Supporting Information for: Transition Metal-Free Alkyne Hydrogenation Catalysis with $BaGa_2$, a Hydrogen Absorbing Layered Zintl Phase

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Experimental Section:

Sample Preparation. The synthesis of $BaGa_2$ has been accomplished with greater than 90% phase purity via a sealed quartz tube reaction in an alumina crucible by slowly heating up stoichiometric quantities of barium and gallium to 900 °C and holding at that temperature for 12 hours. The reaction is then cooled to 100 °C over 12 hours and reheated to 800 °C and held for 24 hours. The impurity phase, $BaGa_4$, was also synthesized by heating up stoichiometric barium and gallium over 12 hours to 900 °C, held for 12 hours and then cooled to room temp over 12 hours. $BaGa_2H_2$ was synthesized by annealing $BaGa_2$ at 50 bar H_2 and 175 °C for 5 days.

General Procedure for the Catalytic Hydrogenation Reactions. For atmospheric pressure experiments, $BaGa_2$ is ground in a mortar and pestle, massed out and added to a 10 mL round bottom flask followed by the addition of the dry, degassed solvent and phenylacetylene. In a typical reaction, 0.9 mmol of substrate and 10 mg of catalyst are mixed in 2.4 mL of solvent. The material is then removed from the glovebox, and a balloon filled with hydrogen gas is added to the flask. The reaction progress as a function of time is monitored via HPLC with an external calibration to monitor phenylacetylene to styrene to ethylbenzene progress. For high pressure experiments, the catalyst, solvent, and substrate are added to a 20mL vial in a Parr bomb. Once the Parr bomb is brought out of the glovebox it is pressurized with hydrogen gas and then brought up to temperature on a hot plate. To calculate the surface specific activity (SSA), Equations 1, 2, and 3 were used.

$$(1)\ \mathrm{SSA} = {}^{n_0 C}/_{t\, n_{cat}}$$

$$(2)\ n_{cat} = {}^{m_{cat} N_{Ga\ sites}}/_{N_A}$$

$$(3)\ N_{Ga\ sites} = S_{BET} \times \frac{2\ \mathrm{Ga\ atoms}}{S_A}$$

Where n_0 is the initial moles of substrate, C is the conversion of the substrate at reaction time t, n_{cat} is the moles of Ga atoms exposed on the surface, m_{cat} is the mass of the catalyst, $N_{Ga\ sites}$ is the amount of exposed Ga atoms per gram of catalyst, N_A is Avogadro's constant, S_{BET} is the specific

surface area of the material, and S_A is the surface area of the gallium atoms. A surface of $BaGa_2$ has 2 Ga atoms per 17 $Å^2$ surface area, thus S_A would correspond to 17 $Å^2$ in equation 3.

When making comparisons, the $BaGa_2$ catalyst used was from the same synthetic batch to eliminate differences in the relative amount of $BaGa_4$ impurity (though typically this is below 5%), surface areas per gram, and changes in the amount of surface oxidation. For instance, the $BaGa_2$ catalyst used in the kinetic traces in figure 2b and 2c was collected from the same synthetic batch.

Gas Adsorption Measurements: A micrometrics 3Flex Surface Characterization Analyzer was used to measure single component, gas adsorption isotherms. The measurements were performed using ultra high purity krypton (99.999%) purchased from Praixair (Kr: 5.0RS-Q2000). Prior to analysis 311 mg of $BaGa_2$ was transferred to oven-dried sample tubes equipped with TransSeals™ (Micrometrics) and heated to 100 °C (1 °C min^{-1}) under vacuum until the outgas rate was less than 3 mbar min^{-1}. Surface areas were calculated from Kr adsorption isotherms (77K) by fitting the isotherm data to the BET equation with the pressure range ($0.0001 \leq P/P_0 \leq 0.4$).

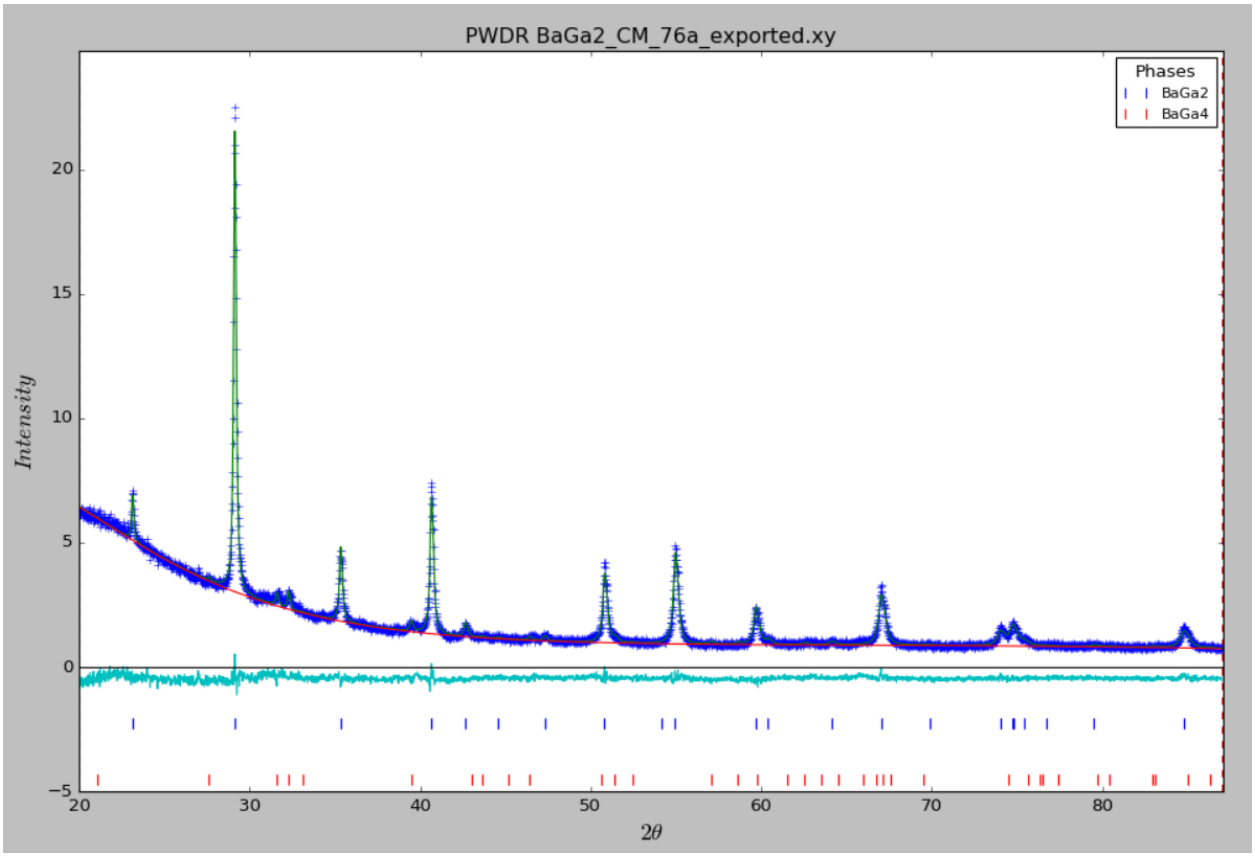

Figure S1. Rietveld refinement of the powder XRD scan of $BaGa_2$, performed using GSAS-II. The observed data, calculated fit, and difference curve are shown using blue marker, green line, and light blue line, respectively.

Table S1. Crystallographic Data on $BaGa_2$

Empirical Formula	$BaGa_2$
Formula Weight (g/mol)	276.77
Space group	P6/mmm
a (Å)	4.4320(3)
c (Å)	5.0731(2)
V ($Å^3$)	86.301
T (K)	295
λ (Å)	1.5406
ρ (g cm^{-3})	5.325
Pattern range (2θ,°)	15-87
Step size (2θ,°)	0.015342
Step scan time (s)	2.0
No. of contributing reflns	4368
R_{wp}	0.0492
R_p	0.0377
$R(F^2)$	0.0565
$BaGa_2$ Phase Fraction	0.9773
$BaGa_4$ Phase Fraction	0.0276

Table S2. Atomic coordinates and displacement parameters U_{iso} ($Å^2$) for $BaGa_2$.

Element	x	y	z	U_{iso}
Ga	0.33333	0.66667	0.50000	0.01265
Ba	0.00000	0.00000	0.00000	0.00559

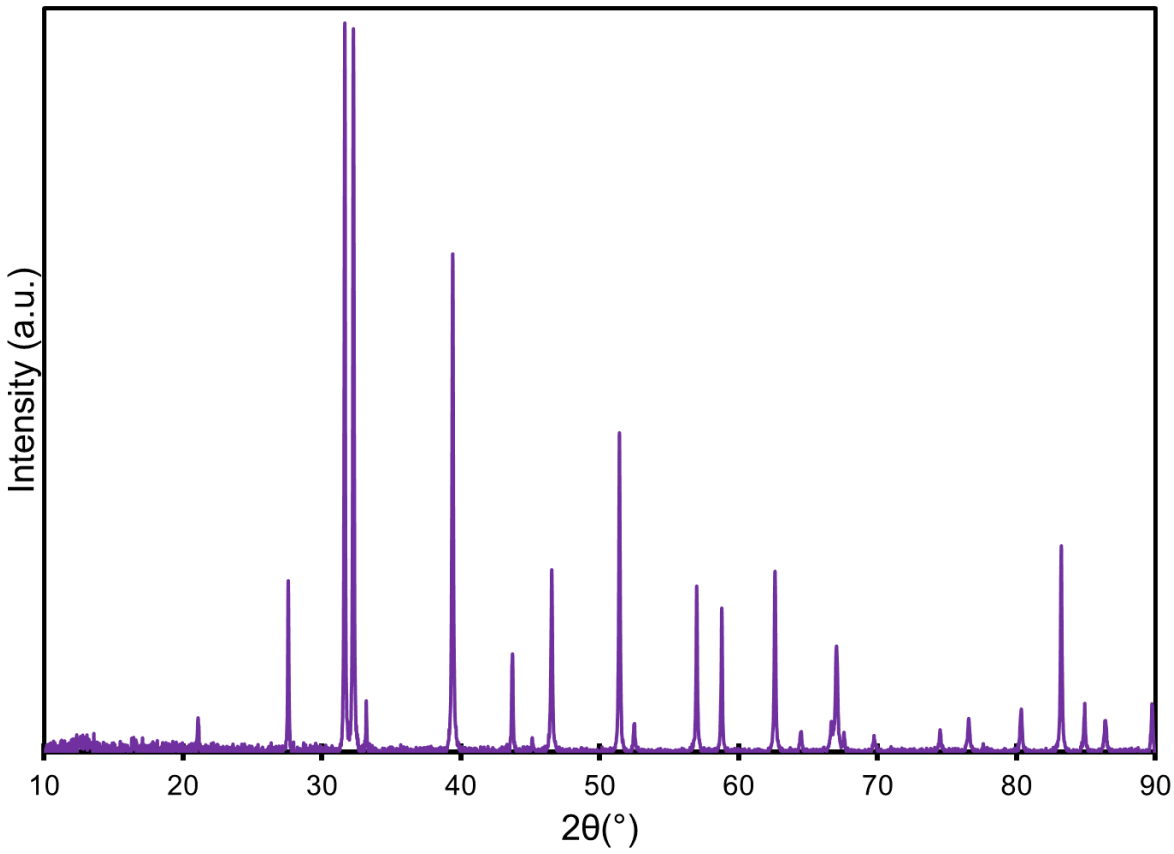

Figure S3. Powder XRD pattern of $BaGa_4$

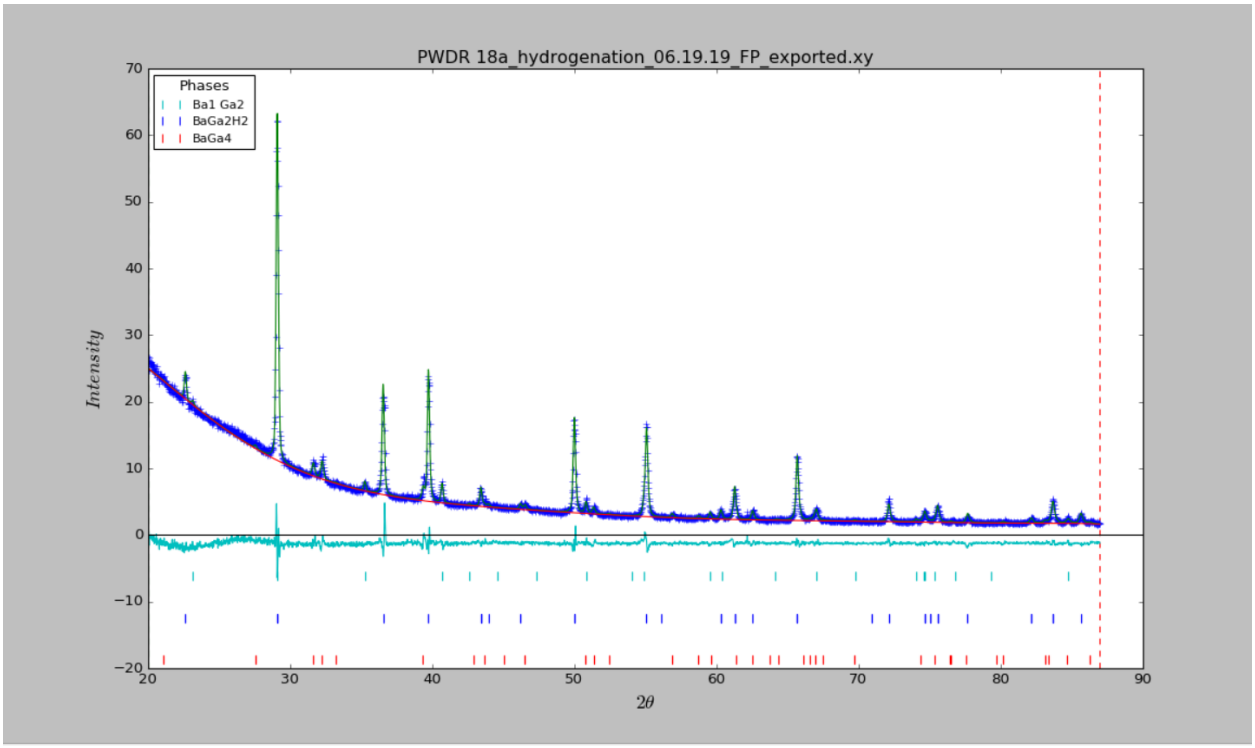

Figure S2. Rietveld refinement of the powder XRD scan of $BaGa_2H_2$, performed using GSAS-II. The observed data, calculated fit, and difference curve are shown using blue marker, green line, and light blue line, respectively.

Table S3. Crystallographic Data on $BaGa_2H_2$

Empirical Formula	$BaGa_2H_2$
Formula Weight (g/mol)	278.79
Space group	P-3m1
a (Å)	4.530(8)
c (Å)	4.910(9)
V	86.385
T	295
λ	1.5406
ρ (g cm^{-3})	5.302
Pattern range (2θ,°)	15-87
Step size (2θ,°)	0.020
Step scan time (s)	1.00
No. of contributing reflns	3397
R_{wp}	0.0481
R_p	0.0355
$R(F^2)$	0.0814
$BaGa_2$ Phase Fraction	0.116
$BaGa_4$ Phase Fraction	0.0365
$BaGa_2H_2$ Phase Fraction	0.847

Table S4. Atomic coordinates and displacement parameters U_{iso} ($Å^2$) for $BaGa_2H_2$, * marks positions/ parameters that were not refined (due to the low electron density of Hydrogen).

Element	x	y	z	U_{iso}
Ga	0.33333	0.66667	0.458(2)	0.0162(26)
Ba	0.00000	0.00000	0.00000	0.0237(3)
H	0.33333	0.66667	0.09760*	0.01*

*not refined

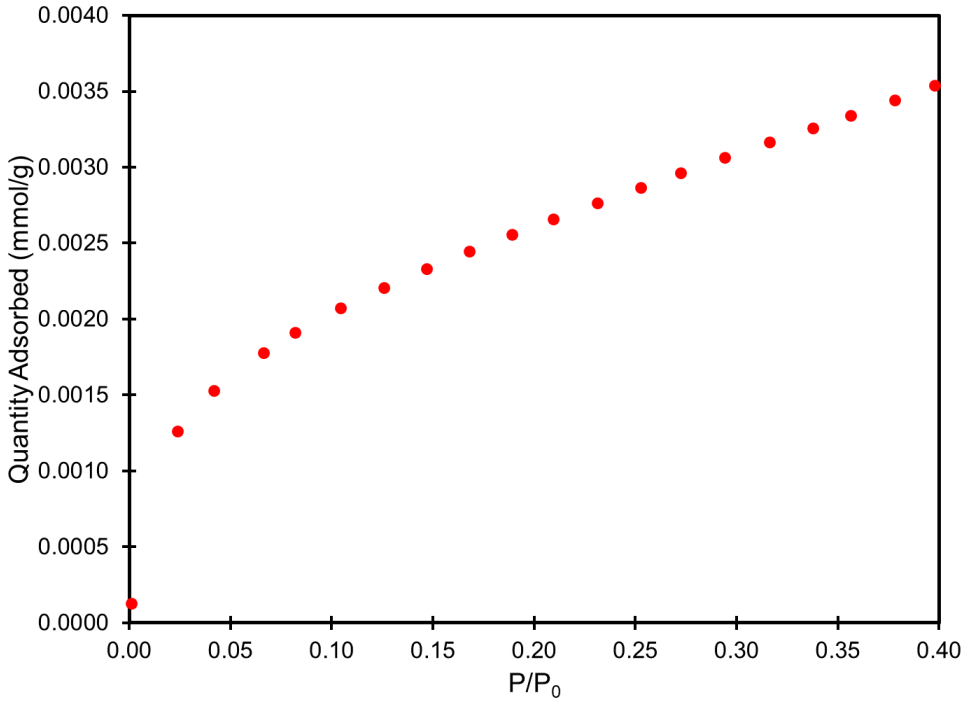

Figure S4. Kr adsorption isotherm of $BaGa_2$.

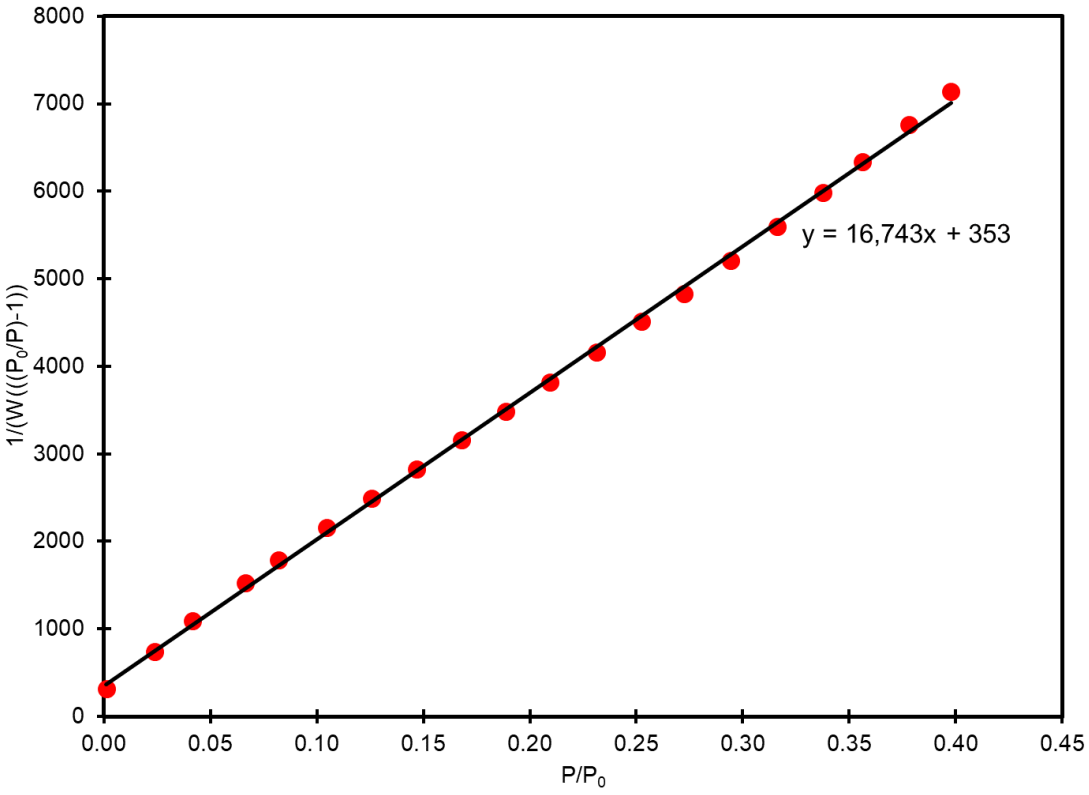

Figure S5. Multipoint fitting of BET measurement of $BaGa_2$ powder, to determine surface area.

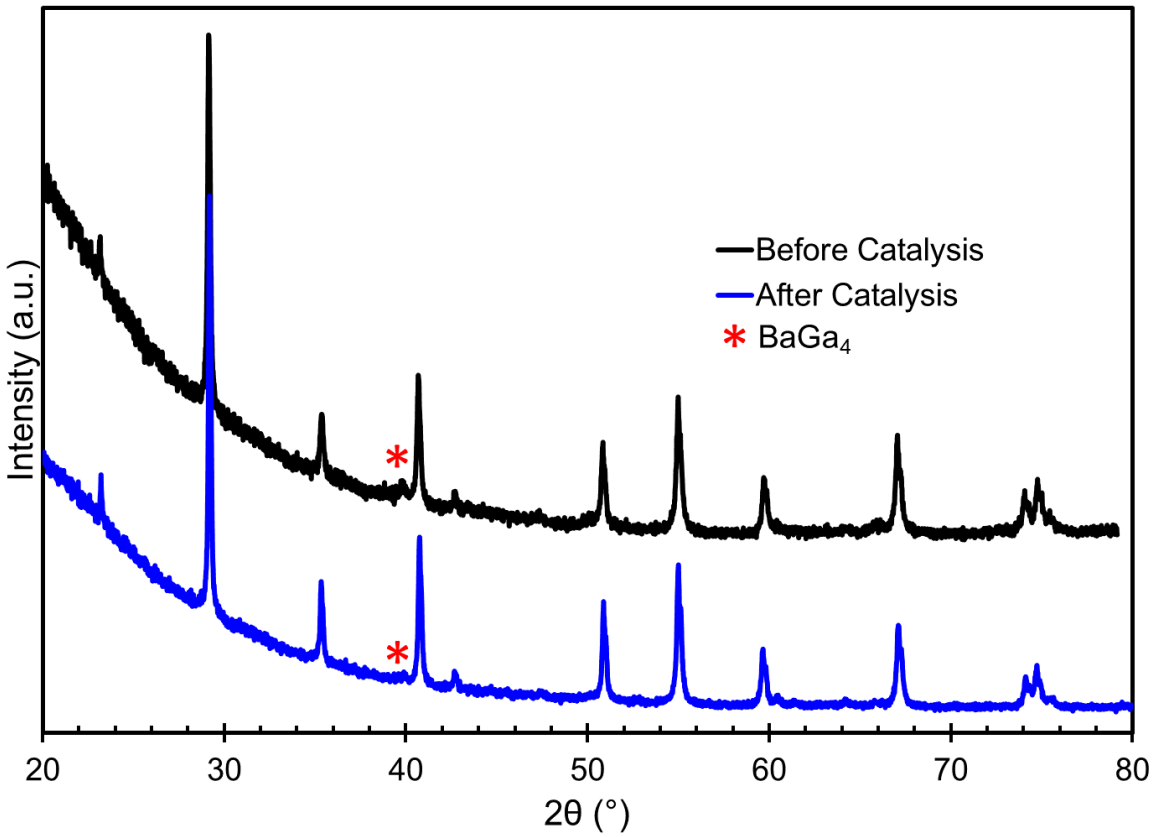

Figure S6. Powder XRD patterns of $BaGa_2$ before and after catalysis, highlighting the absence of structural transformations or $BaGa_2H_2$ formation.

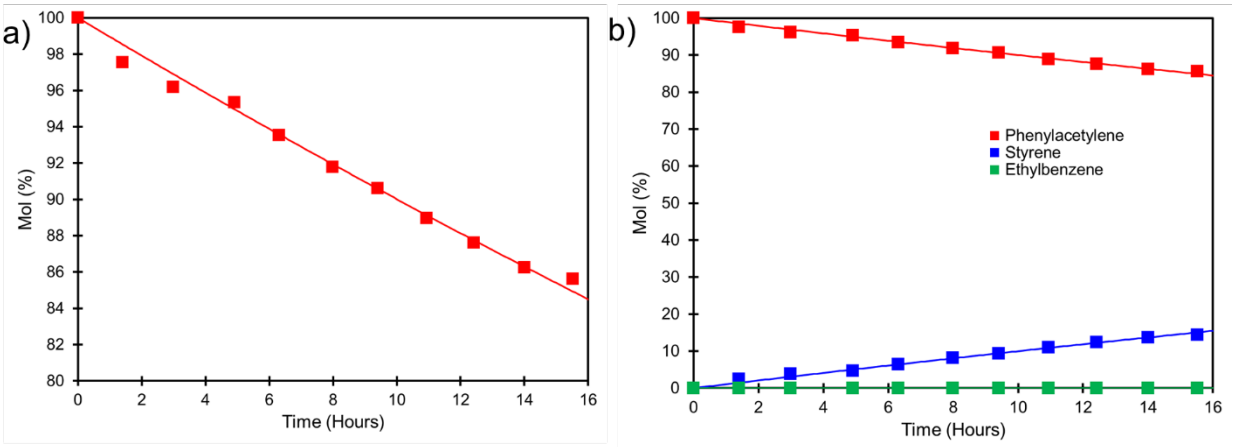

Figure S7. a,b). Time dependent conversion products using 1 bar H_2, 40 ºC, 2.4 mL DMF, 1.1 mmol phenylacetylene, and 0.28 mmol $BaGa_2$ catalyst. The conversion of phenylacetylene to styrene is fit to first order kinetics with k_1= 0.0105(12) h^{-1}.

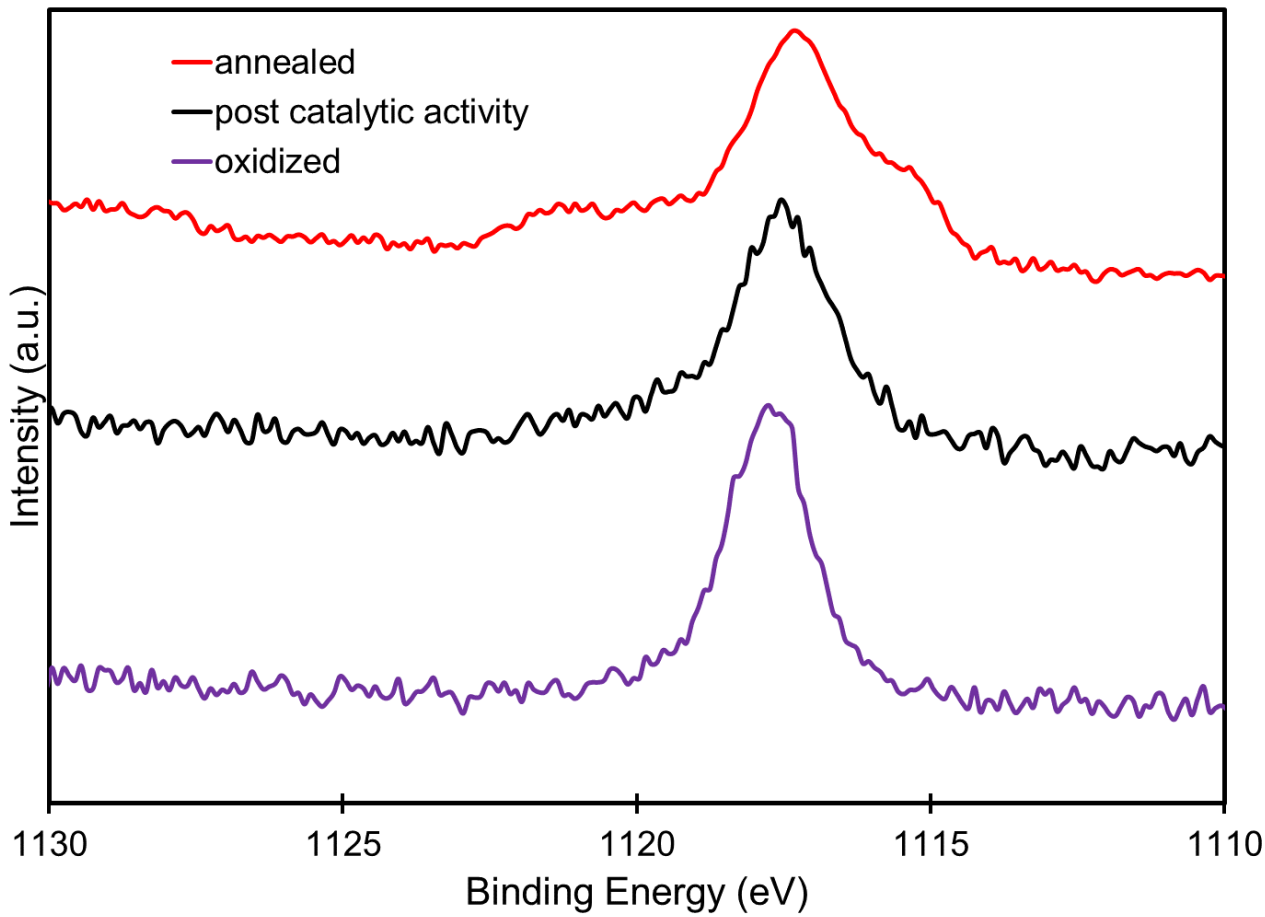

Figure S8. X-ray photoelectron spectroscopy of the Ga $2p_{3/2}$ peak for the 800 ^{o}C annealed (regenerated) $BaGa_2$ (red), $BaGa_2$ after loss of catalytic activity in butanol(black), and air-exposed $BaGa_2$ (purple).

Table S3. Comparison of the catalytic activities of phenylacetylene to styrene with different catalysts.

Catalyst	Conditions	Surface specific activity, or activity per mole of catalyst	Reference
$BaGa_2$	**51 bar H_2, 40 °C, DMF**	**8390 h^{-1} (per surface Ga)**	**This Work**
$BaGa_2$	**1 bar H_2, 40 °C, DMF**	**425 h^{-1} (per surface Ga)**	**This Work**
Pt/C	**1 bar H_2, 40 °C, DMF**	**8950 h^{-1} (per mol Pt)**	**This Work**
Lindlar's Catalyst	**1 bar H_2, 40 °C, DMF**	**860 h^{-1} (per mol Pd)**	**This Work**
Ni_3Ga	5 bar H_2, 40 °C, Hexanes	5.16 x 10^{-3} h^{-1} (per surface Ni)	(S1)
Pd/Carbon Nanotubes	H_2 flow (30 mL/ min), 50 °C, Methanol	3600 h^{-1} (per surface Pd)	(S2)
Au/graphene oxide	H_2 flow (0.2 mL/min), 60 °C, Ethanol	360 h^{-1} (per surface Au)	(S3)
PdZn/ZnO	6 bar, 0 °C, Toluene	15840 h^{-1} (per surface Pd)	(S4)
$Pd/Fe_3O_4@SiO_2(50)$	1bar H_2, 40 °C, Ethanol	47304 h^{-1} (per surface Pd)	(S5)
Lindlar's Catalyst	Continuous flow, 1 bar H_2, Methanol, 30 °C, 1,4-dioxane	1866 h^{-1} (per surface Pd)	(S6)
Pd+Polyethyleneimine(B) @HSS_cal	Continuous flow 1bar H_2, 30 °C, Methanol, 1,4- dioxane	6751 h^{-1} (per surface Pd)	(S6)
Pd/FDU-12	1 bar of H_2, 25 °C, Ethanol	1840 h^{-1} (per surface Pd)	(S7)

References

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