

Supporting Information

Precisely-Controlled Porous Alumina Overcoating on Pd Catalyst by Atomic Layer Deposition: Enhanced Selectivity and Durability in Hydrogenation of 1,3-butadiene

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Experimental section

1. Catalyst synthesis

ALD was carried out on a viscous flow reactor (GEMSTAR-6TM Benchtop ALD, Arradiance). Ultrahigh purity N₂ (99.999%) was used as carrier gas at a flow rate of 200 ml/min. Pd ALD was performed at 150 °C using palladium hexafluoroacetylacetate (Pd(hfac)₂, Sigma-Aldrich, 99.9%) and formalin (Aldrich, 37% HCHO and 15% CH₃OH in aqueous solution).¹⁻² The Pd(hfac)₂ precursor was heated to 65 °C to get sufficient vapor pressure, and the inlet lines were heated to 110 °C to avoid any condensation. The Pd/Al₂O₃ catalyst was synthesized on spherical alumina powder (Nanodur, 99.5% Alfa Aesar) by Pd ALD for one cycle. The timing sequence was 300, 200, 90, and 200 sec for Pd(hfac)₂ exposure, N₂ purge, formalin exposure and N₂ purge, respectively. Al₂O₃ ALD coating on the Pd/Al₂O₃ catalyst was performed by alternative exposures to trimethylaluminum (TMA, Sigma-Aldrich, 99%) and de-ionized water at 200 °C for different cycles.³⁻⁵ The Pd loading was determined to be 0.25% by an inductively coupled plasma atomic emission spectrometer (ICP-AES).

Pt ALD was conducted using trimethyl(methylcyclopentadienyl)-platinum(IV) (MeCpPtMe₃, Sigma-Aldrich, 98 %) and O₂ at 250 °C.⁶⁻⁷ Here the MeCpPtMe₃ precursor was contained in a sealed stainless steel bottle at 65 °C to get sufficient vapor pressure, and the inlet lines were heated to 110 °C to avoid any condensation. The Pt/Al₂O₃ catalyst was synthesized on the spherical alumina powder by Pt ALD for one cycle. The timing sequence was 300, 200, 250, and 180 sec for MeCpPtMe₃ exposure, N₂ purge, O₂ exposure and N₂ exposure, respectively. The Pt loading was determined to be 1.4% by ICP-AES.

Another Pd/Al₂O₃ sample was also synthesized using a wet-impregnation method (Pd/Al₂O₃-WI).³ Therein, 0.1 g of Pd(NO₃)₂ · 2H₂O (Aladdin, ≥97.7%) and 0.436 g of citric acid (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%) were dissolved in 2.57 ml water to form a Pd-citric acid solution. Then 4.36 g spherical Al₂O₃ powder (Nanodur, Alfa Aesar, 99.5%) was added to the solution and mixed uniformly, and the mixture was dried overnight at 125 °C. Finally, the dried material was calcined in 10% O₂ in He at 300 °C for 5 h, then reduced at 250 °C for 30 min in 10% H₂ in He. The Pd loading was determined to be 1% by ICP-AES.

2. Characterization

The morphology of catalysts was characterized on an aberration-corrected HAADF-STEM instrument at 200 kV (JEOL-2010F, University of Science and Technology of China). The DRIFTS CO chemisorption measurements were performed on a Nicolet iS10 spectrometer equipped with an MCT detector and a low temperature reaction cell (Praying Mantis Harrick). After loading a sample into the cell, the sample was calcined in 10% O₂ in He at 150 °C for 1 h followed by reduction in 10% H₂ in He at 150 °C for 1 h. After cooling the sample to room temperature under He, a background spectrum was collected. Subsequently, the sample was exposed to 10% CO in He at a flow rate of 20 ml/min for about 30 min until saturation. Next, the sample was purged with He at a flow rate of 20 ml/min for another 30 min to remove the gas phase CO and then the DRIFT spectrum was collected with 256 scans at a resolution of 4 cm⁻¹. The N₂ physisorption measurements were conducted using a Micromeritics ASAP 2020 system. Therein all the samples were degassed at 150 °C in the vacuum for 12 h before the measurements.

3. Reaction test

Selective hydrogenation of 1,3-butadiene was conducted in a fixed-bed flow reactor. The feed gas consisted of 1.9% 1,3-butadiene, 4.7% H₂ with Ar as the balance gas. For the reaction in the presence of propene, the feed gas was adjusted to 1.9% 1,3-butadiene, 4.7% H₂, 70% propene and Ar as the balance gas. The total flow rate was kept at 25 ml/min in both cases. The amount of uncoated Pd/Al₂O₃ catalyst was 50 mg, while the amount of alumina coated Pd/Al₂O₃ catalyst was adjusted to keep the same Pd content. All catalysts were diluted with 1 g of 60-80 mesh quartz chips. Prior to the reaction test, all catalysts were first calcined in 10% O₂ in Ar for 1 h, then reduced in 10% H₂ in Ar at 150 °C for another 1 h. The reaction products were analyzed using an online gas chromatography equipped with a FID detector and a capillary column (ValcoPLOT VP-Alumina-KCl, 50 m x 0.53 mm).

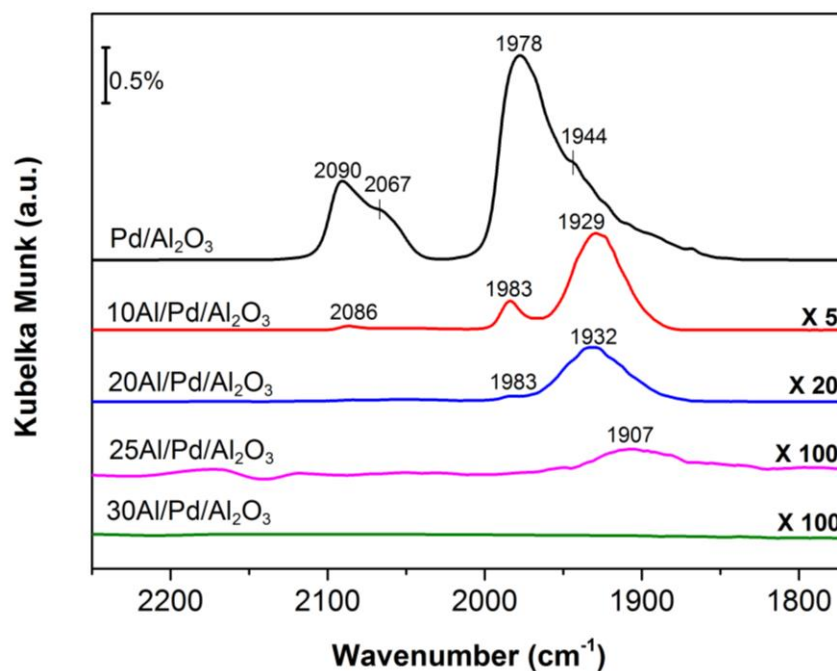


Figure S1. DRIFT spectra of CO chemisorption on the Pd/Al₂O₃ samples with and without ALD alumina overcoats at the CO saturation coverage: uncoated Pd/Al₂O₃, and as-prepared xAl/Pd/Al₂O₃ (x = 10, 20, 25 and 30) samples. For the purpose of clear vision, the spectra of ALD alumina coated samples are magnified to different extents as indicated on the right side of this figure.

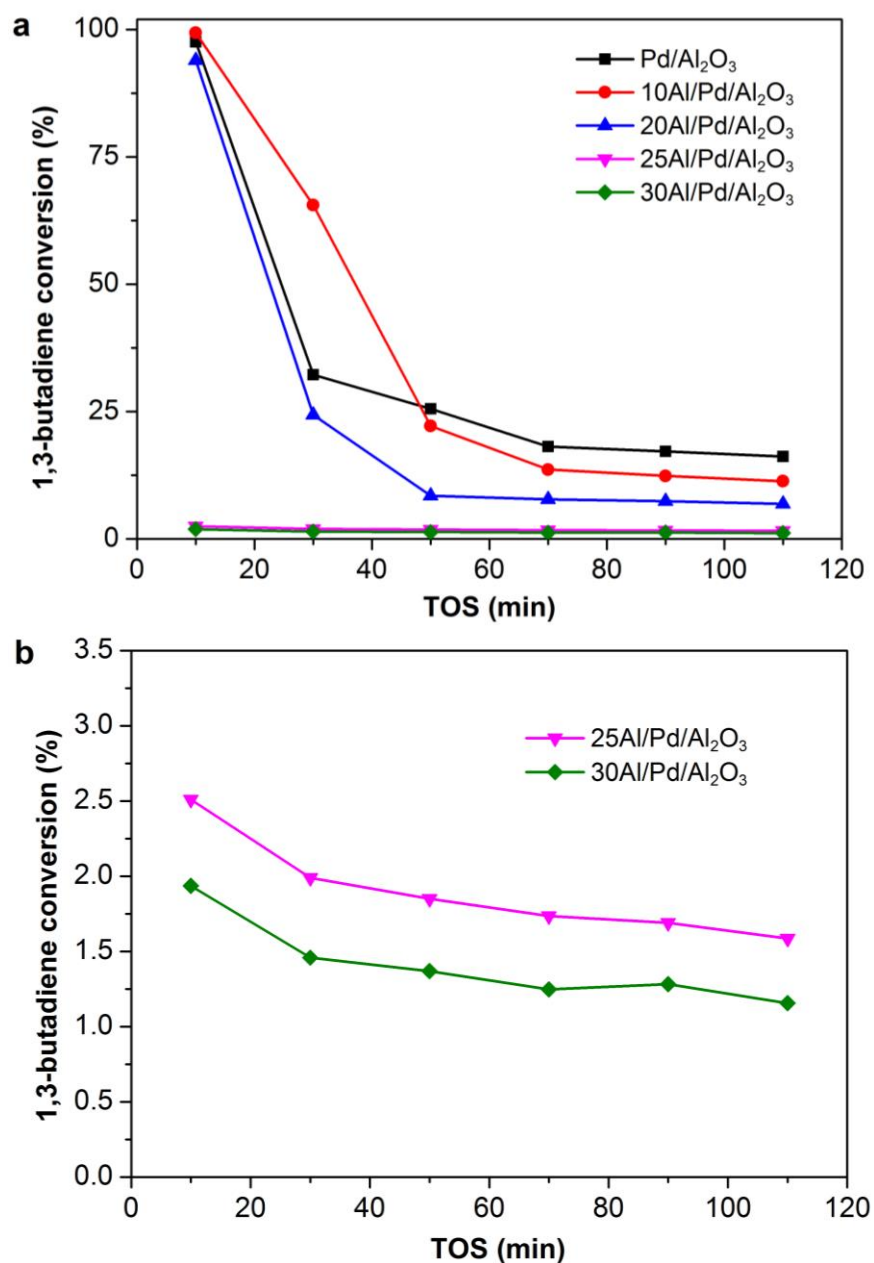


Figure S2. (a) The initial deactivation behaviors of the various uncoated and ALD alumina coated Pd/Al₂O₃ catalysts; (b) The initial deactivation behaviors of the 25 and 30 cycles of ALD alumina coated Pd/Al₂O₃ catalysts (25Al/Pd/Al₂O₃ and 30Al/Pd/Al₂O₃) for a clear illustration.

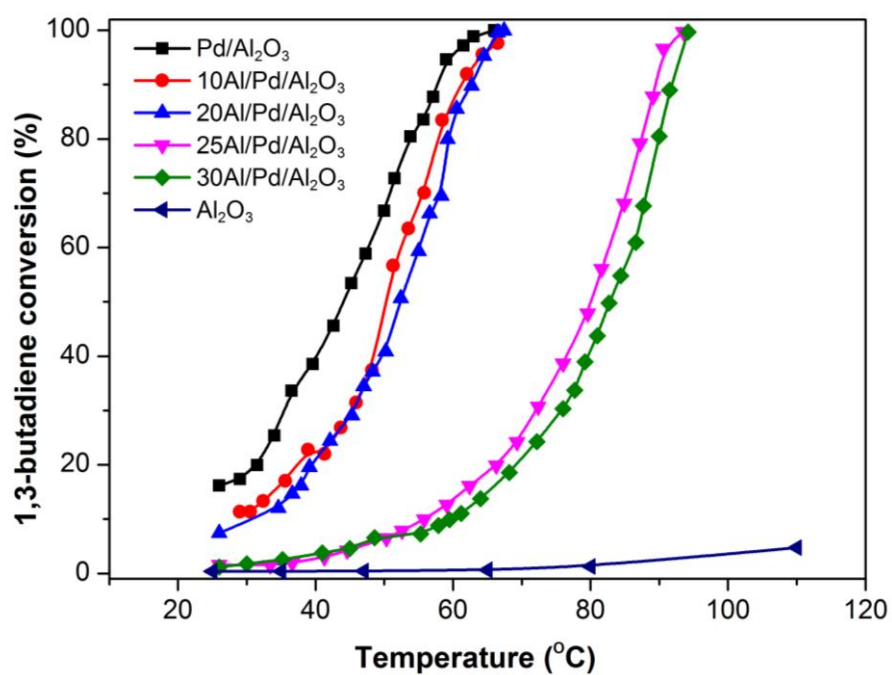


Figure S3. 1,3-butadiene conversion as a function of reaction temperature on the various uncoated and ALD alumina coated Pd/Al₂O₃ catalysts after the initial catalyst deactivation. The Al₂O₃ substrate was also examined as a control experiment.

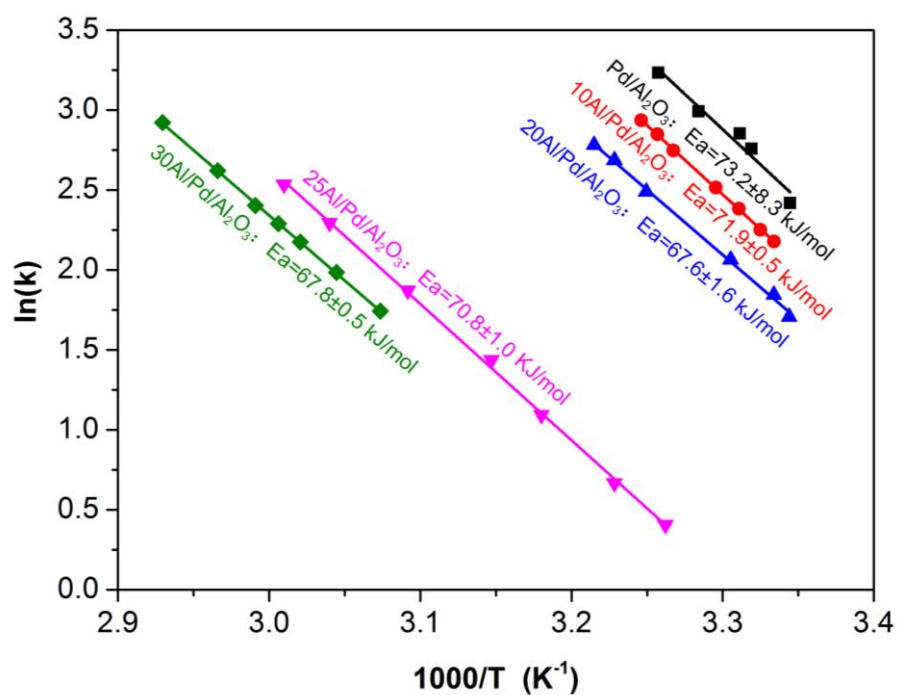


Figure S4. Arrhenius plots on the various uncoated and ALD alumina coated Pd/Al_2O_3 catalysts after the initial catalyst deactivation. The activation energies of these samples are indicated.

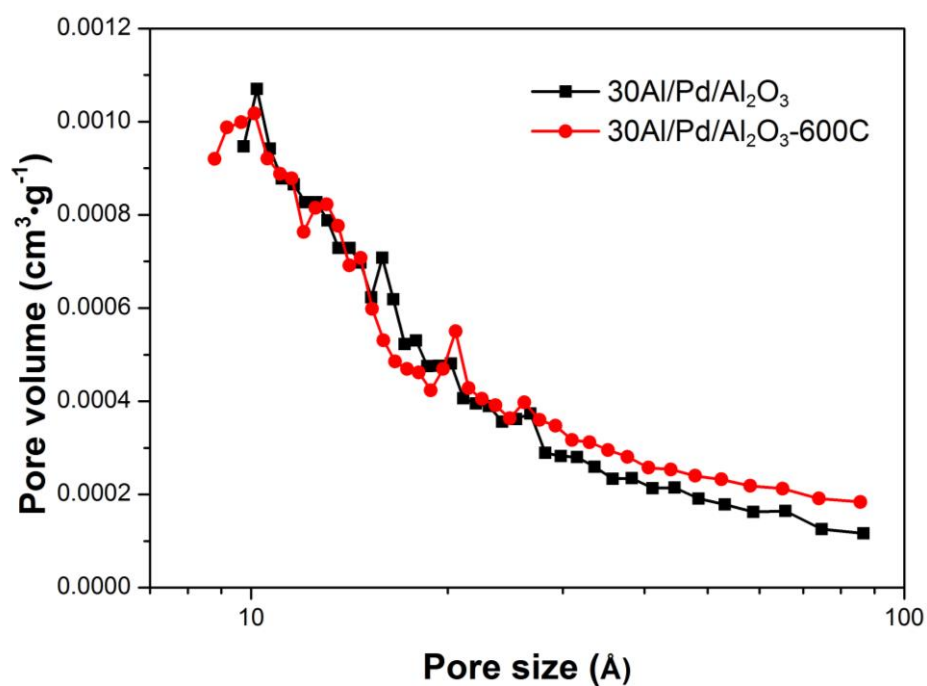


Figure S5. Pore size distributions calculated based on the DFT model from the N₂ adsorption isotherms of the as-prepared 30Al/Pd/Al₂O₃ and 30Al/Pd/Al₂O₃-600C samples. Here the 30Al/Pd/Al₂O₃-600C catalyst was obtained by calcining the 30Al/Pd/Al₂O₃ sample at 600 °C in 10% O₂ in Ar for 2 h followed by reduction at 250 °C in 10% H₂ in Ar for another 1h.

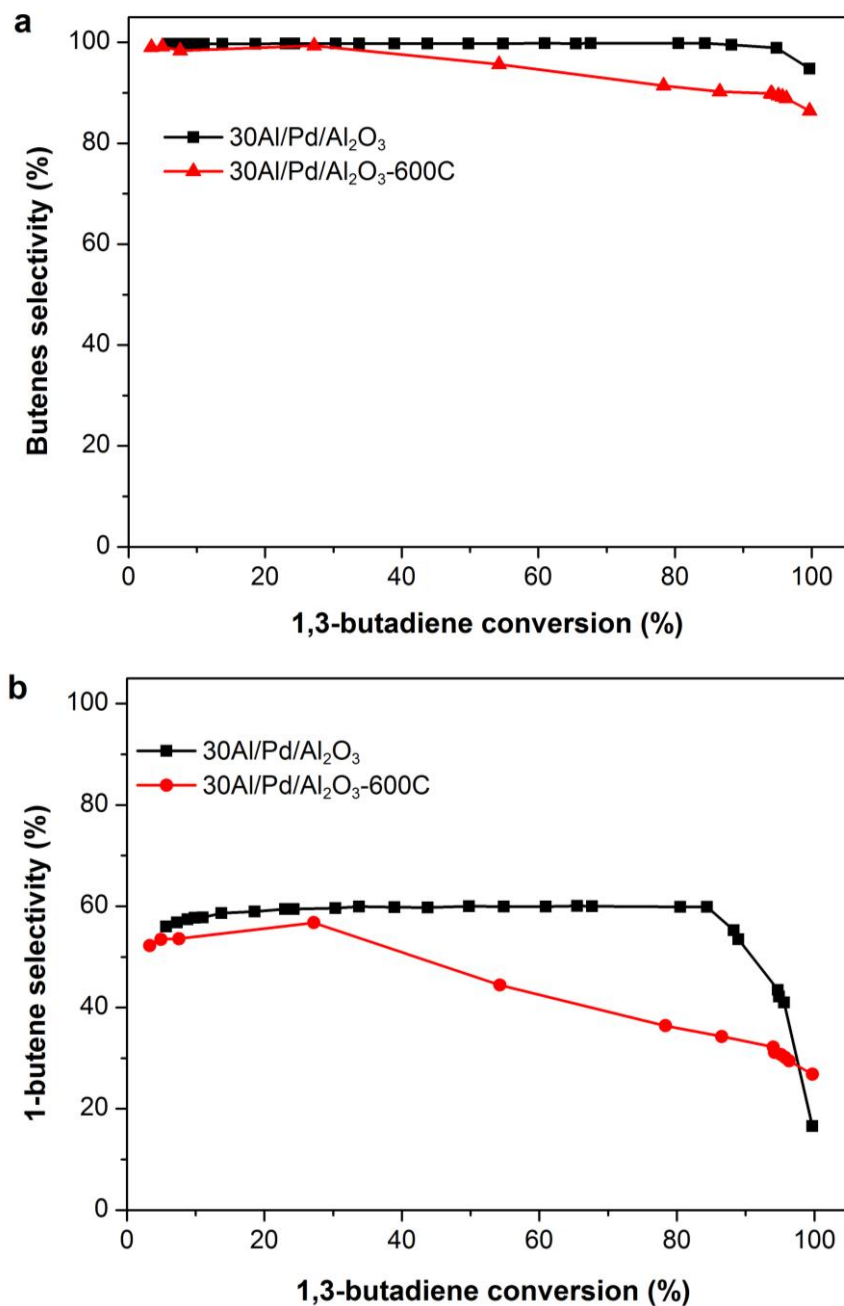


Figure S6. Catalytic performance of the as-prepared 30Al/Pd/Al₂O₃ and 30Al/Pd/Al₂O₃-600C catalysts in selective hydrogenation of 1,3-butadiene in the absence of propene. a) Selectivity to all butenes as a function of 1,3-butadiene conversion; b) 1-butene selectivity as a function of 1,3-butadiene conversion. Here the 30Al/Pd/Al₂O₃-600C catalyst was obtained by calcining the 30Al/Pd/Al₂O₃ sample at 600 °C in 10% O₂ in Ar for 2 h followed by reduction at 250 °C in 10% H₂ in Ar for another 1h.

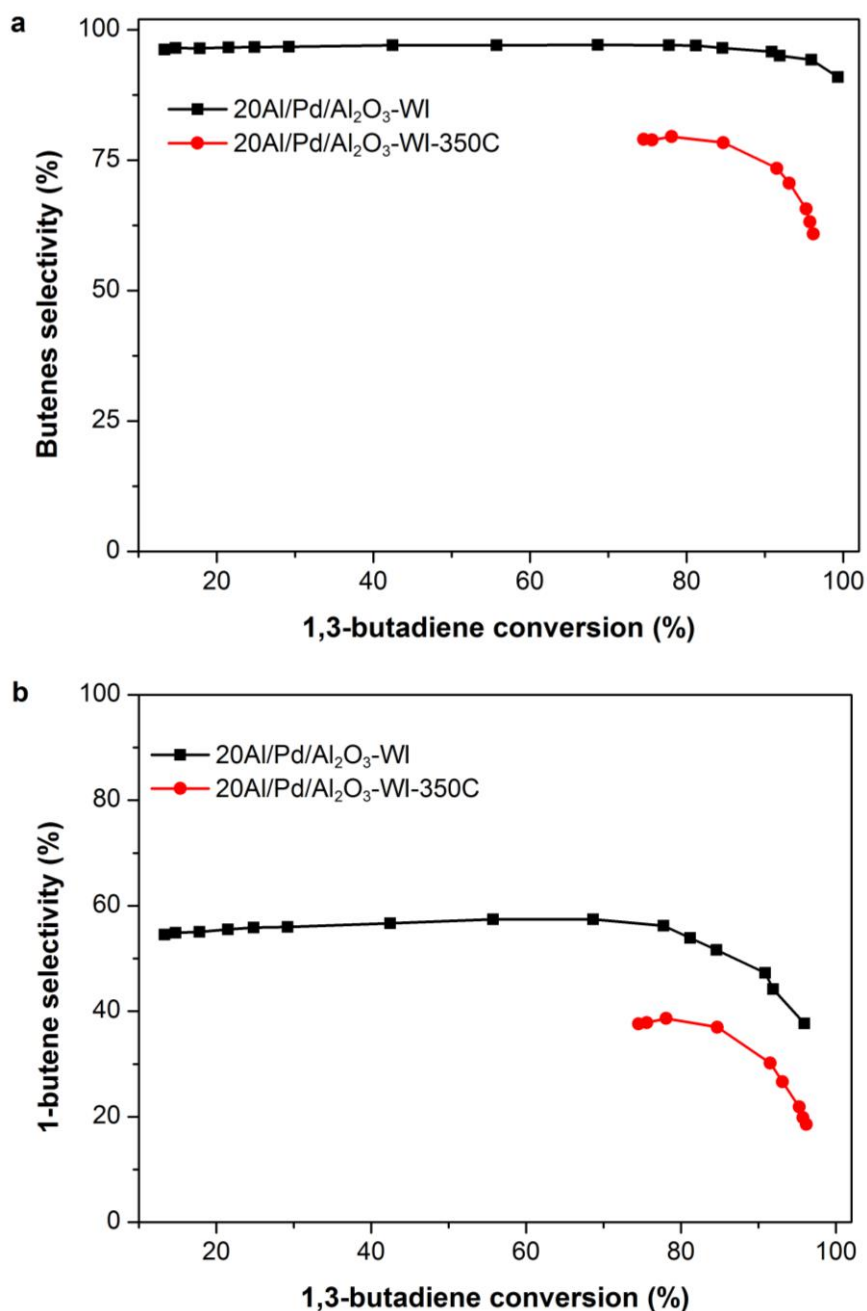


Figure S7. Catalytic performance of the as-prepared 20Al/Pd/Al₂O₃-WI and 20Al/Pd/Al₂O₃-WI-350C catalysts in selective hydrogenation of 1,3-butadiene in the absence of propene. a) Selectivity to all butenes as a function of 1,3-butadiene conversion; b) 1-butene selectivity as a function of 1,3 butadiene conversion.

Here the 20Al/Pd/Al₂O₃-WI-350C sample was obtained by calcining the 20Al/Pd/Al₂O₃-WI sample at 350 °C in 10% O₂ in Ar for 1 h followed by reduction at 150 °C in 10% H₂ in Ar for another 1 h. Because the conversion of 1,3-butadiene was already about 75% on the 20Al/Pd/Al₂O₃-WI-350C sample at room temperature, we only showed the selectivity-conversion relationship at above ~75% conversion on this sample.

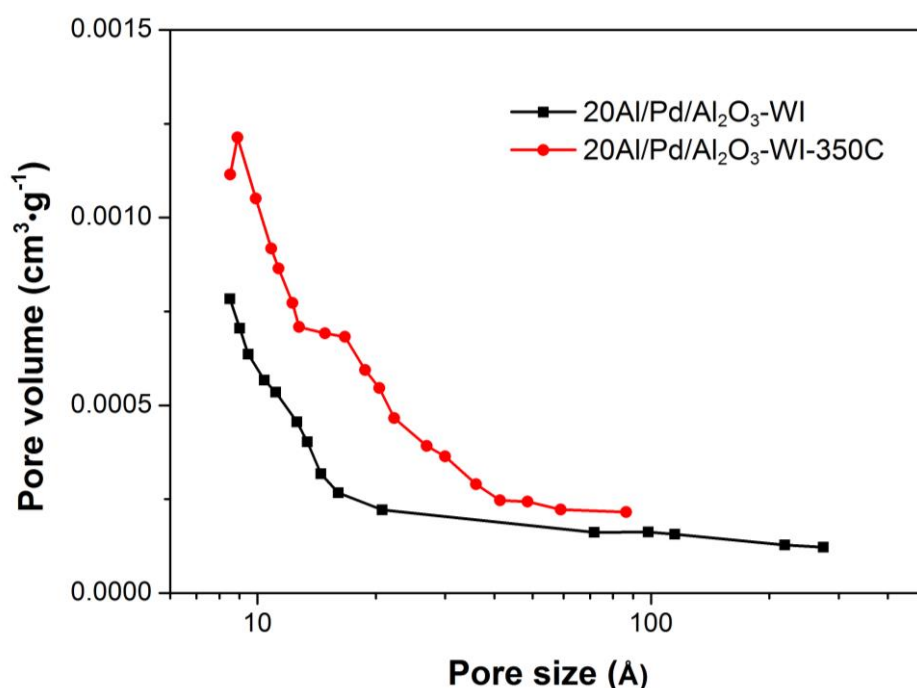


Figure S8. Pore size distributions calculated based on the DFT model from the N₂ adsorption isotherms of the as-prepared 20Al/Pd/Al₂O₃-WI and 20Al/Pd/Al₂O₃-WI-350C samples. Here the 20Al/Pd/Al₂O₃-WI-350C sample was obtained by calcining the 20Al/Pd/Al₂O₃-WI sample at 350 °C in 10% O₂ in Ar for 1 h followed by reduction at 150 °C in 10% H₂ in Ar for another 1 h.

On the Pd sample synthesized by Pd ALD, the porosity did not change significantly even after calcination at 600 °C (Figure S4). Only a slight increase in pore volume was observed with the pore size between ~3-9 nm. However, a significant change in pore size distribution was observed on the Pd sample synthesized using the WI method. Therein, larger pores with a size between 2-4 nm were formed even after calcination at 350 °C in 10% O₂ for 1 h (Figure S7), consistent with our previous results.³ Apparently, larger pores seem to be much more easily formed on the 20Al/Pd/Al₂O₃-WI sample than the 30Al/Pd/Al₂O₃ sample.

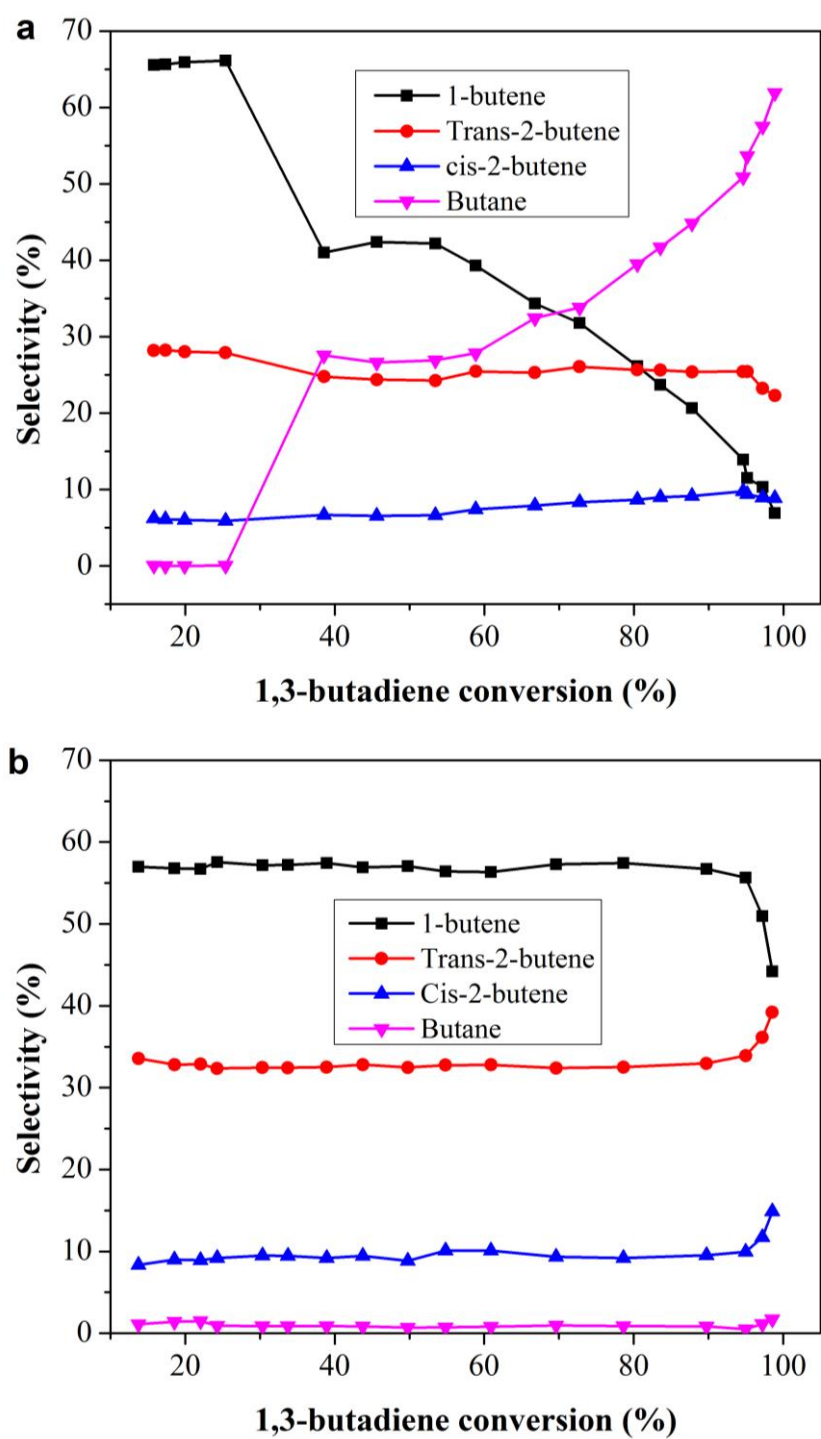


Figure S9 Plots of selectivity as a function of 1,3-butadiene conversion on Pd/Al₂O₃ (a) and 30Al/Pd/Al₂O₃ (b) catalysts in selective hydrogenation of 1,3-butadiene in the absence of propene.

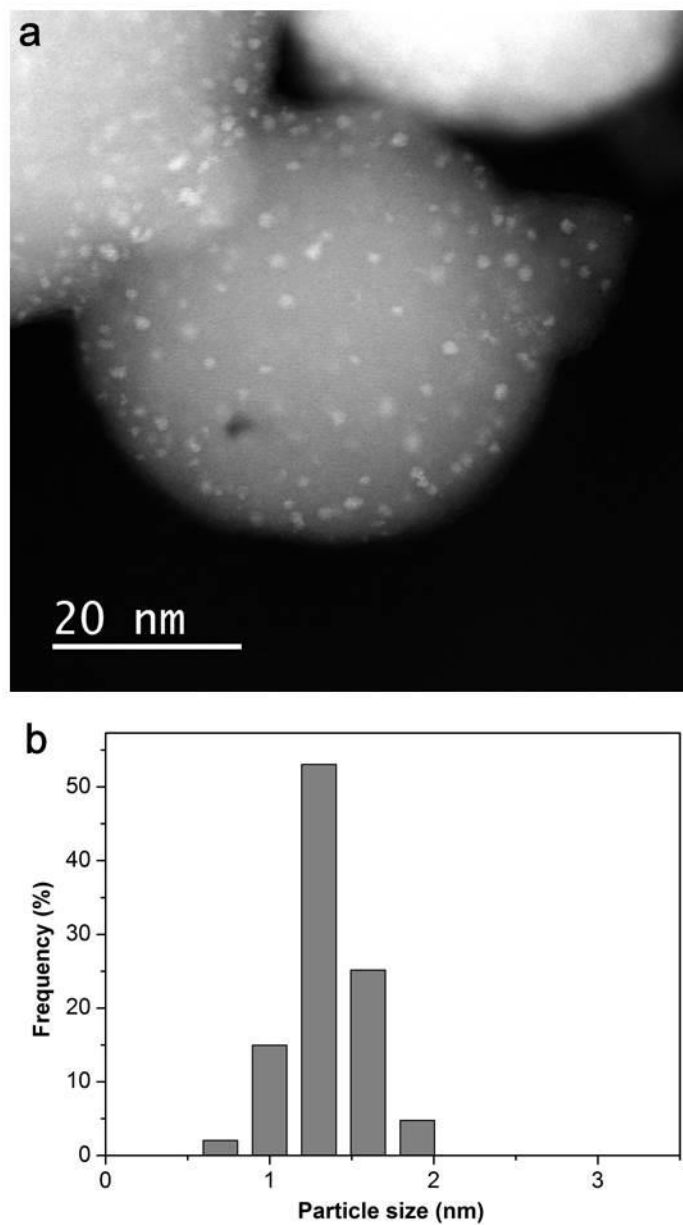


Figure S10. (a) A representative abbreviation-corrected HAADF STEM image of the as-prepared Pt/Al₂O₃ sample using Pt ALD at 250 °C. (b) The particle size distribution histogram of Pt nanoparticles on this sample.

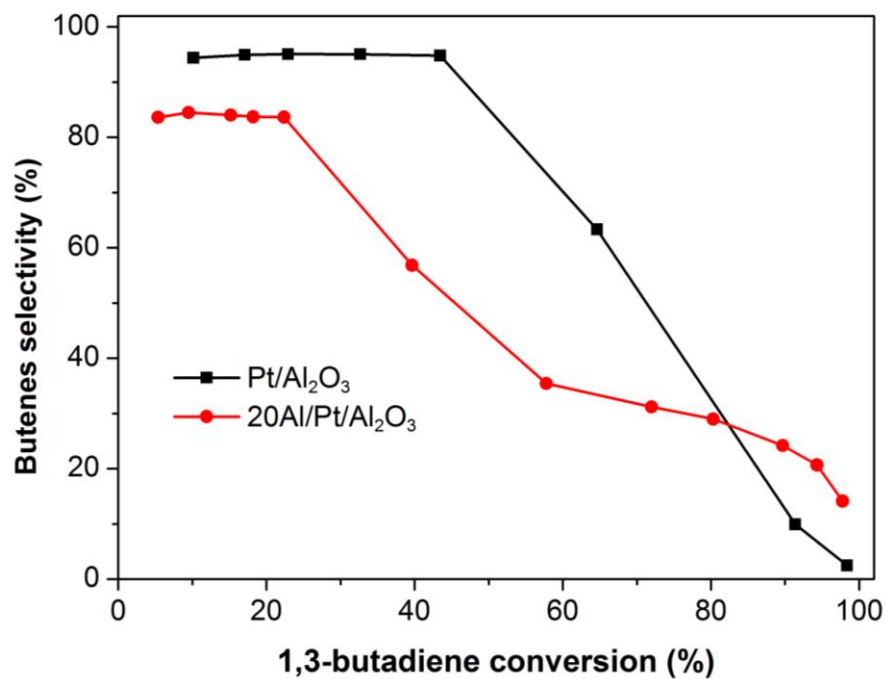


Figure S11. Catalytic performance of the uncoated and 20 cycles of ALD alumina overcoated Pt/Al₂O₃ catalysts in selective hydrogenation of 1,3 butadiene in the absence of propene.

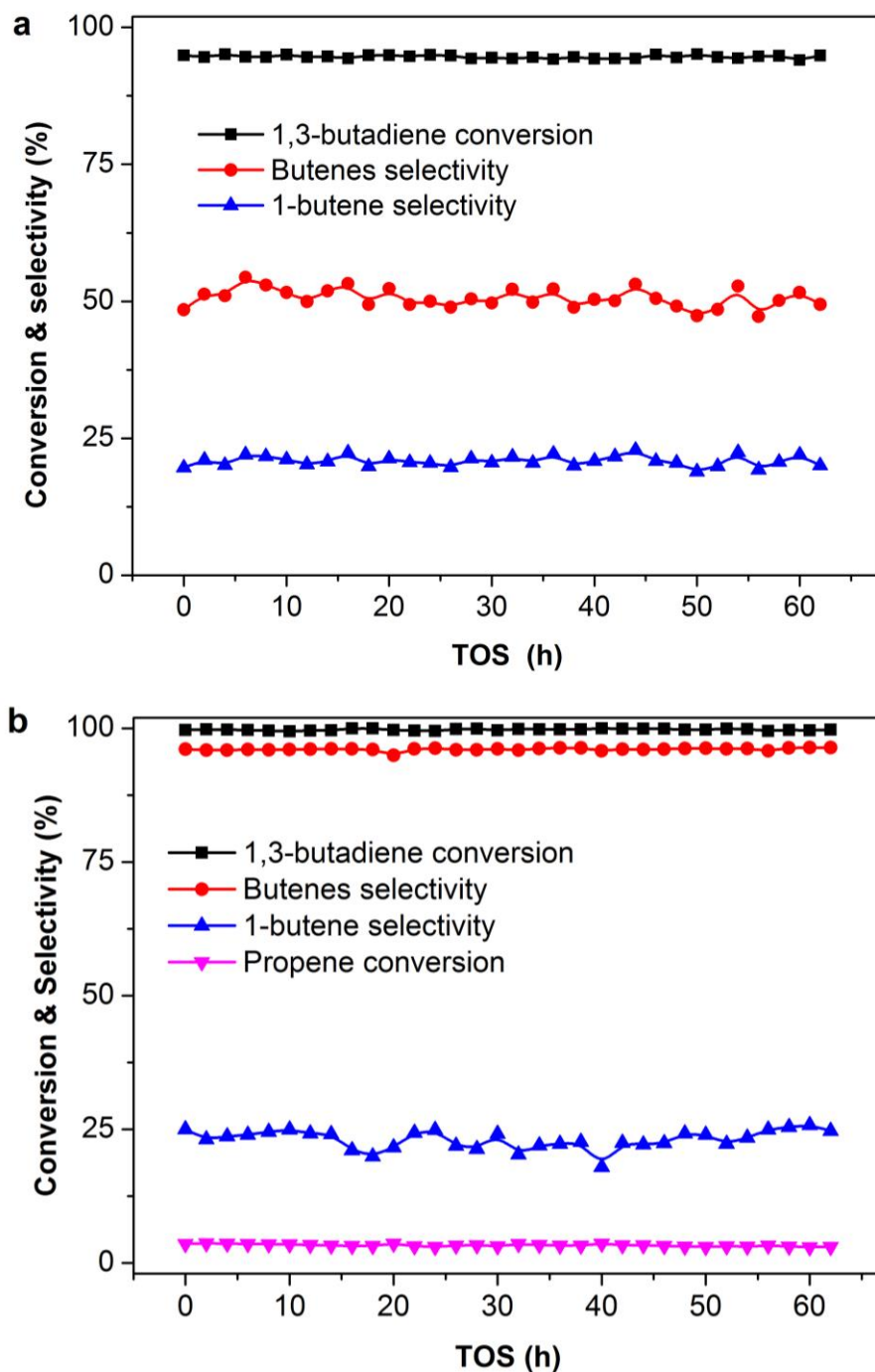


Figure S12. Durability test on the uncoated Pd/Al₂O₃ sample at 44 °C first in the absence of propene for 62 h (a), and then in the presence of 70% propene for another 62 h (b) at high 1,3-butadiene conversions. The propene conversion was 3.9%. TOS = time on stream.

Table S1: Catalytic performances of the Pd/Al₂O₃-WI samples with and without ALD alumina overcoats in the presence of an excess of propene. The feed gas was 1.9% 1,3-butadiene, 4.7% H₂, and 70% propene with Ar as the balance gas at a total flow rate of 25 ml/min.

Samples	Reaction Temp. (°C)	Propene Conv. (%)	1,3-Butadiene Conv. (%)	Selectivity (%)		
				1-butene	trans-2-butene	cis-2-butene
Pd/Al ₂ O ₃ -WI	54	3.6	97	18	54	25
10Al/Pd/Al ₂ O ₃ -WI	68	3.5	97	29	45	23
15Al/Pd/Al ₂ O ₃ -WI	57	1	98	43	41	15
20Al/Pd/Al ₂ O ₃ -WI	61	0.4	100	51	36	12
20Al/Pd/Al ₂ O ₃ -WI-350C	30	3.3	100	23	46	23

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