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Rhenium-promoted Pt/WO3/ZrO2: An efficient catalyst for aqueous glycerol hydrogenolysis under reduced H2 pressure

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1. Glycrerol hydrogenolysis with extended reaction times

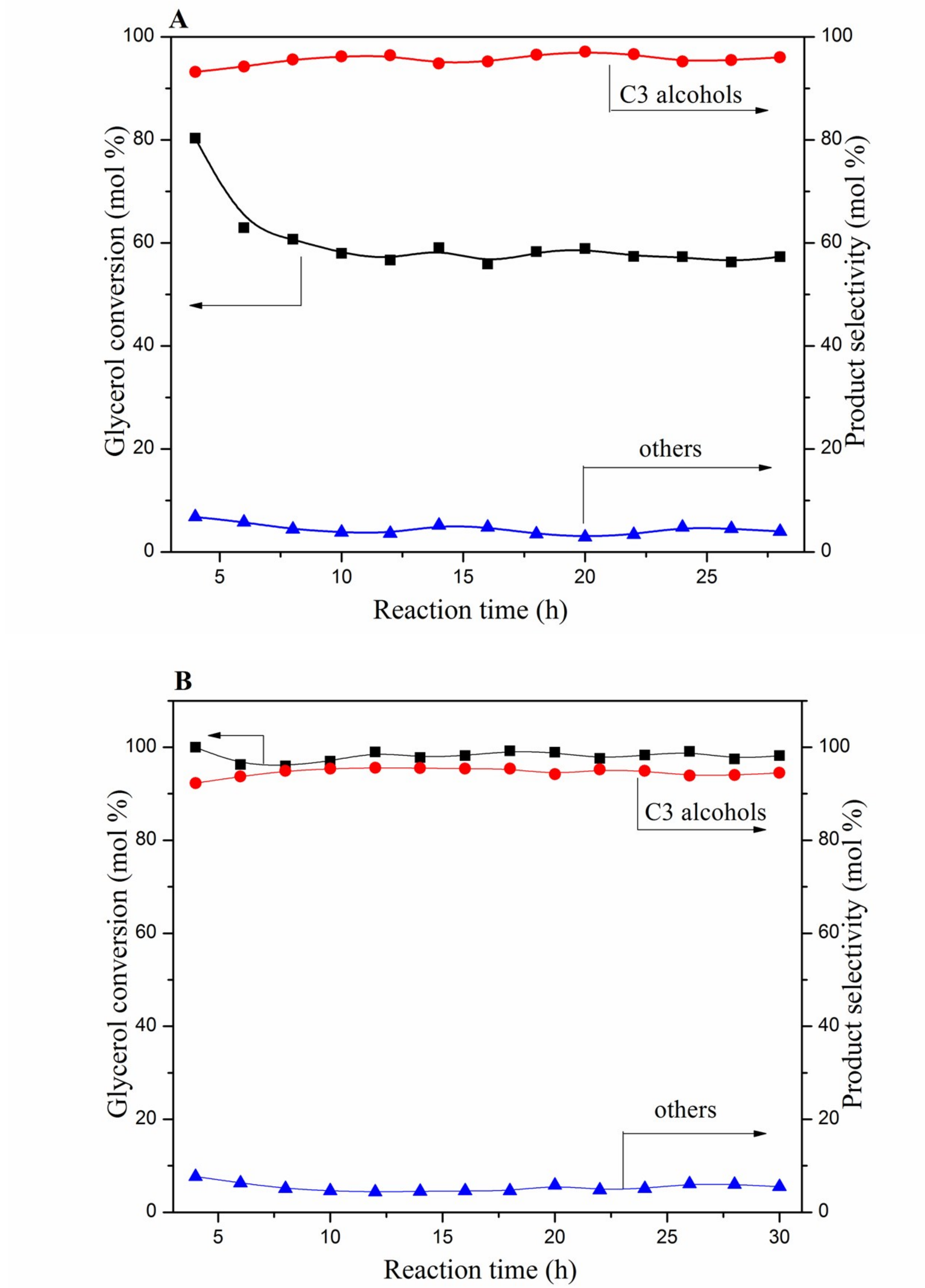

Figure S1 Catalytic perfomance of (A) 2%Pt/WO_3/ZrO_2, (B) 2%Pt-0.8%Re/WO_3/ZrO_2 catalysts.

2. TEM images of the catalysts

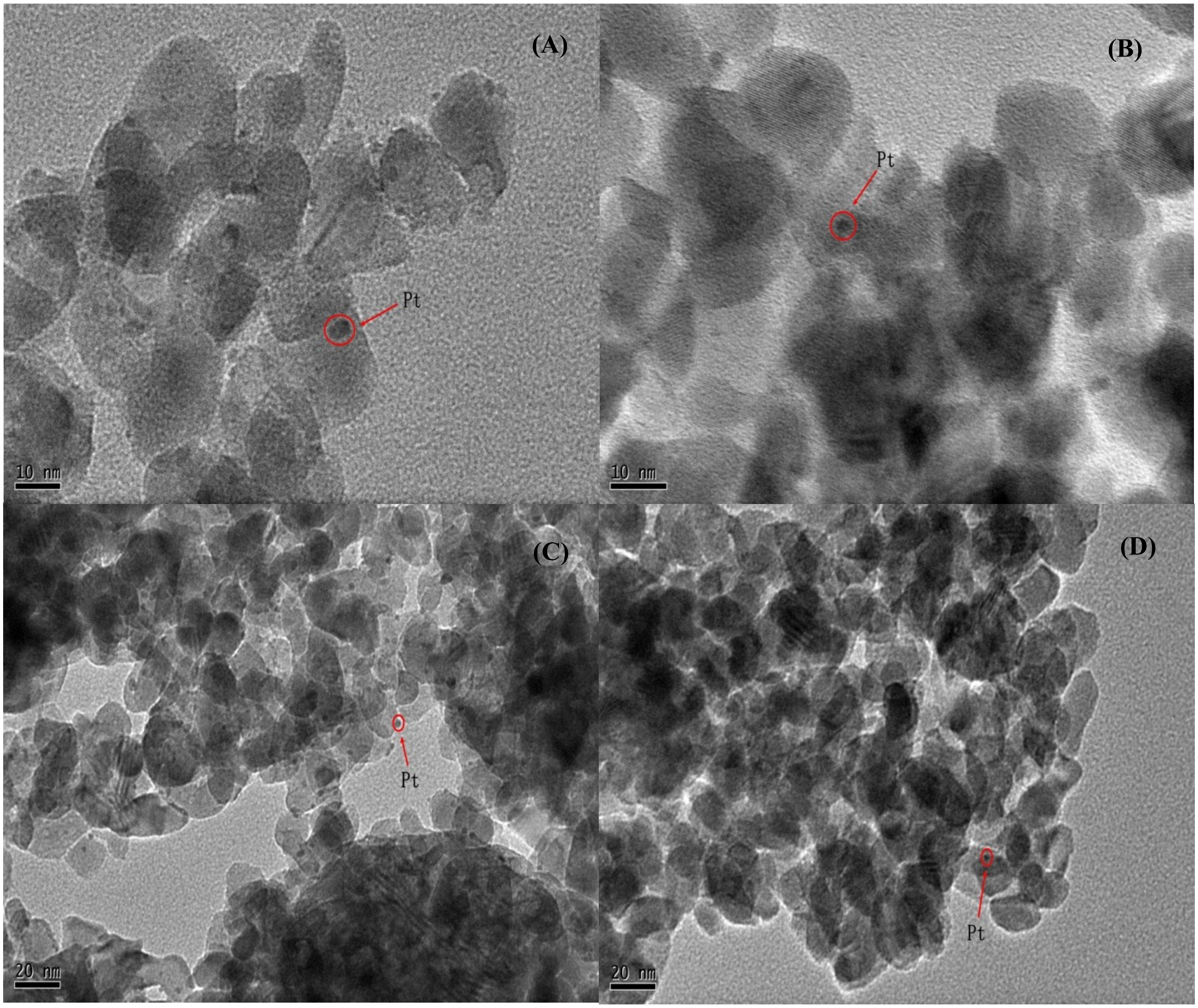

Figure S2 TEM images of (A) 2 %Pt/WO_3/ZrO_2 (10 nm), (B) 2 % Pt-0.8 %Re/WO_3/ZrO_2 (10 nm), (C) 2 % Pt/WO_3/ZrO_2 (20 nm) , (D) 2 % Pt-0.8 % Re/WO_3/ZrO_2 (20 nm) catalysts.

3. The catalytic performance comparison of glycrerol hydrogenolysis between 2Pt/WO_3/ZrO_2 and 1.5Pt-0.8Re/WO_3/ZrO_2 catalysts (Figure 1 in text)

Table S1 Catalytic performance of glycerol hydrogenolysis over 2% $Pt/WO_3/ZrO_2$ and 1.5 % Pt-0.8 % Re $/WO_3/ZrO_2$ catalysts[a]

Entry	Gl.Conv.[b] (mol%)	C3 alcohols selectivity (mol%)					Others selectivity[c] (mol%)
		1,3-PDO	1,2-PDO	1-PO	2-PO	Total	
1[d]	57.7	28.9	14.6	46.9	6.4	96.8	3.2
2[e]	68.2	25.9	27.3	34.4	6.8	95.7	4.3

[a] Data after 14 h reaction; reaction conditions：2g catalysts, 10 wt.% glycerol aqueous solution, H_2 pressure=2.5 MPa，reaction temperature=175 ^oC, WHSV=0.12 h^{-1}; [b] glycerol conversion; [c] others: acetone, propionate acid and ethylene glycerol; [d] 2 % $Pt/WO_3/ZrO_2$ catalyst; [e] 1.5 % Pt-0.8 % $Re/WO_3/ZrO_2$ catalyst.

4. Catalytic performance of glycrerol hydrogenolysis over 2Pt-Re/WO_3/ZrO_2 catalysts (Figures 2-3 in text)

Table S2 Catalytic performance of glycerol hydrogenolysis over 2 % Pt-Re/WO_3/ZrO_2 catalysts [a]

Entry	xRe (wt. %)	Gl.Conv.[b] (mol%)	C3 alcohols selectivity (mol%)					Others selectivity[c] (mol%)
			1,3-PDO	1,2-PDO	1-PO	2-PO	Total	
1	0	57.7	28.9	14.6	46.9	6.4	96.8	3.2
2	0.10	99.9	16.5	8.4	60.4	10.4	95.7	4.3
3	0.36	99.7	18.8	12.1	53.3	10.8	95.0	5.0
4	0.80	99.0	20.4	13.4	51.3	10.5	95.6	4.4
5	1.00	69.9	15.9	14.8	54.6	9.4	94.7	5.3
6	2.00	67.3	9.4	33.7	39.4	12.6	95.1	4.9
7[d]	2.00	11.6	0.6	84.6	3.3	2.3	93.7	6.3

[a] Data after 14 h reaction; reaction conditions：2g catalysts, 10 wt.% glycerol aqueous solution, H_2 pressure=2.5 MPa，reaction temperature=175 ^oC, WHSV=0.12 h^{-1}; [b] glycerol conversion;[c] others: acetone, propionate acid and ethylene glycerol; [d] 2 % $Re/WO_3/ZrO_2$ catalyst.

5. Catalytic performance of glycerol hydrogenolysis over 2Pt-0.8Re/WO_3/ZrO_2 catalysts under different reaction temperatures (Figure 4 in text)

Table S3 Catalytic performance of glycerol hydrogenolysis over 2 % Pt-0.8 % Re/WO_3/ZrO_2 catalysts under different reaction temperature [a]

Entry	t (°C)[b]	Gl.Conv.[c] (mol%)	C3 alcohols selectivity (mol%)					Others selectivity [d] (mol%)
			1,3-PDO	1,2-PDO	1-PO	2-PO	Total	
1	135	6.4	40.4	21.0	25.2	6.2	92.9	7.1
2	155	30.5	37.9	9.2	42.6	7.6	97.3	2.7
3	165	45.7	29.8	9.6	49.4	8.3	97.2	2.8
4	170	56.2	26.2	12.9	47.3	8.9	95.3	4.7
5	175	99.0	20.4	13.4	51.3	10.5	95.6	4.4

[a] Data after 14 h reaction; reaction conditions：2g catalysts, 10 wt.% glycerol aqueous solution, H_2 pressure=2.5 MPa, WHSV=0.12 h^{-1}; [b] reaction temperature; [c] glycerol conversion; [d] others: acetone, propionate acid and ethylene glycerol.

6. Catalytic performance of glycerol hydrogenolysis over 2Pt-0.8Re/WO_3/ZrO_2 catalysts under different H_2 pressure (Figure 5 in text)

Table S4 Catalytic performance of glycerol hydrogenolysis over 2 % Pt-0.8 % Re/WO_3/ZrO_2 catalysts under different H_2 pressure [a]

Entry	P.[b]	Gl.Conv.[c] (mol%)	C3 compounds selectivity (mol%)						Others selectivity [d] (mol%)
			1,3-PDO	1,2-PDO	1-PO	2-PO	acetol	Total	
1	0.1[e]	96.8	1.8	13.7	13.4	3.2	63.1	95.2	4.8
2	0.5	99.7	19.1	28.6	24.4	7.1	12.8	92.0	8.0
3	1.0	94.8	15.8	31.7	37.4	7.8	2.6	95.4	4.6
4	1.5	99.1	20.4	32.3	35.4	6.3	1.8	96.3	3.7
5	2.0	99.6	20.8	27.8	40.0	5.9	0.7	95.3	4.7
6	2.5	99.0	20.4	13.4	51.3	10.5	/	95.6	4.4

[a] Data after 14 h reaction; reaction conditions：2g catalysts, 10 wt.% glycerol aqueous solution, reaction temperature=175 °C, WHSV=0.12 h^{-1}; [b] H_2 pressure; [c] glycerol conversion; [d] others: acetone, propionate acid and ethylene glycerol. [e] Atmospheric pressure.

7. Catalytic performance of glycerol hydrogenolysis over $2Pt/WO_3/ZrO_2$ and 2Pt-0.8Re/WO_3/ZrO_2 catalysts under N_2 atmosphere (Figure 6 in text)

Table S5 Catalytic performance of glycerol hydrogenolysis over 2 % Pt/WO_3/ZrO_2 and 2 % Pt-0.8 % Re/WO_3/ZrO_2 catalysts under N_2 atomsphere [a]

Entry	catalysts	Gl. Conv.[b] (mol%)	C3 compounds selectivity (mol%)							Others selectivity (mol%)[c]
			1,3-PDO	1,2-PDO	1-PO	2-PO	actone	acetol	Total	
1	2Pt/WO_3/ZrO_2	19.6	/	35.1	4.7	13.6	10.7	26.4	90.5	9.5
2	2Pt-0.8Re/WO_3/ZrO_2	18.9	1.4	21.4	10.3	12.2	27.9	17.8	91.0	9.0

[a] Data after 14 h reaction; reaction conditions：2g catalysts, 10 wt.% glycerol aqueous solution, reaction temperature = 175 ^oC, N_2 pressure=2.5 MPa, WHSV=0.12 h^{-1}; [b] glycerol conversion; [c] others: propionate acid and ethylene glycerol, ethanol.

8. Comparison of the methods

As described in introduction part in text, although 1,3-PDO are important raw material in the synthesis of polytrimethylene terephthalate (PTT), the other C3 alcohols and acetol are also useful chemicals in industrial production. 1-PO, the major product of this article with > 50% selectivity (Table S1, entry 4), is also very important an important solvent or starting material in pesticide, medicine and perfume industries and its **market demand** is growing fast in recent years. Therefore, **total selectivity of C3 alcohol** is a very important parameter to evaluate the catalysts. Low total selectivity of C3 alcohol means the generation of large amount of wastes, which is **not allowed** in large-scale production. In this work (Table S2, entry 23), we got >95% total C3 alcohol selectivity. Compared with reported works that reached the similar technical level (C3 alcohol selectivity >90%, Table S2, entries 3, 5, 6-7, 9, 12-13, 17-22), the **glycerol conversion** of our work (>99%) is higher than all of them. The complete glycerol conversion of our work leads to high capacity in industrial production, which is also very important factor. In addition, our work requires the **lowest H_2 pressure** (2.5 MPa, Table S2, entries 23 *vs.* 1-22), which reduces the equipment requirements and energy consumption. Reference in Table S2, entry 20 obtained the highest 1,3-PDO selectivity (60.4%) and excellent C3 alcohol selectivity (99.6%), but unfortunately, the glycerol conversion was very low (33.1%).

Table S6 comparison of the methods

Entry	Catlysts	P (MPa)[a]	C (%)[c]	1,3-PDO (%)[d]	C3 (%)[e]	Ref.[f]
1	2% Pt/19.6% WO_3/ZrO_2	8.0	78.4	24	64.2	3*a*
2	3% Pt/10% WO_3/ZrO_2	4.0	70.2	45.6	70.1	3*b*
3	5% Pt/W/ZrSi	5.0	54.3	52.9	97.6	3*c*
4	2% Pt/WO_3/ZrO_2	5.5	31.6	34.9	64.0	4*a*
5	5.7 %Pt-4.6 %Re/C	4.0	20.0	34	100	4*b*

6	2% Pt/ASA	4.5	19.8	4.5	90.2	4*c*
7	2%Pt/WO_3/TiO_2/SiO_2	5.5	15.3	50.5	93.6	4*d*
8	2% Pt/ Mesoporous WO_3	5.5	18.0	39.3	84.3	4*e*
9	2% Pt-H4Si$W_{12}O_{40}$/SiO_2	6.0	81.2	38.7	>90	4*f*
10	5% Pt/A_2O_3+STA	4.0	49	28	/	4*h*
11	2 % Pt/$Ti_{80}W_{20}$	5.5	55.4	26.9	76.8	4*i*
12	2% Pt–$H_4SiW_{12}O_{40}$/ZrO_2	5.0	26.7	38.9	91.6	4*j*
13	2% Pt–15%$H_4SiW_{12}O_{40}$/ZrO_2	5.0	24.1	48.1	90.9	4*k*
14	5% Pt-Re/CNTs	4.0	20.0	~21	82	4*l*
15	2% Pt/$AlPO_4$	vapor phase	100	35.4	70.2	4*m*
16	9% Pt/8%WO_x/Al_2O_3	4.5	53.1	51.9	86.2	4*n*
17	2% Pt–15%WO_x/Al_2O_3	5.0	53.4	58.9	92.0	4*o*
18	5% Rh/SiO_2 +Amberlyst	8.0	14.3	9.8	90.9	5*a*
19	4% Rh–ReO_x/SiO_2	8.0	79.0	14.0	99.4	5*b*
20	4% Ir–ReO_x/SiO_2 +H_2SO_4	8.0	33.1	60.4	99.6	6*a*
21	4% Ir–ReO_x/SiO_2+ H-ZSM-5	8.0	58.8	44.7	98.7	6*c*
22	Ru-4% Ir–ReO_x/SiO_2	8.0	65.8	36.9	99.4	6*e*
23	2% Pt-0.8% Re/5%WO_3/ZrO_2	2.5	>99	20.4	95.6	This work

[a] H_2 pressure; [b] Reaction temperature; [c] glycerol conversion (%); [d] 1,3-PDO selectivity (%); [e] C3 alcohol selectivity (%); [f] Reference NO. cited in text.