Supporting Information

Title: Are Fermentation Products Promising Feedstock for High-Density Bio-Fuel? Domino Reactions for Upgrading Aqueous Acetone–Butanol–Ethanol Mixtures

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Materials and chemicals:

Polyethylene-polypropylene glycol (F127), Tetraethyl orthosilicate (TEOS) were purchased from Energy Chemical Co. $Mg(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Sigma-Aldrich Co. Mg-Al hydrotalcite, γ-Al_2O_3 were purchased from J&K Chemical Co. Acetone (99.9%), 1-butanol (99.9%) and ethanol (99.9%) were purchased from Fisher Chemical Co., J&K Chemical Co., and Shanghai Macklin Biochemical Co., respectively. Toluene (99.9%) and *n*-heptane (99.5%) were purchased from Shanghai Macklin Biochemical Co. The proportions of each substance in the mimic ABE mixtures are shown in Table S1.

Table S1. Detailed compositions of aqueous ABE mixtures with different water content.

Ethanol (g)	Acetone (g)	Butanol (g)	Water (g)	Water content (%)
0.27	3.38	5.37	0.98	9.8
0.22	3.24	5.34	1.21	12.1
0.28	3.28	4.86	1.58	15.8
3.89	4.90	0.00	1.21	12.1

Catalyst preparation:

Synthesis of SBA-16: In a 120 mL glass vessel, 2 g of F127, 78 mL of water and 3.3 mL of HCl (10 M) were added. After completely dissolved, 9 mL TEOS was injected to the mixture. Stirring at 40 °C for 20 h, it was moved into a Teflon lining for hydrothermal reaction at 220 °C for 24 h. After being filtered and dried, the product was calcined at 550 °C.

Synthesis of Ni−MgO−SBA-16 with different loading amount of Ni: The catalyst was prepared by impregnation method. In a typical synthetic route, certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were dissolved in 100 mL of water under stirring at room temperature, and 3 g of SBA-16 was added to the aqueous solution subsequently. The mixture was thoroughly evaporated under intensely stirring at 80 °C, and then the sample was reduced by H_2 for 3 h at 550 °C after calcination at 550 °C for 3 h.

Characterizations:

XRD analysis was carried out using a Shimadzu XRD-6100 diffractometer with Cu Kα radiation (60 kV, 50 mA). The 2-theta value was scanned in the range of $5° \leq 2\theta \leq 80°$.

The morphology of the samples (SEM) was observed via ZEISS SUPRA55. The structure, size, and lattice fringes of the samples were examined using HRTEM (JEOL JEM-2011), equipped with an energy-dispersive X-ray spectroscopy (EDS) detector.

The specific surface area was measured using Beishide Instrument 3H-2000PS2 1 by the Brunauer–Emmett–Teller (BET) method based on the N_2 adsorption isotherms. All samples were degassed at 180 °C for 12 h before measurements.

The acidic and basic properties of catalysts were determined using NH_3-TPD and CO_2-TPD, respectively, equipped with a thermal conductivity detector (TCD). The sample (0.1 g) was pretreated in a glass U-tube under He flow (25 mL/min) at 500 °C for 1 h, and then cooled to room temperature. Until the sample was completely degassed, absorption gas was switched to CO_2 or NH_3 to sweep the U-tube for 30 min at room temperature. Then under an atmosphere of pure He, the temperature was increased with a heating rate of 10 °C/min from 100 to 900 °C, recording TCD signals. The surface area and content of Ni was calculated via H_2-TPD. The operation process was the same as CO_2- or NH_3-TPD except that there is a reduction process at the very beginning and hydrogen is used as the adsorbed gas.

Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 214 Polyma differential scanning calorimeter using Concavus Pan Al with a nitrogen flow of 40 or 60 mL/min. High purity indium was used to calibrate the calorimeter. Sample sizes were between 30−40 mg and the samples were ramped from -150 ℃ to 25 ℃, down to -150 ℃ and then back to 25 ℃, all at 5 ℃ /min. The energy density was determined by standard bomb calorimetry methods using KD ZDHW-8A oxygen bomb calorimeter.

Activity tests:

A mixture of acetone, *n*-butanol, and ethanol with water were used as the model ABE fermentation. In a typical reaction process, 1 g of the as-prepared catalyst, 10 g of the ABE mixtures and certain amount of internal standard were added into the reactor. Then the reactor was purged with nitrogen gas three times and then heated to 240 °C with a stirring speed of 600 rpm for 24 h. Afterwards, the reactor was cooled to room temperature by an ice-water bath.

The trimer condensation of methyl ketones was conducted in a 50 mL sealed stainless-steel autoclave or a Dean-Stark apparatus. In a typical reaction process, 1 g of the solid base catalyst, 1 g anhydrous $CaCl_2$, 1.5 g of the methyl ketone, 20 g heptane and certain amount of internal standard were added into the reactor. Then the reactor was purged with nitrogen gas three times and then heated to 180 °C with a stirring speed of 600 rpm for 2 h.

The HDO of the as-prepared products was conducted in a 50 mL sealed stainless-steel autoclave. In a typical reaction process, oxygenates (0.4 g), 7 wt% Ni−$MgSiO_3$ catalyst (0.4 g), and cyclohexane (8 g) were transferred into the autoclave. The reactor was then sealed, purged with H_2 for three times and charged to 2.5 MPa H_2 pressure. The reaction was then carried out at 180 °C and 2.5 MPa under magnetic stirring for 12 h. After the reaction, the autoclave was quenched in an ice-water bath to room temperature.

All the reaction product was analyzed by internal standard method through Shimadzu GC-2014 Chromatograph, using dodecane as the internal standard.

Parameter of Gas Chromatography (GC):

The chromatographic column is HP-5 (30 m × 0.32 mm, d_f = 0.5 μm). The oven temperature was maintained at 313 K for 2 min and then heated up to 493K at 5 K/min. Nitrogen with a flow rate of 180 mL min^{-1} was used as the carrier gas. The flow rate of hydrogen gas and air was 40 and 400 mL min^{-1}, respectively.
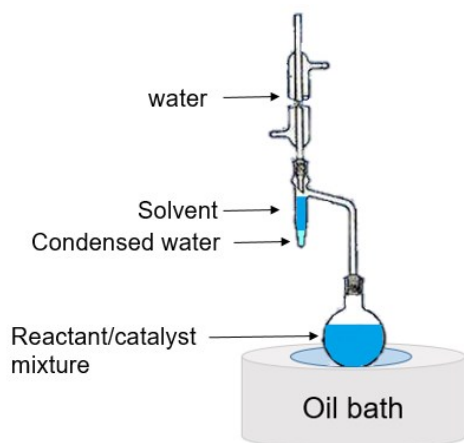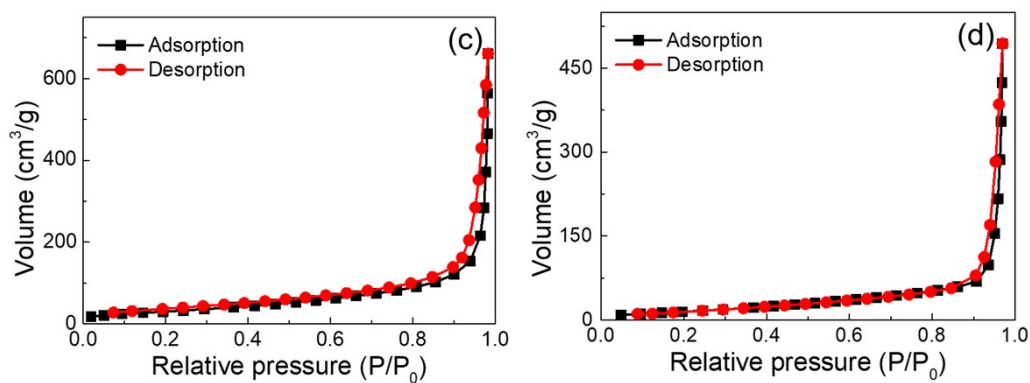
Fig. S1. Diagram of Dean Stark apparatus used in the several exploratory reactions.
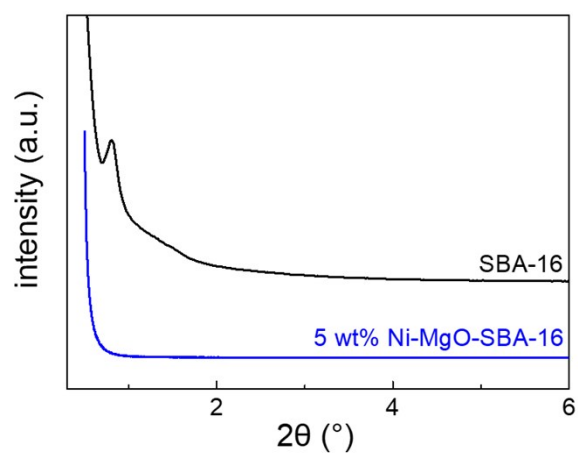
**Fig. S2.** Small-angle XRD patterns for SBA-16 and 5 wt% Ni−MgO−SBA-16.
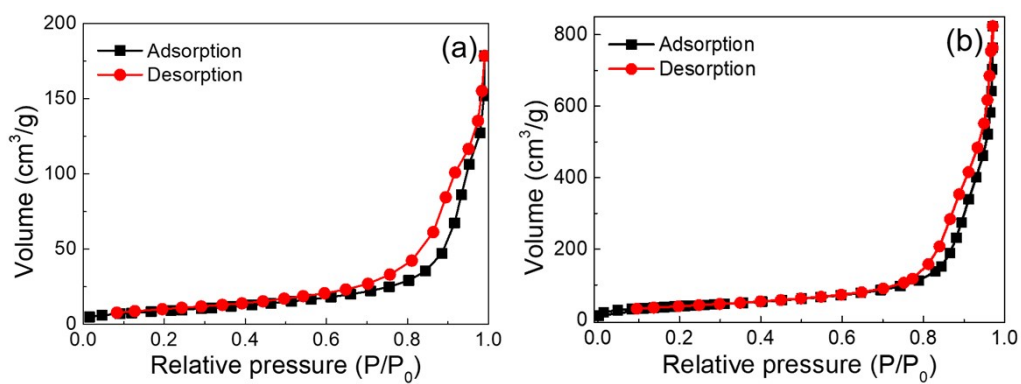
Fig. S3. N$_2$ adsorption/desorption isotherm of (a) 5 wt% Ni−MgO−SBA-16 catalyst, (b) γ-Al$_2$O$_3$ catalyst, (c) MgAl-MMO catalyst and (d) MgO catalyst.

**Table S2.** BET surface areas of 5 wt% Ni−MgO−SBA-16 catalyst and the prepared catalysts used in step two.

Catalyst	Surface Area (m^2/g)
5 wt% Ni−MgO−SBA-16	34.2
γ-Al$_2$O$_3$	230.8
MgAl-MMO	192.6
MgO	178.4
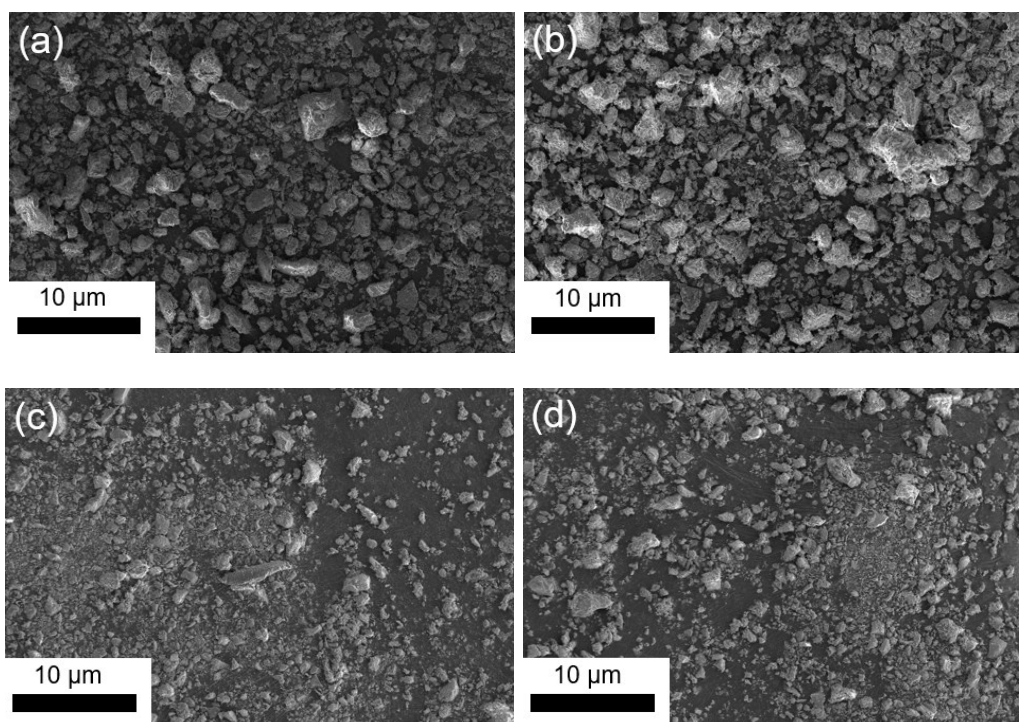
Fig. S4. SEM images of the (a) 2 wt% Ni−MgO−SBA-16 catalyst, (b) 5 wt% Ni−MgO−SBA-16 catalyst, (c) 7 wt% Ni−MgO−SBA-16 catalyst and (d) 10 wt% Ni−MgO−SBA-16 catalyst.
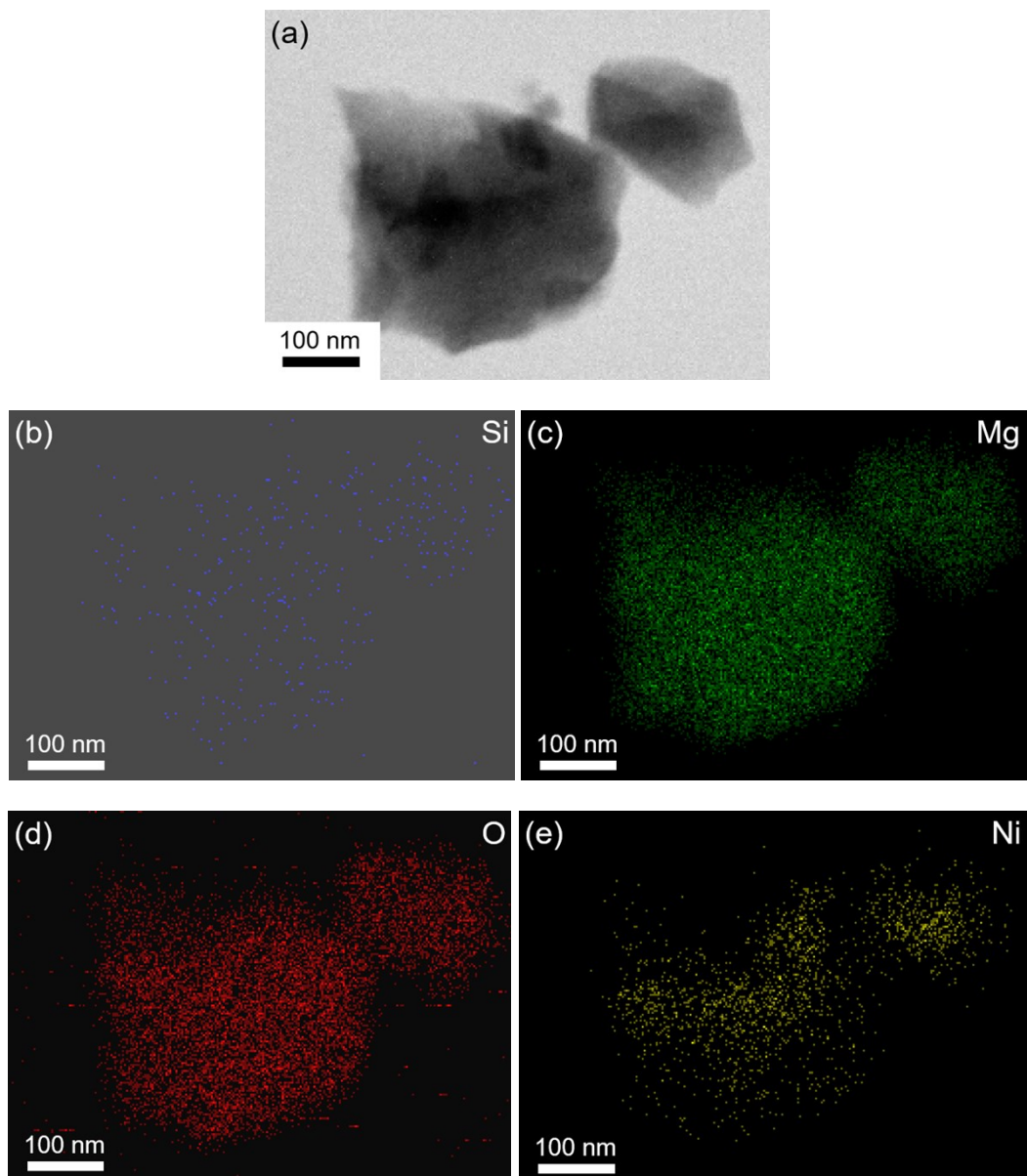
Fig. S5. (a) TEM images and (b−e) EDS mappings of the 2 wt% Ni−MgO−SBA-16 catalyst.
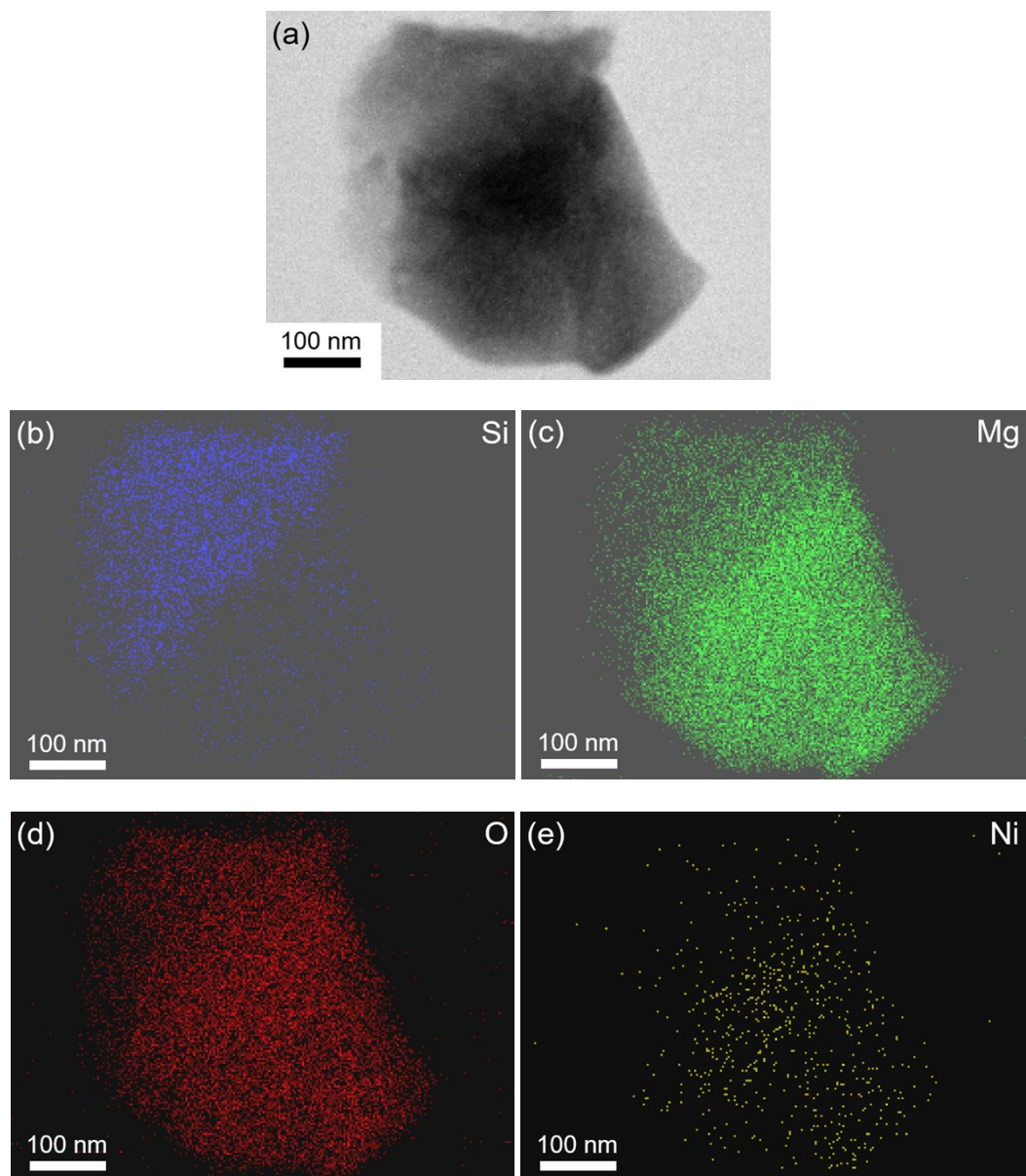
Fig. S6. (a) TEM images and (b−e) EDS mappings of the 7 wt% Ni−MgO−SBA-16 catalyst.
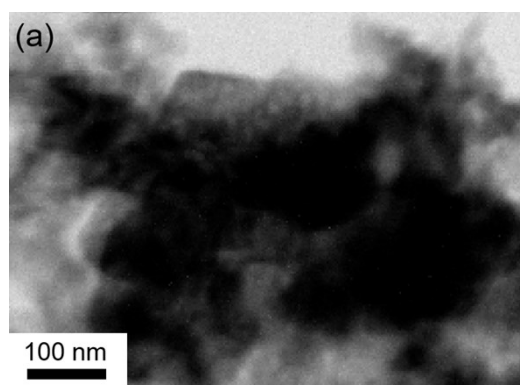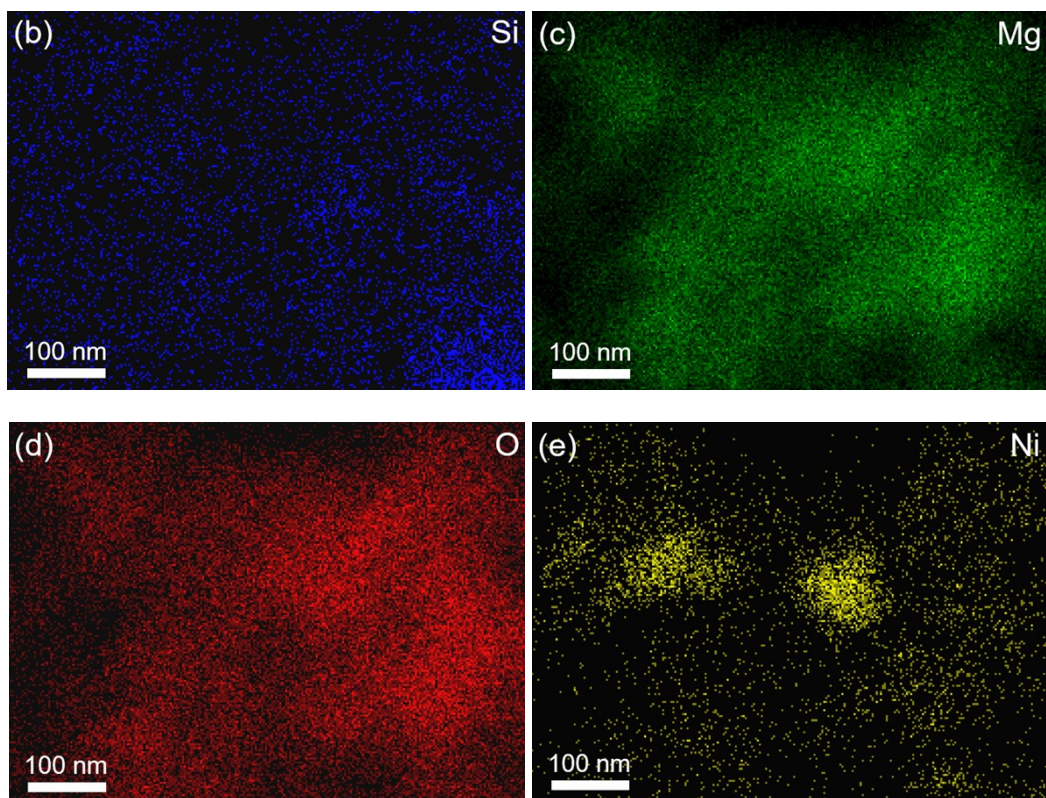
Fig. S7. (a) TEM images and (b−e) EDS mappings of the 10 wt% Ni−MgO−SBA-16 catalyst.
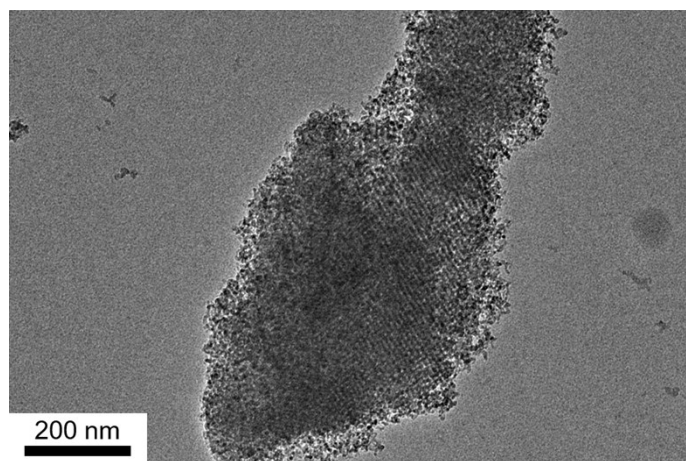
Fig. S8. The HR-TEM image of synthesized SBA-16.

Table S3. Effect of Ni loading amount on catalytic performance over Ni−MgO−SBA-16 catalysts.

Reaction conditions: 12 wt% water containing ABE mixture (10 g), dodecane (1 g), Ni−MgO−SBA-16 catalyst (1 g), reaction temperature (240 °C), and 24 h.

| Ni loading amount	ABE conversion	Selectivity (%)				
(wt %)	(%)	Heptane	2-$C_{5(=O)}$	2-$C_{7(=O)}$	2-$C_{7(-OH)}$	C_{8-15}
2	16.8	2.1	8.7	55.9	19.7	7.7
5	55	5.4	4.7	59.2	11.2	15
7	57.2	10.5	5.6	56.4	2.9	15.9
10	59.4	46.3	3.5	29.5	9.7	13.1
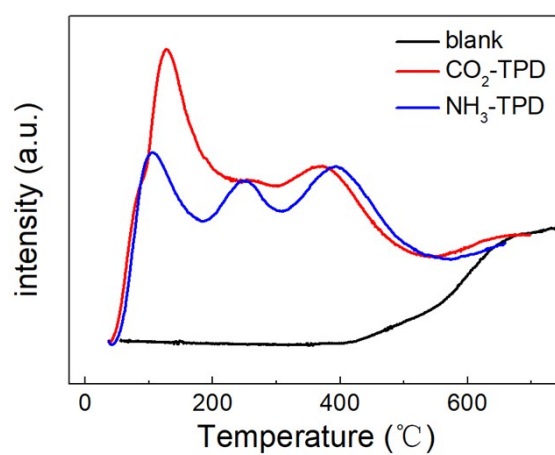
Fig. S9. CO_2 and NH_3-TPD patterns of the γ-Al_2O_3 catalyst.
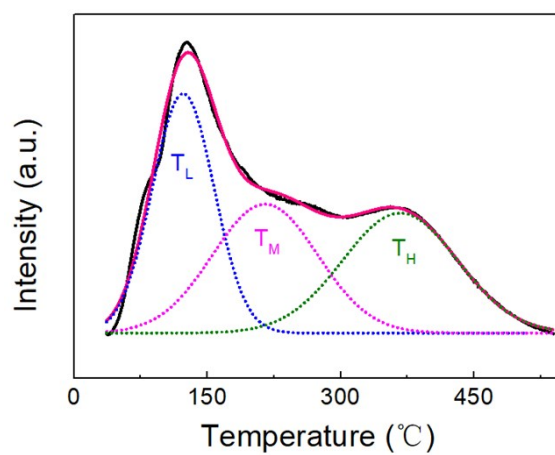
Fig. S10. CO_2-TPD profiles of the γ-Al_2O_3 catalyst.
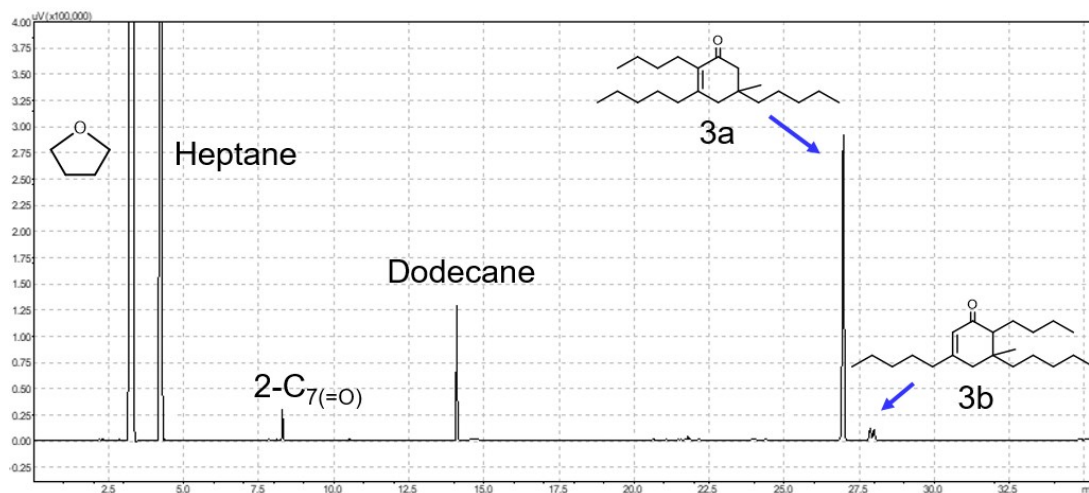
Fig. S11. GC trace of C_{21} oxygenates (3a and 3b) from trimer condensation of 2-$C_{7(=O)}$.
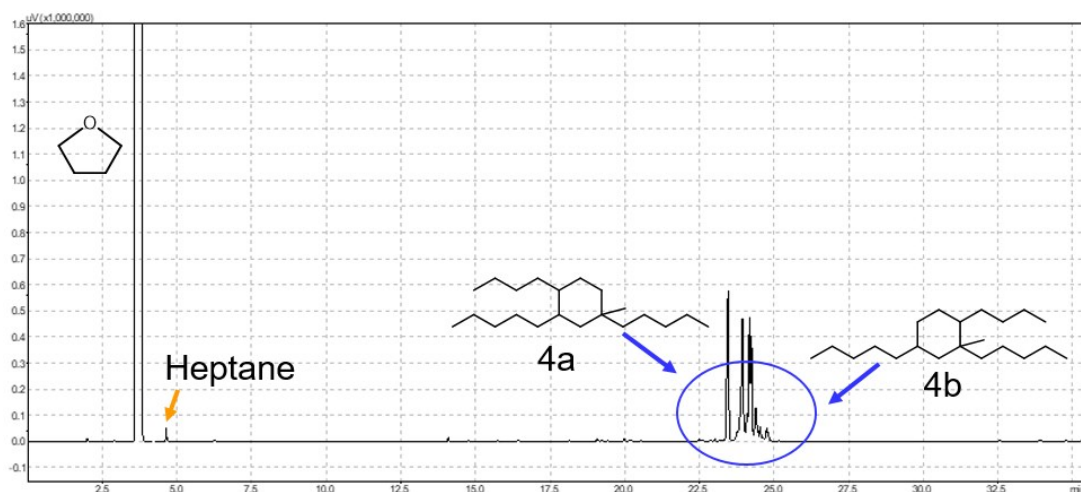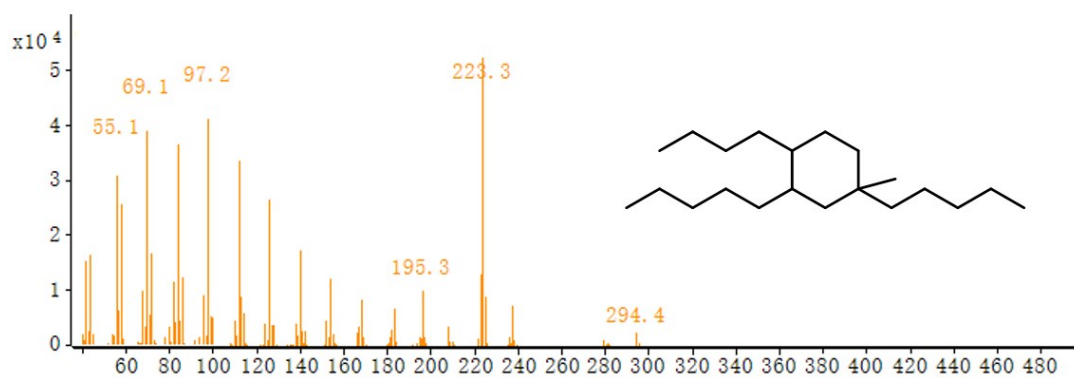

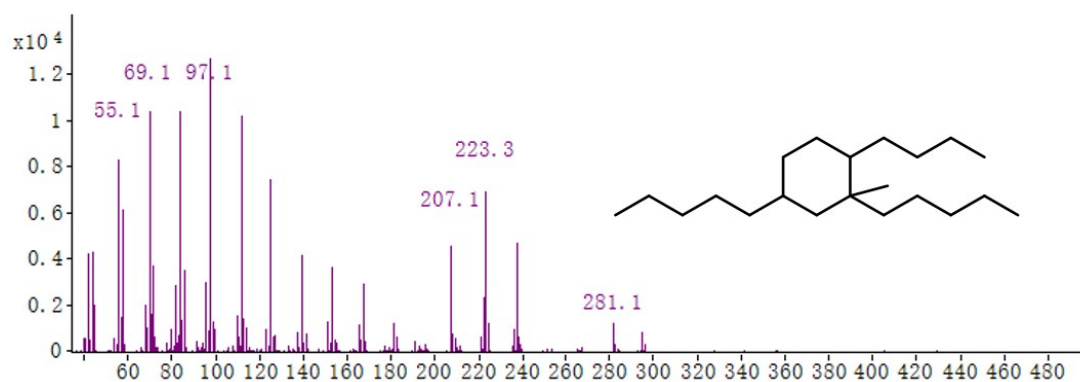**Fig. S12.** GC trace of the HDO products C_{21} alkanes (4a and 4b).
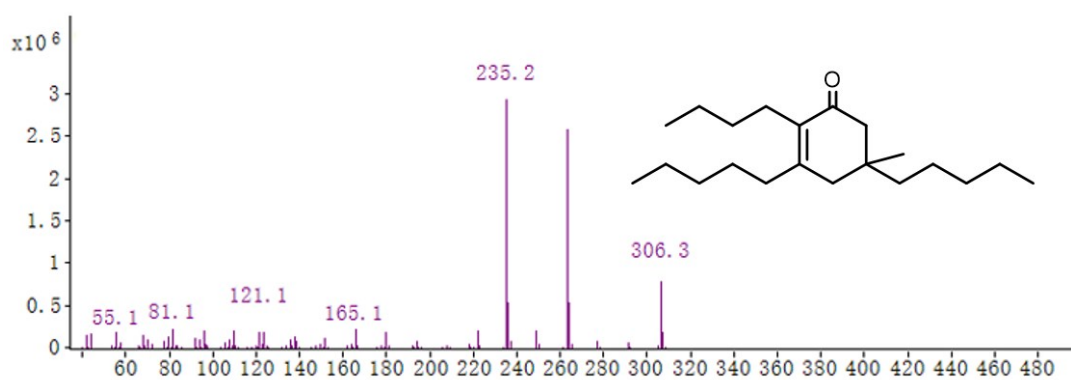
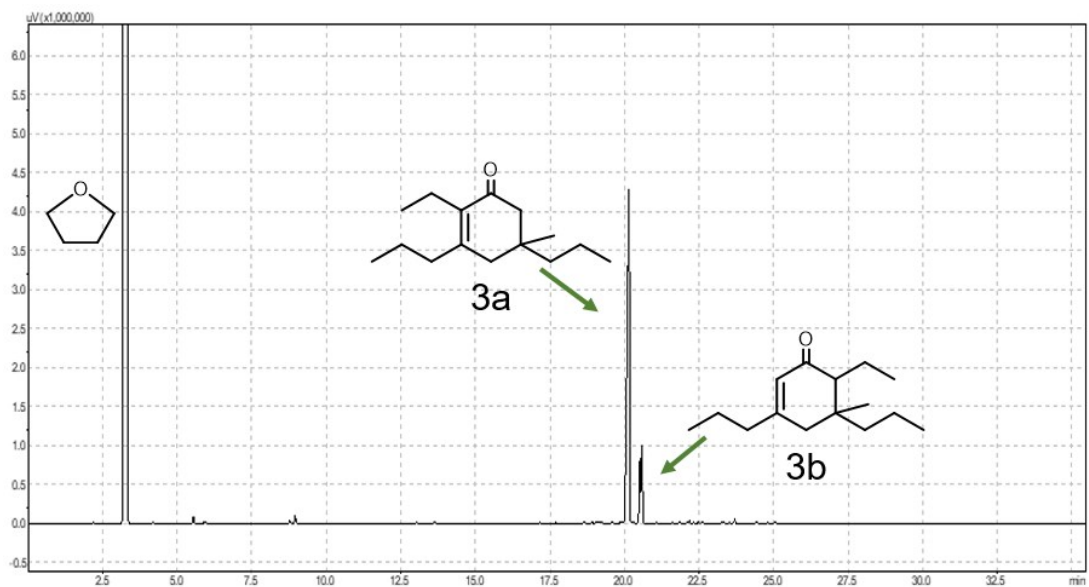**Fig. S13.** Mass spectrum of C_{21} oxygenates (3a).
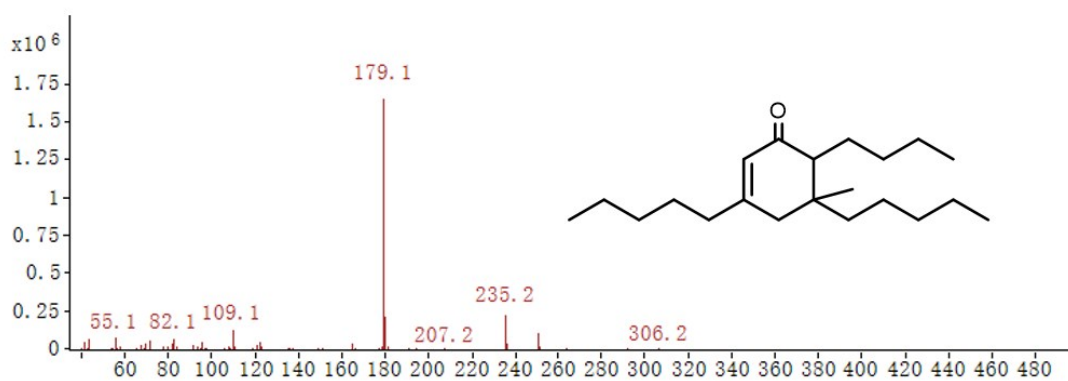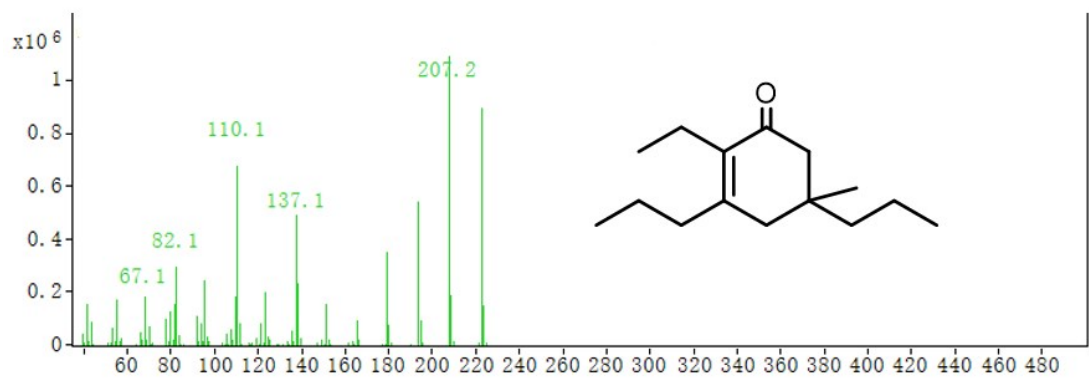
Fig. S14. Mass spectrum of C$_{21}$ oxygenates (3b).
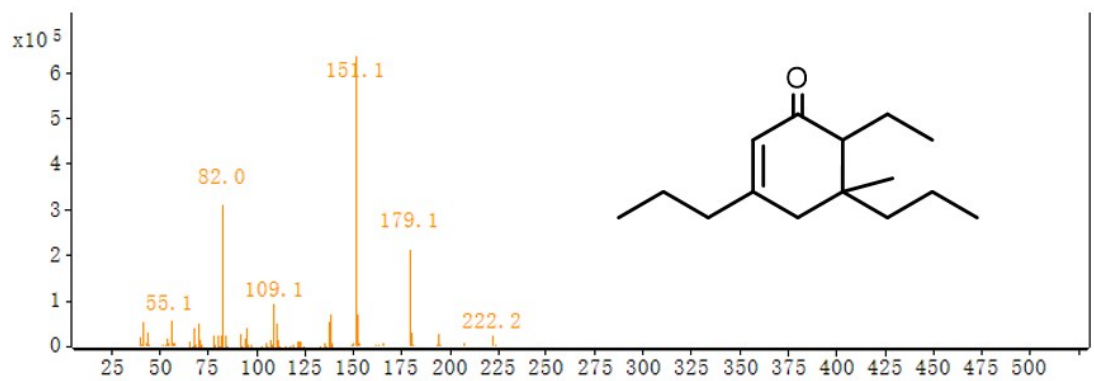

Fig. S15. Mass spectrum of C$_{21}$ alkanes (4a).
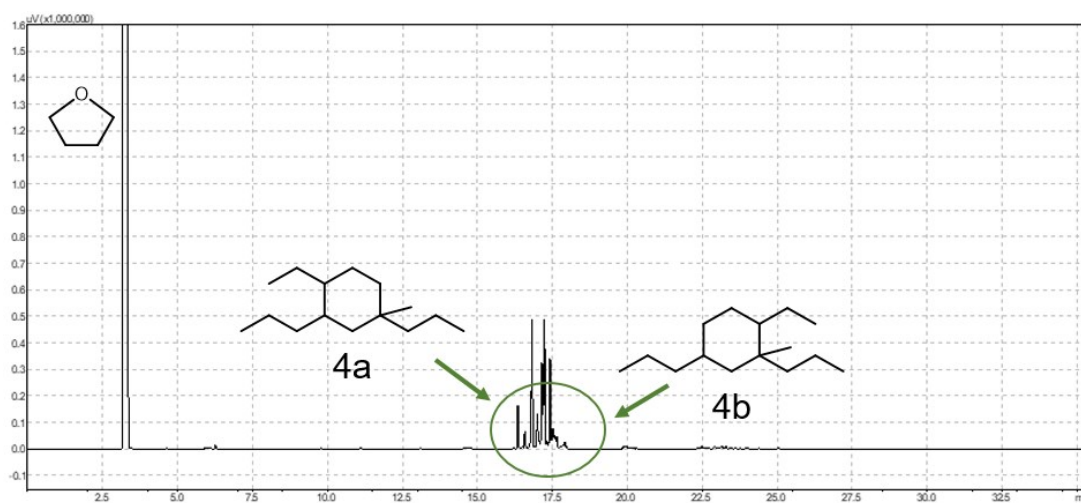

Fig. S16. Mass spectrum of C$_{21}$ alkanes (4b).

Fig. S17. GC trace of C$_{15}$ oxygenates (3a and 3b) from trimer condensation of 2-C$_{5(=O)}$.

**Fig. S18.** Mass spectrum of C$_{15}$ oxygenates (3a)

**Fig. S19.** Mass spectrum of C$_{15}$ oxygenates (3b).

Fig. S20. GC trace of the HDO products C$_{15}$ alkanes (4a and 4b).

Table S4. The physical property data of several chemicals used in the first step (at normal temperatures and pressures).

| Chemicals	Boiling point (K)	Density (g/cm³)
Acetone	329.4	0.78
Butanol	390.6	0.81
Ethanol	351.0	0.79
2-Pentanone	374~378	0.81
2-Heptanone	422~423	0.82
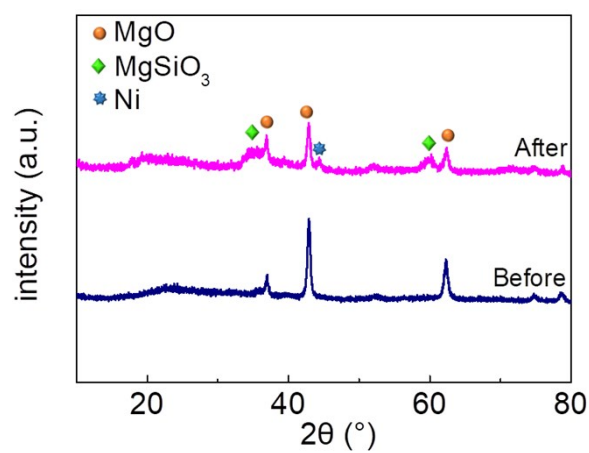
Fig. 21. XRD patterns of the 5 wt% Ni–MgO–SBA-16 catalyst before and after reaction with 12.1 wt% water content ABE mixtures.
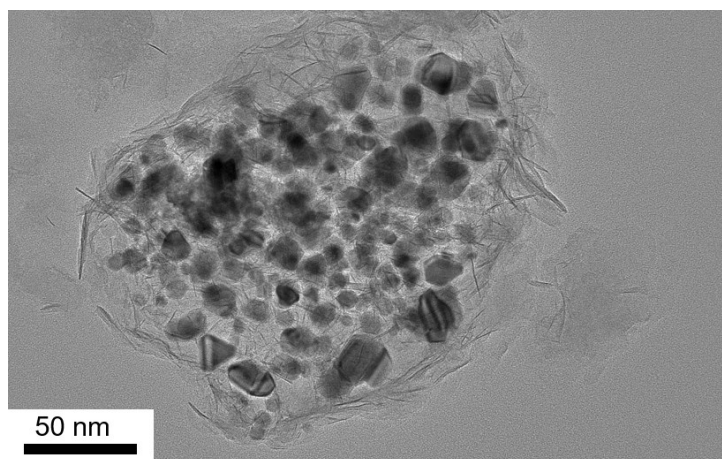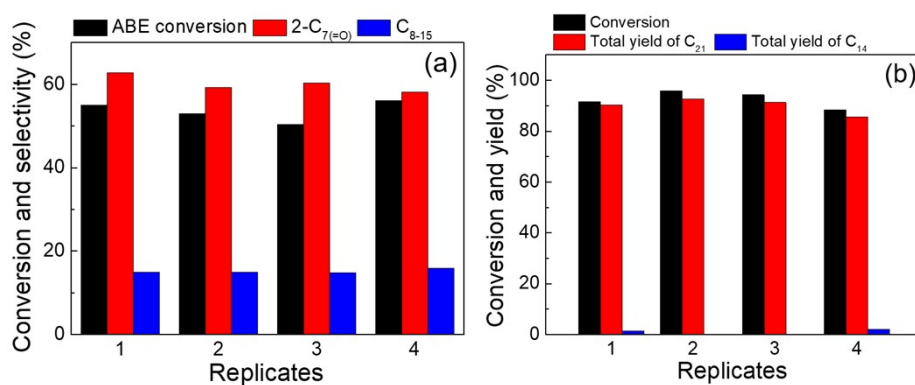

Fig. S22. The HR-TEM image of the spent 5 wt% Ni–MgO–SBA-16 catalyst.

Table S5. BET results of the initial and spent γ-Al$_2$O$_3$ catalyst.

Recycle times	Surface area (m^2/g)
0	230.8
1	160.5
2	143.6
3	130.3
5(calcination)	219.7
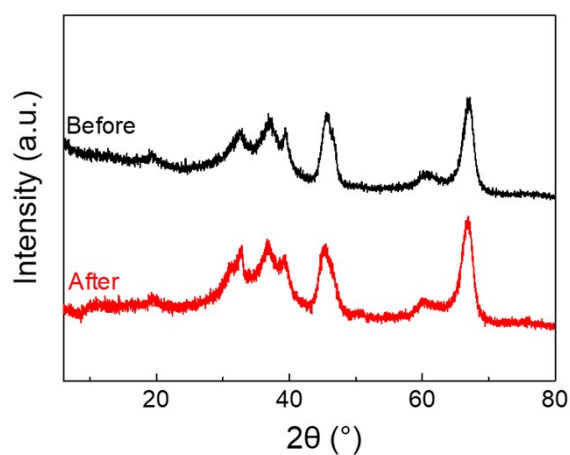
Fig. S23. XRD patterns of the γ-Al$_2$O$_3$ catalysts before and after reaction with 2-heptanone.

Fig. S24. (a) Replicated experiments of the 5 wt% Ni−MgO−SBA-16 catalyst. Reaction conditions: 12.1 wt% water containing ABE mixtures (10 g), dodecane (1 g), catalyst (1 g), reaction temperature (240 °C), and 24 h. (b) Replicated experiments of the γ-Al$_2$O$_3$ catalyst. Reaction conditions: 2-heptanone (1.5 g), heptane (20 g), dodecane (0.3 g), γ-Al$_2$O$_3$ (2 g), anhydrous CaCl$_2$ (1 g), 2 h, 180 ℃.