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Octanoic acid hydrodeoxygenation over bifunctional Ni/Al-SBA-15 catalysts

Khairul Basyar Baharudin[a,b], Mahashanon Arumugam,[c] James Hunns,[d] Adam F. Lee,[d] Edwin Mayes,[d] Yun Hin Taufiq-Yap,[c,e] Karen Wilson,[d*] Darfizzi Derawi[a*]

[a]Laboratory for Biolubricant, Biofuels and Bioenergy Research, Center for Advanced Materials and Renewable Resources, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

[b]Faculty of Biotechnology and Biomolecular Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

[c]Catalysis Science and Technology Research Centre (PutraCat), Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

[d]School of Science, RMIT University, 124 La Trobe Street, Melbourne, Victoria 3000, Australia.

[e]Chancellery Office, Universiti Malaysia Sabah (UMS), 88400 Kota Kinabalu, Sabah, Malaysia.

S1. Experimental

a) Synthesis of Al-SBA-15 support

The Al-SBA-15(R) catalyst support with different Si:Al molar ratios was prepared by using the true liquid crystal templating method (TLCT), where R denotes the Si:Al molar ratio (5, 25, 50 and 75). In polypropylene bottle, appropriate amounts of $Al(NO_3)_3.(9H_2O)$ were dissolved in acidified water, pH 2 (hydrochloric acid, HCl), then 2g of Pluronic P123 was added to the dissolved solution which was immersed in an ultrasonic water bath at 40 °C for 2 hours to produce a homogenous gel. Next, 4.08 ml of tetramethylortosilicate (TMOS) was added to the gel and the mixture stirred until a smooth clear gel was observed. Methanol evolved in the reaction was removed under light vacuum (100 mbar) at 40 °C for 18 hours in a vacuum oven. The fine white powder obtained after grinding was then subjected to calcination in a muffle furnace at ramp rate of 1.5 °C min^{-1} to desired temperature, 550 °C and maintained for 5 hours.

b) Synthesis of Ni/Al-SBA-15

Support material were impregnated with 5 wt.% Ni loading via wet impregnation using $Ni(NO_3)_2.6H_2O)$ as the Ni precursor. 0.25 g of $Ni(NO_3)_2.6H_2O$ was dissolved into 40 ml ethanolic solution, ethanol:water (1:1)., then 1g of finely ground Al-SBA-15 catalyst support powder was the added to the solution, which was continuously stirred at ambient temperature. After 3 hours, the light green milky slurry was heated slowly with stirring to ~80 °C and maintained at temperature until a dry solid was obtained. The resulting catalysts were air dried for 18 hours in an electrical oven at 80 °C, then calcined in a muffle furnace at ramp rate of 3°C min^{-1} to 550 °C, where it was maintained for 5 hours. Subsequently, the catalyst was reduced at 500 ^{o}C under 10 ml/min flowing H_2 for 4 hours to yield 5 wt% Ni/Al-SBA-15(R).

c) Catalyst Characterization

X-ray diffraction (XRD) pattern of Al-SBA-15(R) support and corresponding 5 wt% Ni/Al-SBA-15(R) catalyst was recorded using a Bruker D8 Advance diffractometer fitted with a LynxEye X'celerator detector at CuKα (λ = 1.54 Å). Diffractograms were collected between 10° to 80° with a step size of 0.02° and a scan rate of 1 s for wide angle scan and between 0.45 to 8°, with a step size of 0.01° and scan rate of 0.6 for low angle scans. The Scherrer equation was used to calculate the volume-averaged crystallite diameters. The elemental composition of Al-SBA-15 catalyst support, Si:Al molar ratio and Ni loading of NI/Al-SBA-15 catalyst were analysed through X-ray fluorescence (XRF) using a Bruker S8 Tiger instrument equipped with a rhodium tube operating at 4 kW. Samples were analysed without any special pre-treatment. A Quantachrome AUTOSORB instrument was used to analyse the textural properties of catalysts by N_2 physisorption. All catalysts were degassed at 150 °C for 4h under vacuum, (P< 10-5 mm Hg) to remove moisture and unknown gases before the nitrogen gas adsorption-desorption measurements were conducted at -196 °C

The acidic properties of all supports and corresponding Ni catalysts were analysed through temperature programmed reaction of propylamine using thermogravimetric analysis coupled with mass spectrometry (TGA-MS), Mettler Toledo TGA/DSC2 STAR. Prior to analysis, 30 mg of catalyst was wet-impregnated with a small amount of propylamine (Sigma-Aldrich, ≥ 99%) and dried in a fume hood under lamellar flow for 1 hours and further drying in 40°C vacuum oven for 18 hours. The impregnated catalyst was analysed under flowing nitrogen (30 ml/min) at a ramp rate of 10 °C/min start from temperature of 40°C until 800 °C. The amount of catalyst acidity based on the reactively formed propene quantification of the acid sites. Thus, the effluent gas from TGA was passed and carefully monitored through a Pfeiffer Vacuum ThermoStar MS at m/Z = 41 for propene desorption.

Brønsted and Lewis acid sites were identified by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using pyridine as a probe molecule. Prior to analysis, the catalysts were ground with KBr (50 wt.%) into a fine powder, wetted with 0.1 mL of pyridine and left to dry under a fume hood for 1 hour before drying overnight in a vacuum oven at 40 °C. In absorbance mode, DRIFT spectra were recorded at ambient temperature using a Thermo scientific Nicolet iS50 FTIR spectrometer. High-resolution transmission electron microscopy (HRTEM) analysis was performed using a JEOL 2100F TEM operating at 200 kV. Samples were prepared on a Cu holey carbon grid using the drop cast method.

Solid-state ^{27}Al nuclear magnetic resonance (NMR) spectra was recorded at 104.20 MHz, using a Bruker Avance III HD spectrometer attached to a 4 mm magic-angle spinning (MAS) probe. ^{27}Al spectra were obtained using direct excitation with a pulse angle of approximately 30 degrees, with a 0.2 s recycle delay and a sample spin-rate of approximately 14 kHz. Spectral referencing was made with respect to an external sample of aqueous 1 M aluminium nitrate.

d) Catalytic Hydrodeoxygenation of Octanoic Acid

Hydrodeoxygenation reactions were undertaken in a 100 mL stainless steel autoclave, Parr 5500 series. In a typical experiment, the glass liner was charged with 150 mg of the Ni supported catalyst and 30 ml of reactant stock solution comprising 2.5 mmol octanoic acid in n-dodecane with tetradecane as calibration standard (the stock solution was prepared from 3 g octanoic acid with 4.2 ml tetradecane made up to 250 ml with dodecane). The glass liner was inserted in the reactor and sealed then the reactor was purged by nitrogen gas three times to ensure the reactor was under an inert atmosphere with no gas leakage. The reactor was heated at 260°C without stirring and once the desired temperature was reached, the first sample, t=0 was collected through the reactor dip-tube sampling system. Later, the vessel was pressurised to 40 bar with H_2 and stirring commenced at 900 rpm. The samples were collected based on sampling series of 10, 20, 30, 60, 120 ,180 and 300 minutes. Periodic samples (1ml) diluted 1:1 v/v with dichloromethane solvent prior to yield analysis and an aliquot of approximately 1 µl injection into the calibrated Bruker Scion 456 gas chromatograph equipped with ZB-50 high polarity column (length: 30 m × inner diameter: 0.32 mm × film thickness: 0.25 µm) and flame ionization detector (FID). All analyses were repeated several times with the same condition to validate the reliability of the results.

The percentage Conversions (*X*) across the reaction duration were calculated by:

$$X = \frac{(no - nt)}{no} \times 100\%$$

where: *n*t is the number of mmol octanoic acid at time, t and *n*o is the initial octanoic concentration prior to addition of hydrogen

The percentage selectivity (*S*) of the major liquid phase product were calculated by:

$$S = \frac{nx = i}{\sum nx} \times 100\%$$

where: $nx = i$ is number of moles of product, *i*= n-octane, n-heptane, octyl-octanoate, octanol, iso-octane and nx = total amount of products detected.

S2. Results

Table S1: Physicochemical properties of the synthesized Al-SBA-15(R) catalyst supports

Catalyst	**BET surface area (m^2g^{-1})^a**	**Pore volume (cm^3g^{-1})^b**	**Average Pore size (nm)^c**	**Si/Al molar ratio^d**	**Acid site loading ($mmol.g^{-1}$)^e**
SBA-15	698	0.98	6.2	-	-
Al-SBA-15(75)	410	0.40	3.4	113.5	0.22
Al-SBA-15(50)	384	0.42	4.5	69.5	0.23
Al-SBA-15(25)	386	0.32	3.2	38.2	0.30
Al-SBA-15(5)	309	0.36	3.6	7.8	0.49

a. Errors in surface area ±10%

b. BJH desorption pore volume (Error = ±10%)

c. BJH desorption average pore diameter (Error = ±0.2 nm)

d. Estimated from XRF analysis (Errors in Si/Al= ±20%).

e. Propylamine TGA-MS analysis (Error ±10%)

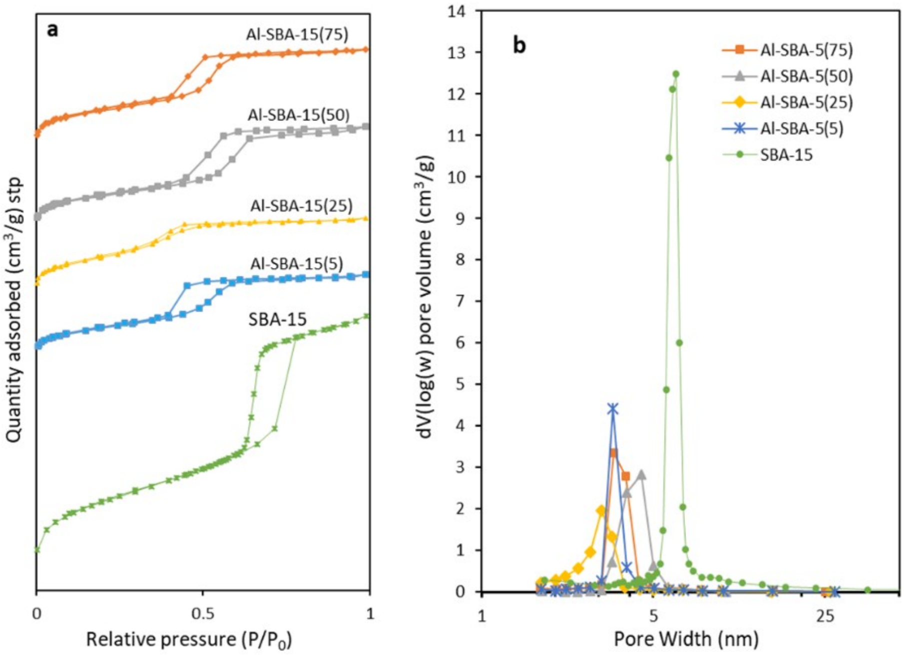

Figure S1. a) N_2 adsorption-desorption isotherms and b) Pore size distribution of parent Al-SBA-15 (R) and SBA-15 catalyst supports

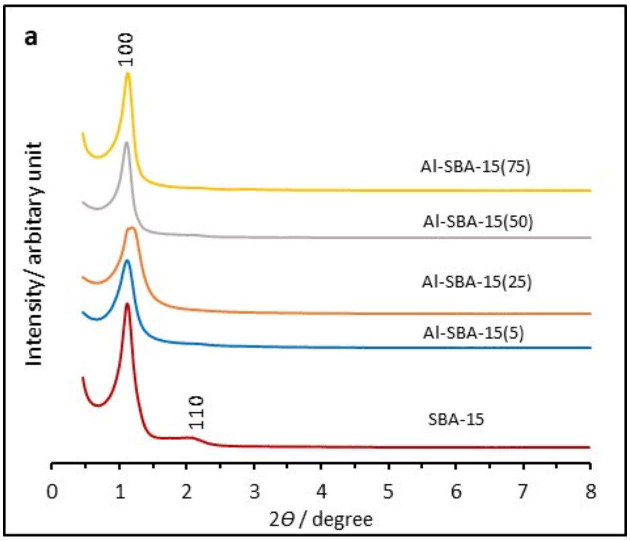

Figure S2 Low-angle XRD patterns for SBA-15 and Al-SBA-15 (R) supports with different Si:Al ratios

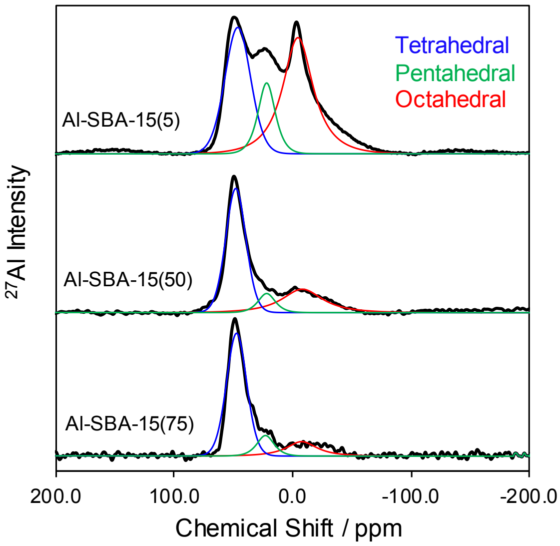

Figure S3. Deconvoluted ^{27}Al MAS-NMR of Al-SBA-15 (R) supports showing evolution of species with Si:Al ratio (Quantification of framework and extra framework Al species is shown in **Figure S6**)

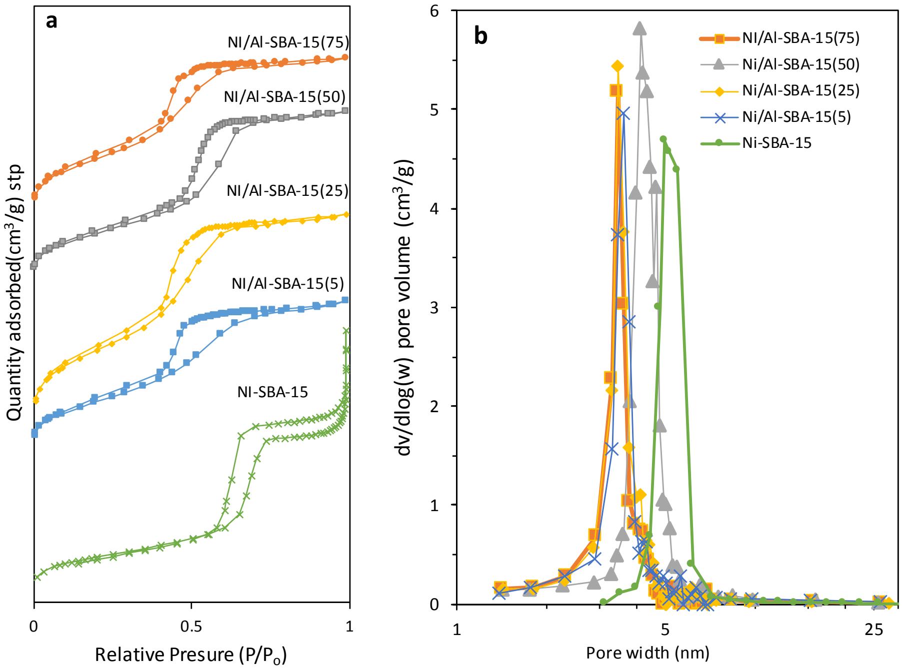

Figure S4. a) N_2 adsorption-desorption isotherms and b) Pore size distribution of synthesized 5 wt% Ni/Al-SBA-15 (R) and 5 wt% Ni/SBA-15 catalysts.

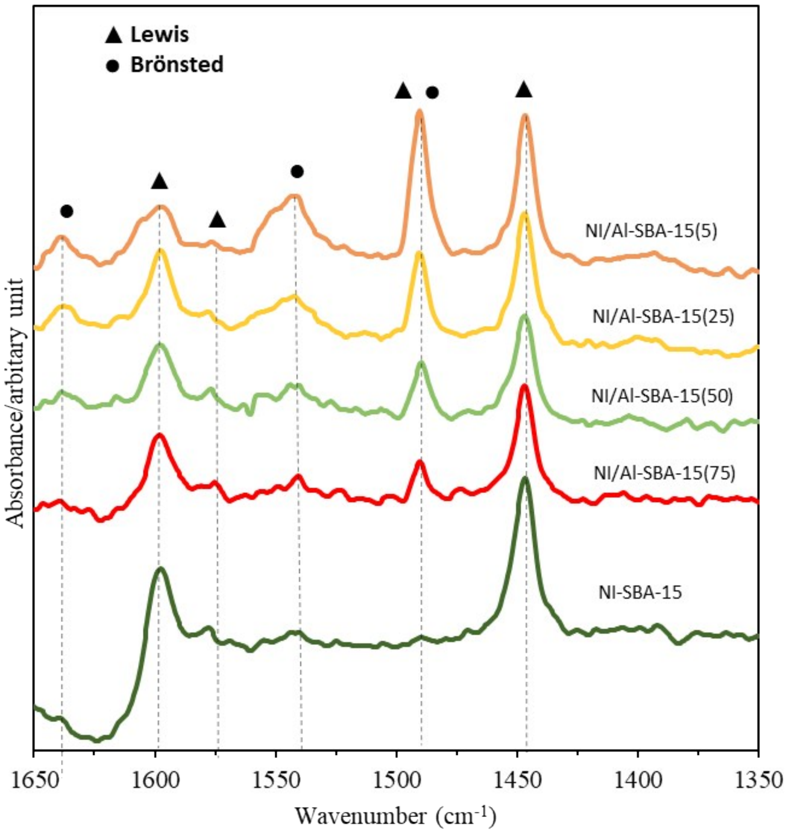

Figure S5. DRIFT spectra of chemisorbed pyridine on 5 wt% Ni/Al-SBA-15 (R) and 5 wt% Ni/SBA-15 catalysts.

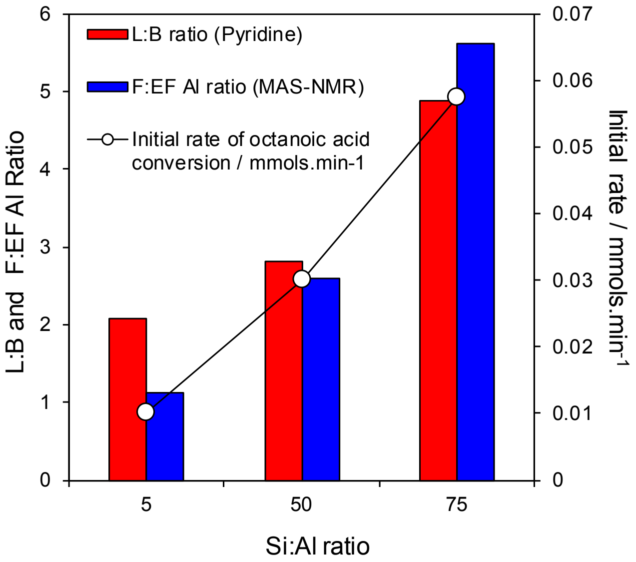

Figure S6. Quantification of framework:extra framework Al species from MAS-NMR and correlation with initial rate of octanoic acid conversion and Lewis:Brønsted acid site ratio.

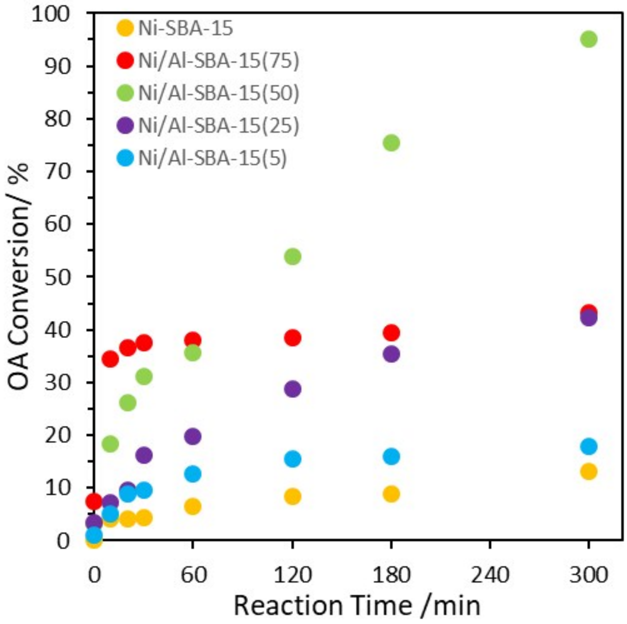

Figure S7. Octanoic acid conversion over 5 wt% Ni/Al-SBA-15 (R) and 5 wt% Ni/SBA-15 catalysts. Conditions: 260 °C, 40 bar H_2 and 150 mg catalyst in 30 ml reactant (2.5 mmol octanoic acid in dodecane solution)

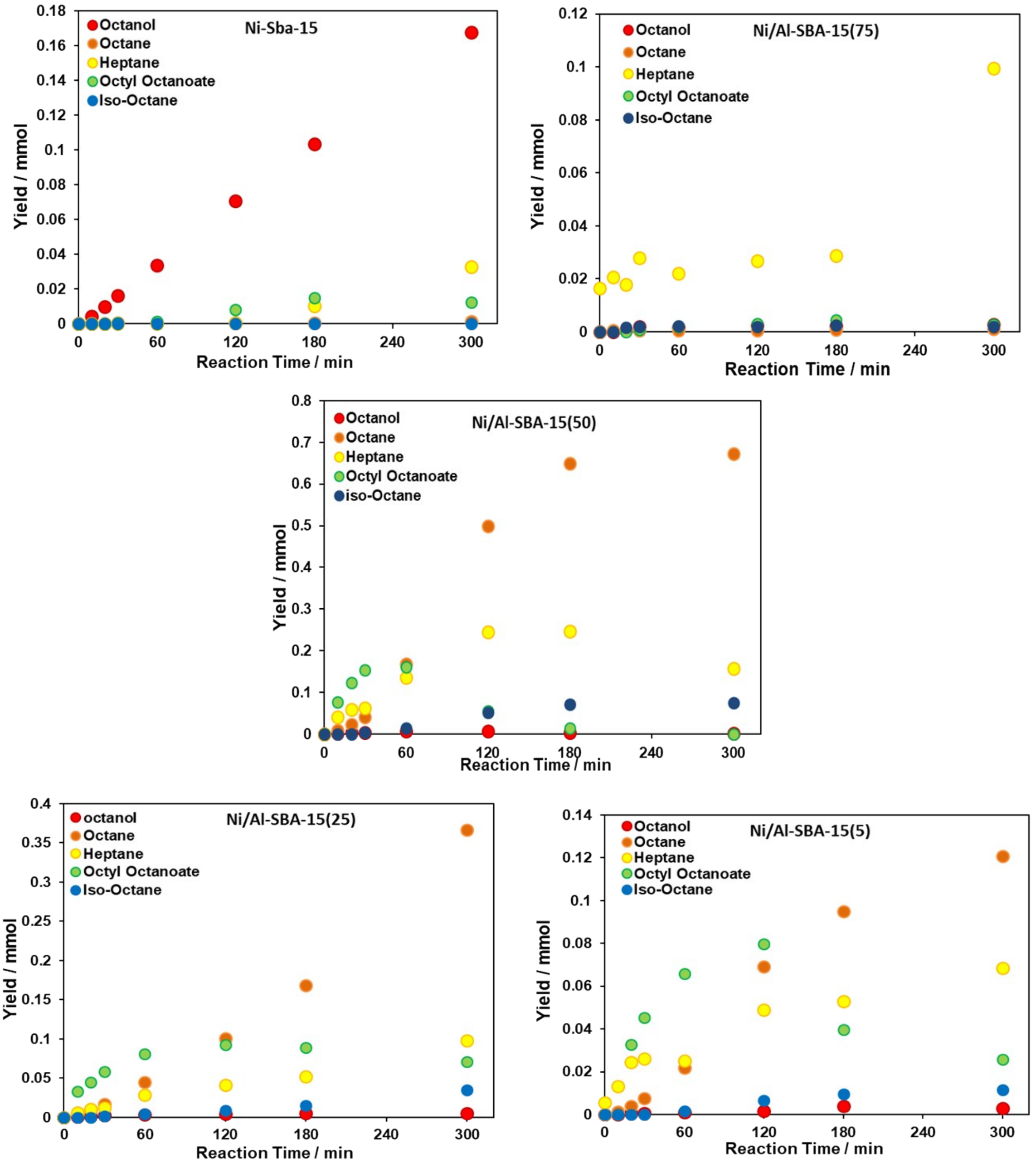

Figure S8. Time-dependent product yields of over 5 wt% Ni/Al-SBA-15(R) and 5 wt% Ni/SBA-15 catalysts. Conditions: 260 °C, 40 bar H_2 and 150mg catalyst in 30 ml reactant (2.5 mmol octanoic acid in dodecane solution).

Table S2. Product selectivity and carbon balance at 13-20% octanoic acid conversion during hydrotreatment over 5 wt% Ni/Al-SBA-15(R) and 5 wt% Ni/SBA-15 catalysts. Conditions: 260 °C, 40 bar H_2 and 150mg catalyst in 30 ml reactant (2.5 mmol octanoic acid in dodecane solution)

Catalyst	**Selectivity at 13-20% iso-conversion (%)**					
	Octanol	OCOT	n-C7	n-C8	[a]iso-C8	[b]CX
Ni-SBA-15	78.2	5.8	15.5	0.6	0	99.2
Ni/Al-SBA-15 (75)	3.2	0	94.0	2.9	0	87.6
Ni/Al-SBA-15 (50)	1.7	59	32.5	6.9	0	91.8
Ni/Al-SBA-15 (25)	2.5	65.5	14.0	18.3	1.7	91.5
Ni/Al-SBA-15 (5)	0.8	57	21.7	18.9	1.5	95.1

[a] n-octane isomerization, 2-metylheptane and 3-metylheptane; [b] Calculated carbon balance (errors = ±2%)

Table S3. Elemental analysis of spent 5 wt% Ni/Al-SBA-15 and 5 wt% Ni/SBA-15 catalysts

	Percentage (%)[a]	
Spend Catalyst	Ni	Si/Al
Ni-SBA-15	6.68	
Ni/Al-SBA-15(5)	5.86	5.98
Ni/Al-SBA-15(25)	6.91	29.73
Ni/Al-SBA-15(50)	7.60	48.13
Ni/Al-SBA-15(75)	5.77	81.88

a. Estimated from XRF analysis (errors in Si/Al= ±20%).

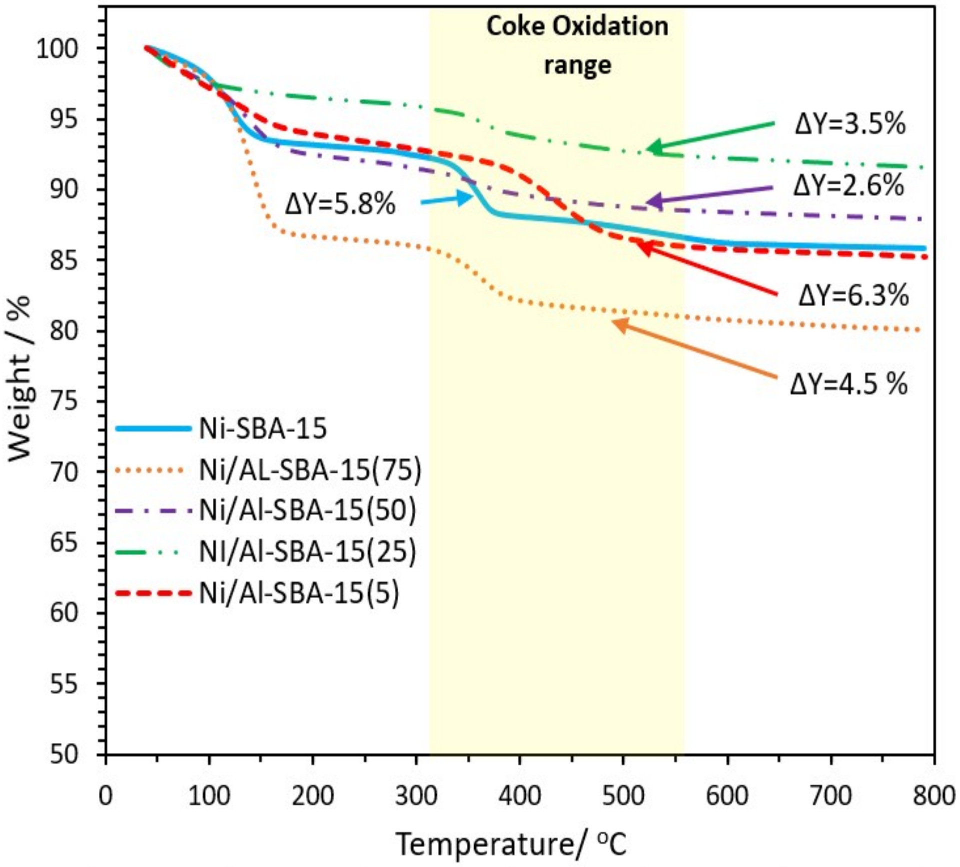

Figure S9. Temperature programmed oxidation of spent 5 wt% Ni/Al-SBA-15 (R) and 5 wt% Ni/SBA-15 catalysts.