Biofuels

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

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In this era of diminishing petroleum reserves, it is imperative that industrialized society should develop ways to utilize more effectively the abundant and renewable biomass resources available to provide new sources of energy and chemical intermediates.[1] To this end, various processes have been developed to convert biomass and biomass-derived molecules into specialty chemicals (methanol), light alkanes (C_1–C_6), liquid fuels (ethanol and C_7–C_{15} alkanes), and synthesis gas.[2] As a new direction, we show herein that glycerol can be converted over platinum-based catalysts into gas mixtures of H_2 and CO (synthesis gas) at temperatures from 498 to 620 K. These temperatures are lower than those for conventional gasification of biomass (e.g. 800–1000 K).[3,4] Synthesis gas can be used to produce fuels and chemicals; therefore, the endothermic conversion of glycerol into synthesis gas can be combined with exothermic Fischer–Tropsch and methanol syntheses to provide low-temperature and energy-efficient routes for the production of these compounds. The glycerol used can be sourced from waste glycerol streams that are currently generated as by-products from the production of biodiesel. This heat-integrated catalytic process could also be a less energy-intensive alternative to current methods of converting carbohydrates into fuel-grade ethanol.

Synthesis gas production methods for conventional Fischer–Tropsch plants require either an O_2 plant or a large Fischer–Tropsch reactor to process the synthesis-gas stream diluted with N_2 from air, thereby increasing the capital costs of such facilities.[5] Furthermore, Hamelinck et al. showed that nearly 50 % of the cost of producing Fischer–Tropsch liquids from biomass is related to capital cost,[6] of which 50 % stems from biomass gasification, gas cleaning, and synthesis-gas processing. The method we present herein may allow for economic operation of a small-scale Fischer–Tropsch reactor by producing an undiluted H_2/CO gas mixture. Indeed, our method reduces the capital cost of the Fischer–Tropsch plant by eliminating the O_2 plant or biomass gasifier and subsequent gas-cleaning steps.

The conversion of glycerol into CO and H_2 takes place by Equation (1). The endothermic enthalpy change of this

$$C_3O_3H_8 \rightarrow 3\,CO + 4H_2 \tag{1}$$

reaction (350 kJ mol^{-1}) corresponds to about 24 % of the heating value of the glycerol (−1480 kJ mol^{-1}). The heat generated by Fischer–Tropsch conversion of the CO and H_2 to liquid alkanes such as octane (−412 kJ mol^{-1}) corresponds to about 28 % of the heating value of the glycerol. Thus, combining these two reactions results in the following exothermic process, with an enthalpy change (−63 kJ mol^{-1}) that is about 4 % of the heating value of the glycerol:

$$C_3O_3H_8 \rightarrow \frac{7}{25}C_8H_{18} + \frac{19}{25}CO_2 + \frac{37}{25}H_2O \tag{2}$$

One source of glycerol for our catalytic process is the low-value waste stream from the transesterification of plant oils[1,7] and animal fat[1] in the production of biodiesel. This waste contains glycerol in water at high concentrations (e.g. 80 %).[8] The current production levels of biodiesel in the United States and Europe are 1×10^8 and 2×10^9 L year^{-1}, respectively, and are expected to double in the near future.[8,9] Selling waste glycerol solution can lower the production costs of biodiesel by 6 %.[10] The production of methanol from this glycerol is an attractive alternative that could help alleviate the burden of low-value waste glycerol and decrease the production costs of biodiesel by lowering the dependence on natural-gas-derived methanol.

Glycerol can also be produced by fermentation of sugars such as glucose, either directly[11] or as a by-product of the industrial conversion of lignocellulose into ethanol.[12] This form of ethanol production in the U.S. is expected to increase to 30×10^9 L year^{-1} by 2020 (three times the expected increase in ethanol production from corn over the same period);[13] this growing industry may be a major biofuel provider in the future. Technical and economic analyses show that the co-production of glycerol with ethanol lowers production costs and increases profit margins.[11,14–16] The process pathways that generate liquid fuels and chemicals from glycerol are outlined in the Supporting Information.

Although the fermentation of glucose produces ethanol at concentrations of about 5 wt % in water, it can be carried out to produce glycerol at concentrations of at least 25 wt %.[11] This higher concentration of glycerol decreases the energy costs required to remove water from the oxygenated hydrocarbon fuel. Indeed, distillation is one of the most energy-intensive steps involved in the production of fuel-grade ethanol from glucose.[17,18] For example, the energy required to vaporize a 5-wt % aqueous solution of ethanol (as an estimate of the energy of distillation) is 1680 kJ mol^{-1}, which

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corresponds to 1.4 times the lower heating value of the ethanol product ($-1241\,\mathrm{kJ\,mol^{-1}}$). In contrast, the energy required to vaporize a 25-wt % aqueous solution of glycerol ($531\,\mathrm{kJ\,mol^{-1}}$) corresponds to 0.33 times the lower heating value of the liquid-alkane products ($-1418\,\mathrm{kJ\,mol^{-1}}$, assuming octane as the product molecule and utilizing the enthalpy change in Equation (2)). Detailed energy calculations are presented in the Supporting Information.

Figure 1 shows results for the gas-phase conversion of glycerol into synthesis gas over supported Pt catalysts at 623 K and atmospheric pressure with a feed solution of glycerol in water (30 wt %). This concentration is similar to that reported by Gong et al.[11] Moreover, the energy required to separate the glycerol from water is similar to that of vaporizing the solution and condensing the water after the glycerol has reacted. Catalysts consisting of Pt supported on Al_2O_3, ZrO_2, CeO_2/ZrO_2, and MgO/ZrO_2 exhibited deactivation during time-on-stream, whereas the Pt/C catalyst showed stable conversion of glycerol into synthesis gas for at least 30 h (Figure 1 a). The catalyst with the most acidic support, Pt/Al_2O_3, showed a period of apparently stable catalytic activity, followed by a period of rapid catalyst deactivation. Because the reactor initially operates at 100 % conversion, glycerol is present only in the upstream portion of the catalyst bed in the tubular reactor, and a deactivation front moves from the reactor inlet to the outlet as olefinic species are formed from glycerol on acid sites associated with alumina, followed by deposition of coke from these species on the Pt surface sites. The most basic catalyst support, MgO/ZrO_2, showed rapid deactivation for all times-on-stream. The most stable oxide-supported catalyst appears to be Pt on CeO_2/ZrO_2; however, the performance of this catalyst is inferior to that of Pt supported on carbon.

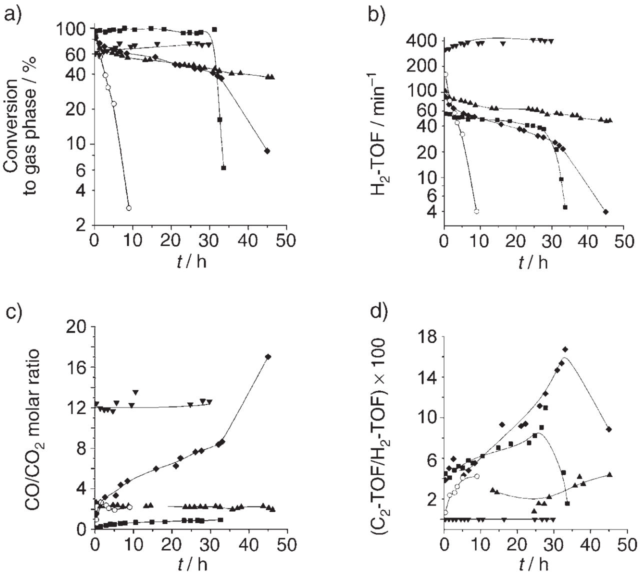

Figure 1. Performance of supported Pt catalysts. Variation with time-on-stream of a) percentage glycerol conversion to gas-phase products, b) H_2-turnover frequency, c) CO/CO_2 molar ratio, and d) C_2-TOF/H_2-TOF ratio for Pt catalysts supported on Al_2O_3 (■), CeO_2/ZrO_2 (▲), C (▼), ZrO_2 (◆), and MgO/ZrO_2 (○). Percentage conversion to gas phase is calculated as [(C atoms in gas-phase product stream)/(total C atoms into reactor as feed)]×100. Reactions were carried out at 1 bar and 623 K with aqueous glycerol feed solution (30 wt %) over oxide-supported Pt catalysts (1.0 g) or Pt/C catalyst (0.060 g) and a feed rate of $0.32\,\mathrm{cm^3\,min^{-1}}$. See Supporting Information for further experimental details.

The different deactivation profiles displayed in Figure 1 for the various catalysts suggest that the support plays an important role in the deactivation process. Figure 1 d shows the rate of formation of C_2-hydrocarbons (ethane and ethylene) normalized to the rate of H_2 production for the various supported Pt catalysts. Negligible amounts of C_2-hydrocarbons were formed on the Pt/C catalyst. In contrast, catalysts consisting of Pt supported on the various oxides formed measurable amounts of C_2-hydrocarbons, and the C_2-TOF/H_2-TOF ratio (TOF = turnover frequency) increased with time-on-stream. This behavior suggests that one of the modes of catalyst deactivation is caused by dehydration on the oxide catalyst supports, which leads to the formation of unsaturated hydrocarbon species that form carbonaceous deposits on the Pt surface, thereby decreasing the rate of H_2 production and increasing the C_2-TOF/H_2-TOF ratio.

Table 1: Experimental data for catalytic processing of glycerol into synthesis gas under various conditions.

Conditions		Conversion into gas phase [%]	H_2-TOF [min^{-1}]	H_2/CO	CO/CO_2	CH_4/H_2
Feed flow rate [cm^3 min^{-1}][a]	0.08	68	111	1.6	5.7	0.038
	0.16	71	241	1.4	8.8	0.036
	0.32	64	373	1.3	12	0.045
	0.64	39	449	1.3	17	0.038
Glycerol concentration [wt %][b]	20	64	265	1.4	8.7	0.025
	30[c]	50	285	1.3	14	0.032
	50	26	267	1.2	37	0.050
T [K][d]	573	17	104	1.31	90	0.037
	623	54	335	1.31	17	0.027
	673	100	600	1.33	11	0.027
	673[e]	72	450	1.38	–	–
	723	61	419	1.68	4.6	0.019
	723[e]	43	300	1.83	–	–

For these studies of reaction kinetics, 0.060 g of 5 wt % Pt/C was used. [a] Glycerol feed 30 wt %, 623 K, 1 bar. [b] Feed flow rate $0.32\,\mathrm{cm^3\,min^{-1}}$, 623 K, 1 bar. [c] Point taken after 2 h time-on-stream. [d] Glycerol feed 30 wt %, $0.32\,\mathrm{cm^3\,min^{-1}}$, 1 bar. [e] Point taken after 3 h time-on-stream.

The H_2/CO ratio for the product stream from the Pt/C catalyst is approximately 1.3:1 (Table 1), which is in agreement with the stoichiometry of Equation (1). In contrast, the H_2/CO ratios obtained over the other catalysts were higher than 1.5:1, which indicates some contribution from water–gas shift (WGS). This behavior is demonstrated more clearly by the CO/CO_2 ratio (Figure 1 c). The initial CO/CO_2 ratio for Pt/C is 12:1, whereas for the other catalysts it is less than 3:1. Thus, it appears that the WGS reaction is facilitated by the presence of the oxide support, as reported in other studies of WGS over supported metal catalysts.[19–21]

Reaction conditions (Table 1) that result in lower conversions of glycerol (i.e. higher flow rates of the glycerol feed (30 wt%) and higher glycerol concentrations at constant feed flow rate) lead to higher CO/CO_2 ratios. This behavior suggests that the primary reaction in glycerol conversion is the formation of CO and H_2, and the production of CO_2 by WGS is a secondary reaction. Therefore, water acts primarily as a diluent in the production of synthesis gas from glycerol, thus leading to higher conversions (Table 1). The important consequence of this behavior is that it is possible to adjust the space velocity of the catalytic process to ensure that the conversion of glycerol is complete, while simultaneously controlling the H_2/CO ratio for the Fischer–Tropsch synthesis step. We note that the rate of methane formation remained low for all of the conditions in Table 1.

The results in Table 1 show that the rate of H_2 production passes through a maximum with respect to reaction temperature at constant-feed conditions. The rate increases with increasing temperature from 573 to 623 K (with an activation energy of about 70 $kJ\,mol^{-1}$). However, although the rate of hydrogen production increases further when the temperature is initially increased to 673 K, the Pt/C catalyst eventually undergoes deactivation at this higher temperature. We suggest that at high temperatures, dehydration is fast relative to H_2 formation, thus leading to catalyst deactivation.

Figure 2 a and b show the performance of the Pt/C catalyst under different pressures (1 and 20 bar) for the 30-wt% glycerol feed, and at different glycerol feed concentrations (30 and 50 wt%) at a pressure of 1 bar. The catalyst showed good stability for at least 48 h time-on-stream for both the higher glycerol feed concentration (50 wt%) and the higher reaction pressure (20 bar). It also showed excellent stability for converting a 30-wt% glycerol feed into synthesis gas at 20 bar, with a H_2/CO ratio ($\approx$2:1) that is appropriate for Fischer–Tropsch[22] or methanol synthesis.[23]

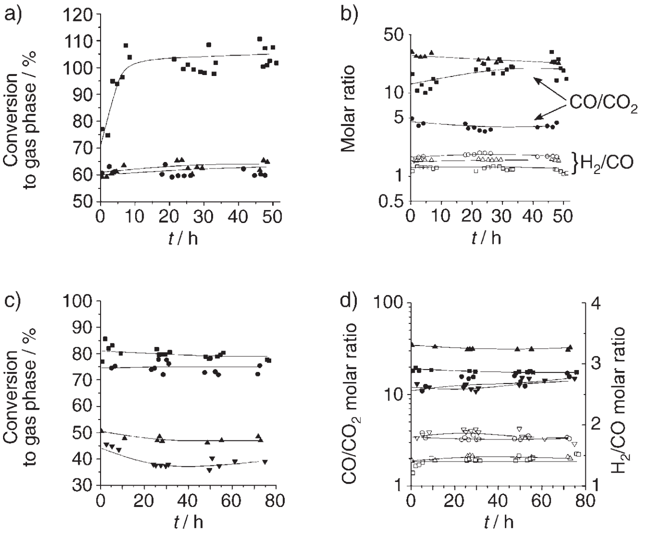

Figure 2. Performance of carbon-supported Pt and Pt-bimetallic catalysts under various process conditions. Variation with time-on-stream of a) percentage glycerol conversion to gas-phase products and b) molar ratios for conversion of 30 wt% glycerol at 1 bar (■), 50 wt% at 1 bar (▲), and 30 wt% at 20 bar (●) over 0.090 g Pt/C at 623 K. Variation with time-on-stream of c) percentage glycerol conversion to gas-phase products and d) CO/CO_2 (filled symbols) and H_2/CO (empty symbols) molar ratios for conversion of 30 wt% glycerol at 1 bar over Pt–Ru/C at 548 K (triangles; 0.435 g catalyst) and 573 K (squares; 0.513 g catalyst) and over Pt–Re/C at 498 K (inverted triangles; 0.535 g catalyst) and 523 K (circles; 0.535 g catalyst). A feed rate of 0.16 $cm^3\,min^{-1}$ for a) and b) and 0.08 $cm^3\,min^{-1}$ for c) and d) was used.

To allow the efficient combination of the endothermic conversion of glycerol into synthesis gas with the exothermic Fischer–Tropsch or methanol-synthesis steps, the former should be performed at the lowest-possible temperature. In doing so, flexibility in the Fischer–Tropsch materials used (e.g, Co-based versus Fe-based catalysts) becomes possible. Therefore, we carried out studies of glycerol conversion into synthesis gas at 498–573 K. The catalytic conversion of polyols to H_2, CO_2, and CO involves the preferential cleavage of C–C bonds as opposed to C–O bonds,[24,25] and Pt-based catalysts are particularly active and selective for this process. Under these reaction conditions, the surface is covered primarily by adsorbed CO species;[26] therefore, a strategy for a catalyst that converts polyols into synthesis gas and is active at low temperatures is to facilitate the desorption of CO, thereby suppressing the subsequent WGS step and improving the turnover of the catalytic cycle by regenerating vacant surface sites. Accordingly, we require materials that possess the catalytic properties of Pt with respect to selective cleavage of C–C versus C–O bonds, but that have less exothermic enthalpy changes for CO adsorption; Pt–Ru and Pt–Re alloy catalysts fit this description.[27,28]

Figure 2 c and d show that the percentage conversion of glycerol and the product-gas ratios remained constant for at least 72 h time-on-stream at these low temperatures over Pt–Ru and Pt–Re (atomic ratio 1:1) bimetallic catalysts. The overall carbon balances for these runs came to within 10%. The main condensable organic compound in the effluent streams of the catalysts was unconverted glycerol, with smaller amounts of ethylene glycol, methanol, hydroxypropanone, and ethanol. These results demonstrate that the conversion of glycerol to synthesis gas can, in fact, be accomplished at temperatures well within the ranges employed for Fischer–Tropsch and methanol syntheses,[22,23,29] thus allowing for the efficient combination of these processes. Moreover, the H_2/CO ratio can be adjusted by adding a WGS functionality (see Supporting Information).

We have presented a low-temperature catalytic route for converting glycerol into H_2/CO gas mixtures that are suitable for combination with Fischer–Tropsch and methanol syntheses. This new route opens new opportunities for use with processes that produce polyols, such as glycerol through fermentation of carbohydrate feedstocks, at high concentrations in water.

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