

Supporting Information

Graphite Oxide Activated Zeolite NaY: Applications in Alcohol

Dehydration

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General Considerations. NaY, NH₄Y, and HY (Si/Al = 5.1) were purchased from Zeolyst International and used as received. Unless otherwise noted, all reagents were purchased from commercial sources and used as received. 7-tridecanol was synthesized according to the literature.¹ ¹H and ¹³C NMR spectra were recorded on a Varian Unity INOVA 400 MHz. Chemical shifts (δ) are expressed in ppm downfield from Si(CH₃)₄ using residual solvent peak as an internal standard (CDCl₃, 7.24 ppm for ¹H and 77.0 ppm for ¹³C NMR). IR spectra were recorded on a Thermo Scientific Nicolet iS5 system equipped with an iD3 attenuated total reflectance (ATR) attachment (germanium crystal). Gas chromatography (GC) measurements were performed using an Agilent 6850 Series II using a DB-1 (dimethylpolysiloxane) column (length = 30 m, inner diameter = 0.53 mm, and film thickness = 0.25 μ m) with H₂ as the carrier gas at a flow rate of 1.5 mL/min. The inlet temperature was 250 °C and the oven was programmed for 50 °C for 3 min, then a 5 °C/min ramp to 200 °C, followed by a 10 °C/min ramp to 250 °C, and then held at 250 °C for 1 min. The BET surface area analyses were performed on a Quantachrome NOVA 2000 surface analyzer using nitrogen adsorption. Elemental combustion analyses were performed by Midwest Microlabs, LLC (Indianaapolis, IN). Powder X-Ray diffraction (XRD) measurements were taken on an R-Axis Spider diffractometer using CuK α radiation with an exposure time of 10 min. pH measurements were recorded using a VWR SympHony pH meter outfitted with an Orion probe.

Preparation of Graphite Oxide (GO). A 250 mL round-bottom flask was charged with a stir bar, natural flake graphite (6.04 g, Bay Carbon SP-1), concentrated H₂SO₄ (150 mL), and then cooled in an ice bath. The flask was slowly charged with KMnO₄ (18.13 g, 114.74 mmol) over 2 h which produced a dark colored mixture. After stirring at 0 °C for an additional 1 h, the mixture was then stirred at room temperature for 2 h and finally at 35 °C for 3 h. After cooling to room temperature, the mixture was added to deionized water (3 L) which resulted in an exotherm. To the resulting suspension was added a 30% aqueous solution of H₂O₂ (15 mL) and the resulting vibrant yellow suspension was allowed to sit overnight. The GO was isolated by centrifugation and subsequent decantation of the supernatant after being washed with 6 N HCl (3 L) and deionized water (6 L) respectively. The precipitate was collected and dried under high vacuum to afford the product (11.15 g) as a dark brown powder which was characterized by elemental combustion, FT-IR spectroscopy, and BET analysis.

Representative Alcohol Dehydration Procedure. A pressure tube was charged with a stir bar, 4-heptanol (160.0 mg, 1.38 mmol), GO (12.0 mg), NaY (12.0 mg), and CDCl₃ (0.3 mL). The tube was sealed with an o-ring line cap and heated to 150 °C for 30 min. The vessel was allowed to cool to room temperature upon which mesitylene (10 μ L) was added as an internal standard, and the mixture was filtered through a syringe filter (0.2 μ m, PTFE) directly into a NMR tube. Conversions were determined by ¹H NMR and the product distribution for the optimized reaction was determined by GC.

BET Measurements. The samples were degassed at room temperature to avoid thermal decomposition of GO and measurements were determined using a 7-point BET method using molecular nitrogen as the adsorbate.² The analyses were performed in triplicate and averaged. The surface area of NaY listed in Table S1 was lower than the reported 902 m²/g reported by Zeolyst International due to residual water.

Table S1. BET Surface Area Analyses of GO and NaY^a

Entry	Material	Surface Area (m ² /g)
1	GO	2.5
2	Spent GO ^b	6.1
3	NaY ^c	286.7
4	GO/NaY	130.6
5	Spent GO/NaY ^d	118.0
6	Spent GO then NaY ^e	217.9

^a The samples were degassed at room temperature overnight prior to data collection. ^b GO was used as a catalyst for the dehydration of 4-heptanol under optimized conditions (15 wt%, 150 °C, 30 min), and the carbon material was recovered and analyzed. ^c The surface area reported by Zeolyst International was 902 m²/g; however, the degas procedure did not remove all the residual H₂O from the zeolite which resulted in a lower measured surface area. ^d Recovered GO/NaY from optimized dehydration of 4-heptanol (15 wt% (1:1), 150 °C, 30 min). ^e Zeolite recovered from the experiment summarized in Entry 6, Table 3.

Table S2. Summary of the Combustion Analysis Data

Element	Starting GO Material
Carbon	51.02
Hydrogen	1.65
Nitrogen	none found
Oxygen	44.50
Sulfur	1.85
Chlorine	0.92

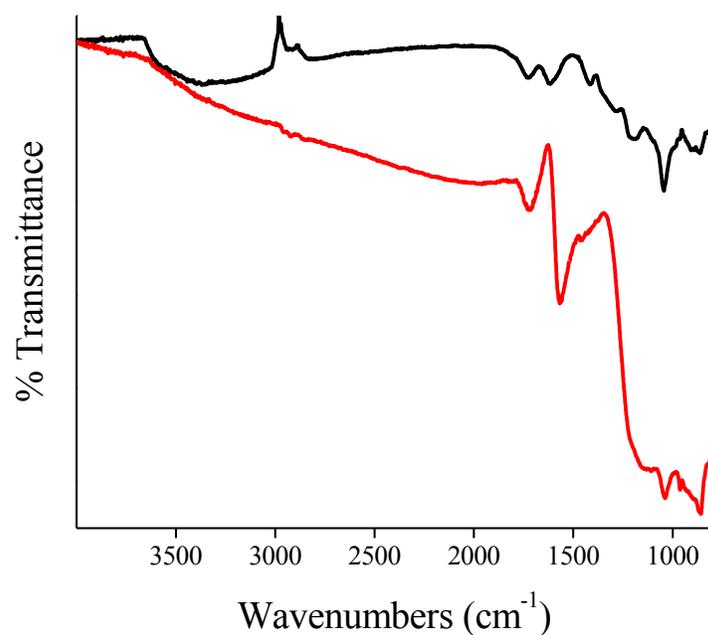


Figure S1. IR spectra of freshly prepared GO (black line) and the material recovered (red line) after being subjected to the dehydration conditions optimized for 4-heptanol (15 wt% GO/NaY (1:1), 150 °C, 30 min).

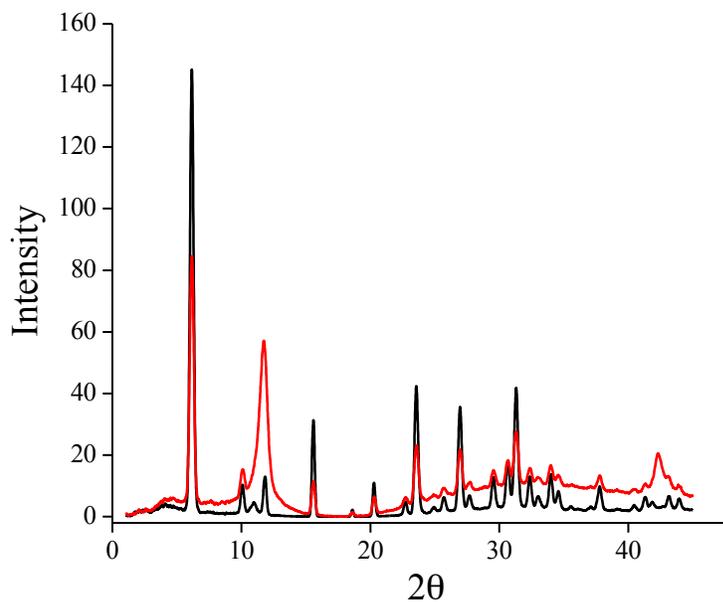


Figure S2. Powder XRD spectral overlay of the freshly prepared GO/NaY mixture (red line) and the material recovered (black line) after being subjected to the dehydration conditions optimized for 4-heptanol (15 wt% GO/NaY (1:1), 150 °C, 30 min).

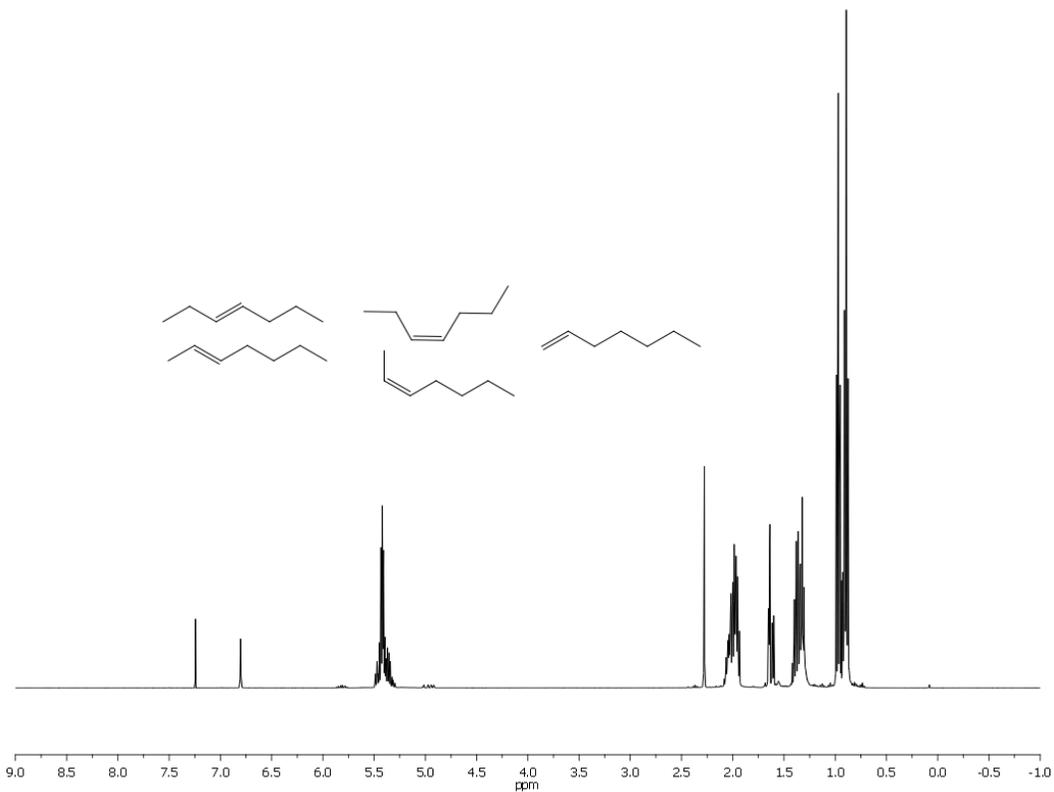


Figure S3. ¹H NMR spectrum of the heptene isomers obtained from the dehydration of 4-heptanol under the optimized conditions.

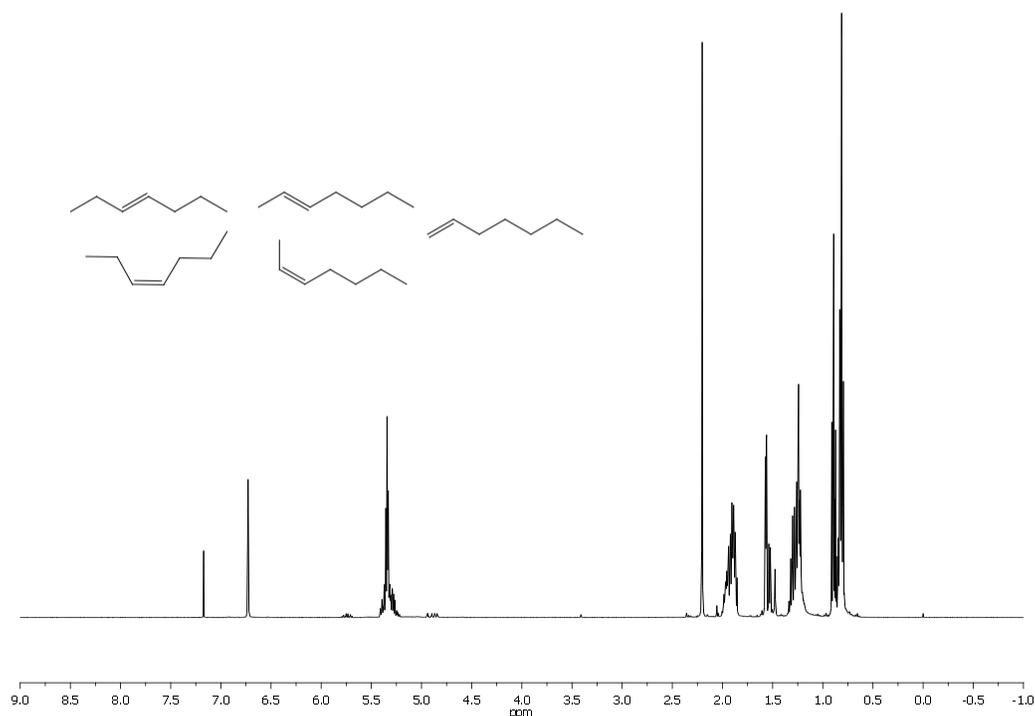


Figure S4. ¹H NMR spectrum of the heptene isomers obtained from the dehydration of 2-heptanol under the optimized conditions.

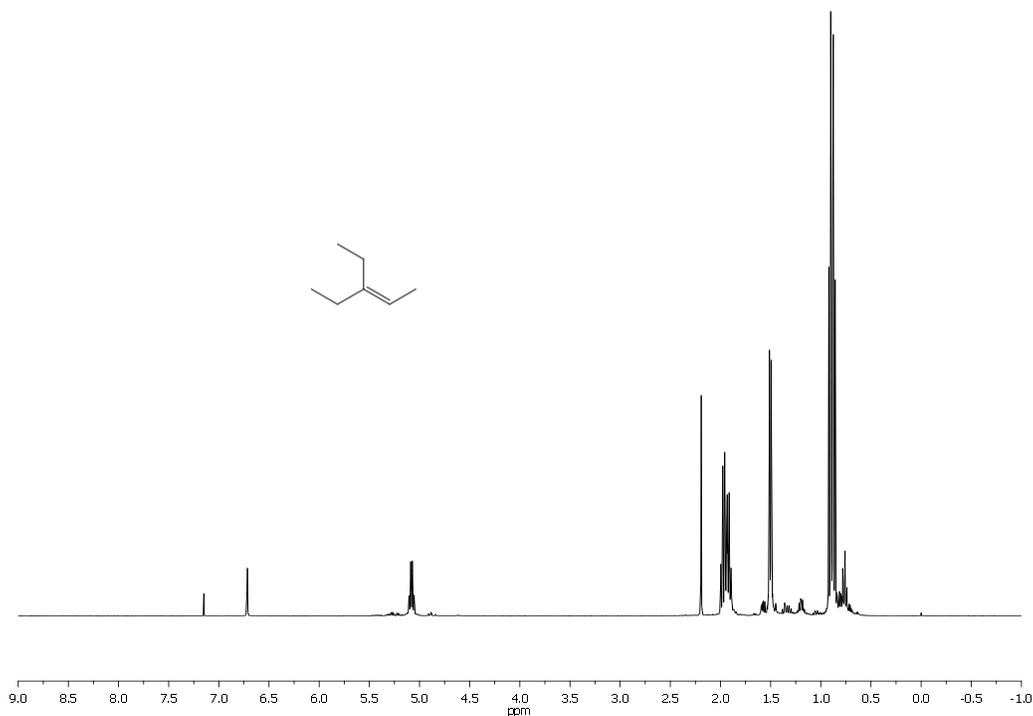


Figure S5. ¹H NMR spectrum of 3-ethyl-pent-2-ene obtained from the dehydration of 3-ethyl-3-pentanol under the optimized conditions.

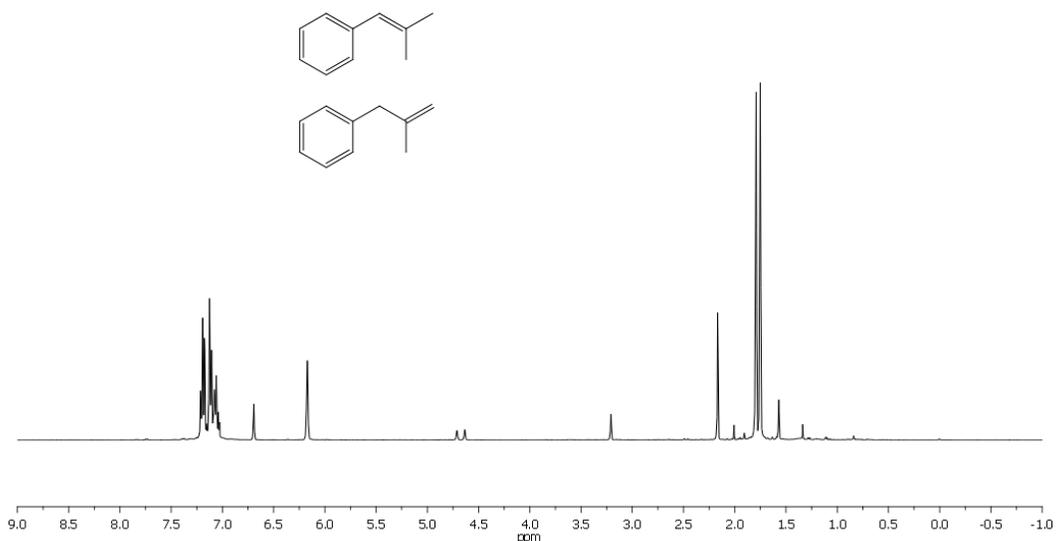


Figure S6. ¹H NMR spectrum of (2-methyl-propenyl)-benzene and (2-methyl-allyl)-benzene from the dehydration of 2-methyl-1-phenylpropan-2-ol under the optimized conditions.

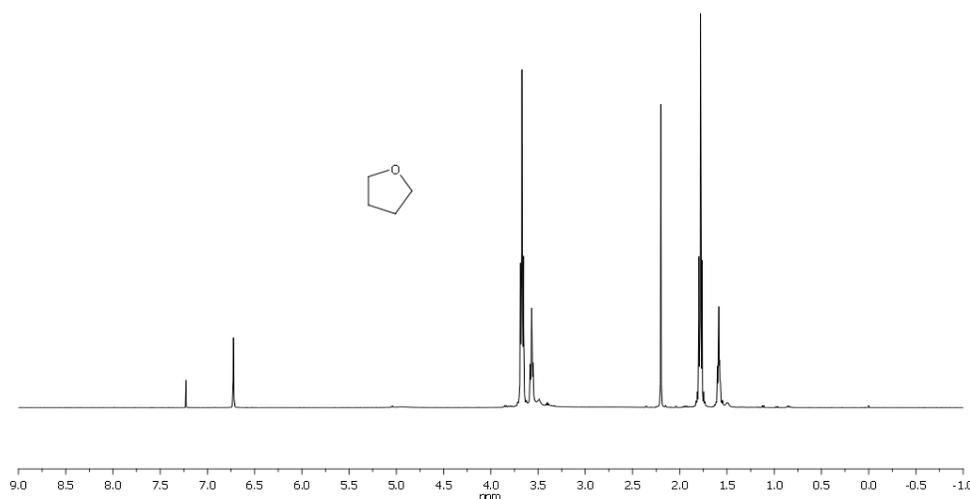


Figure S7. ¹H NMR spectrum of tetrahydrofuran with an oligomeric species present obtained from the dehydration of 1,4-butanediol under the optimized conditions.

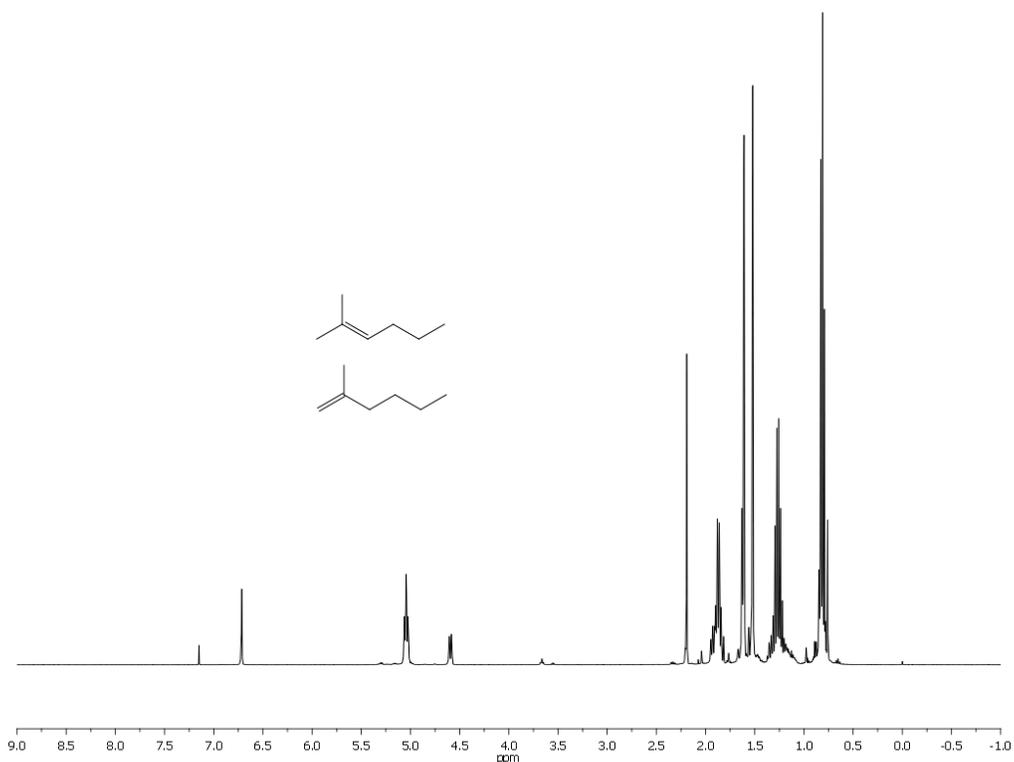


Figure S8. ¹H NMR spectrum of 2-methyl-hex-2-ene and 2-methyl-hex-1-ene obtained from the dehydration of 2-methyl-hexan-2-ol under the optimized conditions.

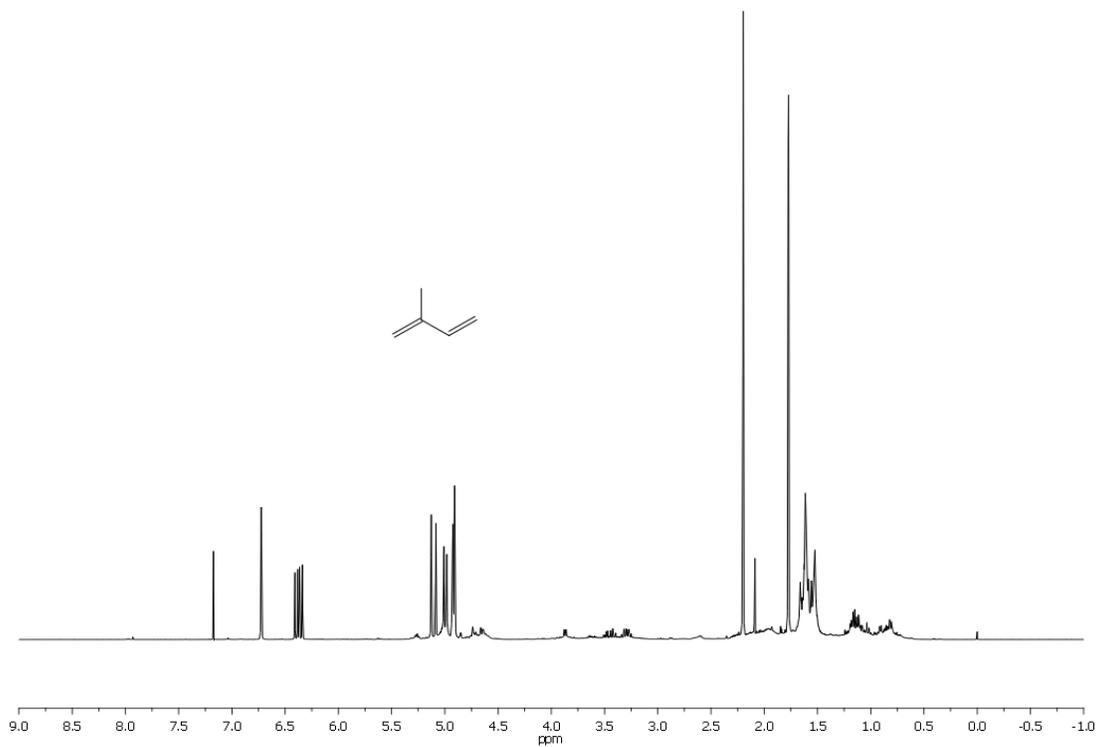


Figure S9. ¹H NMR spectrum of isoprene with an oligomeric species present obtained from the dehydration of 3-methyl-but-2-en-1-ol under the optimized conditions.

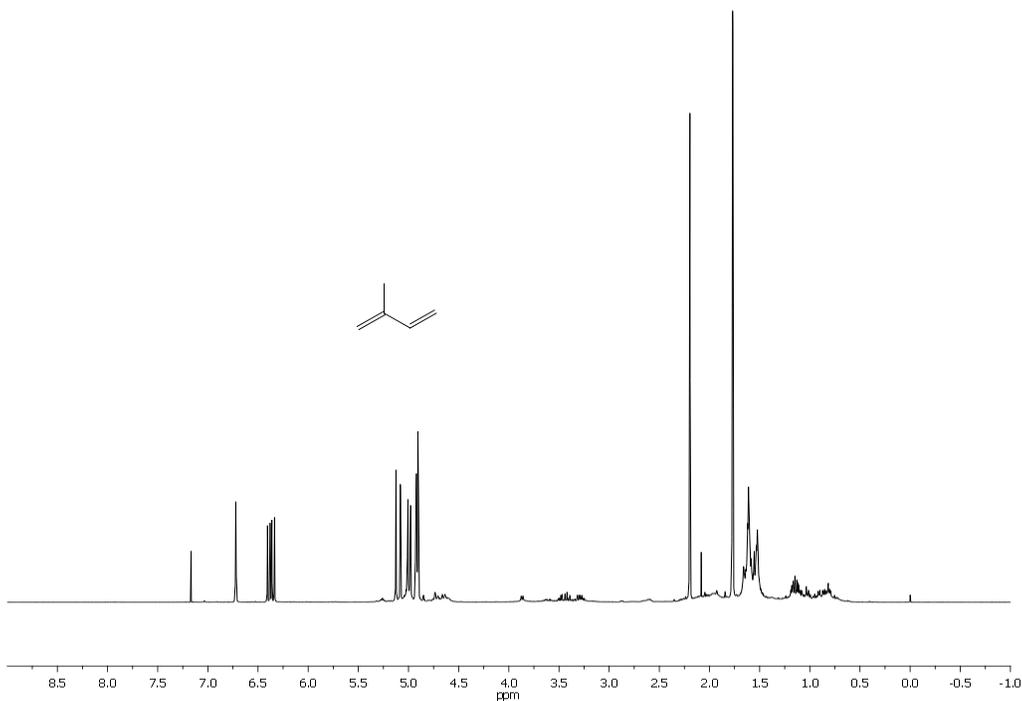


Figure S10. ¹H NMR spectrum of isoprene with an oligomeric species present obtained from the dehydration of 2-methyl-but-3-en-2-ol under the optimized conditions.

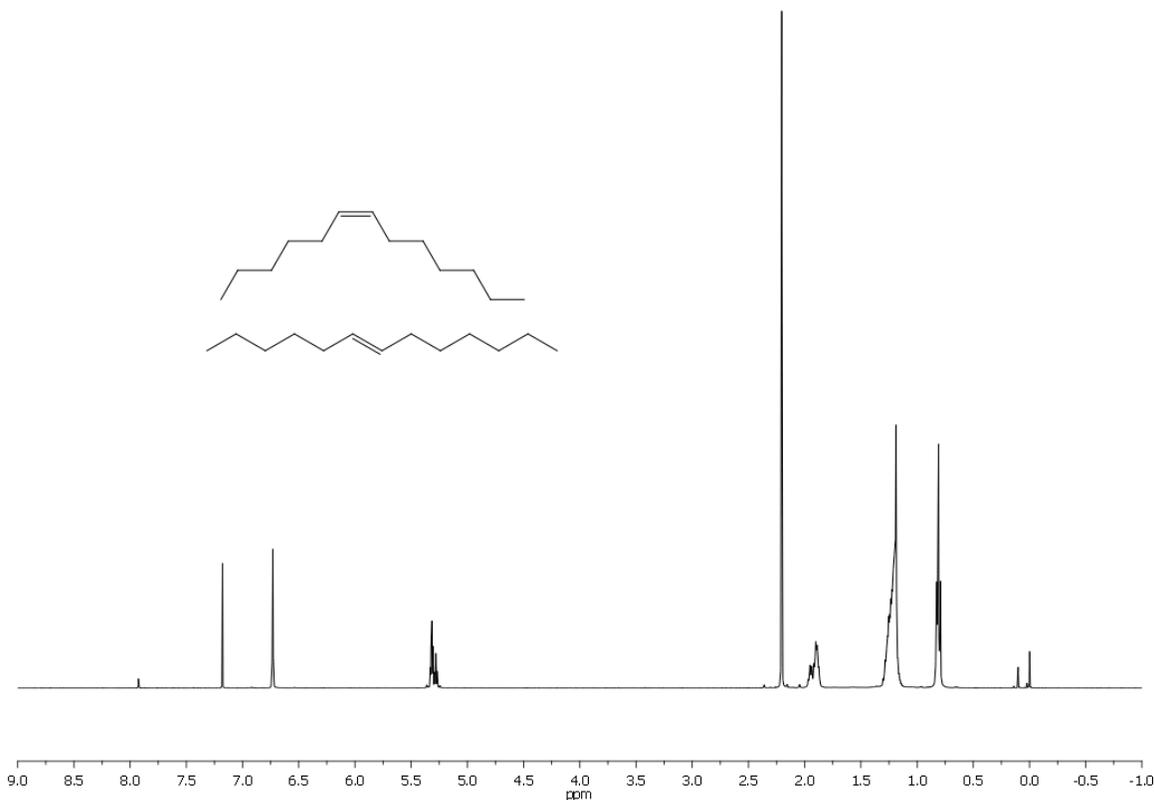


Figure S11. ^1H NMR spectrum of (E)-6-tridecene and (Z)-6-tridecene obtained from the dehydration of 7-tridecanol under the optimized conditions

References

1. Yue, W.; Zhao, Y.; Shao, S.; Tian, H.; Xie, Z.; Geng, Y.; Wang, F. *J. Mater. Chem.* **2009**, *19*, 2199-2206.
2. Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309-319.