

From crude industrial waste glycerol to biopropene *via* Ru-mediated hydrodeoxygenation in ionic liquids

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Summary on the glycerol to propene literature

Table S1: State of the art conversion of glycerol to propene.

Catalyst	Conditions	Yield (%)	Glycerol Feed	MeOH / salts
316 stainless steel & HOTf or [Ru(H ₂ O) ₃ (4'-phenyl-terpyridine)](OTf) ₂ ¹	5.5 MPa H ₂ , 250 °C, 24h	96	4 wt% in H ₂ O	<i>none / none</i>
Hydrogen iodide & AcOH ²	6.9 MPa H ₂ , 210 °C, 5h	78	14 wt% in H ₂ O	1 wt% MeOH / 1 wt% salts
Ir/ZrO ₂ & ZSM-5-30 ³	Continuous H ₂ flow, 250 °C	85	30 wt% in H ₂ O	<i>none^a / none</i>
Fe-Mo/C ^{4,5}	Continuous H ₂ flow, 300 °C	90	2 wt% in H ₂ O	<i>none / none</i>
WO ₃ -Cu/Al ₂ O ₃ & SiO ₂ -Al ₂ O ₃ ⁶	Continuous H ₂ flow, 250 °C	85	20 wt% in H ₂ O	<i>none / none</i>
MoO ₃ -Ni ₂ P/Al ₂ O ₃ & ZSM-5-30 ⁷	Continuous H ₂ flow, 250 °C	72	59 wt% in H ₂ O	15 ^b wt% MeOH / <i>none</i>
Ru[CO] ₃ Br ₂ (<i>in situ</i>) & HBr/ <i>n</i> -Bu ₄ PBr ⁸	4.0 MPa H ₂ , 210°C, 1h	57	100 wt% (pure)	<i>none / none</i>

^a Reaction was performed on crude glycerol (Glycerol/methanol/NaCl at 84:1:15 ratio) for the partial conversion to 1-propanol. However, there was no report on the conversion of crude glycerol to propene. ^b Simulated crude glycerol (Glycerol/methanol at 85:15 mass ratio), the reaction temperature was increased to 450 °C to promote propylene selectivity.

Chemicals

Tetrabutylphosphonium bromide (Sigma-Aldrich, 98%), glycerol (Sigma-Aldrich 99%), *n*-dodecane (J&K, 95%), *n*-tetradecane (TCI, 99%), N₂ (Air Liquide, α1), H₂ (Air Liquide, N40), CO (Air Liquide, N37), HBr (Sigma-Aldrich, 48% in water), ruthenium(III) bromide hydrate (Alfa, Ru 25% min), trirutheniumdodecacarbonyl (Arcos, 99%), tricarbonyldichlororuthenium(II) dimer (Sigma Aldrich), formaldehyde (Sigma-Aldrich, ACS reagent, 37 wt.% in H₂O, contains 10-15% methanol as stabilizer) *N,O*-bis(trimethylsilyl)trifluoroacetamide (Sigma-Aldrich, BSTFA + TCMS 99:1), sodium chloride (Fisher Scientific, +99%), sodium bromide (Sigma-Aldrich, 99%), potassium bromide (Acros, 99%), potassium chloride (VWR, 99%), hydrogen chloride (VWR, 37 wt.% in H₂O), methanol (VWR, +99%), sulfuric acid (Merck, 98%), pyridine (Acros, 98%), 1,2,4-butanetriol (Alpha-Aesar, 96%), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (Alpha-Aesar, 97%, MSTFA), AgNO₃ (Sigma-Aldrich, 99%), NaSCN (Acros, 98%), (NH₄)₂Fe(II)(SO₄)₂ (Sigma-Aldrich, 98%), benzene (Carl Roth 99%), chloroform (Fisher, 99%), hexane (Acros, 97%), Br₂ (Sigma-Aldrich, +99.5%) and crude glycerol (OleonNV, ex-biodiesel production). All chemicals were used as received unless mentioned otherwise.

Catalytic reaction

First, the active catalyst is formed *in situ* during a pretreatment step using a CO source. Standard experiments start from RuBr₃·xH₂O (10 μmol, 4.0 mg), HBr (25 μmol, 2.8 μL), Bu₄PBr (1.7 mmol, 577 mg) and formaldehyde (25 equivalents, 18.6 μL) or CO gas (certain pressure). All components are loaded in a glass liner inside a stainless steel pressure reactor and stirred for 30 minutes under 40 bar H₂ at 180 °C. After pretreatment the reactor is cooled on ice and the remaining H₂/CO is released to the waste exhaust. Secondly, the actual catalytic hydrodeoxygenation of (crude) glycerol is performed. Glycerol + additives (0.5 mmol, additives on wt% basis), dodecane (1 mL, as an extracting apolar layer) and tetradecane (0.5 mmol, 0.13 mL, internal standard in dodecane layer) were additionally loaded into the reactor containing the pretreated catalyst. The reaction is performed typically for 1h under 40 bar H₂ at 220 °C, after which the reactor is again cooled, and a gaseous sample (for FT-IR gas phase analysis) is taken *via* a syringe. The yield of the apolar compounds is determined *via* GC analysis of the dodecane layer. Finally, an additional derivatisation step is performed using BSTFA (1mL), silylating the remaining unconverted polar intermediates in the polar IL layer for GC analysis.

Product analysis

After reaction a spontaneous phase separation occurs between the IL and the dodecane layer.⁸ A liquid aliquot of the dodecane layer was taken for GC analysis, performed on a Shimadzu GC-2013 instrument equipped with a DB-FFAP column as this allows for the separation of propene and propane and quantification of even highly volatile compounds.⁸ GC analysis of the silylated polar intermediates (alcohols) was performed on a Shimadzu GC-2010 instrument equipped with a CP SIL-5 CB column.

However, at high conversions and propene selectivities, the amount of propane is very low compared to propene. Therefore, to maintain high accuracy on the exact propene/propane selectivity, in addition to quantitative GC analysis, we performed an independent analysis to determine the propene vs propane selectivity. Fourier Transformed Infrared (FT-IR) spectroscopy was performed on the gas in the headspace of the reactor, injecting a gas sample into a N₂ flow on a Gasetm DX 4000 FT-IR gas analyzer. Spectra were processed using Calcmet standard software (v. 12.161), and corresponded well with the liquid phase composition. The use of FT-IR relies on a difference in vibrations of the =C-H alkene stretch (above 3000 cm⁻¹) compared to the -C-H alkane stretch (2800-3000 cm⁻¹). The Calcmet software allows for the accurate calculation of the propene vs propene+propane ratio, thus indicating the selectivity of the system even at very low concentrations (below 1% of the formed C₃-compounds is present in the gaseous phase).

Apart from propene/propane and CO/CH₄, originating from the catalyst pretreatment and HDO of formaldehyde and methanol additives, no additional gaseous compounds were detected, indicating that no fragmentation of C₃ to C₂ products occurs (also confirmed with GC-MS). In the first liquid extraction, apart from acetone, all side products are below 2% yield, unless mentioned otherwise. The other detected compounds include mono-bromopropanes, propanal, and C₆ compounds (hexanones and hexenes) (Scheme 1, 5). In the extraction after a derivatisation reaction, increased amounts of polar intermediates were observed in case of slow dehydration. These products were categorized as hydroxy compounds (Scheme 1, 4) comprising glycerol, 1,2-propanediol, 2-propanol and 1-propanol. Hydroxyacetone and 1,3-propanediol were occasionally detected, but always in amounts below 1%.

Crude glycerol (real vs. simulated)

Simulated crude glycerol blends were all made weighing the corresponding components in a glass vial and applying intensive stirring on a vortex mixer. All samples are blended on weight percentage (wt%) basis. For example, the simulated blend used in entries 9, 12, 15 and 18 contains 80 wt% of glycerol, 10 wt% of water, 5 wt% of NaCl and 5 wt% MeOH. This represents an extreme scenario in which no purification of the waste glycerol is performed, with rather high residues of saponification and acidification reagents. The real ex-biodiesel crude glycerol was kindly provided by Oleon^{NV} (±80 wt% glycerol).

Crude glycerol analysis

Additional experiments were performed to analyze the composition of the industrial glycerol. The industrial sample was simply filtered over a 0.45 μm filter (Merck, Millipore Millex HP) to remove solid particles, obtaining a homogeneous, amber colored liquid. The glycerol content was determined according to a literature procedure.⁹ Crude glycerol was weighed (100 mg), acidified by 100 μL 1:1 HCl (v/v) and dissolved in pyridine (10 mL). Then, a 100 μL aliquot and 100 μL of an 1,2,4-butanetriol standard solution (8.7 mg/mL) were derivatized using *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA, 100 μL) for 15 min at 38°C in a GC vial. After reaction the sample was cooled down and measured on a Shimadzu GC-2010 instrument equipped with an CP SIL-5 CB column. A calibration curve based on pure glycerol was used, indicating a 78±2 wt% of glycerol content. Karl Fisher titration was performed (870 KF Titrino plus, Metrohm) indicating 20±1 wt% water. Chloride content was determined *via* Volhard titration. Crude glycerol (500 mg) was diluted in water (5 mL) and stirred with excess AgNO₃ (1 mmol, 169.9 mg) forming AgCl in suspension. Then, the remaining Ag⁺ ions were back-titrated with NaSCN (0.1M) using (NH₄)₂Fe(II)(SO₄)₂ as an indicator. At the equivalence point the solution turned from light yellow to dark red, indicating a total chloride content of 2 wt%.

Synthesis of [RuBr₂(CO)₃]₂

The ruthenium bromide carbonyl complex was synthesized according to a literature procedure.^{8,10} Ru₃(CO)₁₂ (0.064 g, 0.10 mmol) was dissolved in dry benzene resulting in an orange solution. Excess Br₂ was added and the solution was stirred vigorously for 3 hours. The solvent and unreacted Br₂ were removed under reduced pressure. The crude product was purified by recrystallization in chloroform/hexane resulting in a yellow solid. The identity of the [RuBr₂(CO)₃]₂ complex was confirmed with FT-IR spectroscopy and Electrospray Ionization Mass Spectrometry (ESI-MS). The FTIR sample was analyzed in a Bruker IFS 66v/S FTIR spectrometer under vacuum. The data were analyzed using OriginPro. The ESI-MS was conducted in positive ion mode with a Thermo Finnigan LCQ Advantage mass spectrometer. ν(CO): (KBr) 2138 cm⁻¹ (s), 2078 (s) cm⁻¹, ESI-MS (MH⁺ in CH₃CN): 387.75; found, 388.0.

Catalyst recycling experiments

The reaction was performed as described under optimal conditions (Table 2, entry 21). After reaction, the gaseous phase and dodecane layer were removed and analyzed. Derivatisation of polar compounds remaining in the ionic liquid layer was not carried out in between cycles, as unreacted BSTFA and unwanted side products could remain in the IL and hinder the catalytic

performance. The IL layer was dried overnight at 110°C under reduced pressure (30 mbar) after which HBr was added and the catalyst was pretreated as usual (0.1 MPa CO, 4.0 MPa H₂, 30 min, 180°C). After pretreatment the catalyst was loaded with fresh, crude glycerol and extraction solvent. After the 8th cycle the remaining polar compounds are quantified *via* a derivatisation step using BSTFA, as described under product analysis.

Characterization and stability of the (recycled) catalyst

Solid phase Fourier transform infrared (FT-IR) spectroscopy was performed on fresh and recycled Ru-catalyst, entrapped in the solidified ionic liquid (after 8th cycle). Both catalysts were pretreated as described above (0.1 MPa CO, 4.0 MPa H₂, 30 min, 180°C). The samples were analyzed in a Bruker Vortex v70 FT-IR spectrometer. The data were analyzed using OPUS software.

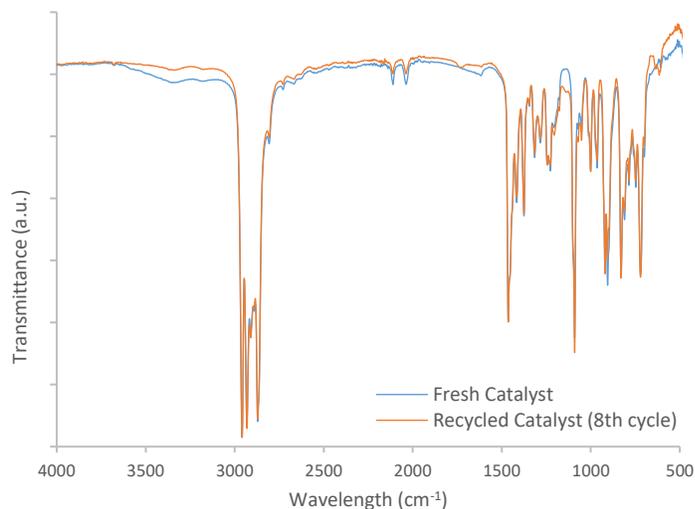


Fig. S1 Fourier transformed infrared spectroscopy of fresh and recycled Ru-catalyst

To confirm the catalyst stability in combination with preservation of high selectivity, we exposed both fresh and recycled pretreated catalyst (after 8th cycle) to 0.1 MPa of pure propylene gas under relevant reaction conditions (0.01 mmol Ru_{cat}, 1.7 mmol Bu₄PBr, 25 μmol HBr, 1 mL dodecane, 0.5 mmol tetradecane (IS), 4.0 MPa H₂, 1h, 220°C). After reaction only the propene vs propane ratio was analyzed as described under Product Analysis. Both reactions showed very low propane formation (>90% of the C₃ fraction is still propene), showing that overhydrogenation of the desired olefin is avoided.

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