

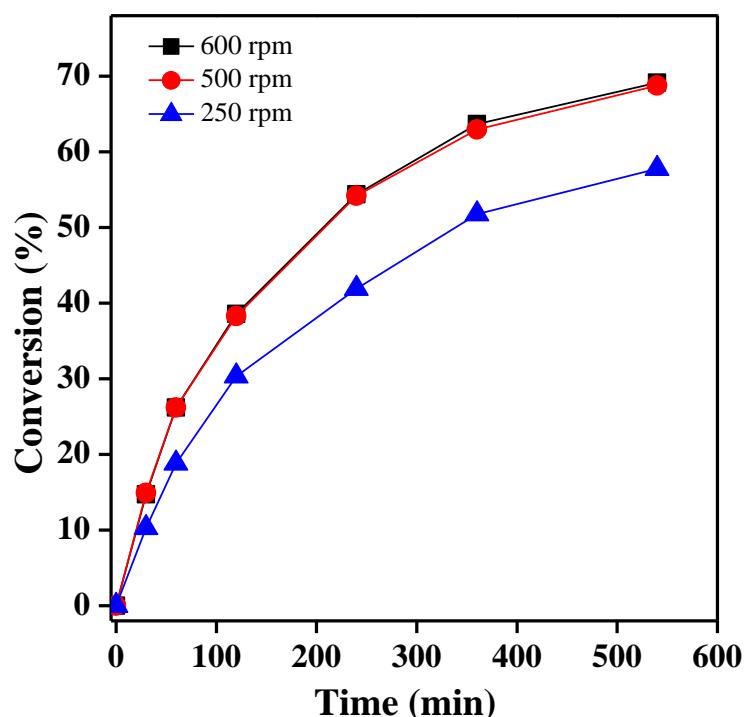
## **Electronic Supporting Information**

### **Size effects of Pt nanoparticles supported on carbon nanotubes for selective oxidation of glycerol in a base-free condition**

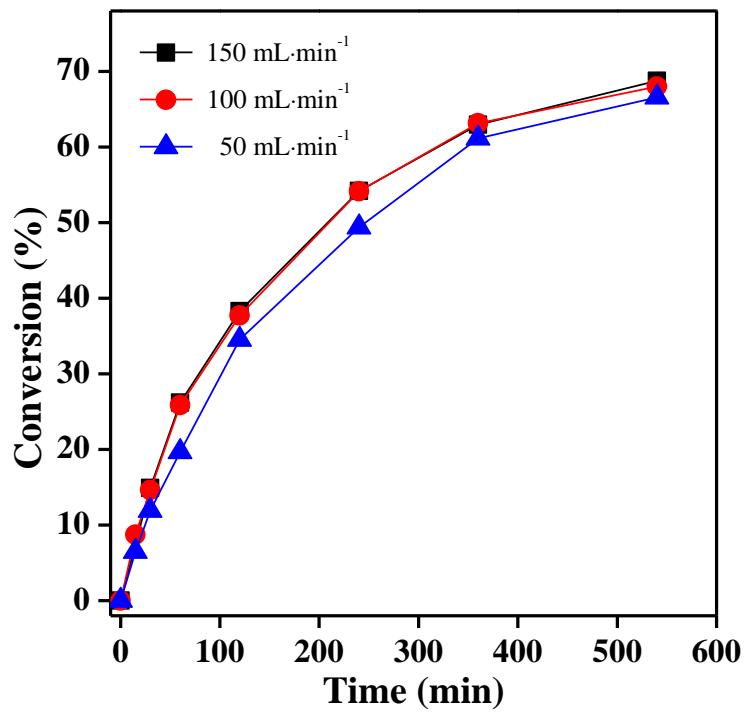
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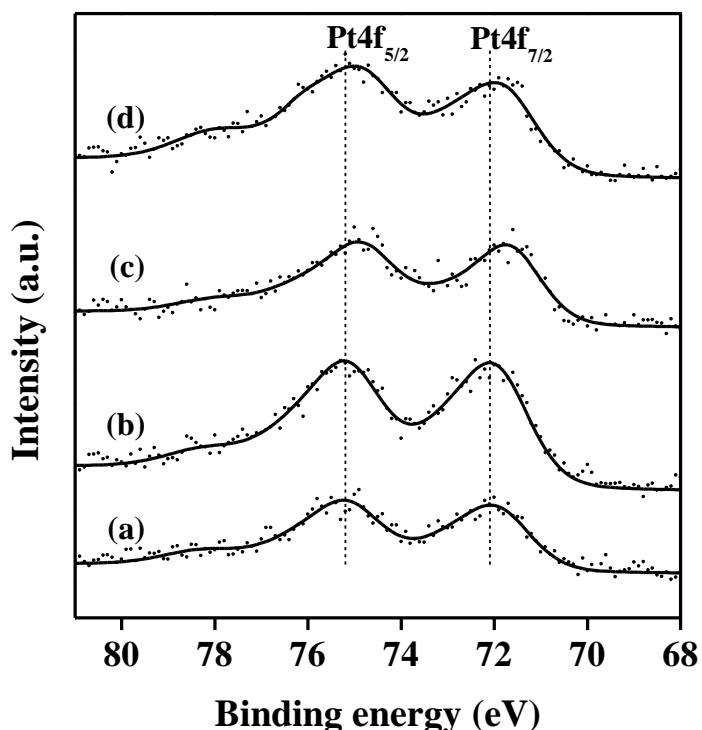
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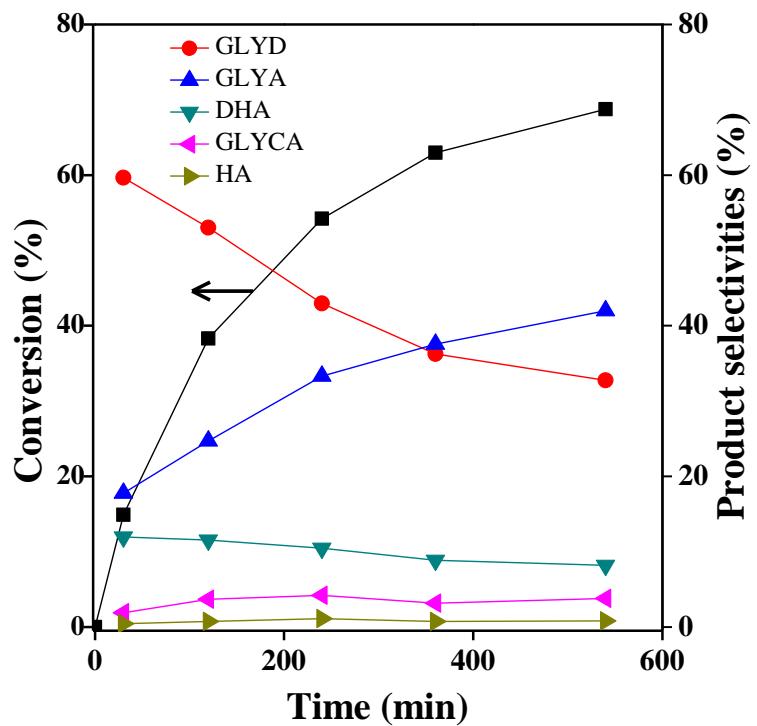
**Figure S1** Influence of agitation speed on the catalytic activity of 5.0 wt% Pt/CNTs. Reaction conditions: 30 mL glycerol aqueous solution ( $0.1 \text{ g}\cdot\text{mL}^{-1}$ ), glycerol/Pt molar ratio 890,  $T=60^\circ\text{C}$ ,  $F_{\text{O}_2}=150 \text{ mL}\cdot\text{min}^{-1}$ .



**Figure S2** Influence of oxygen flow rate on the catalytic activity of 5.0 wt% Pt/CNTs. Reaction conditions: 30 mL glycerol aqueous solution ( $0.1 \text{ g}\cdot\text{mL}^{-1}$ ), glycerol/Pt molar ratio 890,  $T=60^\circ\text{C}$ , 500 rpm.



**Figure S3** XPS spectra for the Pt 4f regions of Pt catalysts: (a) 3.0 wt% Pt/CNTs, (b) 5.0 wt% Pt/CNTs, (c) 3.0 wt% Pt/CNTs after reaction for 9 h, (d) 5.0 wt% Pt/CNTs after reaction for 9 h. The dotted profile represents the original XPS spectra while the bold black line represents the fitted Pt spectra.



**Figure S4** Glycerol oxidation over 5.0 wt% Pt/CNTs catalyst. Reaction conditions: 30 mL glycerol aqueous solution ( $0.1 \text{ g}\cdot\text{mL}^{-1}$ ), glycerol/Pt molar ratio 890,  $T=60^\circ\text{C}$ ,  $F_{\text{O}_2}=150 \text{ mL}\cdot\text{min}^{-1}$ , 500 rpm.

**Table S1** Binding energies of Pt catalysts

catalyst	Pt 4f (eV)	
	4f <sub>7/2</sub>	4f <sub>5/2</sub>
3.0 wt% Pt/CNTs	72.1	75.2
5.0 wt% Pt/CNTs	72.1	75.2
used 3.0 wt% Pt/CNTs	71.7	74.9
used 5.0 wt% Pt/CNTs	71.9	75.1

**Table S2** Comparison of activities and selectivities after 6 h reaction for glycerol oxidation over different Pt/CNTs catalysts in a base-free condition

Pt catalyst	glycerol/Pt molar ratio	$P_{O_2}$ (bar)	specific rate <sup>a</sup> (mol·h <sup>-1</sup> ·mol <sup>-1</sup> Pt)	product selectivity <sup>b</sup> (%)					Ref.
				GLYA	GLYD	DHA	GLYCA	HA	
5.0 wt% Pt/CNTs	890	1	90.4	37.6	36.2	8.8	2.5	0.7	This work
5.0 wt% Pt/CNTs	445	1	55.3	48.1	9.8	8.9	3.8	2.2	This work
5Pt/MWNTs	445	1	35.7 <sup>c</sup>	65.9	3.7	2.8	1.4	7.1	[1]
5Pt/H <sub>2</sub> O <sub>2</sub> -MWNTs	445	1	52.0 <sup>c</sup>	69.8	3.0	2.8	2.2	0	[2]
5Pt/S-MWNTs	445	1	67.2 <sup>c</sup>	68.3	1.3	13.3	5.9	0	[1]
PtC/MWNTs	1250	3	122	34.0 <sup>d</sup>	42.0 <sup>d</sup>	11.0 <sup>d</sup>	2.0 <sup>d</sup>	-	[3]

<sup>a</sup> Calculated as: (mol of converted glycerol)/(mol of total Pt added)/(reaction time, h). <sup>b</sup> Calculated as: (mol of product in reaction mixture)\*(the number of carbon atom in the product)/(mol of glycerol converted\*3)\*100%. <sup>c</sup> Recalculated according to the reported data. <sup>d</sup> Product selectivities at 40% glycerol conversion.

## **REFERENCES**

- (1) Liang, D.; Gao, J.; Wang, J. H.; Chen, P.; Hou, Z. Y.; Zheng, X. M. Selective Oxidation of Glycerol with Oxygen in a Base-Free Aqueous Solution over MWNTs Supported Pt Catalysts. *Appl. Catal. B: Environ.* **2011**, *106*, 423.
- (2) Gao, J.; Liang, D.; Chen, P.; Hou, Z. Y. ; Zheng, X. M. Oxidation of Glycerol with Oxygen in a Base-Free Aqueous Solution over Pt/AC and Pt/MWNTs Catalysts. *Catal. Lett.* **2009**, *130*, 185.
- (3) Rodrigues, E. G.; Pereira, M. F.; Chen, X. W. ; Delgado, J. J.; Órfão, J. J. M. Selective Oxidation of Glycerol over Platinum-Based Catalysts Supported on Carbon Nanotubes. *Ind. Eng. Chem. Res.* **2013**, *52*, 17390.