Electronic Supplementary Material (ESI) for Faraday Discussions.

Aligning time-resolved kinetics (TAP) and surface spectroscopy (AP-XPS) for a more comprehensive understanding of ALD-derived 2D and 3D model catalysts.

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Supporting Information

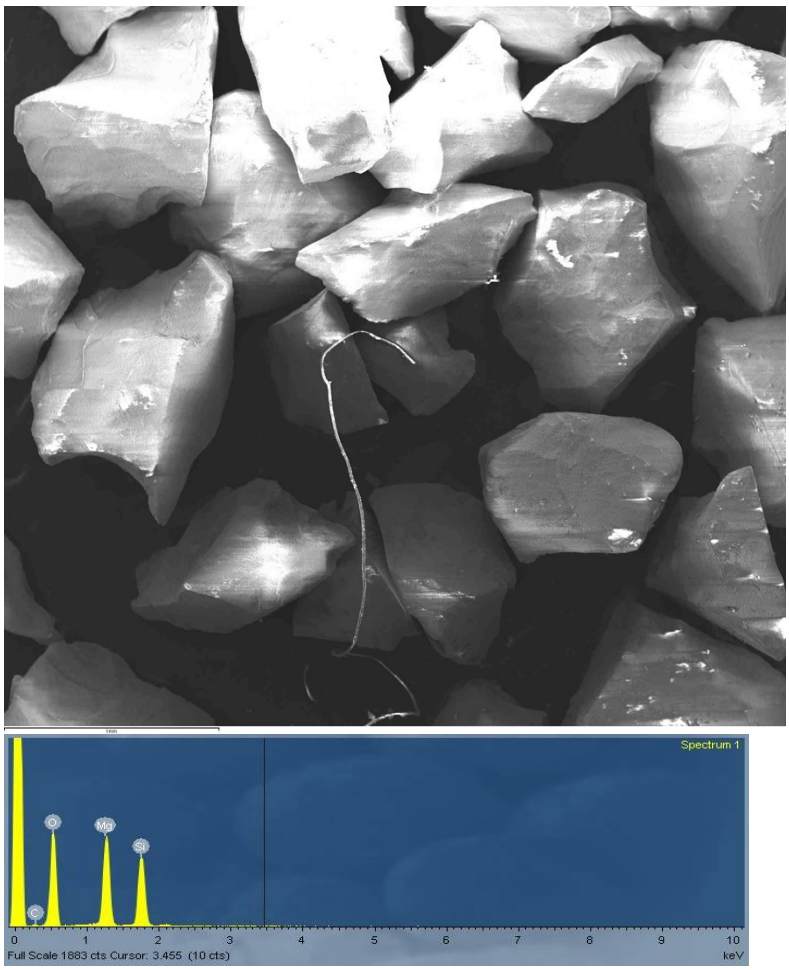


Figure S1. SEM/EDX of the 3D quartz support after MgO ALD.

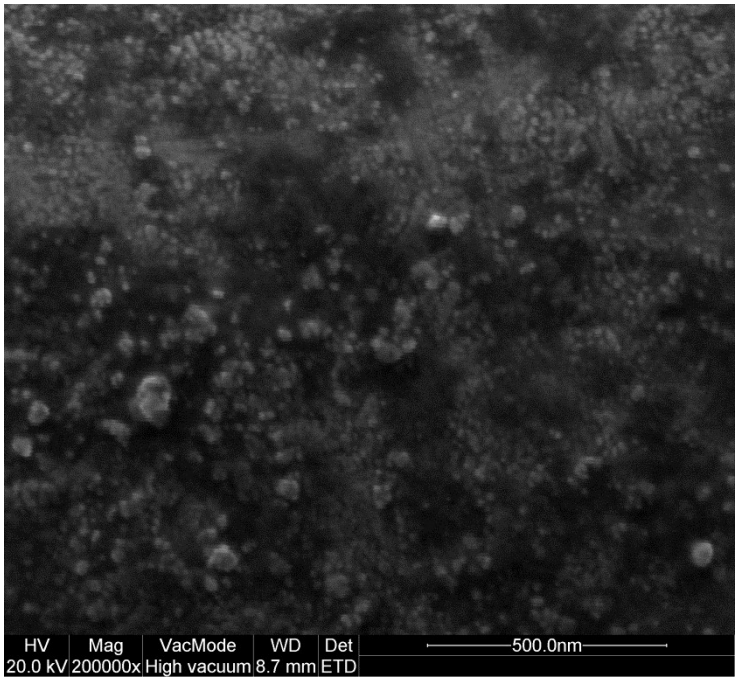
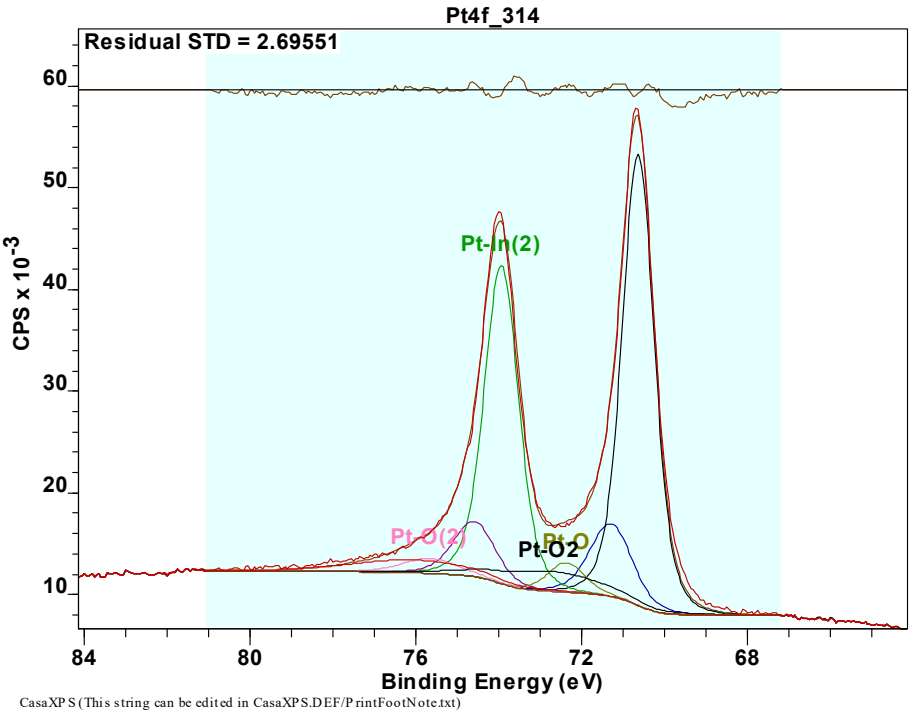


Figure S2. SEM/EDX of the 2D Si-wafer support after MgO ALD.

XPS deconvolution

Pt4f

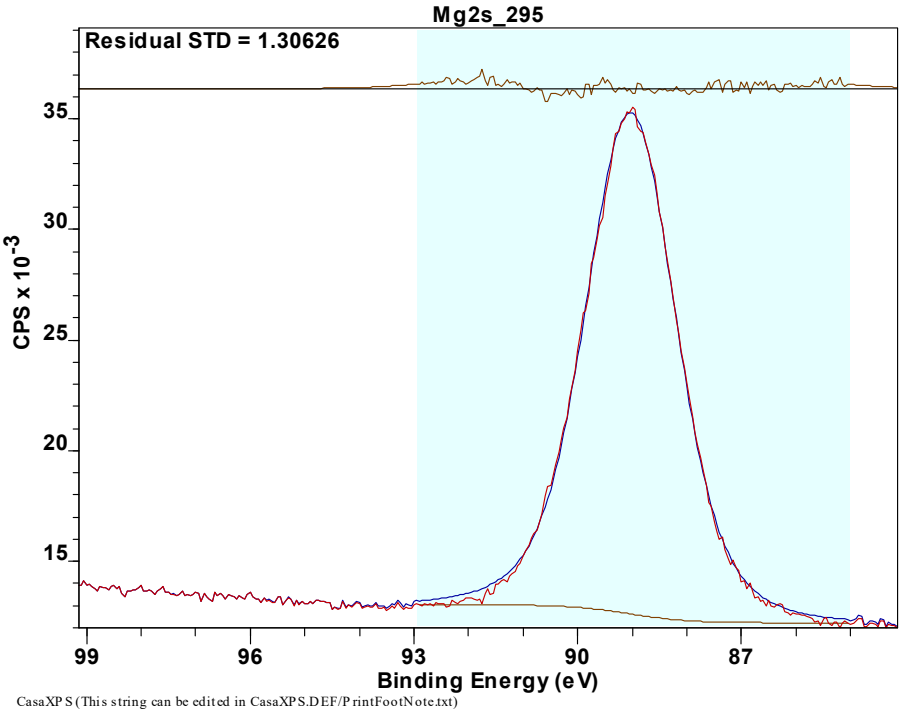
Name	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Goodness of Fit
Pt-M	71.29	1.20	9805.33	8.46	4440.71
Pt-In	70.63	0.91	46259.3	39.92	
Pt-In(2)	73.93	0.97	34694.4	29.94	
Pt-M(2)	74.59	1.19	7354	6.35	
Pt-O	72.36	1.05	3470.86	3.00	
Pt-O(2)	75.66	1.57	2603.15	2.25	
Pt-O2	72.78	3.0	6680.12	5.76	
Pt-O2(2)	76.08	3.44	5010.09	4.32	



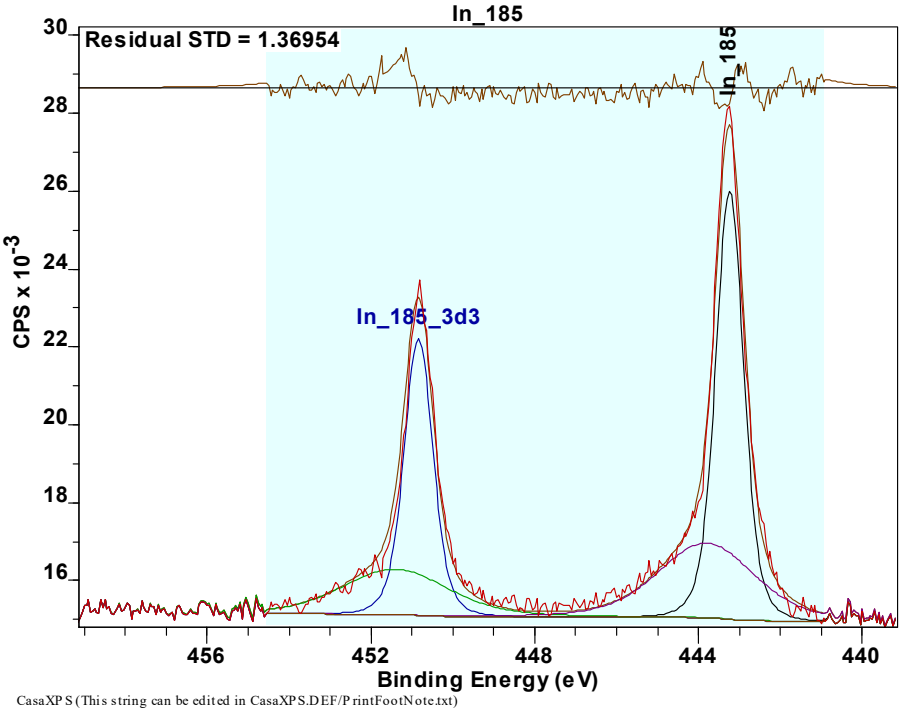
Two major doublet components can be assigned to the pure Pt metal (71.29/74.59 eV) and the alloyed Pt within PtIn alloy (70.63/73.93 eV), respectively. We have also assessed Pt 4f spectrum of a control Pt/SiO_2 sample using C 1s for normalization in that sample. Metallic Pt gave a single doublet with the 7/2 component at 71.72 eV. To compare this pure Pt peak to the pure Pt component (Pt-M) of our main $PtIn/MgO/SiO_2$ sample, we also re-calibrated Pt 4f 7/2 peak for the latter sample to C 1s to yield 72.17 eV. It can be concluded that the pure Pt in the alloyed sample is up-shifted in BE by 0.45 eV with respect to the monometallic reference sample. It can be hypothesized that this difference is due to a combination of three factors: the difference in Pt particle sizes, the influence of MgO support, and the influence of the PtIn alloy which is in electronic constant with pure Pt domains. The downshift of 0.66 eV observed between the pure metal and alloyed contribution within the $PtIn/MgO/SiO_2$ sample is a larger effect in comparison with the 0.45 eV upshift between pure metal components in the two samples.

Mg2s

Name	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Goodness of Fit
Mg2s_295	89.03	1.95	50339.2	100	1521

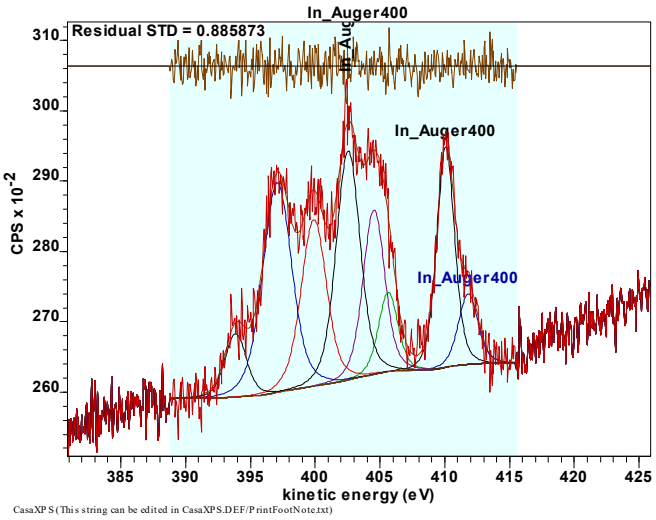


In3d



Name	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Goodness of Fit
In_185_3d5	443.24	0.8	10024.8	37.22	2206.58
In_185_3d5bis	443.80	2.8	6131.78	22.77	
In_185_3d3	450.84	0.82	6686.56	24.83	
In_185_3d3bis	451.40	3.08	4089.9	15.19	

In MNN Auger

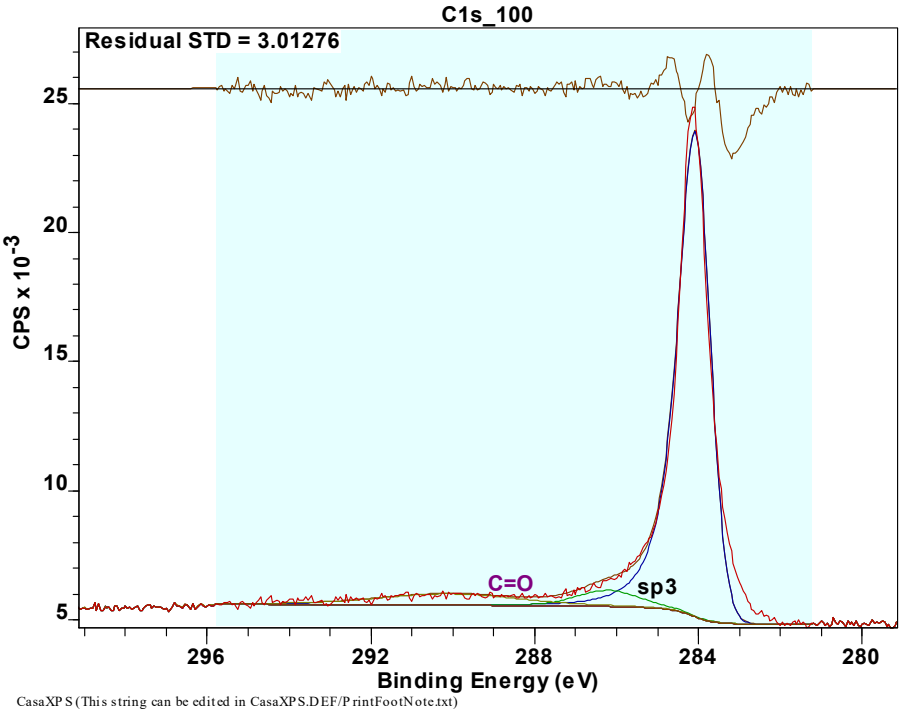


Name	Position (Ekin)	FWHM	%At Conc	Goodness of Fit
In_Auger400_1	411.80	1.75	4.96	2411.68
In_Auger400_2 or $In_4M_{4,5}M_{4,5}$	410.07	1.61	14.26	
In_Auger400_3	405.63	1.75	5.58	
In_Auger400_4	404.53	1.96	12.94	
In_Auger400_5 or $In_5M_{4,5}M_{4,5}$	402.54	2.16	19.86	
In_Auger400_6	399.89	2.3	15.39	
In_Auger400_7	397.06	2.62	22.04	
In_Auger400_8	393.85	1.95	4.97	

Based on the PHI element page for In, the kinetic energy of $In_4M_{4,5}M_{4,5}$ is required together with the binding energy of In3d, to assess the state of In. Based upon the above tables of fitting, the $In_4M_{4,5}M_{4,5}$ Auger peak with Ek = 410.07eV and the In core level 3d 5/2 peak with the Eb = 443.24eV result in the Auger parameter of 853.31eV. The latter positions our material in the neighborhood of indium telluride and indium metal.

C1s:

Name	Position	FWHM	Area/(RSF*T*MFP)	%At Conc	Goodness of Fit
sp2	284.09	0.86	17359.4	84.16	3442.33
Sp3	285.00	1.9	0	0.0	
C-O	286.20	1.8	1286.26	6.24	
C=O	288.60	1.8	0	0.0	
pi-pi*	290.09	4.0	1981.27	9.61	



Simulation parameters for TAP experiments

Theoretical exposure evaluation

time of a single pulse simulation: t= 0.0 to 5.0 s, 0.001 s steps
pulse intensity range: Np = 1e-9 to 1e-8 mol/pulse, 0.01e-9 mol steps
number of pulses in the sequence: n_{pls} = 0 to 1000 pulses, 10 pulses steps
Knudsen diffusivity in the one zone reactor: D = 2e-3 m^2/s
cross-sectional area of the reactor: A = 1.28e-5 m^2
length of a single-zone reactor: L = 50.0e-3 m
void fraction of the packed bed: eps = 0.4

Experiment evaluation

time of a single pulse simulation: t= 0.0 to 3.0 s, 0.001 s steps
pulse intensity range: Np = 1e-8 (actual intensities of Ne signal were used for pulse-wise normalization)
number of pulses in the sequence: n_{pls} = 0 to 490 pulses
Knudsen diffusivity in the one zone reactor at 800K: D_{Ne} = 8.3e-3 m^2/s
cross-sectional area of the reactor: A = 1.28e-5 m^2
length zones in the reactor: L = [0.01778, 0.01952, 0.0119] m
void fraction of the packed bed: eps = 0.4
catalyst loading: m_{cat} = 0.280e-3 kg
concentration of Pt sites: C_{Pt} = 0.2e-3 mol/kg

The total surface area of the catalyst was estimated assuming quartz density of ρ_{SiO2} = 2.65e3 kg/m^3, the mean particle diameter of d_p = (250e-6+500e-6)/2.0.

Numerical parameters:
the number of gridpoints per m of reactor length: 1.d5.

the absolute tolerance passed to subroutine lsode: 1.d-7

the relative tolerance passed to subroutine lsode: 1.d-99