Supporting Information

Continuously Efficient Hydrodeoxygenation of Glycerol into 1,3-propandiol over Pt/WO$_x$/Beta Catalysts

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For the calculation of mass transfer limitations based on Weisz-Prater and Mears criteria

The effects of mass transfer limitations on HDO of glycerol into 1,3-propanediol were evaluated by Mears criteria (C_M) and Weisz-Prater (C_{WP}) [1-2]. The detailed calculations are presented:

$$C_M = \frac{-r_A' \rho_b R_p n}{k_c C_{Ab}} \ll 0.15$$

$$C_{WP} = \frac{-r_A' \rho_c R_p^2}{D_{eA} C_{As}} \ll 1$$

Where $-r_A'$ is the observed reaction rate (kmol·kg^{-1}·s^{-1}); R_p is the catalyst particle radius (m); ρ_b is the bulk density of catalyst bed (kg·m^{-3}), $\rho_b = (1-\varepsilon)\rho_c$; ρ_c is the solid catalyst density (kg·m^{-3}); ε is the catalyst porosity; C_{Ab} is the bulk concentration of glycerol (kmol·m^{-3}); k_c is the mass transfer coefficient of glycerol in the liquid phase (m·s^{-1}); n is the reaction order; C_{As} is the bulk concentration of glycerol at the external surface of the catalyst (kmol·m^{-3}); D_{eA} is the effective diffusivity of glycerol (m^2·s^{-1}).

The parameters were computed using reaction conditions of 160 °C, 4.0 MPa, and WHSV 1.0 h^{-1}.

k_c was calculated using Eqs. (S1) to (S4).

$$k_c = \frac{D_{AB} Sh}{d_p} \tag{S1}$$

$$Sh = 2 + 0.6 Re_p^{1/2} Sc^{1/3} \tag{S2}$$

$$Re_p = \frac{d_p u \rho_f}{\mu} \tag{S3}$$

$$Sc = \frac{\mu}{\rho_f D_{AB}} \tag{S4}$$

where Sh is the Sherwood number; d_p is the particle diameter (m); ρ_f is the fluid density (kg·m^{-3}); μ is the viscosity of glycerol (Pa·s); $(Re)_p$ is the Reynolds number considering the diameter of the particle; u is the linear velocity in pores; Sc is the Schmidt number; D_{AB} is diffusion coefficient.

For the Pt/WO$_x$/Beta catalyst,
$d_p = 3.75 \times 10^{-4}\, m$
$R_p = 1.875 \times 10^{-4}\, m$
$n = 0.827$
$\varepsilon = 0.375$

$$-r_A' = k\, C^{0.827} = 2.216 \times 10^{-4}\, mol^{0.173} L^{0.827} h^{-1} g^{-1} \times (5.3763\, mol \cdot L^{-1})^{0.827} = 2.4 \quad s^{-1}$$

$\rho_b = 600\, kg \cdot m^{-3}$
$\rho_c = 960\, kg \cdot m^{-3}$
$C_{As} = C_{Ab} = 500 g \cdot L^{-1} = 5.4295\, mol \cdot L^{-1} = 5.4295\, kmol \cdot m^{-3}$
$\rho_f = 1.1035 \times 10^3\, kg \cdot m^{-3}$

$$\mu = 1.748 \times 10^{-12} e^{\frac{8056}{273.15 + 160}} = 0.209 \times 10^{-3}\, Pa \cdot s = 0.209 \times 10^{-3}\, kg \cdot m^{-3}$$

$$d_p = 3.75 \times 10^{-4}\, m$$

$$u = 2.8313 \times 10^{-5}\, m \cdot s^{-1}$$

$$\tau = 3$$

$$D_A \approx D_{AB} = 3.5034 \times 10^{-8}\, m^2 \cdot s^{-1}$$

$$D_{eA} = \frac{D_A \varepsilon}{\tau} = \frac{3.0534 \times 10^{-8} \times 0.375}{3} = 3.8168 \times 10^{-9}\, m^2 \cdot s^{-1}$$

; where τ is the catalyst tortuosity.

the reactor inner diameter: 1.5×10^{-2} m

$$Sc = \frac{\mu}{\rho_f D_{AB}} = \frac{0.209 \times 10^{-3}\, kg \cdot m^{-1} \cdot s^{-1}}{1.1035 \times 10^3\, kg \cdot m^{-3} \times 3.5034 \times 10^{-8}\, m^2 \cdot s^{-1}} = 5.406$$

$$Re_p = \frac{d_p u \rho_f}{\mu} = \frac{3.75 \times 10^{-4}\, m \times 2.8313 \times 10^{-5}\, m \cdot s^{-1} \times 1.1035 \times 10^3\, kg \cdot m^{-3}}{0.209 \times 10^{-3}\, kg \cdot m^{-1} s^{-1}} = 0.0561$$

$$Sh = 2 + 0.6 Re_p^{1/2} Sc^{1/3} = 2 + 0.6 \times (0.0561)^{1/2} \times (5.406)^{1/3} = 2.2494$$

$$k_c = \frac{D_{AB} Sh}{d_p} = \frac{3.5034 \times 10^{-8}\, m^2 \cdot s^{-1} \times 2.2494}{3.75 \times 10^{-4}\, m} = 2.1015 \times 10^{-4}\, m \cdot s^{-1}$$

$$C_M$$

$$= \frac{-r_A' \rho_b R_p n}{k_c C_{Ab}} = \frac{2.474 \times 10^{-7}\, kmol \cdot kg^{-1} s^{-1} \times 600\, kg \cdot m^{-3} \times 1.875 \times 10^{-4}\, m}{2.1015 \times 10^{-4}\, m \cdot s^{-1} \times 5.3763\, kmol \cdot m^{-3}}$$

$$\ll 0.15$$

$$C_{WP}$$

$$= \frac{-r_A' \rho_c R_p^2}{D_{eA} C_{As}} = \frac{2.474 \times 10^{-7}\, kmol \cdot kg^{-1} s^{-1} \times 960\, kg \cdot m^{-3} \times (1.875 \times 10^{-4}\, m)}{3.8168 \times 10^{-9}\, m^2 \cdot s^{-1} \times 5.4295\, kmol \cdot m^{-3}}$$

Therefore, the mass transfer limitations can be neglected.

The effects of heat transfer limitations on HDO of glycerol into 1,3-propanediol were evaluated by Mears criteria (C_H). The detailed calculations are presented:

$$C_H = \frac{-r_A' |\Delta H_r^0| \rho_b R_p E_A}{h R_g T_b^2} \ll 0.15$$

Where $-r_A'$ is the observed reaction rate (kmol·kg^{-1}·s^{-1}); ΔH_r is the reaction enthalpy, h is the heat transfer coefficient; R_p is the catalyst particle radius (m); R_g is the universal gas constant (8.314 J·mol^{-1}·K^{-1}); ρ_b is the bulk density of catalyst bed (kg·m^{-3}), E_A is the activation energy (kJ·mol^{-1}); T_b is the bulk fluid temperature (K).

$$\rho_b = 600\, kg \cdot m^{-3}$$

$$R_g = 8.314\, J \cdot mol^{-1} \cdot K^{-1}$$

$$R_p = 1.875 \times 10^{-4}\, m$$

$$-r_A' = k\, C^{0.827} = 2.474 \times 10^{-4}\, mol \cdot kg^{-1} s^{-1}$$

$$T_b = 160 + 273.15 = 433.15\, K$$

$E_A = 51.688 \, kJ \cdot mol^{-1}$

$\Delta H_r^0 = -101.64 \, kJ \cdot mol^{-1}$

For the catalyst bed, $h = 61.2 \sim 320 \, kJ \cdot m^{-2} \cdot h^{-1} \cdot K^{-1} = 0.017 \sim 0.089 \, kJ \cdot m^{-2} \cdot s^{-1} \cdot K^{-1}$

$$C_H$$

$$= \frac{2.474 \times 10^{-4} \, mol \cdot kg^{-1} s^{-1} \times 101.64 \, kJ \cdot mol^{-1} \times 600 \, kg \cdot m^{-3} \times 1.875 \times 10}{(0.017 \sim 0.089) kJ \cdot m^{-2} \cdot s^{-1} \cdot K^{-1} \times 8.314 \times 10^{-3} kJ \cdot mol^{-1} \cdot K^{-}}$$

$= (1.053 \sim 5.514) \times 10^{-3} \ll 0.15$

Therefore, the heat transfer limitation can be neglected.

Table S1 Reaction performance of the synthesized catalyst [a].

Entry	Catalysts	Conversion, %	Selectivity, %				
			1,3-PDO	n-PrOH	1,2-PDO	i-PrOH	C_{3-}
1	$1.5Pt/WO_x(APT)$	1.8	19.6	23.1	12.3	8.9	36.1
2	1.5Pt/Beta	3.8	23.6	28.2	5.9	3.2	39.1
3	1.5Pt/0.5W(APT)/Beta	40.5	43.5	23.6	1.1	2.6	29.2
4	1.5Pt/0.5W(APT)/ZSM-5	16.4	41.2	21.3	1.2	4.3	32.0
5	1.5Pt/0.5W(APT)/USY	16.5	45.4	26.8	11.4	8.3	8.1
6	1.5Pt/0.5W(APT)/HY	7.92	48.4	20.7	8.6	4.3	18.0
7	$1.5Pt/0.5W(WCl_6)/Beta$	36.1	35.7	25.1	2.1	2.3	34.8
8	$1.5Pt/0.5W(Na_2WO_4)/Beta$	28.3	36.7	19.6	2.0	3.5	38.2
9	1.5Pt/0.5W(AMT)/Beta	37.3	34.1	24.2	2.0	2.8	36.9
10	$1.5Pt/0.5W(HSiWO_x)/Beta$	28.9	36.8	25.0	1.8	2.4	34.0
11	1.5Pt/0.1W(APT)/Beta	9.9	43.4	25.8	6.4	4.9	19.5
12	1.5Pt/0.3W(APT)/Beta	23.6	41.9	23.8	2.2	2.6	29.5
13	1.5Pt/0.7W(APT)/Beta	31.1	38.6	30.9	2.5	2.6	25.4
14	1.5Pt/1.0W(APT)/Beta	29.5	33.7	23.4	1.9	2.6	38.4
15	1.5Pt/1.5W(APT)/Beta	22.8	29.7	22.7	2.6	2.6	42.4
16	1.5Pt/8.5W(APT)/Beta	5.4	27.1	29.6	6.8	7.6	28.9
17	0.5Pt/0.5W(APT)/Beta	19.7	30.4	21.4	2.8	3.7	41.7
18	1.0Pt/0.5W(APT)/Beta	24.6	38.1	26.1	2.1	4.6	29.1
19	3.0Pt/0.5W(APT)/Beta	26.0	37.8	28.5	3.8	5.2	24.7

[a] Reaction condition: 10 ml of 30 g/L glycerol, 0.2 g catalysts at 160 °C of reaction temperature, 4.0 MPa of initial hydrogen pressure and 3h of reaction time.

C_{3-} indicates the total products of C-C breakage in the aqueous products, including ethanol, methanol, and ethylene glycol, etc.

Table S2 Acidic properties of the different supports

Catalysts	[a] DT, 100°C		[a] DT, 200 °C		[a] DT, 350 °C	
	n_B, μmol/g	n_L, μmol/g	n_B, μmol/g	n_L, μmol/g	n_B, μmol/g	n_L, μmol/g
Beta	180.9	332.7	179.5	152.3	154.7	71.8
WO_x(APT)	0	0.9	0	0	0	0
WO_x/Beta	290.8	57.6	256.6	54.6	178.7	51.6

[a]DT is short for desorption temperature.

Table S3 Elemental analysis of fresh and used Pt/WO$_x$/Beta.

Catalysts	[a] Ratio of W, %	[a] Ratio of Pt, %	[b] Ratio of Al, %	[b] Ratio of Si, %
Fesh Pt/WO$_x$/Beta	0.471	1.497	3.191	40.083
Spent Pt/WO$_x$/Beta	0.468	1.509	3.028	42.633

[a] W and Pt weight ratio are determined by ICP-AES

[b] Si and Al weight ratio are determined by XRF.

Table S4 Reaction performance of different substrates over Pt/WO$_x$/Beta catalyst [a]

Entry	Substrates	Conversion, %	Selectivity, %				
			1,3-PDO	n-PrOH	1,2-PDO	i-PrOH	C$_3$-
1	Glycerol	40.5	43.5	23.6	1.1	2.6	29.2
2	1,2-PDO	61.5	--	69.4	--	3.3	27.3
3	1,3-PDO	4.6	--	71.6	--	--	28.4

[a] Reaction condition: 10 ml of 30 g/L substrates, 0.2 g catalysts at 160 °C of reaction temperature, 4.0 MPa of initial hydrogen pressure and 3 h of reaction time.

C$_3$- indicates the total products of C-C breakage in the aqueous products, including ethanol, methanol, and ethylene glycol, etc.
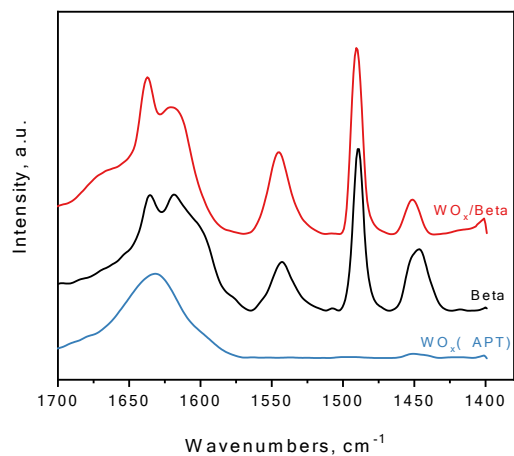
Fig. S1 Infrared Spectroscopy of the different supports after adsorbing pyridine followed by desorption at 200 °C. The pyridine adsorption/desorption in situ infrared study determined the type of acids on the catalyst and the used support shows abundant acid sites containing Brønsted acid (1540 cm^{-1}) and Lewis acid (1450 cm^{-1} and 1612 cm^{-1}).
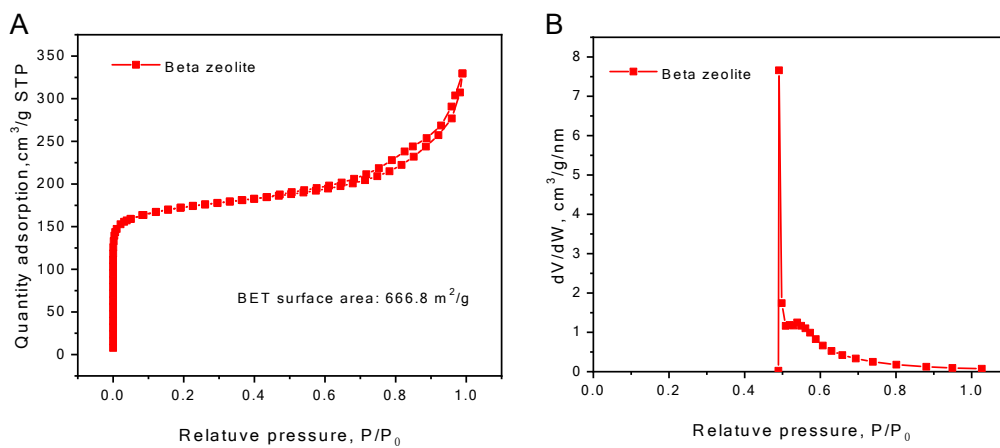
A

B

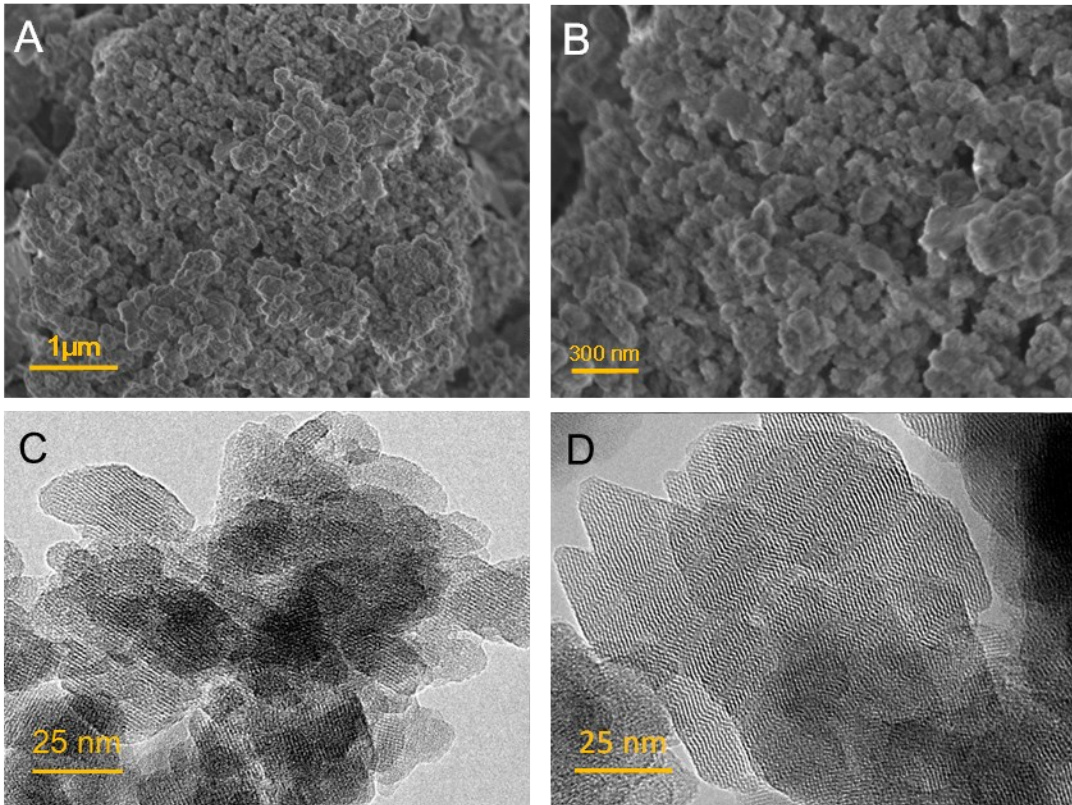**Fig. S2** A) N_2 adsorption isotherm linear plot and B) pore diameter distribution of Beta zeolite.

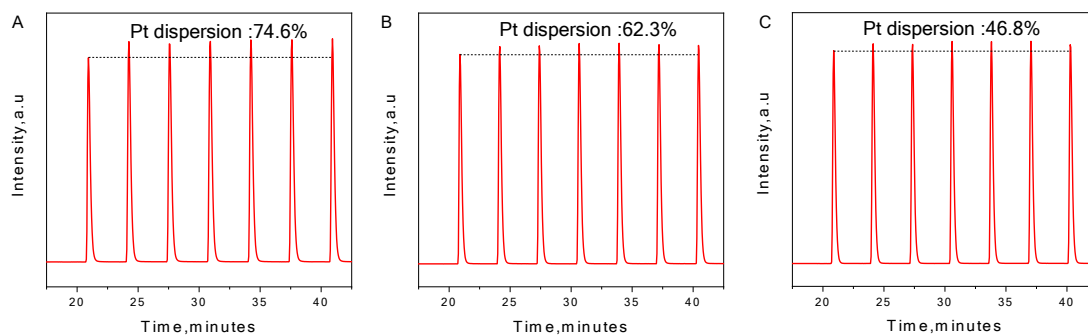**Fig. S3** SEM (A and B) and TEM (C and D) images of Beta zeolite.

Fig. S4 CO pulse images of Pt/WO$_x$/Beta catalyst with different Pt loading, A) 0.5%Pt/WO$_x$/Beta, B) 1.5%Pt/WO$_x$/Beta, C) 3.0%Pt/WO$_x$/Beta.
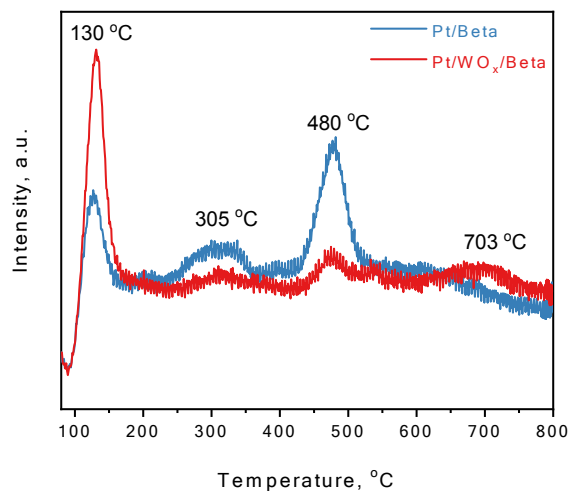
Fig. S5 H_2 DRIFT of Pt/WO$_x$/Beta catalyst at high temperature (300 °C).

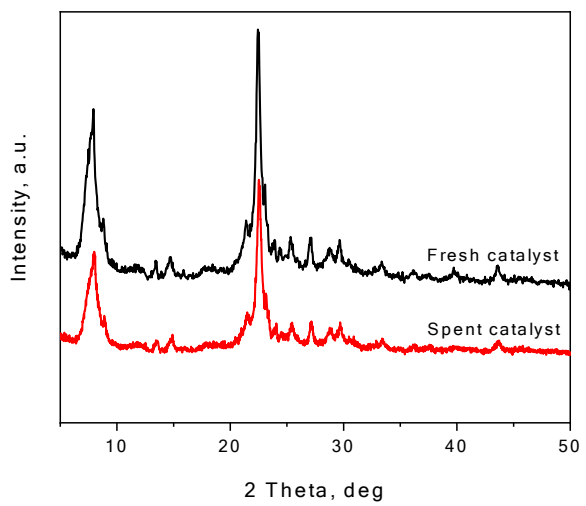**Fig. S6** H_2 TPR curves of Pt/WO$_x$/Beta and Pt/Beta catalyst.

Fig. S7 XRD patterns of fresh and spent Pt/WO$_x$/Beta catalyst.
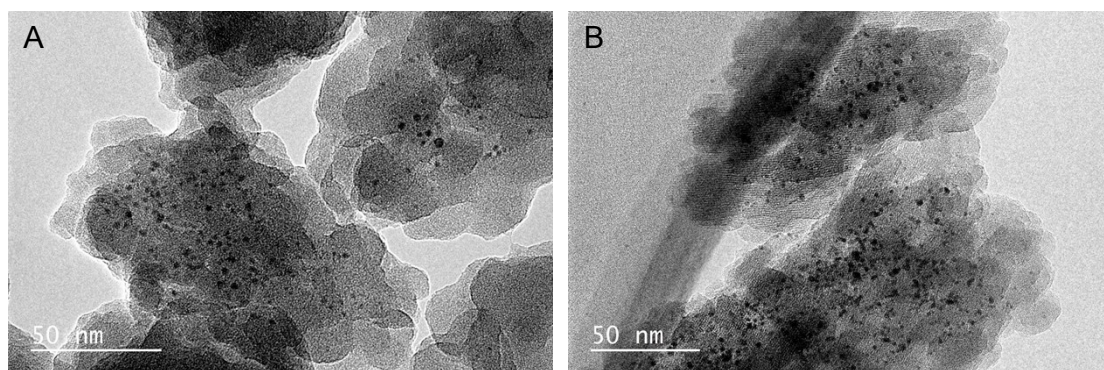
Fig. S8 TEM images of A) fresh and B) spent Pt/WO$_x$/Beta catalysts.
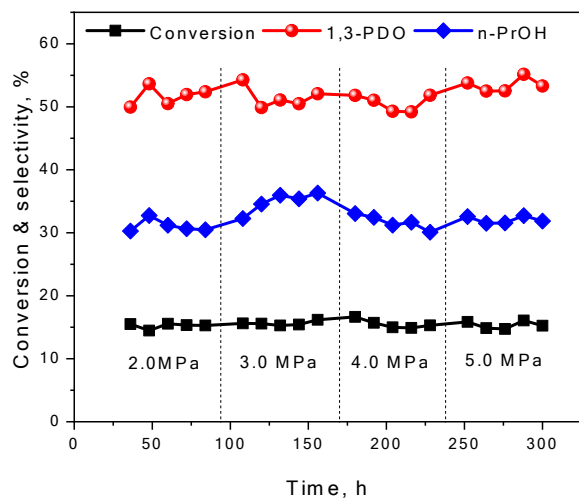
Fig, S9 The effect of H_2 initial pressure on the glycerol conversion and product selectivity, reaction temperature: 160 °C, glycerol aqueous flow rate: 0.1 ml/min, glycerol concentration: 500 g/L.

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References

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