Supporting Information

Highly dispersed Pt studded on CoO_x nanoclusters for CO preferential oxidation in H_2

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Methods

 γ -Al₂O₃ supported cobalt oxide samples are synthesized via a deposition– precipitation method. Firstly, the as-calcined (650 °C 5h, atmosphere) γ -Al₂O₃ powder (1 g) is added in 100 mL deionized water with vigorous stirring for 1 hour. Then, 0.05g Co(NO₃)₂·6H₂O (Co nominal ratio: 1%) is dissolved in deionized water and added to the suspended liquid dropwise. Na₂CO₃ aqueous solution (0.5 mol/L) is added into the above solution drop by drop until the pH value of the liquid reached about 9. After stirring for 2 hours at room temperature, the stock solution is centrifuged at 3500r/min and then washed by deionized water for three times. Then the powder is dried at 100 °C overnight. Finally, it is calcined in still air at 400 °C for 4 h (ramping rate: 2 °C/min). The as prepared sample is denoted as CoO_x/Al₂O₃. Similar deposition–precipitation method is utilized to prepare pure CoO_x powder without γ -Al₂O₃ support denoted as CoO_x. Pt deposited on the pure CoO_x powder is denoted as Pt/CoO_x.

The Pt ALD process is performed in a fluidized ALD reactor. The base pressure for during Pt ALD is about 1.2 torr. 200 mg powder is weighted and loaded in the designed powder holder. The deposition temperature for Pt ALD process is kept at 150 °C with the Pt precursor of trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe₃, 98%, Sigma-Aldrich). The Pt precursor is held in a stainless steel bottle kept at 65 °C during Pt ALD. The pulse time and purge time for MeCpPtMe₃ are 200 s and 200 s. For Pt ALD on γ -Al₂O₃ powder, O₃ is used as counter reactant with the pulse time and purge time of 200 s and 200 s. Note that, all Pt contained catalysts in this paper are prepared with one cycle. Pt deposited on Al_2O_3 substrate is denoted as Pt/Al_2O_3 . After Pt deposition on CoO_x/Al_2O_3 powder, the catalyst is denoted as $Pt-CoO_x/Al_2O_3$ (O₃ as Pt precursor) and $Pt/CoO_x/Al_2O_3$ (O₂ as Pt precursor), respectively. All the catalytic tests are performed in a U-type vertical quartz reactor. In CO PROX reaction activity tests, 50 mg of catalysts are heated to 200 °C with a controlled rate of 2 °C/min. The reactant gas consists of 1% CO, 0.5% O₂, 50% H₂ balanced with He with a flow rate of 50 mL/min. The concentration of the outlet gas after catalytic reaction is detected by the Mass spectrometry (MS; AMETEK Dycor System 200 LCD).

Density functional theory (DFT) calculations are carried out by using the Vienna Ab initio Simulation Package (VASP). The exchange and correlation energy are in the form of generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) and the plane wave cutoff energy was expanded to 400 eV. We constructed the (110) surface of CoO (80 atoms) and Co₃O₄ (72 atoms) with five layers and 4×2 supercell (8.15Å×11.53Å for Co₃O₄ and 8.56Å×12.10Å for CoO) was adopted in x-y plane. The thickness of vacuum layer was set to 15 Å along z direction to avoid the interactions between periodic images. The Brillouin zones were sampled with gammacentered Monkhorst-Pack k-meshs of $3\times3\times1$. The atoms were allowed to relax and optimal atomic positions are obtained once the Hellmann-Feynman force on each atom was smaller than 0.05 eV/Å. To get the minimum energy path of O₂ dissociation and CO oxidation, the climbing image nudged elastic band (CI-NEB) was used and four intermediate images were linearly interpolated to make sure the intermediate images were linearly interpolated.



Figure S1: (a) TEM images of 1% CoO_x nanoclusters supported on γ -Al₂O₃ powder

(b) STEM images of Pt/CoO_x/Al₂O₃ catalysts



Figure S2: XRD patterns of Pt/Al₂O₃, Pt/CoO_x/Al₂O₃ and CoO_x sample as prepared,

after reduction and after PROX reaction.



Figure S3: TEM images of (a) 1, (b) 2, (c)4 cycles of Pt deposited by O3. (d) HRTEM images of Pt NPs.



Figure S4: Spectroscopic ellipsometer measurements of the growth rate for Pt

deposition on CoO_x and Al_2O_3 substrates at 150 °C using O_2 as co-reactant



Figure S5. Raman spectra of CoO_x , CoO_x/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts.



Figure S6. N₂ adsorption-desorption isotherms of Pt/CoO_x, Pt/Al₂O₃, Pt/CoO_x/Al₂O₃

and Pt/CoO_x/Al₂O₃-red.



Figure S7. H_2 TPR profile of CoO_x



Figure S8: long time stability of $Pt/CoO_x/Al_2O_3$ -red in CO PROX reaction stream at

30°C



Figure S9. Arrhenius curve in single CO oxidation for Pt/Al_2O_3 , $Pt/CoO_x/Al_2O_3$ and $Pt/CoO_x/Al_2O_3$ -red catalysts

Table S1. CO and H2 oxidation rate in CO oxidation and CO PROX reaction at 120 °C.The unit of the specific rate is mmol g_{Pt}^{-1} s⁻¹

sample	CO avidation rate	CO oxidation rate	H ₂ oxidation rate	
	CO oxidation rate	(PROX)	(PROX)	
Pt/Al ₂ O ₃	0.010	0.165	0.307	
Pt/CoO _x /Al ₂ O ₃	0.043	0.262	0.146	
Pt/CoO _x /Al ₂ O ₃ -red	0.237	0.554	0.112	

catalysts	Nobel	Feed gas(%)		GHSV	Max	Temperature		Notes	
	metal	СО	02	H2		СО	Т	ΔΤ	
Pt/CoO _x /Al ₂ O ₃	0.82	1	0.5	50	60000	~95	15-60	45	-
PtCo	1	1	1	50	24000	100	65-110	45	1
Pt-Co/SiO2	3	2	2	35	162000	100	~120	0	2
K-PtCo/Al2O3	1	1	1.5	50	120000	48	120-160	40	3
PtCo-Al	3.2	1	0.6	60	276000	93.4	109	0	4
Pt0.5Co0.5	unsupport	1	1	98	80000	100	45-50	5	5
Pt-CoOx	unsupport	1	1	98	14000	100	25-53	28	5
1.5Co1Pt	1	0.97	0.49	73.98	120000	70	110	0	6
PtCo/ETS10	1.4	1	1	74	30000	100	125-150	25	7
Fe-Pt/SiO2	3.6	1	0.5	48	36000	100	-73-103	180	8
Au/CeO2	1	1	1	40	30000	97.9	30	0	9
Pt-Ni-Al	0.56	1	0.5	50	12000	60.9	200	0	10
Pt/Fe	2.5	1	1	40	18750	100	20-70	50	11
Pt-Fe/Al2O3	0.71	1	1	50	20000	100	25-80	55	12
Pt-Fe/SiO2	4	1	0.5	98.5	36000	100	27-47	20	13
PtFe/Carbon	4	1	0.5	50	30000	100	30-45	15	14
Pt-Ni/Al2O3	3.43	1	0.5	70	120000	100	110	0	15
Au/CeO2–CuO	6.0	1	1	50	40000	100	95-155	60	16

Table S2. Comparison of our catalysts with other noble metal based catalysts



Figure S10. The atomic structures of (a) Co_3O_4 (110) slab and (b) CoO (110) slab. The blue and red spheres represent Co and O atoms, respectively. O atoms in different environments on the reconstructed (c) Co_3O_4 (110) surface and (d) CoO (110) surface.

Table S3. E_{0_v} of CoO (110) surface and Co₃O₄ (110) surface. E_{0_v} is calculated by $E_{0_v} = E_{slab-0} + E_{0_2}/2 - E_{slab}$, where E_{slab-0} , E_{0_2} and E_{slab} are energies of the surface with an oxygen vacancy, O₂ molecule and ideal surface, respectively. The vacancy number of CoO (110) surface corresponds to **Fig. S8** (c). The result shows that the lattice O atom is hard to be snatched.

Surface			Co ₃ O ₄ (110)				
Vacancy	1	2	3	Λ	5	6	
Number	1	2	3	4	5	0	
$E_{O_{v}}(eV)$	2.48	2.46	1.69	2.06	2.67	2.56	3.47



Figure S11. The energetic route of O_2 molecule adsorption and dissociation at the CoO (110) and Co_3O_4 (110).



Figure S12. The atomic structures of (a) Pt/Co_3O_4 and (b) Pt/CoO interface. The blue, red and gray spheres represent Co, O and Pt atoms, respectively.

Table S4. The CO adsorption energies $({}^{E_{CO}^{ads}}(eV))$ in different adsorption configurations on the CoO_x (110) surface. ${}^{E_{CO}^{ads}}$ is calculated by ${}^{E_{CO}^{ads}} = {}^{E_{slab}} + {}^{CO} - {}^{E_{CO}} - {}^{E_{slab}}$, where ${}^{E_{slab}} + {}^{CO}$, ${}^{E_{CO}}$ and ${}^{E_{slab}}$ are the total energies of CoO_x (110) surface adsorbed CO, isolated CO molecule and pure CoO_x (110) surface. The blue, red, gray and brown spheres represent Co, O, Pt and C atoms, respectively. The difference between Type A and Type C is that the angle of Co-C-Pt in these two adsorption configurations is different. The result indicates that CO molecule prefers to adsorb on Pt and Co atoms like Type A.

The Types of	Type A	Type B	Type C
Different	~	1	
Adsorption			
Configurations	0 00	000	000
CoO (110) Surface	-1.61	-1.38	-1.11
Co ₃ O ₄ (110)	1.07	1.67	1 55
Surface	-1.97	-1.0/	-1.55

- 1. Wang, C. et al. Appl. Catal. B: Environ., 2013, 136-137, 48-55
- 2. Furukawa, S., Ehara et al. Catal. Sci. Technol., 2016, 6, 1642-1650
- 3. Yu. et al. Applied Catalysis B: Environ., 2013,140-141, 588-597
- 4. D.I. Potemkin et al. Chemical Engineering Journal, 2012, 207-208, 683-689
- 5. D.I. Potemkin et al. Catalysis Communications, 2017, 100, 232-236
- Guillermo J. Siri et al. International Journal of Hydrogen Energy, 2016, 41, 19005
- 7. Silvia Irusta et al. Applied Catalysis A: General, 2016, 528, 86-92
- 8. Lu. et al. Nature, 2019, 565, 631
- Apanee Luengnaruemitchai et al. Chemical Engineering Journal, 2018, 344, 545–555
- 10. Z. Mohamed et al. Appl. Catal. B: Environ., 2016, 180, 687-697
- 11. Tao Zhang et al. ACS Catal. 2014, 4, 2113–2117
- 12. Zhang, H. et al. Appl. Catal. B: Environ. 2016, 180, 237-245
- 13. Fu, Q. et al. Science, 2010, 328, 1141-1144
- 14. Xu, H. et al. Energy Environ. Sci. 2012, 5, 6313-6320
- 15. Pan Y. et al., ACS Catal., 2018, 8, 5777-5786
- 16. Jing G. et al., CrystEngComm, 2019, 21, 363-371