deolefin of gas oil fraction were performed at WHSV 1.0 h^{-1}, 653 K, 1.5 MPa and H$_2$/C 4.0 (mol/mol).

Supporting References

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