



Supporting Information

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Glycerol as a Source for Fuels and Chemicals by Low-Temperature Catalytic Processing

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Experimental Methods

Catalyst Preparation and Characterization

Supported Pt catalysts were prepared by incipient wetness impregnation of Al_2O_3 (Catapal B, Sasol), $\text{CeO}_2/\text{ZrO}_2$, MgO/ZrO_2 , and ZrO_2 using chloroplatinic acid hexahydrate (Strem Chemicals) for ZrO_2 and $\text{CeO}_2/\text{ZrO}_2$ and tetraamine platinum (II) nitrate (Strem Chemicals) for Al_2O_3 and MgO/ZrO_2 . Following impregnation, the Pt/ZrO_2 and $\text{Pt}/\text{CeO}_2/\text{ZrO}_2$ catalysts were dried in air at 393 K for 15 h and calcined at 773 K for 4 h in a muffle furnace. During calcination, the temperature was increased from room temperature to 373 K and held for 1 h, then increased by increments of 100 K to 773 K, holding at each increment for 1 h. The MgO/ZrO_2 and Al_2O_3 supported Pt catalysts were dried in air for 15 h at 393 K and then calcined in flowing O_2/He gas mixtures (20% for $\text{Pt}/\text{MgO}/\text{ZrO}_2$ and 10% for $\text{Pt}/\text{Al}_2\text{O}_3$, using a flowrate of $300 \text{ cm}^3(\text{NTP}) \text{ min}^{-1}$) to 533 K (at 1.3 K min^{-1}) for $\text{Pt}/\text{Al}_2\text{O}_3$ and 723 K (at 3.6 K min^{-1}) for $\text{Pt}/\text{MgO}/\text{ZrO}_2$ and held at these temperatures for 2 h. The carbon-

supported Pt catalyst and Pt:Ru (atomic ratio of 1:1) alloy catalyst were purchased from E-TEK. The carbon-supported Pt:Re catalyst (atomic ratio of 1:1) was prepared via incipient wetness impregnation of Pt/C (E-TEK) using perrhenic acid (Strem Chemicals). Prior to reaction kinetics or gas adsorption measurements (i.e., CO chemisorption, BET surface area), each catalyst was reduced in flowing H₂ (180 cm³(NTP) min⁻¹) at temperatures of 533 K (Al₂O₃, MgO/ZrO₂, and C-supported catalysts; ramped at 0.5 K min⁻¹ and held for 2 h) or 773 K (CeO₂/ZrO₂ and ZrO₂ supported catalysts; ramped at 0.5 K min⁻¹ and held for 1 h). The Pt:Ru/C catalyst was reduced in flowing H₂ (140 cm³(NTP) min⁻¹) at the reaction temperature (548 K or 573 K; ramped at 0.5 K min⁻¹), while Pt:Re/C was reduced at 723 K (ramp rate of 0.5 K min⁻¹) for 2 h in flowing H₂ (140 cm³(NTP) min⁻¹). Table S1 shows the characteristics of each catalyst. The irreversible CO uptakes and BET surface areas were measured using a standard gas adsorption apparatus described elsewhere.^[1]

The preparation of ZrO_2 and CeZrO_2 supports is described in detail elsewhere.^[2] Briefly, these oxide supports were prepared by co-precipitation, starting from an aqueous solution containing 0.12 M of both zirconyl nitrate (Sigma-Aldrich) and cerium ammonium nitrate (Sigma-Aldrich) and using an excess ($\text{Me}^{4+}:\text{OH}^- = 8$) of ammonium hydroxide (28-30 wt % NH_3 , Sigma-Aldrich) as the precipitation agent. The precipitates were washed in de-ionized (DI) water and calcined at 773 K in air in a muffle furnace. A similar procedure for preparation of MgO/ZrO_2 is described elsewhere.^[3] The MgO/ZrO_2 support was prepared using an aqueous solution containing 0.2 M of magnesium nitrate (Sigma-Aldrich) and 0.02 M of zirconyl nitrate (Sigma-Aldrich). The solution was stirred at room temperature while NaOH solution (25 wt%) was added until a pH of 10 was reached and the corresponding gel was formed. The gel was aged for 72 h and vacuum filtered. The precipitate formed was washed with DI water until the Na concentration in the filtrate was below 10 ppm as measured by ICP analysis. The sample was then dried

in air at 393 K for 16-24 h. The MgO/ZrO₂ support was calcined in flowing O₂ (100 cm³(NTP) min⁻¹) to 873 K (3.2 K min⁻¹) and then held at this temperature for 3 h.

Reaction Kinetics Measurements

Figure S1 shows a schematic of the apparatus used to conduct reaction kinetics measurements. Fresh catalyst was loaded into a ¼-inch outer diameter tubular stainless steel reactor. For experiments at low temperature conditions (*i.e.*, 498 - 573 K over Pt:Ru/C and Pt:Re/C), a ½-inch outer diameter tubular stainless steel reactor was used. For both tubular reactor types, the catalyst bed was contained between an end plug of quartz wool (Alltech) and fused SiO₂ granules (-4+16 mesh; Sigma-Aldrich) which aid in vaporization of the liquid feed. The Pt/C, Pt:Ru/C, and Pt:Re/C catalyst powders were mixed with equal volumes of crushed SiO₂ granules before loading in the reactor to decrease the pressure drop across the catalyst bed. Type-K thermocouples (Omega) were attached to the outside of the reactor to measure reactor temperature, which was controlled with

a series 16A type temperature controller (Dwyer Instruments). Fresh catalyst was reduced in flowing H₂ as outlined above. Mass-flow meters (5850 Brooks Instruments) were used to control the flowrate of H₂. An HPLC pump (Model 301, Alltech) was used to introduce the aqueous feed solution into the liquid injection unit above the reactor. The unit is comprised of a 6-inch needle with a point 5 style tip (Hamilton) soldered into a section of 1/8-inch stainless steel tubing. The needle extends into the reactor just above the fused SiO₂ granules. The effluent from the reactor was water-cooled in a double-pipe heat exchanger. The effluent liquid was drained periodically for GC analysis (Agilent 6890 with an FID detector and HP-Innowax column or Shimadzu GC-2010 with an FID detector and DB 5 column) and total organic carbon analysis (Shimadzu TOC-V CSH). Each effluent was tested for the presence of glycerol and other liquid byproducts.

The effluent gas stream passed through a back-pressure regulator (GO Regulator, Model BP-60) which controlled the

system pressure. The effluent gas was analyzed with three different gas chromatographs: a) H₂ was analyzed with a Carle GC (series 8700) using a TCD, b) CO, CH₄, and C₂-hydrocarbons were analyzed using an HP-5890 GC with TCD and washed molecular sieve 5A 80/100 column (Alltech), and c) CO₂ was analyzed using a Shimadzu GC-8A with TCD and a Haysep DB 100/120 column (Alltech).

All feed solutions were prepared by mixing glycerol (99.5%, ACS reagent, Sigma-Aldrich) with DI water.

Variation of H₂:CO ratio via 2-bed catalytic system

A catalytic system to produce synthesis gas with varying H₂:CO ratios can be fashioned using two catalyst beds, the first of which is a Pt/C bed to achieve 100% conversion of glycerol to produce a H₂/CO gas mixture, followed by a second catalyst that is effective for water-gas shift, such as 1.0% Pt/CeO₂/ZrO₂ containing redox sites to promote water-gas shift.^[4, 5] As shown in Figures S2A and S2B, this two-bed catalyst system achieved 100% conversion of glycerol, and the H₂:CO and CO:CO₂ ratios

remain stable for at least 48 h time-on-stream. The values of 1.33 and 14 for the H₂:CO and CO:CO₂ ratios, respectively, for the Pt/C catalyst indicate a negligible contribution from the water-gas shift reaction; however, the significant increase in the H₂:CO ratio and the corresponding decrease in the CO:CO₂ ratio for the two-bed catalyst system indicate that the Pt/CeO₂/ZrO₂ catalyst has achieved effective water-gas shift conversion.

Calculation of Heats of Reaction

Heats of reaction were calculated using the standard heats of formation and heat capacities from Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds for each species. Table S2 lists the thermodynamic quantities for each species. Heat capacities were assumed constant over the temperature range. The following reaction network was used for the formation of liquid alkanes (*e.g.*, octane) from glycerol. This network includes the water-gas shift reaction to achieve the necessary H₂:CO ratio as well as to produce hydrogen for the hydrogenation of the unsaturated alkene product.



Table S3 lists the heats of reaction for reactions 1-4 at 523 K.

The sum of these reactions gives the following net exothermic process with $\Delta H = -63 \text{ kJ mol}^{-1}$



The lower heating value of the organic species is the energy released from the combustion of the organic molecule to CO_2 and H_2O vapor.

The energies to vaporize 5 wt% ethanol in water and 25 wt% glycerol in water solutions were calculated by multiplying the molar ratio of water to organic molecule by the heat of vaporization of water.

Pathways for Glycerol Processing

Figure S3 shows a schematic of the overall processes for converting glycerol to liquid fuels and chemicals. Glycerol is available as either an 80 wt% aqueous stream from biodiesel production^[6] or as a 25-30 wt% stream from the fermentation of glucose.^[7] Producing glycerol from the fermentation of glucose is an energy-efficient alternative to ethanol production because higher product concentrations can be formed. The glycerol is converted to synthesis gas via low-temperature catalytic processing, as shown in this communication. The H₂:CO ratio of the syngas can be adjusted through WGS. Liquid fuels and chemicals are produced via subsequent synthesis reactions (Fischer-Tropsch, methanol). Methanol can be recycled to the transesterification process or used as a chemical.

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Table S1. Properties of supported metal catalysts.

Catalyst	Wt%	Irreversible Pt ^a CO Uptake ($\mu\text{mol g}^{-1}$)	BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	CO/Metal Atomic Ratio
Pt/Al ₂ O ₃	3.0	92	218	0.60
Pt/MgO/ZrO ₂	1.5	22	182	0.29
Pt/ZrO ₂	1.0	26	112	0.51
Pt/CeO ₂ /ZrO ₂	1.0	5.5	73.7	0.11
Pt/C-Vulcan XC-72	5.0	110	--	0.42
Pt:Ru/C-Vulcan XC-72	5.0	120	--	0.23
Pt:Re/C-Vulcan XC-72	5.0	110	--	0.20

^aNominal loading**Table S2.** Thermodynamic quantities of reaction species.

species	ΔH_f^0 kJ mol ⁻¹	C_p J mol ⁻¹ K ⁻¹	ΔH_f (523 K) kJ mol ⁻¹
CO	-111	29.2	-104
CO ₂	-394	37.1	-385
H ₂	0	28.8	6.49
H ₂ O(g)	-242	33.6	-234
H ₂ O(l)	-286	75.3	-269
Glycerol(l)	-668	150	-635
Octene(l)	-124	241	-69.2
Octane(l)	-250	189	-207
O ₂	0	29.4	6.60
CH ₃ OH(l)	-239	81.2	-221
Ethanol(l)	-277	112	-252

Table S3. Heats of reaction for coupling of glycerol processing with Fischer-Tropsch synthesis.

Reaction	Heat (kJ mol ⁻¹)
Glycerol to syngas	349
Fischer-Tropsch reaction to octene	-340
Hydrogenation of octene to octane	-40.5
Water-gas shift	-30.7
Overall	-62.9

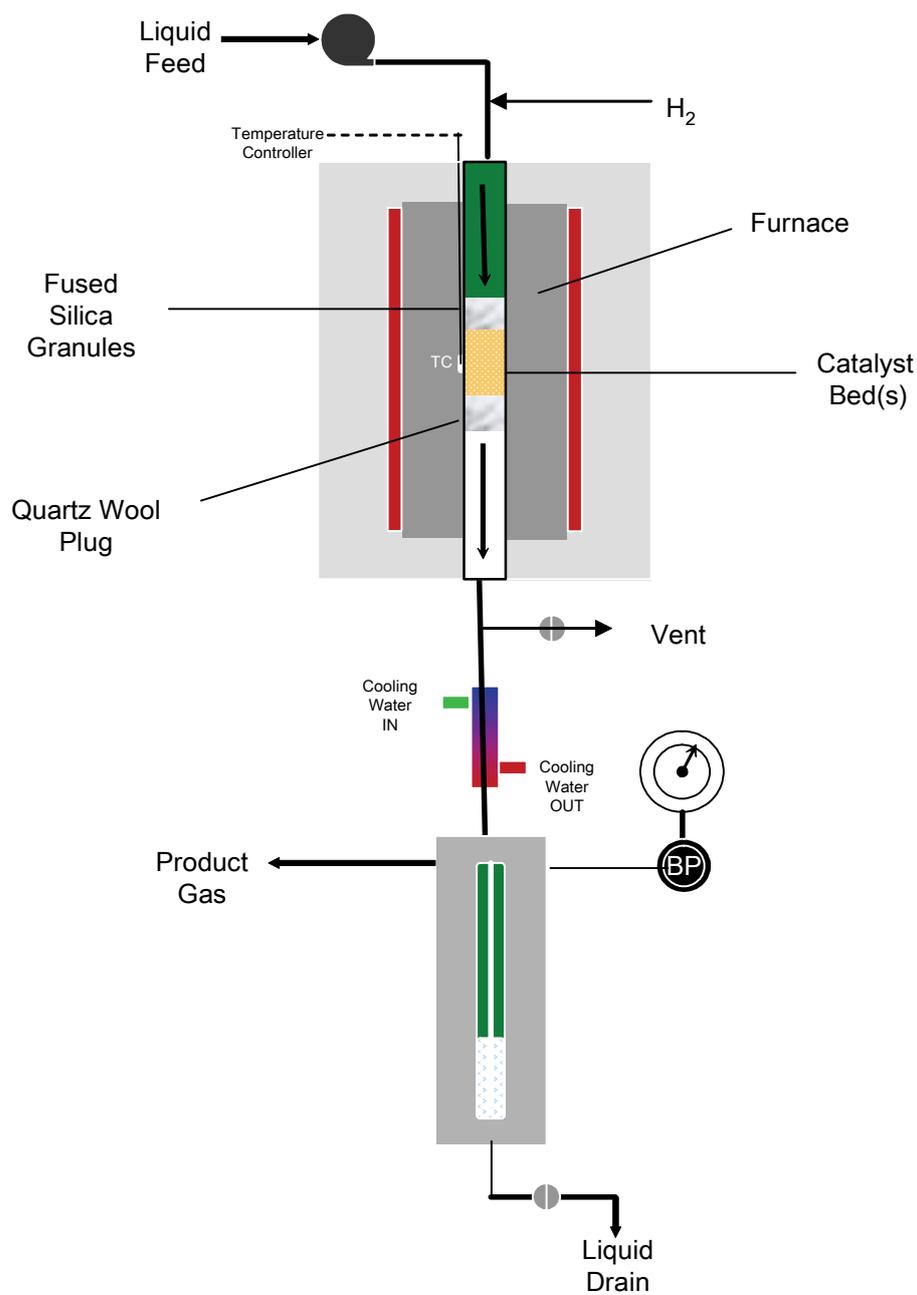


Figure S1. Schematic diagram of reaction kinetics apparatus. H_2 flow is used only during catalyst reduction.

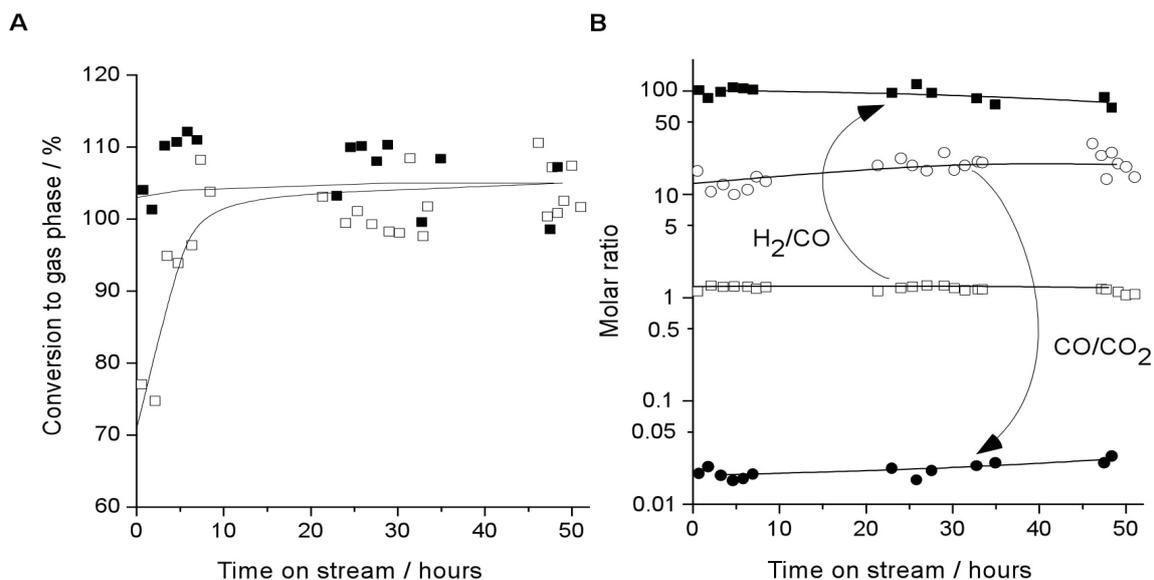


Figure S2. Effect of water-gas shift functionality. Variation of **A)** glycerol conversion to gas phase products and **B)** molar ratios for gas phase conversion of $0.16 \text{ cm}^3 \text{ min}^{-1}$ of 30 wt% glycerol at 1 bar and 623 K for single bed (0.090 g Pt/C; open symbols) and double bed (0.090 g Pt/C, 1.0 g Pt/CeO₂/ZrO₂; closed symbols) systems.

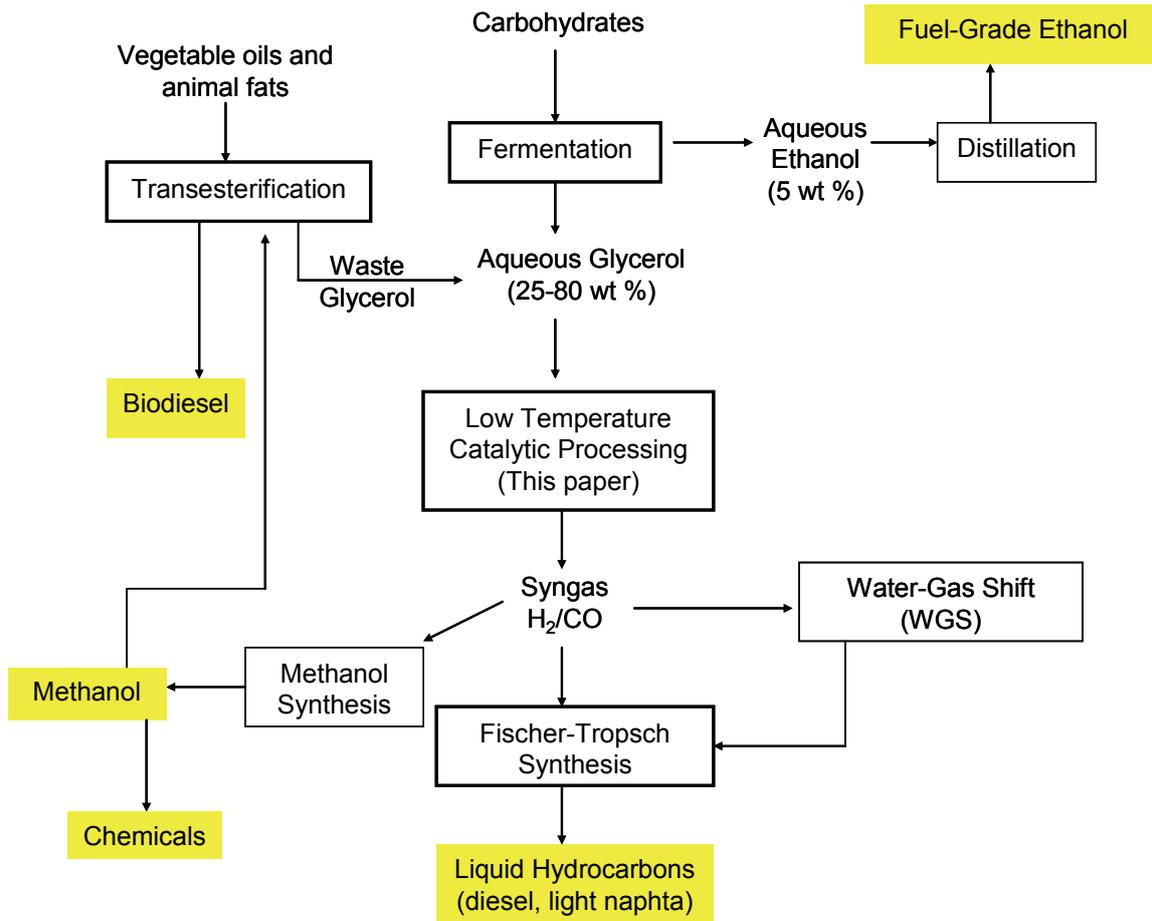


Figure S3. Schematic of liquid fuel and chemical production via catalytic processing of glycerol.