Supporting Information for

Production of Renewable Lubricants via Self-condensation of Methyl ketones

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I. General

Materials: Chemicals were used as received without further purification. Commercially available ketones, 2-methylfuran and octane were purchased from Sigma-Aldrich, USA. All HPLC grade solvents, such as acetone, acetonitrile, dichloromethane, diethyl ether, ethyl acetate, hexanes, tetrahydrofuran and toluene were obtained from Fisher Scientific, USA. Anhydrous inorganic solids (Na₂CO₃, Na₂SO₄ and MgSO₄) were purchased from Fisher Scientific, USA. Catalysts and metal precursors such as synthetic hydrotalcite, tantalum (V) ethoxide and chloroplatinic acid hexahydrate were obtained from Sigma-Aldrich, USA. Niobium phosphate was received in kind from CBMM, Brazil. 2 wt% Pt/NbOPO₄ was synthesized according to the procedure from the literature report.¹ Ketones 1i,² 1j,³ 1k,⁴ and 1l⁵ were synthesized using literature procedures.

Methods: Reaction mixtures were analyzed using a Varian CP-3800 gas chromatograph (GC) equipped with a flame ionization detector (FID) coupled to a Varian 320-MS mass spectrometer (MS). Products were separated using a FactorFour capillary column (VF-5 ms, 30 m length, 0.25 mm diameter) coated with a 0.25 μ m thick stationary phase (5% phenyl and 95% dimethylpolysiloxane). Products were identified by GC/MS and HRMS techniques. The condensates of 2-hexanone (**1a**), the representative example, were confirmed by NMR, IR, and HRMS analyses of chromatographically purified products (**2a**', **2a**'', **3a**, **4a**, and **5a**).

II. Preparation and characterization of catalysts

MgAIO: The commercial synthetic hydrotalcite (Mg/Al = 3:1) was calcined at 700 °C for 2 h in static air by ramping the temperature at 2 °C/min.

4 wt% Ta₂O₅/SBA-15: Prepared *via* incipient wetness impregnation method using synthesized SBA-15.⁶ Tantalum (V) ethoxide (0.375 g, 0.25 mL) was dissolved in absolute ethanol (8.5 mL). This solution was added in multiple portions to SBA-15 (5 g) with grinding to give uniform distribution. It was dried at 100 °C for 16h then calcined at 450 °C for 4 hours by ramping the temperature at 5 °C/min.

2 wt% Pt/NbOPO₄: The commercial niobium phosphate was calcined at 300 °C for 3 h in a tubular oven by ramping at 2 °C/min. An air flow was maintained at 50 mL/min throughout the

course of calcination. Chloroplatinic acid hexahydrate (212 mg) was dissolve in deionized water (1 mL) and impregnated on calcined niobium phosphate (4 g) using the incipient wetness method. This material was dried overnight in an oven at 100 °C and subjected to reduction at 300 °C for 3 h in a tubular oven by ramping at 2 °C/min. The hydrogen flow was maintained at 50 mL/min throughout the course of reduction.

Surface area measurements: Catalyst surface area was determined by Brunauer-Emmett-Teller (BET) analysis using a Micromeritics TriStar system with a FlowPrep 060 degassing system. The material (~200 mg) was degassed in a BET tube at 120°C for 6 hours under flowing argon. The catalyst surface area was determined by the BET isotherm. The surface area for MgAlO, Ta₂O₅/SBA-15, and Pt/NbOPO₄ catalysts were found to be 174 ± 2 , 876 ± 11 , and $157 \pm 1 \text{ m}^2/\text{g}$, respectively.

III. Experimental

IIIa. MgAlO-catalyzed self-condensation of ketones: Dean-Stark reactions for large-scale synthesis of lubricant precursors (2)

A solution of 1 (20 g) in toluene (200 mL) was added with MgAlO (20 g) in a 500 mL round bottom flask (RBF) equipped with a magnetic spin bar. The RBF was then attached to the Dean-Stark apparatus and refluxed with stirring (800 rpm) in a pre-heated oil bath at conditions A given in Table 1 of the manuscript. The by-product water was continuously removed from the reaction mixture and collected in the side-arm of the apparatus during the course of the reaction. The product mixture was then cooled to room temperature and filtered through a fritted funnel by washing the catalyst using ethyl acetate (3×100 mL). The products (2) in the filtrate were recovered after evaporation of the solvents.

IIIb. Ta₂O₅/SBA-15-catalyzed self-condensation of ketones: Parr reactions for large-scale synthesis of lubricant precursors (3)

A solution of **1** (4 g) in toluene (18 mL) was added with $Ta_2O_5/SBA-15$ (2 g) in a 50 mL Parr reactor vessel. The reactor was then sealed and heated with stirring (400 rpm) at conditions A given in Table 1 of the manuscript. The product mixture was then cooled to room temperature and filtered through a fritted funnel by washing the catalyst using ethyl acetate (3×50 mL). The products (**3**) in the filtrate were recovered after evaporation of the solvents.

IIIc. Solvent-free self-condensation of methyl ketone (2-nonanone)

A 250 ml round bottom flask equipped with a thick stir bar was charged with slurry of 2nonanone (55 g) and calcined MgAlO (10 g). A Dean-Stark apparatus and the refluxing condenser were fitted to the flask and then the flask was heated to 190 °C using an oil bath with vigorous stirring. The apparatus was then connected to vacuum line which is maintained at ~50 Torr to simulate industrial reactive distillation conditions to remove water. After completion of set duration, the product mixture was allowed to cool to room temperature, added with an internal standard, and stirred to get homogeneous slurry. It was then allowed to settle and a small aliquot of supernatant was withdrawn and dissolved in toluene for analysis by GC-FID. The above reaction was repeated for various set durations.

Entry	2-nonanone (1c , g)	Calcined MgAlO (g)	Time (min)	Conversion (%)	Selectivity (2c , %)
1	55.01	10	30	72	95
2	55.12	10	60	85	97
3	54.96	10	90	92	96
4	55.04	10	120	92	97

Table S1. Solvent-free self-condensation of 2-nonanone at 190 °C under 50 Torr vacuum.

The GC-FID traces showed that the cyclic enone 2c formed via self-condensation was the major product consistent with the results obtained using toluene as the solvent during the reaction (refer Table 1 of the manuscript). More importantly, as shown in Table S1, the reaction is close to completion within ~ 90 minutes.

IIId. Hydrogenation of condensates (2 and 3) to alkanes (4 and 5)

A solution of **2** or **3** (5 mmol) in octane (5 mL) was added with respective hydrogenation catalysts (metal loadings are calculated with respect to **2** or **3**) in a 25 mL Parr reactor vessel. The reactor was sealed, flushed with nitrogen gas ($2\times$), hydrogen gas ($3\times$) and subsequently charged with the required pressure of hydrogen gas. The Parr reactor was stirred at 500 rpm and subjected to respective conditions mentioned in Table 1, conditions B. The reaction mixture was cooled to room temperature and filtered through a fritted funnel using hexanes as a washing solvent (3×20 mL) to remove the catalyst. The crude products in the filtrate were then analyzed using gas chromatography. The filtrate was concentrated under reduced pressure to recover cyclic alkanes. Substrates possessing furan moieties (**2j-l**) were subjected to two stage hydrogenation which involved the above procedure in each stage.



IV. Strategies to access various methyl ketones for the production of lubricant base-oils



While direct synthesis of C₉, C₁₁ and C₁₃-methyl ketones via the microbial fermentation has been reported,⁷ hybrid routes involving chemical transformations of known fermentationderived platform molecules can considerably help expanding the range of methyl ketones available for upgrading (Scheme S1). For instance, primary alcohols possessing small (C₂ and C₄), medium (C₅–C₁₁), and longer (C₁₂–C₁₅) alkyl chains can be useful building blocks for this purpose. While the fermentation-derived smaller alcohols can be upgraded to higher alcohols through Guerbet coupling,^{8, 9} the medium sized alcohols can be accessed from various transition metal-catalyzed hydrogenations of the appropriate furanic precursors.¹⁰ Renewably sourced fatty alcohols may also be used as building blocks. Such fatty alcohols may be obtained either by the direct hydrogenation of triglycerides or *via* oxidative cleavage of double bonds in high molecular weight unsaturated fatty acids (e.g. C₁₆–C₂₀) followed by reduction.¹¹⁻¹³ Medium sized alcohols (C₈–C₁₂) are particularly interesting for alkylating acetone¹⁴ to produce methyl ketones (**1b**–g, **1i**) which are the precursors for C₃₃–C₄₅ lubricant base-oils. Alternatively, mid-chain fatty alcohols may be dehydrated to terminal olefins and subsequently converted to methyl ketones *via* Wacker-type oxidation^{15, 16} or alkylation¹⁷ of acetone. Finally, in addition to the alkyl methyl ketones (**1b–g**, **1i**), furan-containing methyl ketones (**1j** and **1k**) may also be generated by employing an aldol condensation/hydrogenation sequence to the biomass-derived furanic aldehydes such as furfural and 5-methylfurfual.^{3, 4} Acetone required for the alkylation and aldol condensations may be sourced from biological fermentations. As a special case, the C₁₅-precursor (**1l**) can be sourced exclusively from another furanic platform molecule 2-methylfuran via acid catalyzed trimerization.⁵

V. Characterization of condensates (2 and 3), and cycloalkanes (4 and 5)



Fig. S1. Gas chromatograph trace of MgAlO-catalyzed condensation of 2-hexanone (1a).



Fig. S2. ¹H NMR of **2a**'. ¹H NMR (400 MHz, Chloroform-d) δ 2.28-2.15 (m, 7H), 2.11 (d, *J* = 18.0 Hz, 1H), 1.46-1.19 (m, 12H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H).



Fig. S3. ¹³C NMR of **2a**^{*}. ¹³C NMR (101 MHz, Chloroform-d) δ 199.7, 156.4, 134.5, 50.3, 43.2, 41.3, 35.5, 34.9, 30.1, 27.0, 26.0, 24.9, 23.5, 23.2, 23.0, 14.5, 14.2, 14.1.



Fig. S4. ¹H NMR of single isomer of **2a**". ¹H NMR (400 MHz, Chloroform-d) δ 5.74 (bs, 1H), 2.25 (d, *J* = 18.4 Hz, 1H), 2.13 (td, *J* = 7.2, 2.9 Hz, 2H), 2.00 (dd, *J* = 10.2, 3.4 Hz, 1H), 1.93 (d, *J* = 18.4 Hz, 1H), 1.48-1.15 (m, 14H), 0.94 (s, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H).



Fig. S5. ¹³C NMR of single isomer of **2a**". ¹³C NMR (101 MHz, Chloroform-d) δ 203.1, 161.8, 123.7, 55.8, 40.9, 38.2, 37.5, 29.3, 28.2, 25.1, 24.7, 23.6, 22.5, 21.4, 14.4, 14.2, 14.0.



Fig. S6. FTIR-ATR of 2a'. A characteristic cyclic enone stretch is observed at 1662 cm⁻¹.



Fig. S7. FTIR-ATR of 2a". A characteristic cyclic enone stretch is observed at 1665 cm⁻¹.



Fig. S8. ¹H NMR of 3a (400 MHz, Chloroform-d).



Fig. S9. ¹³C NMR of 3a (101 MHz, Chloroform-d).



Fig. S10. ¹H NMR of isomeric mixture of 4a. ¹H NMR (400 MHz, Chloroform-d) δ 1.80-0.60 (m).



Fig. S11. FTIR-ATR of isomeric mixture of 4a.



Fig. S12. ¹H NMR of isomeric mixture of 5a (400 MHz, Chloroform-d).



Fig. S13. ¹³C NMR of isomeric mixture of 5a (101 MHz, Chloroform-d).



Fig. S14. FTIR-ATR of isomeric mixture of 3a.



Fig. S15. FTIR-ATR of isomeric mixture of 5a.

Molecular Structure	Molecular	Calculated	Measured
	Formula	Mass	Mass
2a	C ₁₈ H ₃₂ O	264.2453	264.2451
	10 02	[M] ⁺	[M]+, EI
0 2b	CalluO	349.3470	349.3469
	02411440	[M+H] ⁺	[M+H]⁺, ESI
○ ○ 2c		391.3940	391.3938
	C ₂₇ H ₅₀ O	[M+H]+	[M+H]⁺, ESI
0 21		433.4409	433.4402
	C ₃₀ H ₅₆ O	[M+H]+	[M+H]⁺, ESI
20		474.4801	474.4795
	C ₃₃ H ₆₂ O	[M] ⁺	[M]⁺, EI
		517.5348	517.5344
	U36H68U	[M+H] ⁺	[M+H]⁺, ESI
0 2g		642.6679	642.6684
	C ₄₅ H ₈₆ O	[M] ⁺	[M]⁺, EI
C C C C C C C C C C C C C C C C C C C	$C_{30}H_{32}O$	409.2531 [M+H]⁺	409.2529 [M+H]⁺, ESI
2i	$C_{33}H_{62}O$	474.4801 [M]+	474.4798 [M] ⁺ , El
	$\mathrm{C}_{24}\mathrm{H}_{26}\mathrm{O}_4$	379.1909 [M+H]⁺	379.1905 [M+H]⁺, ESI
	C ₂₇ H ₃₂ O ₄	421.2379 [M+H]+	421.2377 [M+H]⁺, ESI

Table S2. HRMS Characterization data for condensates 2a-l, and 3a-b, cycloalkanes 4a-l, and 5a-b.



o o	703.3635	703.3632
$C_{45}H_{50}O_7$	[M+H]+	[M+H]⁺, ESI
	0.40.00.40	
C ₁₈ H ₃₀	246.2348	246.2346
	[M]+	[M]⁺, EI
Culture	414.4226	414.4229
C ₃₀ 1 ₅₄	[M] ⁺	[M]+, EI
	252.2817	252.2815
С ₁₈ П ₃₆	[M] ⁺	[M]⁺, EI
	336.3756	336.3748
C ₂₄ I 1 ₄₈	[M] ⁺	[M] ⁺ , EI
C - H	378.4226	378.4219
0271154	[M] ⁺	[M]+, EI
CaeHae	420.4695	420.4698
0301 160	[M] ⁺	[M]+, EI
CasHaa	462.5165	462.5156
0331 166	[M] ⁺	[M]⁺, EI
CooHzo	504.5634	504.5641
036172	[M] ⁺	[M]+, EI
CurHoo	630.7043	630.7047
0451 190	[M] ⁺	[M]+, EI
	462.5165	462.5162
C ₃₃ H ₆₆	[M] ⁺	[M]⁺, EI
0.11	630.7043	630.7024
$C_{45}H_{90}$	[M] ⁺	[M]+, EI
	252.2817	252.2815
$C_{18}H_{36}$	[M] ⁺	[M]+, EI
CaoHeo	420.4695	420.4699
- 30. 100	[M] ⁺	[M]+, EI

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