

# Electronic Supplementary Material

## Thermodynamic analysis of steam reforming of glycerol for hydrogen production at atmospheric pressure

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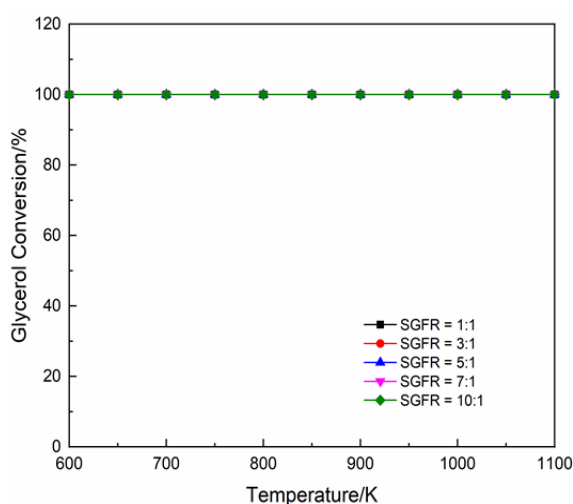
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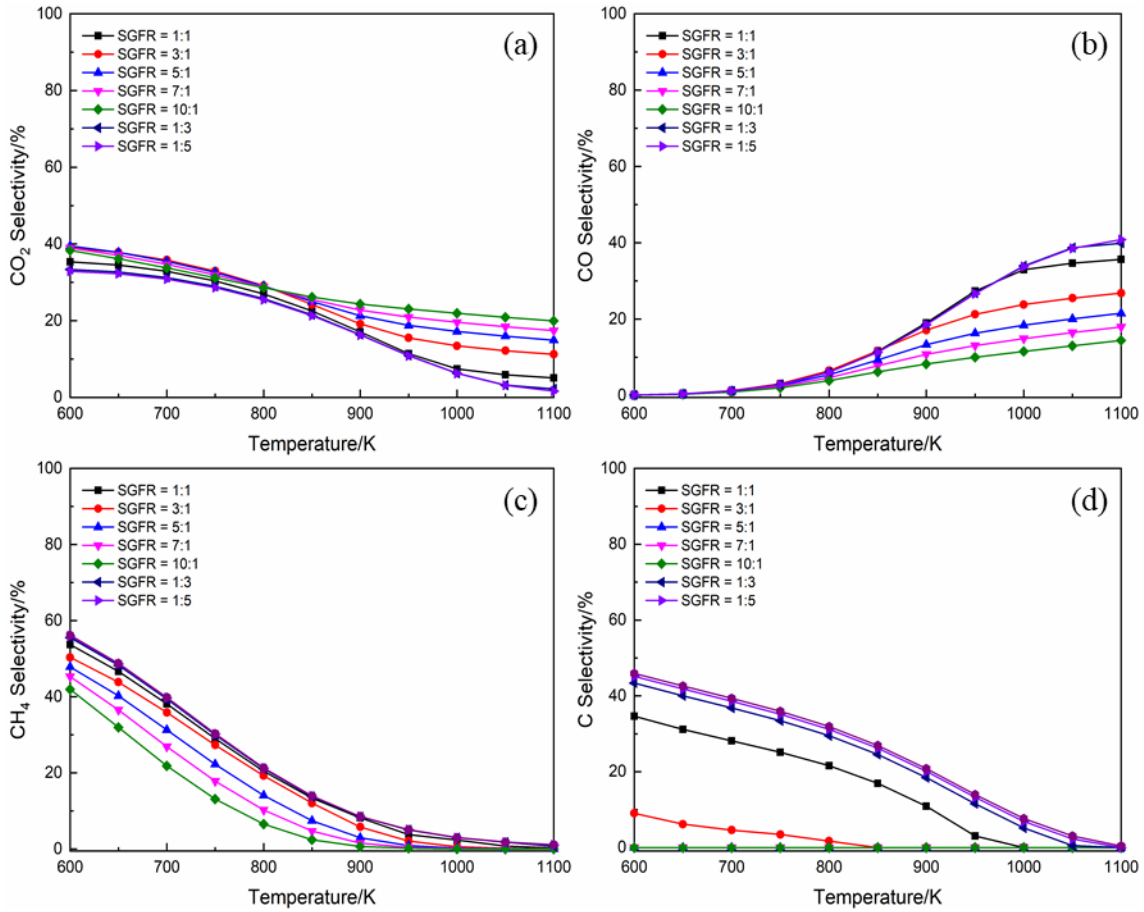
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**Table S1** Summary of possible reactions and associated Gibbs free energy in SRG

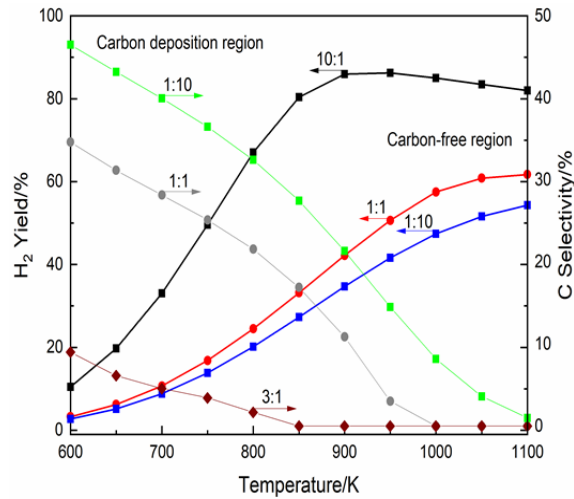
Eq. No.	Reaction	Reaction	$\Delta G_{298}/\text{KJ}\cdot\text{mol}^{-1}$
S1	Steam reforming of glycerol	$\text{C}_3\text{H}_8\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 3 \text{CO}_2 + 7 \text{H}_2$	-48.8
S2	Steam reforming of methane	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2$	141.9
S3	Decomposition of glycerol	$\text{C}_3\text{H}_8\text{O}_3 \rightarrow 3 \text{CO} + 4 \text{H}_2$	37.1
S4	Water gas shift reaction	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	-28.6
S5a	Methanation 1	$\text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$	-141.9
S5b	Methanation 2	$\text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-113.2
S6	Methane dry reforming	$\text{CO}_2 + \text{CH}_4 \leftrightarrow 2 \text{CO} + 2\text{H}_2$	170.5
S7	Methane decomposition	$\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}$	50.5
S8	Boudouard reaction	$2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$	-120.0
S9	CO reduction	$\text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C}$	-91.4
S10	CO <sub>2</sub> reduction	$\text{CO}_2 + 2 \text{H}_2 \leftrightarrow 2 \text{H}_2\text{O} + \text{C}$	-62.8



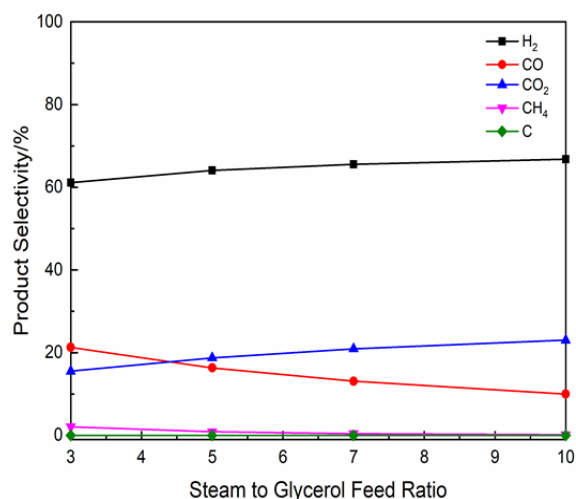
**Fig. S1** Equilibrium conversion of glycerol in SRG as a function of the process temperature.



**Fig. S2** Thermodynamic equilibrium analysis of SRG at atmospheric pressure: Effect of temperature and SGFR on (a) selectivity to  $\text{CO}_2$  (b) selectivity to  $\text{CO}$  (c) selectivity to  $\text{CH}_4$  (d) selectivity to carbon (C).

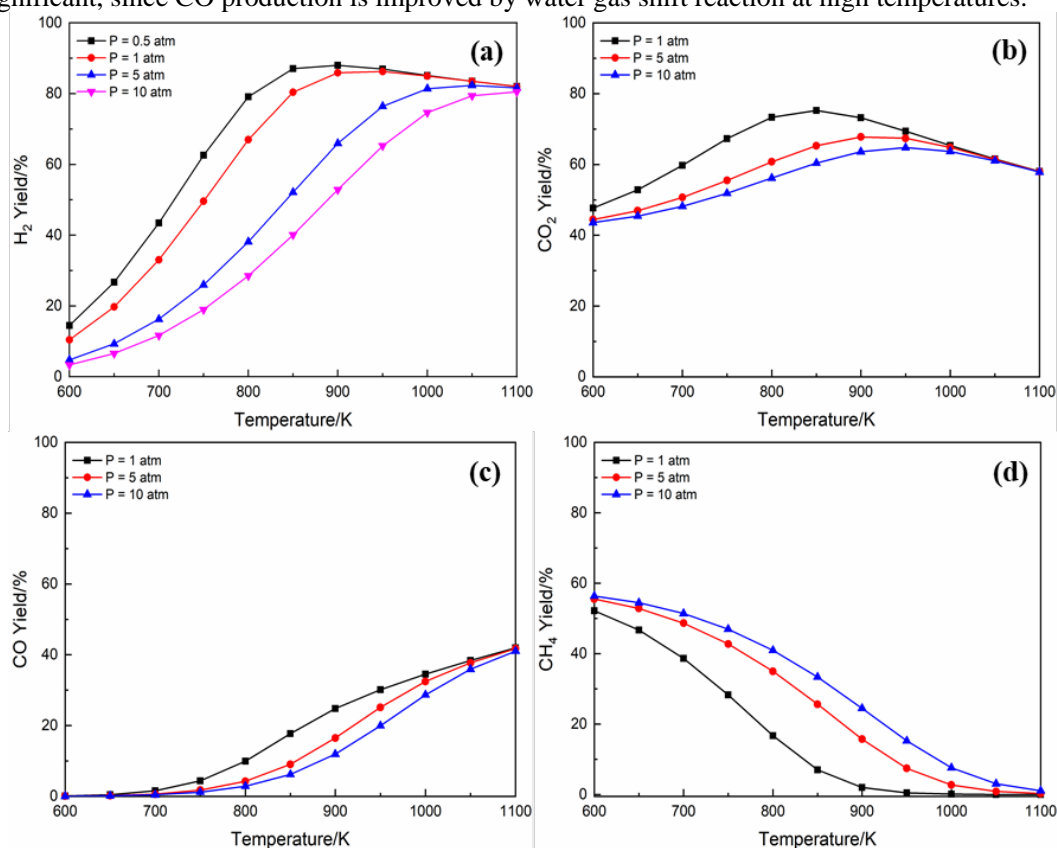


**Fig. S3** Thermodynamic equilibrium analysis of SRG at atmospheric pressure:  $\text{H}_2$  yield and carbon deposition as a function of SGFR and temperature.



**Fig. S4** Effect of SGFR on selectivity to H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and carbon (C) at 950 K and atmospheric pressure.

Fig. S5 shows the effect of pressure variation on equilibrium CO, CO<sub>2</sub> and CH<sub>4</sub> in comparison to H<sub>2</sub> production from SRG at different temperatures. As shown in Fig. S5d, it can be deduced that the yield of methane increases when the pressure of the system increases towards a lower temperature. This can be due to the exothermic nature of methanation reactions (Eq. S5a and S5b), which are favoured at low temperatures. With an increase of the system pressure, the equilibrium of reactions shifts to the product formation, thereby increasing the formation of CH<sub>4</sub> in the system. On the other hand, Figs. S5b and S5c illustrate the formation of CO and CO<sub>2</sub> at different pressures under investigation. It has been observed that a low pressure is beneficial to CO<sub>2</sub> formation. However, at high temperatures, the effect of system pressure is insignificant, since CO production is improved by water gas shift reaction at high temperatures.



**Fig. S5** Effect of pressure variation on (a) H<sub>2</sub> yield (b) CO yield (c) CO<sub>2</sub> yield (d) CH<sub>4</sub> yield at different temperatures (SGFR = 10:1).