Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Enhanced performances of bimetallic PtCo/MCM-41 catalysts for glycerol oxidation in base-free medium

Hao Yan, Hansong Qin, Wei Liang, Xin Jin, Yashuang Zhang, Xiang Feng, Yibin Liu*, Xiaobo Chen, Chaohe Yang*

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China

* To whom correspondence should be addressed: E-mail: liuyibin@upc.edu.cn

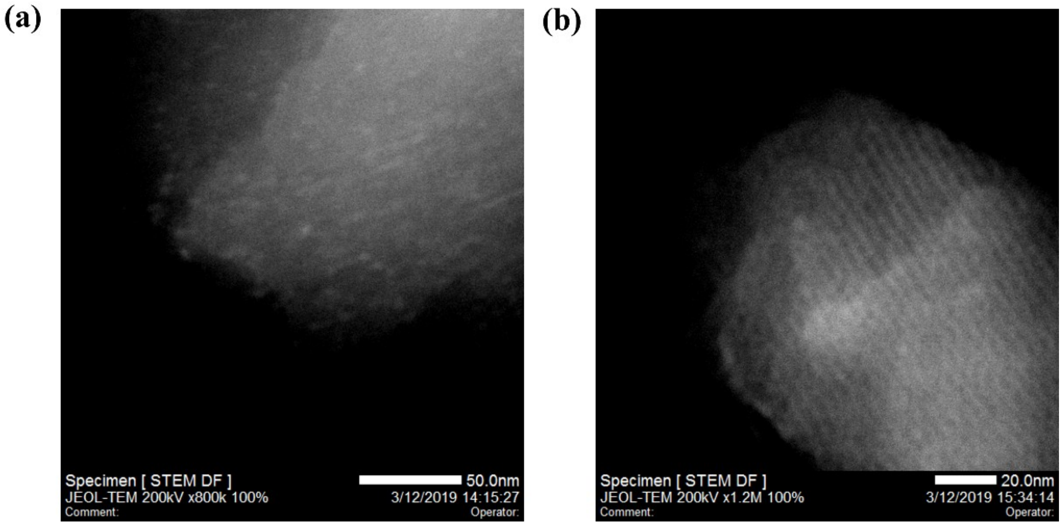

Figure S1. HAADF-STEM images and particle size distribution of (a) Co/MCM-41 (IM) and (b) Co/MCM-41 (200) samples

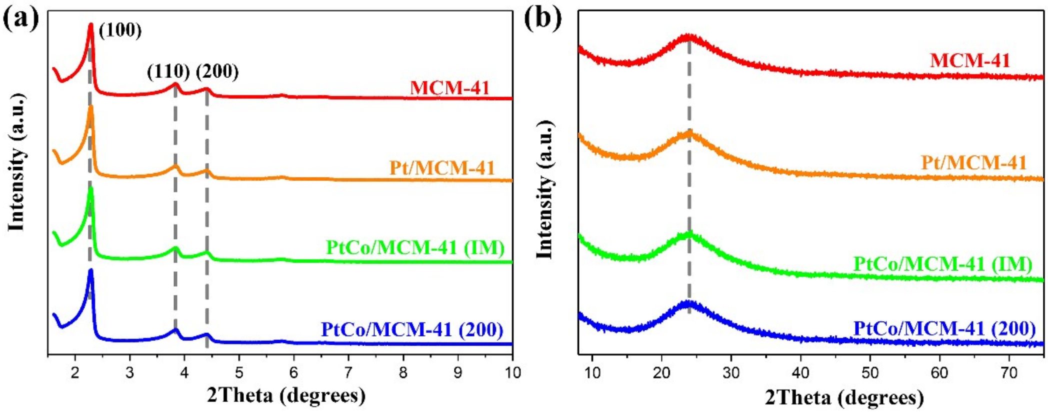

Figure S2. XRD patterns of (a) small-angle and (b) high-angle.

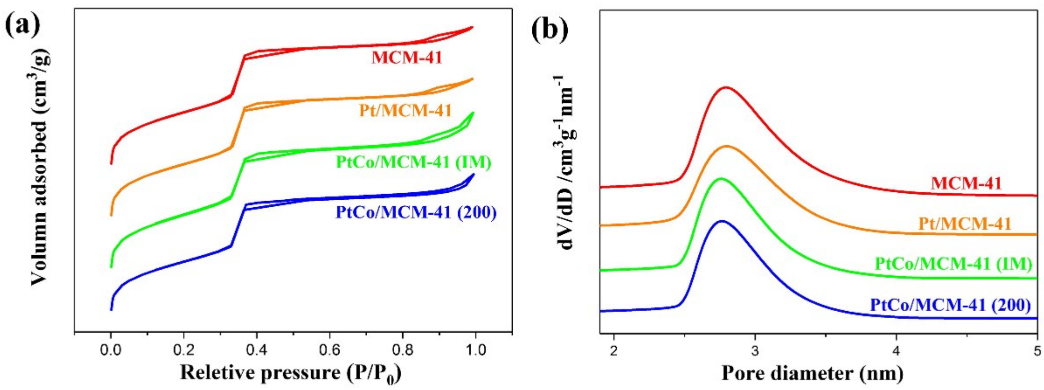

Figure S3. N_2-physisorption isotherms (a) and pore size distribution (b) of MCM-41, Pt/MCM-41, PtCo/MCM-41 (IM) and (b) PtCo/MCM-41 (200) catalyst.

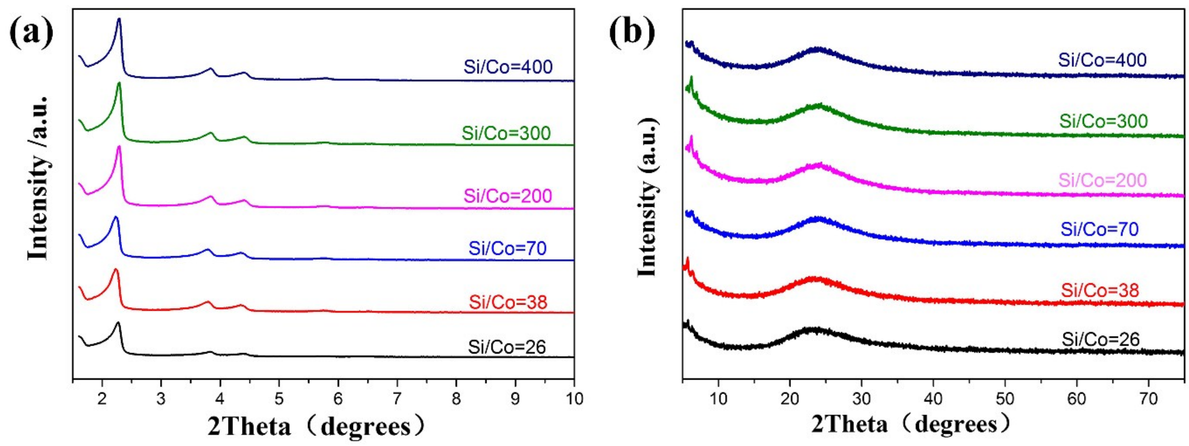

Figure S4. XRD patterns of Co/MCM-41 samples.

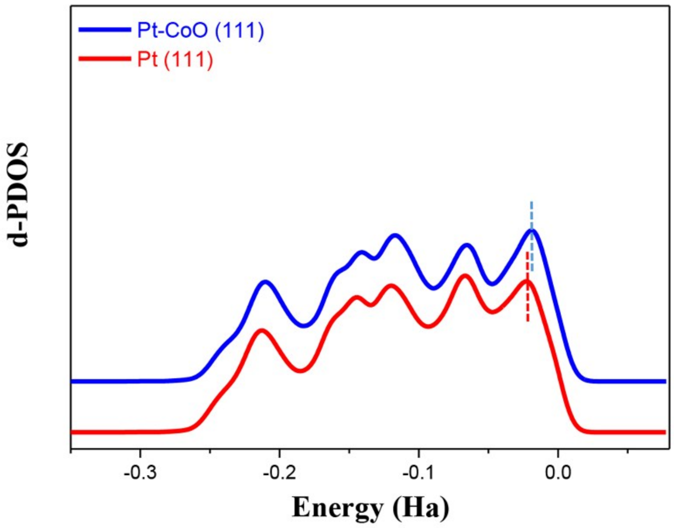

Figure S5. d-partial density of states of Pt (111) and Pt-CoO.

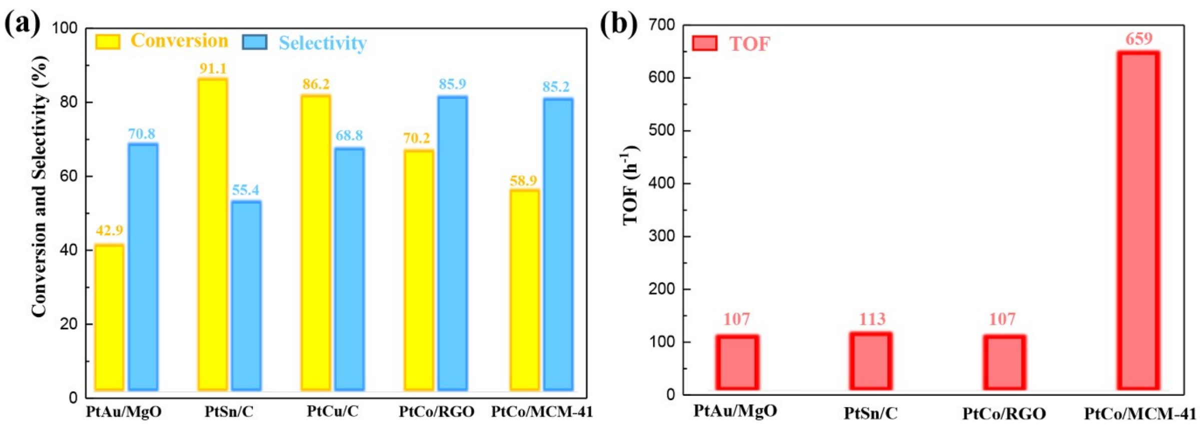

Figure S6. Comparison of PtCo/MCM-41 (200) catalyst with previous work for glycerol oxidation: (a) Conversion and selectivity and (b) TOF (Conditions: T: 60-80 ^{o}C, P_{O2}: 0.1-1 MPa).

The calculation process of ratio of Si/Co in the Co/MCM-41(200) sample

The ratio of Si to C_O is calculated according to the molar ratio of the feed stock. For example, Co/MCM-41 (200) sample means that the amount of Co added is 1/200 of the molar number of Si added. The calculation formula is as follows:

The addition amount of Co:

$$\frac{14.0\ (mL)\cdot 0.9346\left(g/cm^3\right)}{208.33\cdot 200}\cdot 291.03\ =\ 0.09\ \mathrm{g}\ [Co(NO3)2\cdot 6H2O]$$

14.0 mL is the addition amount of TEOS. 0.9346 and 208.33 are the density and relative molecular weight of TEOS, respectively. 291.03 is the relative molecular weight of $Co(NO_3)_2\cdot 6H_2O$.

Table S1. Physicochemical properties of Co/MCM-41 samples

Sample	BET surface area (m2/g)	Pore volume (cm3/g)
PtCo/MCM-41(26)	274.1	0.1
PtCo/MCM-41(38)	322.5	0.2
PtCo/MCM-41(70)	314.7	0.2
PtCo/MCM-41(200)	474.4	0.3
PtCo/MCM-41(300)	585.39	0.5
PtCo/MCM-41(400)	586.25	0.5
Pt/MCM-41	663.2	0.6

Table S2. Oxidation of glycerol over PtCo/MCM-41 catalyst[a]

Catalyst	Loading (wt%)[b]		Dispersion (%)[c]	Selectivity (%)[d]					Conversation (%)	TOF[e] (h^{-1})
	Pt	Co		GLYAD	GLYA	DHA	TA	GLYOA		
PtCo/MCM-41 (26)	0.51	3.25	64.0	10.97	75.06	14.78	0.1	2.62	44.59	376.8
PtCo/MCM-41 (38)	0.57	2.15	69.2	9.68	76.66	13.65	0.08	2.20	45.99	395.6.
PtCo/MCM-41 (70)	0.52	1.39	64.0	8.73	78.45	13.29	0.07	2.43	48.95	527.5
PtCo/MCM-41 (200)	0.58	0.56	61.0	8.16	78.96	12.41	0.09	1.19	55.37	658.6
PtCo/MCM-41 (300)	0.54	0.32	60.6	16.10	67.41	13.60	0.00	0.00	51.54	635.8
PtCo/MCM-41 (400)	0.54	0.15	52.7	20.93	66.26	13.37	0.00	0.00	42.26	469.6
Pt/MCM-41	0.55	0.00	57.3	18.69	62.75	16.41	0.00	0.00	33.33	248.5

a. Reaction conditions: 0.2 catalyst, 25 mL aqueous solution of glycerol (0.22 M), glycerol/Pt molar ration 530, 60℃, 1MPa O_2, 8h

b. Determined by ICP-OES analysis.

c. Measured from TEM images.

d. Most of the rest of the products are CO_2.

e. TOF was calculated as mole of glycerol molecules converted per mole of surface Pt atoms per hour. And the conversion was all less than 10% to ensure that the average reaction rate is equal to the instantaneous reaction rate.

Table S3. Catalyst properties and reaction conditions of PtCo/MCM-41 (200) catalyst with previous work for glycerol oxidation in base-free medium.

Catalyst	Pt loading (%)	Nanoparticle size (nm)	Reaction conditions
Pt/MCN-5	3.1	2.3	glycerol/Pt molar ratio =750, 60℃, 0.3 MPaO_2, 4 h
PtAu/MgO	0.75	2.0	glycerol/Pt molar ratio =1000, 60℃, 0.3 MPaO_2, 4 h
PtSn/AC	2.0	1.8	glycerol/Pt molar ratio =500, 60℃, oxygen (15 mL/min), 8 h

PtCu/AC	5.0	5.0	glycerol/Pt molar ratio =420, 60℃, oxygen (150 mL/min) , 6 h
PtCo/RGO	9.6	2.4	glycerol/Pt molar ratio =420, 60℃, oxygen (30 mL/min) , 3 h
PtCo/MCM-41	0.6	1.9	glycerol/Pt molar ratio =1000, 60℃, 1 MPaO_2 , 8 h