Supporting Information

Bimetallic Pt-Co catalysts for the liquid-phase WGS

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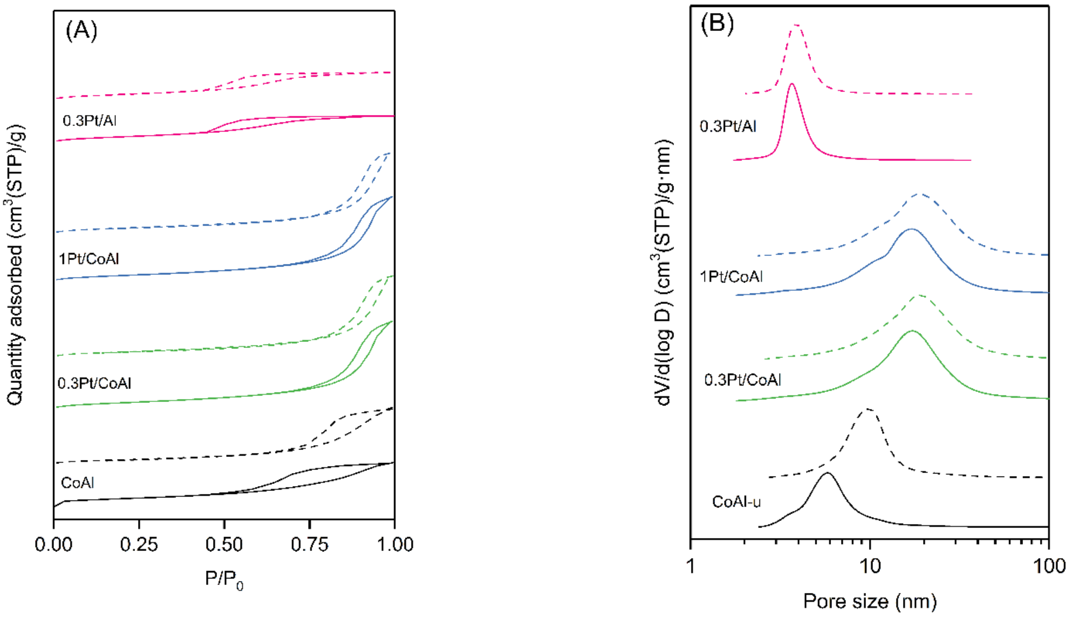
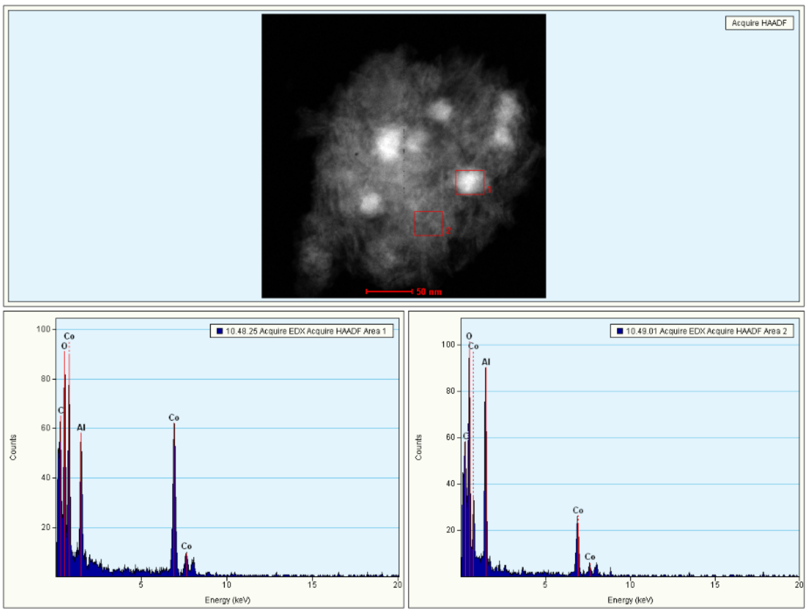


Figure S1. Nitrogen isotherms (A) and pore size distribution (B) of the calcined (solid lines) and reduced (dashed lines) samples.

(A)



(B)

(C)

(D)

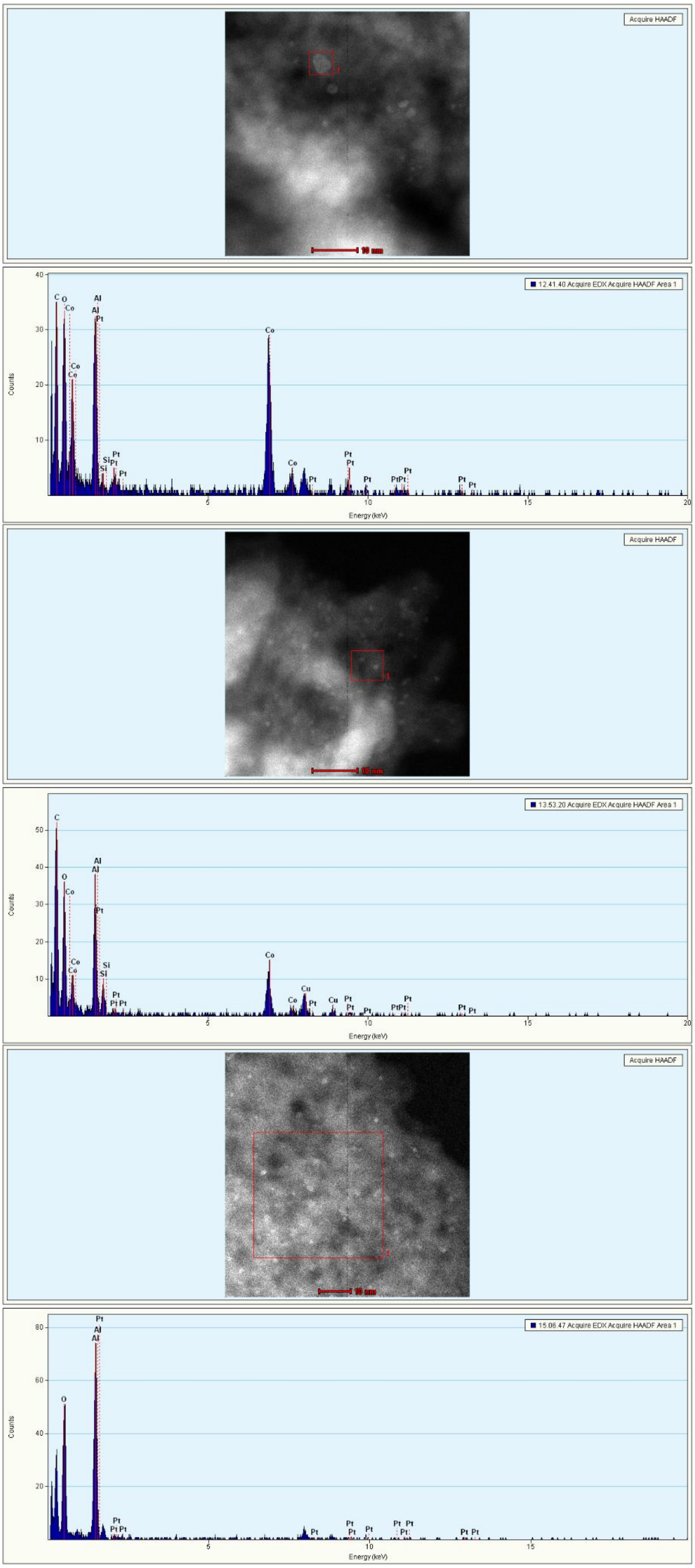


Figure S2. EDX spectrum of reduced samples (A) CoAl (B) 0.3Pt/CoAl (C) 1PtCoAl and (D) 0.3Pt/Al.

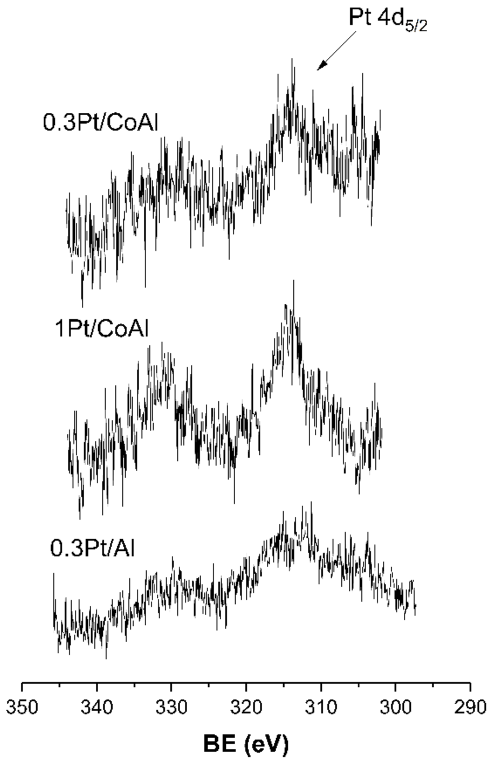


Figure S3. XPS spectra corresponding to Pt $4d_{5/2}$.

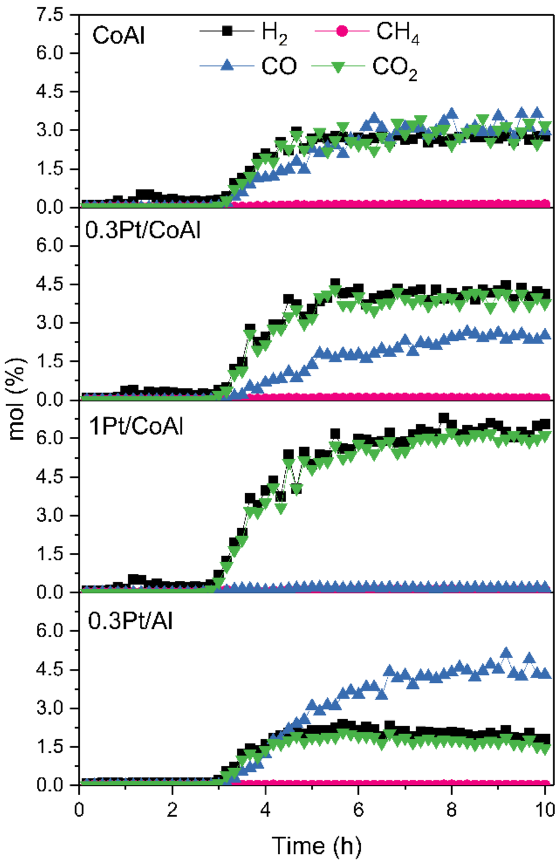


Figure S4. Outlet molar concentration of products during WGS reaction in the absence of hydrogen (H_2/CO = 0). Reaction conditions: 260 °C/50 bar; W_{cat} (0.2 g), water flow (0.04mL/min), CO flow (3.5 mL/min, STP).

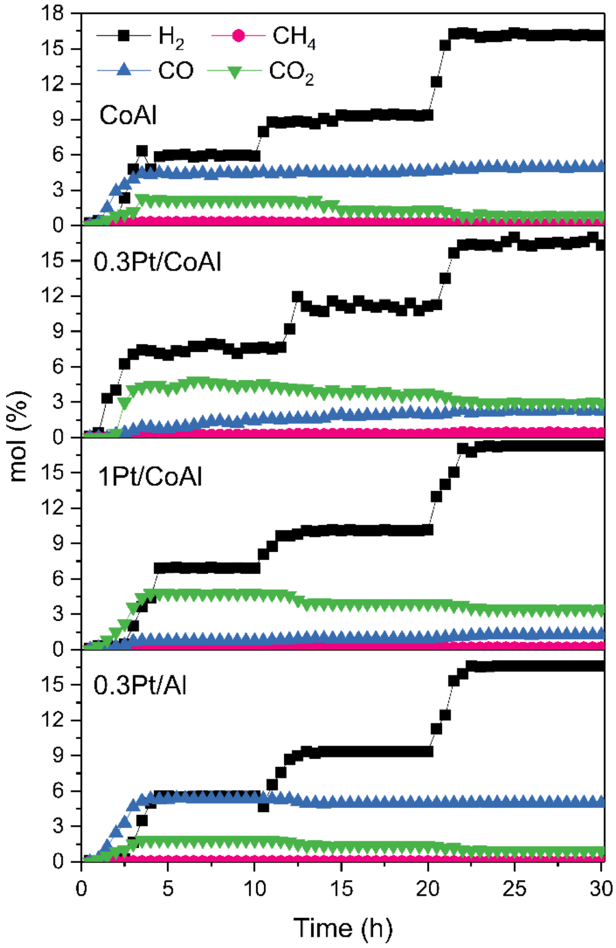


Figure S5. Outlet molar concentration of products during WGS experiments at different H_2/CO ratio. Reaction conditions: 260 °C/50 bar; W_{cat} (0.2 g), water flow (0.04mL/min), CO flow (3.5 mL/min, STP); H_2/CO=4/3 (0-10 h), H_2/CO =7/3 (11-20 h) and H_2/CO=4 (21-30 h).

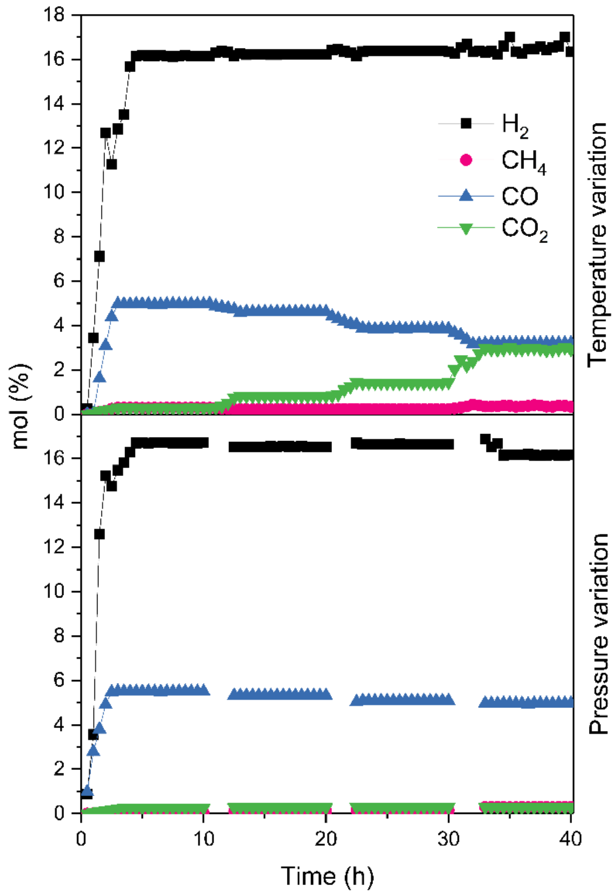


Figure S6. Outlet molar concentration of products during WGS experiments at different temperature and pressure over Pt/CoAl. Reaction conditions: W_{cat} (0.2 g), water flow (0.04mL/min), CO flow (3.5 mL/min, STP), H_2 flow (14 mL/min, STP). Upper part: temperature variation (220, 235, 245, 260 °C) and 50 bar. Lower part: pressure variation (25, 35, 40, 50 bar) and 220 °C.

Table 1S. List of apparent activation energies reported in this work and in the literature for Pt catalysts.

Catalysts	E_a (kJ/mol)	Operating conditions	Reference
0.3%Pt/CoAl	51.5	220-260 °C, liquid-phase	This work
Co_3O_4	91.0	180-280 °C, gas-phase	
0.2%Pt/Co_3O_4	50.1	150-200 °C, gas-phase	[1]
0.2%Pt/Co_3O_4	24.8	300-350 °C, gas-phase	
1%Pt/Al_2O_3	68	285 °C, gas-phase	[2]
0.9% Pt/CeO_2/Al_2O_3	70		
1.5% Pt/ZrO_2	58		
2% Pt/CeO_2	65	250-350 °C, gas-phase	[3]
1.9% Pt/TiO_2	23		
1.5% Pt/Fe_2O_3	44		

Table 2S. Liquid holdup (ε_L), vapor composition and liquid/vapor distribution of CO and H_2.

exp #	H_2/CO	T (˚C)	P (bar)	ε_L (%)	P_{H2O} (bar)	P_{CO} (bar)	P_{H2} (bar)	Liquid/vapor distribution (mol/mol)	
								CO	H_2
1	0	260	50	16.4	47.36	2.64	0	$1.05 \cdot 10^{-04}$	0
2	4/3	260	50	16.2	47.36	1.13	1.51	$4.49 \cdot 10^{-05}$	$1.13 \cdot 10^{-04}$
3	7/3	260	50	16.1	47.36	0.79	1.85	$3.14 \cdot 10^{-05}$	$7.88 \cdot 10^{-05}$
4	12/3	260	50	15.8	47.36	0.53	2.11	$2.11 \cdot 10^{-05}$	$5.29 \cdot 10^{-05}$
5	12/3	245	50	18.8	36.78	2.64	10.58	$1.13 \cdot 10^{-04}$	$2.71 \cdot 10^{-04}$
6	12/3	235	50	15.8	30.78	3.84	15.38	$1.72 \cdot 10^{-04}$	$4.03 \cdot 10^{-04}$
7	12/3	220	50	15.8	23.2	5.36	21.44	$2.60 \cdot 10^{-04}$	$5.80 \cdot 10^{-04}$
8	12/3	220	40	15.3	23.2	3.36	13.44	$1.63 \cdot 10^{-04}$	$3.64 \cdot 10^{-04}$
9	12/3	220	35	15.1	23.2	2.36	9.44	$1.14 \cdot 10^{-04}$	$2.55 \cdot 10^{-04}$
10	12/3	220	25	14.4	23.2	0.36	1.44	$1.74 \cdot 10^{-05}$	$3.89 \cdot 10^{-05}$

Liquid holdup (ε_L) was estimated according to reference [4].

References

1. Zhang, S.; Shan, J.; Zhu, Y.; Frenkel, A.I.; Patlolla, A.; Huang, W.; Yoon, S.J.; Wang, L.; Yoshida, H.; Takeda, S.; Tao, F. WGS Catalysis and In Situ Studies of CoO_{1-x}, $PtCo_n/Co_3O_4$, and $Pt_mCo_{m'}/CoO_{1-x}$ Nanorod Catalysts. *J. Am. Chem. Soc.* **2013**, 135, 8283-8293, DOI 10.1021/ja401967y. Available online: https://doi.org/10.1021/ja401967y.

2. Mendes, D.; Mendes, A.; Madeira, L.M.; Iulianelli, A.; Sousa, J.M.; Basile, A. The water-gas shift reaction: from conventional catalytic systems to Pd-based membrane reactors—a review. *Asia-Pac. J. Chem. Eng.* **2010**, 5, 111-137, DOI 10.1002/apj.364. Available online: https://onlinelibrary.wiley.com/doi/abs/10.1002/apj.364.

3. Thinon, O.; Diehl, F.; Avenier, P.; Schuurman, Y. Screening of bifunctional water-gas shift catalysts. *Catal. Today* **2008**, 137, 29-35, DOI https://doi.org/10.1016/j.cattod.2008.01.001.

4. García-Serna, J.; Gallina,G.; Biasi,P.; Salmi, T. Liquid Holdup by Gravimetric Recirculation Continuous easurement Method. Application to Trickle Bed Reactors under Pressure at Laboratory Scale. *Ind. Eng. Chem. Res.* **2017**, 56, 13294-13300, DOI 10.1021/acs.iecr.7b01810. Available online: https://pubs.acs.org/doi/abs/10.1021/acs.iecr.7b01810 .