

Supporting Information to

Aqueous phase reforming of glycerol over Re-promoted Pt and Rh catalysts

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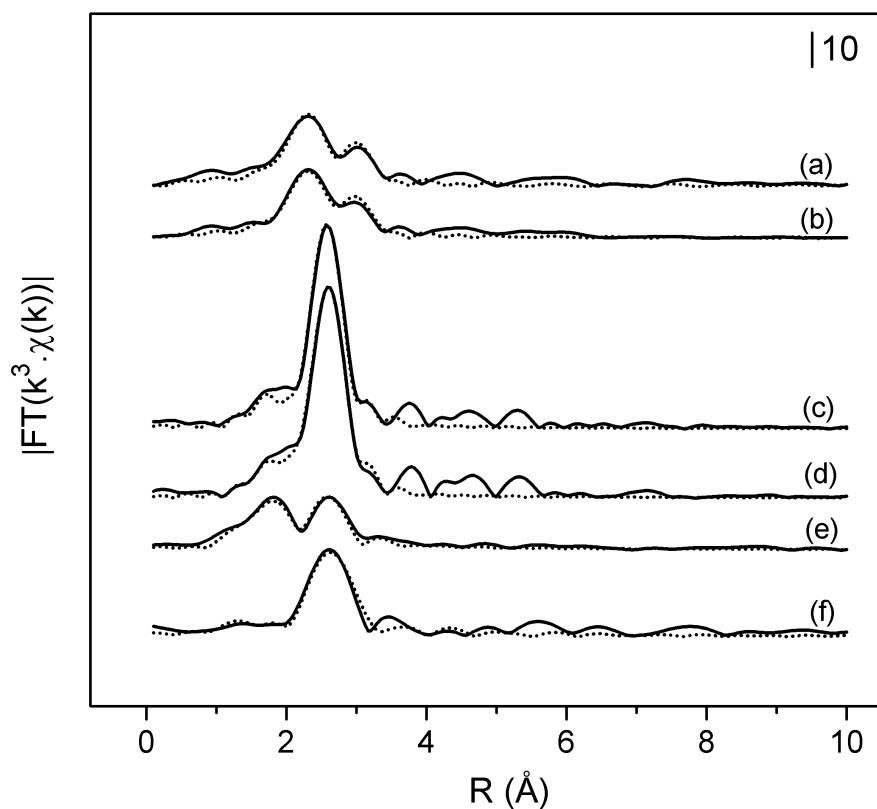
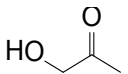
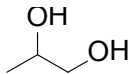
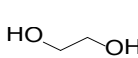


Figure S1 – FT EXAFS functions obtained from the  $k^3$ -weighted Pt  $L_{III}$  edge EXAFS oscillations of Pt/C (a), and PtRe/C (b) during WGS at 300 °C; FT EXAFS functions obtained from the  $k^3$ -weighted Rh K edge EXAFS oscillations of Rh/C (c), and RhRe/C (d) during WGS at 300 °C; FT EXAFS functions obtained from the  $k^3$ -weighted Re  $L_{III}$  edge EXAFS oscillations of RhRe/C (e), and PtRe/C (f) during WGS at 300 °C. Dotted lines represent the fitted spectra.

Table S1 – Product selectivities in APR of glycerol for Pt/C, PtRe/C, Rh/C, RhRe/C and Re/C catalysts after 20 min of reaction.

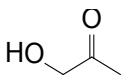
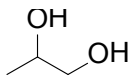
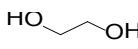
	Conversion	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>				Alcohols <sup>1</sup>	Acids <sup>2</sup>	others <sup>3</sup>
Pt/C	0.3	7.9	-	-	-	92.1	-	-	-	-	-
PtRe/C	0.3	19.4	-	3.1	-	55.8	11.3	-	5.9	4.6	-
Rh/C	0.4	62.5	3.6	7.2	3.3	18.5	1.1	1.1	0.9	-	1.9
RhRe/C	0.4	19.0	2.4	-	-	63.0	4.3	2.5	0.9	2.4	5.5
Re/C	0.1	13.2	-	-	-	86.7	-	-	-	-	0.1

<sup>1</sup>alcohols: methanol, ethanol, 1-propanol, 2-propanol

<sup>2</sup>acids: acetic acid, propanoic acid

<sup>3</sup>others: CO, propionaldehyde, 1,3-propanediol

Table S2 – Product selectivities in APR of glycerol for Pt/C, PtRe/C, Rh/C, RhRe/C and Re/C catalysts after 80 min of reaction.

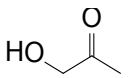
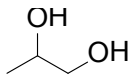
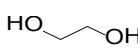
	Conversion	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>				Alcohols <sup>1</sup>	Acids <sup>2</sup>	others <sup>3</sup>
Pt/C	1.7	33.6	3.8	2.0	0.4	42.1	14.1	3.9	-	-	0.1
PtRe/C	2.7	39.9	3.9	5.7	3.3	16.8	24.2	3.5	1.9	0.8	-
Rh/C	0.7	43.2	6.2	3.4	0.7	36.5	3.0	1.0	-	0.8	5.2
RhRe/C	3.8	31.0	3.8	5.8	2.3	26.3	23.6	3.6	0.9	0.7	2.0
Re/C	0.2	11.6	-	-	-	88.2	-	-	-	-	0.2

<sup>1</sup>alcohols: methanol, ethanol, 1-propanol, 2-propanol

<sup>2</sup>acids: acetic acid, propanoic acid

<sup>3</sup>others: CO, propionaldehyde, 1,3-propanediol

Table S3– Product selectivities in APR of glycerol for Pt/C, PtRe/C, Rh/C, RhRe/C and Re/C catalysts after 140 min of reaction.

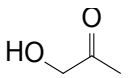
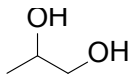
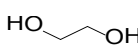
	Conversion	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>				Alcohols <sup>1</sup>	Acids <sup>2</sup>	others <sup>3</sup>
Pt/C	4.0	44.8	7.1	3.4	0.5	16.4	24.6	3.0	-	-	0.2
PtRe/C	8.3	47.1	5.5	10.1	3.2	5.7	22.1	2.8	2.3	0.7	0.5
Rh/C	1.2	40.0	8.2	3.7	0.4	39.2	3.9	0.9	0.3	0.4	3.0
RhRe/C	10.8	42.1	7.1	11.0	4.4	8.6	21.6	2.7	0.9	0.4	1.2
Re/C	0.4	11.1	-	-	-	79.6	9.3	-	-	-	-

<sup>1</sup>alcohols: methanol, ethanol, 1-propanol, 2-propanol

<sup>2</sup>acids: acetic acid, propanoic acid

<sup>3</sup>others: CO, propionaldehyde, 1,3-propanediol

Table S4 – Product selectivities in APR of glycerol for Pt/C, PtRe/C, Rh/C, RhRe/C and Re/C catalysts after 200 min of reaction.

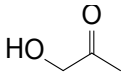
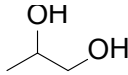
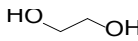
	Conversion	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>				Alcohols <sup>1</sup>	Acids <sup>2</sup>	others <sup>3</sup>
Pt/C	6.6	46.7	8.3	4.2	0.7	14.0	23.1	1.7	1.4	-	-
PtRe/C	12.2	47.8	6.1	11.8	4.1	4.1	18.1	2.3	4.3	0.9	0.5
Rh/C	1.5	49.0	12.4	5.3	0.5	24.4	3.2	0.7	0.5	0.4	3.6
RhRe/C	15.9	43.5	8.2	14.0	5.3	7.0	17.5	1.9	1.2	0.7	0.7
Re/C	0.6	10.2	-	-	-	78.3	11.5	-	-	-	-

<sup>1</sup>alcohols: methanol, ethanol, 1-propanol, 2-propanol

<sup>2</sup>acids: acetic acid, propanoic acid

<sup>3</sup>others: CO, propionaldehyde, 1,3-propanediol

Table S5 – Product selectivities in APR of glycerol for Pt/C, PtRe/C, Rh/C, RhRe/C and Re/C catalysts after 260 min of reaction.

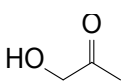
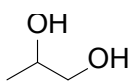
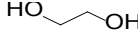
Conversion	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>				Alcohols <sup>1</sup>	Acids <sup>2</sup>	others <sup>3</sup>	
Pt/C	8.5	47.2	9.2	5.4	0.8	11.1	23.1	1.8	1.4	-	-
PtRe/C	16.4	49.3	6.8	14.1	5.3	2.7	14.7	1.9	4.0	0.8	0.4
Rh/C	1.6	51.8	13.7	6.3	0.5	20.5	3.1	0.8	0.2	0.3	2.8
RhRe/C	21.6	43.4	8.5	15.8	5.9	3.4	18.9	2.3	0.6	0.4	0.8
Re/C	0.7	11.2	-	-	-	71.5	17.4	-	-	-	-

<sup>1</sup>alcohols: methanol, ethanol, 1-propanol, 2-propanol

<sup>2</sup>acids: acetic acid, propanoic acid

<sup>3</sup>others: CO, propionaldehyde, 1,3-propanediol

Table S6 – Product selectivities in APR of glycerol for Pt/C, PtRe/C, Rh/C, RhRe/C and Re/C catalysts after 320 min of reaction.

	Conversion	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>				Alcohols <sup>1</sup>	Acids <sup>2</sup>	others <sup>3</sup>
Pt/C	9.0	47.7	9.3	6.2	0.9	8.9	23.5	1.7	1.4	0	0.4
PtRe/C	21.1	46.8	6.5	14.9	6.1	1.9	18.0	2.9	1.4	0.5	0.2
Rh/C	2.1	46.3	13.3	6.2	0.4	25.2	4.0	0.7	0.5	0.4	3.0
RhRe/C	24.0	44.2	8.6	17.3	6.3	2.7	17.0	2.0	0.7	0.4	0.8
Re/C	0.8	10.7	-	-	-	75.3	14.0	-	-	-	-

<sup>1</sup>alcohols: methanol, ethanol, 1-propanol, 2-propanol

<sup>2</sup>acids: acetic acid, propanoic acid

<sup>3</sup>others: CO, propionaldehyde, 1,3-propanediol





Table S7 – Turnover frequencies calculated from reaction rates of glycerol APR, WGS and acetaldehyde decomposition over Pt/C, PtRe/C, Rh/C and RhRe/C taking into account metal dispersions estimated from TEM analysis. The promotional effects of Re on Pt and Rh for each of the reactions are determined by dividing the rates obtained with the bimetallic catalysts to those over their monometallic counterparts.

Catalyst	APR (mol glycerol converted/mol <sub>Pt(Rh)</sub> .h)	WGS (mol CO converted/mol <sub>Pt(Rh)</sub> .h)	Acetaldehyde decomposition (mol CO produced/mol <sub>Pt(Rh)</sub> .h)	Promotional effect of Re (Rate <sub>Pt(Rh)Re</sub> /Rate <sub>Pt(Rh)</sub> )		
				APR	WGS	Acetaldehyde
Pt/C	124	1.5	301	2.2	5.1	1.8
PtRe/C	270	7.5	528			
Rh/C	17	0.9	542	11.7	64.3	1.4
RhRe/C	197	58	731			