Electronic Supplementary Information (ESI)

## Approaching Full-Range Selectivity Control in CO<sub>2</sub> Hydrogenation to Methanol and Carbon Monoxide with Catalyst Composition Regulation

Libo Yao, Yanbo Pan, Dezhen Wu, Jialu Li, Rongxuan Xie and Zhenmeng Peng\*

Department of Chemical, Biomolecular, and Corrosion Engineering, The University of

Akron, Akron, OH 44325, United States.



Figure S1. TEM images of P-regulated In(OH)<sub>3</sub>. (a) P-In-0. (b) P-In-3. (c) P-In-3.5.



Figure S2. TEM image of P-regulated In<sub>2</sub>O<sub>3</sub> (P-In-2).



Figure S3. HR-TEM images for P-regulated materials. (a) P-In-0, (b) P-In-3.5



**Figure S4.** TEM EDX mapping images for P-regulated In<sub>2</sub>O<sub>3</sub> (P-In-3.5). (a) Scanned mapping region. (b)-(d) Mapping images for In, O and P.



Figure S5. P 2p XPS spectra for a, P-In-0, b, P-In-2 and c, P-In-3.5 samples.



**Figure S6.** In 3d (a-c) and O 1s (d-f) XPS spectra for as-prepared P- regulated In<sub>2</sub>O<sub>3</sub>. (a,d) P-In-0, (b,e) P-In-2, (c,f) P-In-3.5.



Figure S7.  $CO_2$  conversion of  $In_2O_3$  with varying P content. Reaction carried out at T = 300

°C, P = 30 bar and GHSV = 18000 ml/( $g_{cat}$ ·h).



Figure S8. T-dependent CO<sub>2</sub> conversion (%) properties for P-In-0, P-In-2 and P-In-3.5 catalysts. Reaction carried out at P = 30 bar and GHSV = 18000 ml/( $g_{cat}$ ·h).



Figure S9. T-dependent space-time yield for methanol (a) and CO (b). Reaction carried out at P = 30 bar and GHSV = 18000 ml/( $g_{cat}$ ·h).



**Figure S10.** Relationship between abundance of oxygen vacancy (represented by Ov percentage obtained from XPS spectra) and space-time yield for methanol and CO.



Figure S11. In situ DRIFTS spectra of CO<sub>2</sub> adsorption experiments on (a) P-In-0, (b) P-In-2

and (c) P-In-3.5

Scherrer equation.					
P/In ratio	Particle size (nm)				
	P-In(OH) <sub>3</sub>	P-In <sub>2</sub> O <sub>3</sub>			
P-In-0	20.81	46.53			
P-In-2	38.12	46.53			
P-In-3	38.12	38.77			
P-In-3.5	28.59	37.22			
P-In-5	28.01	38.12			

Table S1. Particle size of P- regulated  $In(OH)_3$  and  $In_2O_3$  obtained from XRD spectra with

	Condition	$O_V$		O <sub>L</sub>		0
		Position	Area	Position	Area	Usum
P-In-0	Fresh	531.9 eV	5826	530.0 eV	14740	20566
	Reduced	532.4 eV	5378	530.0 eV	14105	19482
P-In-2	Fresh	531.5 eV	4382	530.0 eV	10539	15921
	Reduced	531.5 eV	4053	530.0 eV	11564	15618
P-In-3.5	Fresh	531.3 eV	4185	530.0 eV	11938	16123
	Reduced	531.3 eV	3903	530.0 eV	13447	17350

Table S2. Integrated area of  $O_V,\,O_L$  and  $O_{sum}$  obtained from XPS spectra.