Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Ethane Dehydrogenation Performance and High Temperature Stability of Silica Supported Cobalt Phosphide Nanoparticles

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Experimental Details

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted using a Perkin Elmer Optima 8000. Before analysis samples were first dissolved in a dilute base solution of potassium hydroxide to dissolve the SBA-15 followed by a dilute acid solution of nitric and hydrochloric acid to dissolve the metals.

Pyridine DRIFTS analysis was conducted using a Bruker Vertex FTIR spectrometer equipped with a mercury cadmium tellurium detector. The sample was first pre-treated in-situ at 315°C (temperature limit of the DRIFTS cell) under flowing H_2 (30 ml/min) for 2 hr. The sample was then purged with He for 1.5 hr while still at 315°C. The sample was then cooled and backgrounds were taken at 150°C and 30°C. The sample was then saturated using a stream of He (100 ml/min) passing through a bubbler with pyridine. The sample was then purged at room temperature until the spectra was stable. Then the sample was heated to 150°C while continuing to purge with He. The spectra in Figure S5 were taken after 50 mins of purging at 150°C. The spectra was normalized by dividing by the maximum of each spectra and then the data was smoothed using the FFT smooth function in Origin.

Samples for NH_3 TPD were first pre-treated in flowing H_2 for 2 hr at 550°C, followed by purging with He at 550°C for 90 mins to remove H_2 from the surface. The sample was then cooled to 100°C, exposed to a stream of 2% NH_3 in He for 2 hr, and then purged with He for 3 hr. The sample was then heated to 550°C at 10°C/min. NH_3 in the effluent was monitored using a mass spectrometer analyzing m/z 17.

Thermogravimetric analysis was performed using a TGA/DSC-1. The samples were first heated in air to 250°C and held there for 10 hr to remove water and other adsorbates. Then the sample was heated in air to 800°C at 5°C/min.

Supplementary Data and Figures

Table S1. Catalyst masses and corresponding ethane WHSV for 600°C reactions

Catalyst	Mass Catalyst (mg)	Ethane WHSV[a] (h^{-1})	Initial Ethane Conversion[b] (%)
Co/SBA-15	40	9.2	0.6
Co_2P/SBA-15	1	370	1.4
Co_2P-E/SBA-15	1	370	1.4
Co_2P-CoP/SBA-15	1	370	1.1
CoP-E/SBA-15	3	120	1.1

a. The feed for all reactions was 5%C_2H_6, 5%H_2, balance He, 100 ml/min total flow.
b. Determined by fitting conversion vs time data to Equation 4.

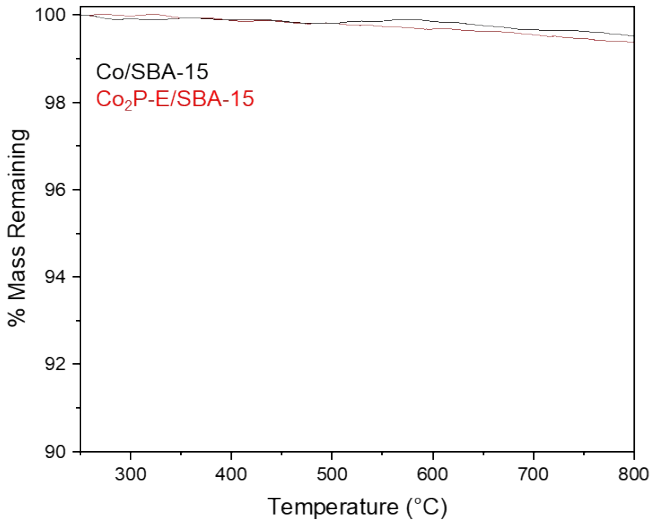

Figure S1. TGA of Co/SBA-15 (black) and Co_2P-E/SBA-15 (red) after EDH. Reaction conditions 600°C, 5% C_2H_6, 5% H_2, balance He, 100 ml/min total flow.

Table S2. Comparison of Co_2P-E/SBA-15 to literature

Catalyst	Temperature (°C)	Feed Comp	Feed Flow ml/min	Ethylene selectivity (%)	TOF[a] (s^{-1})	Reference
Co_2P-E/SBA-15	600	5% C_2H_6, 5% H_2, Balance Inert	100	90	0.9[b]	This work
PtZn/SiO2	600	2.5% C_2H_6, 1% H_2, Balance Inert	150	>99%	0.3[c]	1
Pt_3Sn/Mg(Al)O	600	20% C_2H_6, 25% H_2, Balance Inert	80	96	6.1[d]	2
Pt-In(0.7)	600	5% C_2H_6, 6% H_2, Balance inert	150	99	5.3[b]	3
Ni_3Ga/Al2O3	600	10% C_2H_6, Balance Inert	20	96	0.2[c]	4
Pt@HZSM-5	550	90% C_2H_6, Balance Inert	10	70	0.7[c]	5
Pt/M-TS-1 (EA)	600	75% C_2H_6, Balance Inert	20	>99%	0.6[c]	6

a. TOF = mol ethane reacted / s mol site, sites determined using b. CO, c. H_2, d. estimated using average particle size and surface composition

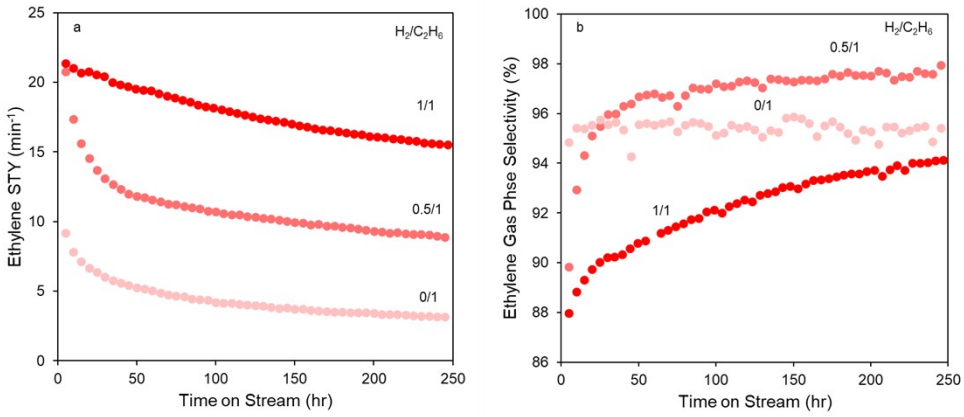

Figure S2. Ethylene STY (a) and ethylene carbon gas phase selectivity (b) as a function of time for varying H_2:C_2H_6 ratio.

Table S3. ICP results

Material	Nominal P:CO Ratio	ICP P:Co Ratio	ICP Co wt%
Co/SBA-15	0	-	5.2
Co_2P/SBA-15	0.5	0.42	4.8
Co_2P-E/SBA-15	1	0.69	5.3
Co_2P-CoP/SBA-15	2	0.98	5.2
CoP-E/SBA-15	4	1.7	3.9

Table S4. XAS results.

Sample	Pre-edge Energy (keV)	XANES Energy (keV)	Scattering Pair	CN	R (Å)	σ^2 (Å^2)	ΔEo (eV)
Co/SBA-15 Precursor: Pre-reduction	7.709	7.7178	Co-O	4.0	2.02	0.005	-7.7
Co/SBA-15 Reduced	-	7.709	Co-O	1.6	2.02	0.005	0.8
			Co-Co	5.3	2.50	0.005	
Co_2P-E/SBA-15 Precursor: Pre-reduction	7.709	7.7178	Co-O	6.0	2.00	0.005	-4.9
Co_2P-E/SBA-15 Reduced	-	7.709	Co-O	2.4	2.00	0.005	2.2
			Co-P	0.5	2.37	0.005	
			Co-Co	1.0	2.60	0.005	
Sample D (Co_2P) (Ref 7)			Co-P	4.7	2.26	0.010464 0.002659	-10, -6.44
			Co-Co	9.9	2.67	0.005416 0.023724	-1.55, -4.12
Sample F (CoP) (Ref 7)			Co-P	5.5		0.008577	-3.03
			Co-Co	7.5		0.010045	-6.49
Co-Al (Ref 8)	7.7092		Co-O	4.2	1.96	.007	1.7
Co-Silicate (Ref 9)	7.7094	7.7177	Co-O	4.34	1.99	.00323	

*CN is the coordination number, R is the bond distance, σ^2 and ΔE_o are EXAFS fitting parameters.

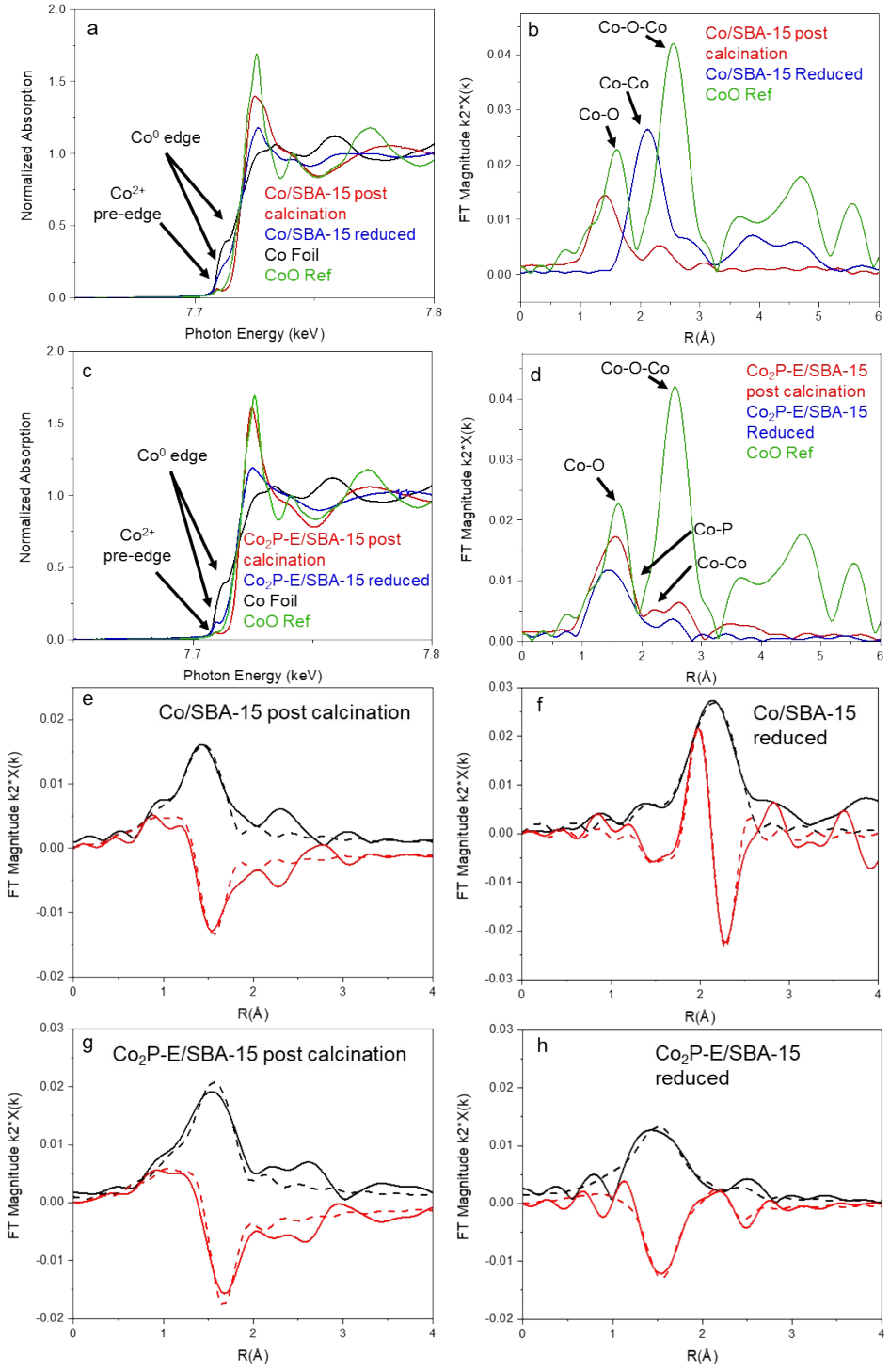

Figure S3. XANES and EXAFS spectra for Co/SBA-15 (a-b) and Co_2P-E/SBA-15 (c-d). The X axis in b and d are uncorrected bond distances. The fits are provided for each sample: Co/SBA-15 post calcination (e) and reduced (f), Co_2P-E/SBA-15 post calcination (g) and reduced (h). The black and red lines indicate the magnitude and imaginary components of the Fourier transform respectively where the solid lines represent the data and dashed lines represent the fit.

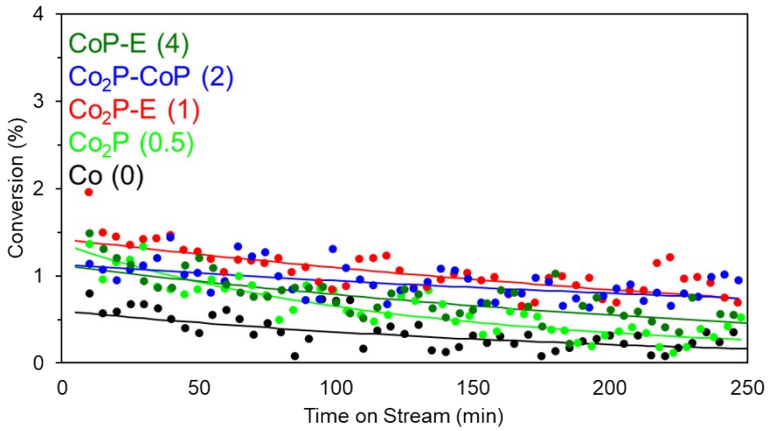

Figure S4. Conversion as a function of time for low temperature dehydrogenation reactions. The lines are the fit of the conversion vs time data to Equation 4. The value in parentheses is the nominal P:Co ratio. Reaction conditions were 600°C, 5% C_2H_6, 5% H_2, balance He, 100 ml/min total flow.

Table S5. Selectivity to all gas phase products for 600°C EDH experiments.

Material	Initial Ethylene Selectivity (%)	Steady State Ethylene Selectivity[a] (%)	Initial Methane Selectivity (%)	Steady State Methane Selectivity[a] (%)
Co/SBA-15	41	58	59	42
Co_2P/SBA-15	85	91	15	9
Co_2P-E/SBA-15	88	93	12	7
Co_2P-CoP/SBA-15	88	91	12	9
CoP-E/SBA-15	88	92	12	8

a. Average selectivity from 1-4 hr TOS.

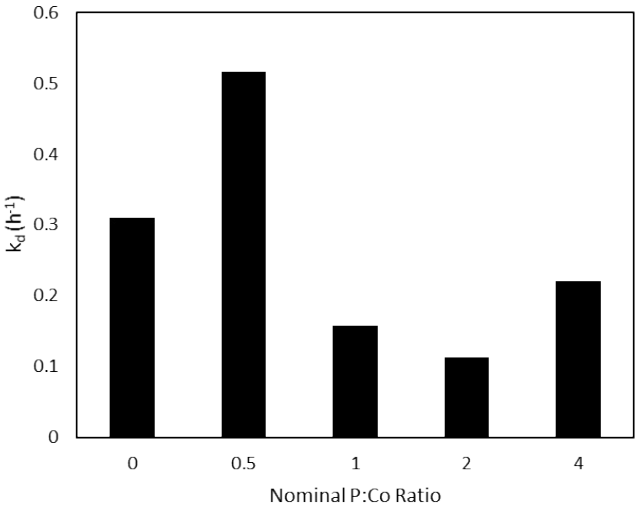

Figure S5. k_d values for different P:Co ratio materials during EDH. Reaction conditions were 600°c, 5% C_2H_6, 5% H_2.

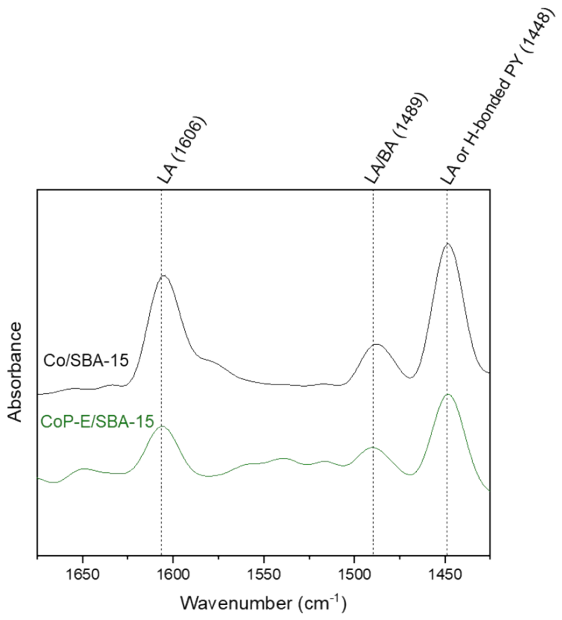

Figure S6. Pyridine DRIFTS of Co/SBA-15 and CoP-E/SBA-15 after purging at 150°C. (LA – Lewis acid feature, BA – Brønstead acid feature)

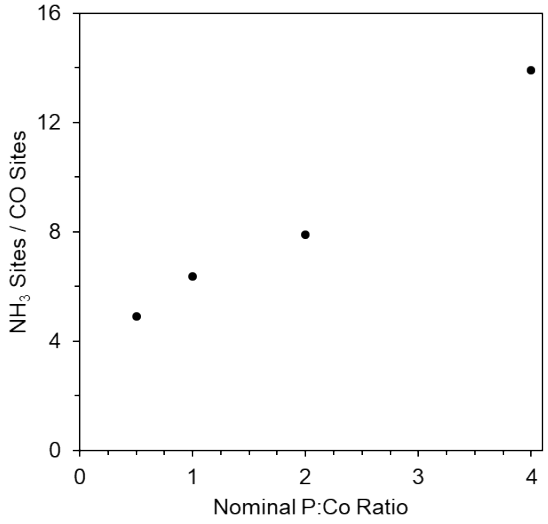

Figure S7. NH_3 sites (from NH_3 TPD) / CO Sites (from CO pulse) as a function of P:Co ratio.

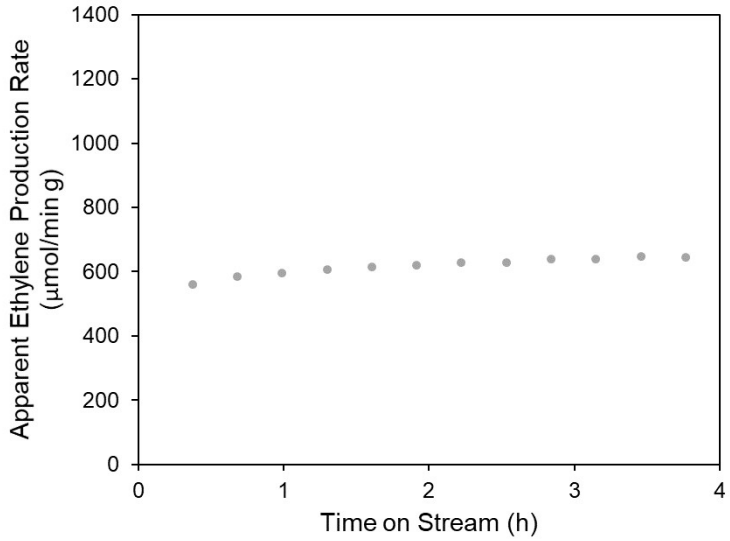

Figure S8. High temperature background runs with SBA-15 (grey). Reaction conditions were 700°C 5% C_2H_6, 5% H_2, balance He, 100 ml/min total flow, 5 mg catalyst.

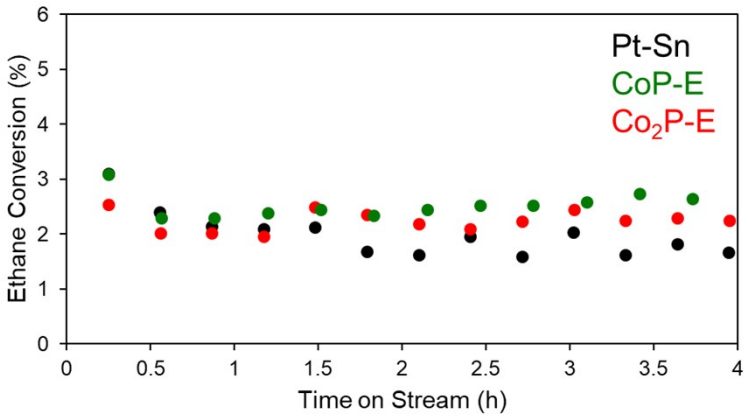

Figure S9. Conversion as a function of time for high temperature dehydrogenation reactions. Reaction conditions were 700°C, 5% C_2H_6, 5% H_2, balance He, 100 ml/min total flow, 5 mg catalyst.

Table S6. Selectivity to all gas phase products for 700°C EDH experiments.

Material	Average Ethylene Selectivity[a] (%)	Average Methane Selectivity[a] (%)
Co_2P-E/SBA-15	98	2
CoP-E/SBA-15	98	2
Pt-Sn/SBA-15	98	2

a. Average selectivity from 0.25-4 hr TOS.

Table S7. Physisorption results, crystallite and particle size, and CO uptake for Pt-Sn/SBA-15

Material	BET Surface Area (m^2/g)	Average Pore Size (nm)	Average Pore Volume (cm^3/g)	Crystallite Size[a] (nm)	Particle Size[b] (nm)	CO Uptake (μmol CO/g)
Pt-Sn/SBA-15	700	6.7	0.54	17	12.3 ± 8.3	10.5

a. From Scherrer equation
b. From TEM

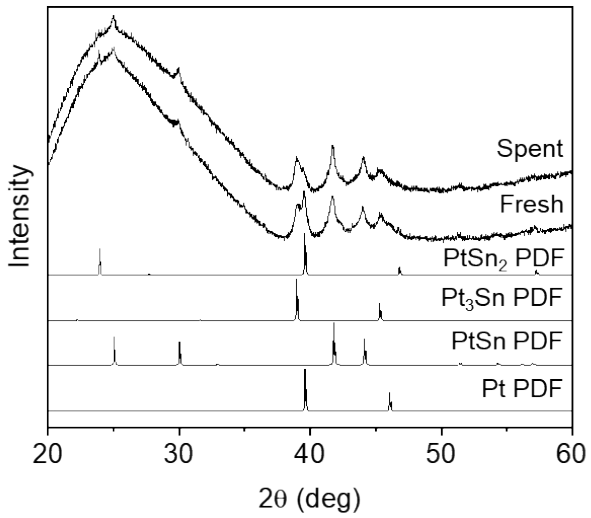

Figure S10. XRD of Pt-Sn/SBA-15 before and after reaction.

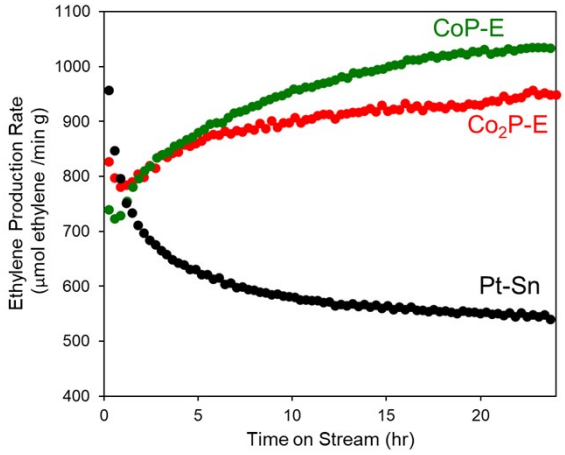

Figure S11. Ethylene production over time with CoP/SBA-15 (green), Co_2P/SBA-15 (red), Pt-Sn/SBA-15 (black). Reaction conditions were 700°C, 5% C_2H_6, 5% H_2, balance He, 100 ml/min, 5 mg catalyst.

References:

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