Supporting Information

Design, testing and characterization of noble-metal catalysts for the heat-release reaction of a molecular solar thermal energy storage isomer pair

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General Considerations

NMR spectroscopy was performed in 5 mm diameter tubes in $CDCl_3$ at 25 °C. ^{1}H NMR spectroscopy was performed on a Bruker Avance spectrometer at 300 MHz with tetramethylsilane (TMS) as a reference. ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 75 or 101 MHz. The chemical shifts are reported in ppm (δ units), and the internal solvent signal (δ = 7.26 ppm for CDCl3) was used as a reference. Au/EC300J catalyst (AuNPs) t (AuNPs <5nm) was purchased from Nanoscientifica Scandinavia.

Isomerization of NBDs took place under the irradiation of a Luzchem UV-Vis photoreactor (LZC-4), provided with 14 8W LZC-UVA/UVB lamps (they can be exchangeable, see below).

Figure S 1UV-Vis Photoreactor Luzchem (LZC-4).

Characterization of NBD1/QC1

^{1}H NMR

- *2-Cyano-3-((4-methoxyphenyl)-norbornadiene (NBD1)*

An NMR tube was filled 700µL of Toluene-d8 with 15.6 mg of NBD1. The ^{1}H NMR spectra were recorded with a Bruker ARX300. Chemical shifts are quoted relative to SiMe4 (external).

NBD1. ^{1}H NMR (300 MHz, Tol) δ 7.66 – 7.52 (m, 2H), 6.66 – 6.54 (m, 2H), 6.46 (ddd, J = 5.1, 2.9, 0.8 Hz, 1H), 6.39 (ddd, J = 5.1, 3.1, 0.9 Hz, 1H), 3.55 (ddtd, J = 3.2, 2.4, 1.6, 0.8 Hz, 1H), 3.43 (ddtd, 1H), 3.25 (s, 3H), 1.75 (ddt, 2H).

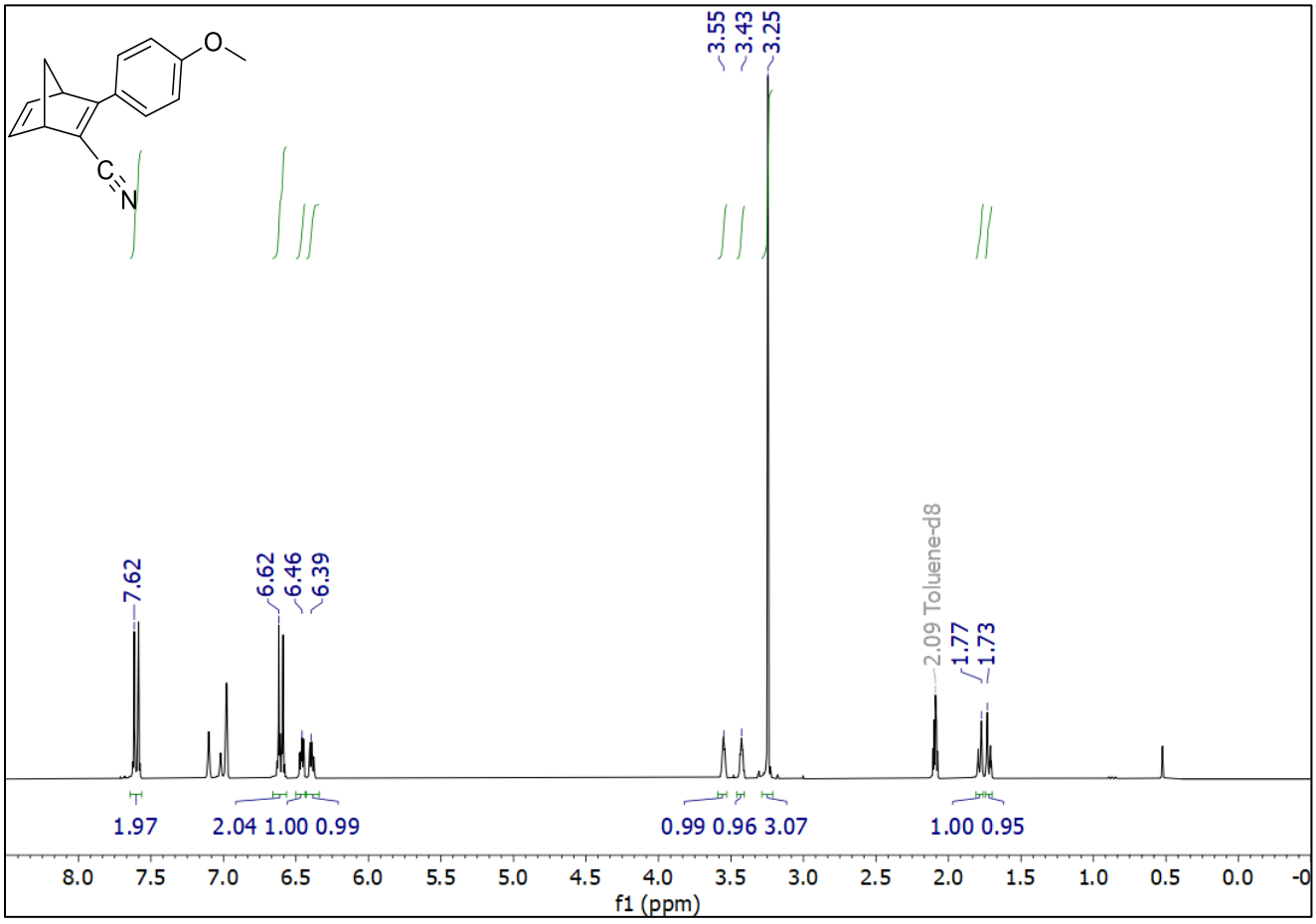


Figure S 2 ^{1}H NMR 300 MHz spectrum of NBD1 in Toluene-d8.

- *2-Cyano-3-((4-methoxyphenyl)-quadricyclane (QC1)*

QC1. ^{1}H NMR (300 MHz, Tol) δ 7.05 (d, 2H), 6.70 (d, 2H), 3.31 (s, 3H), 1.87 (dd, 1H), 1.83 (dt, 1H), 1.65 (dq, 1H), 1.61 (dt, 1H), 1.57 (dq, 1H).

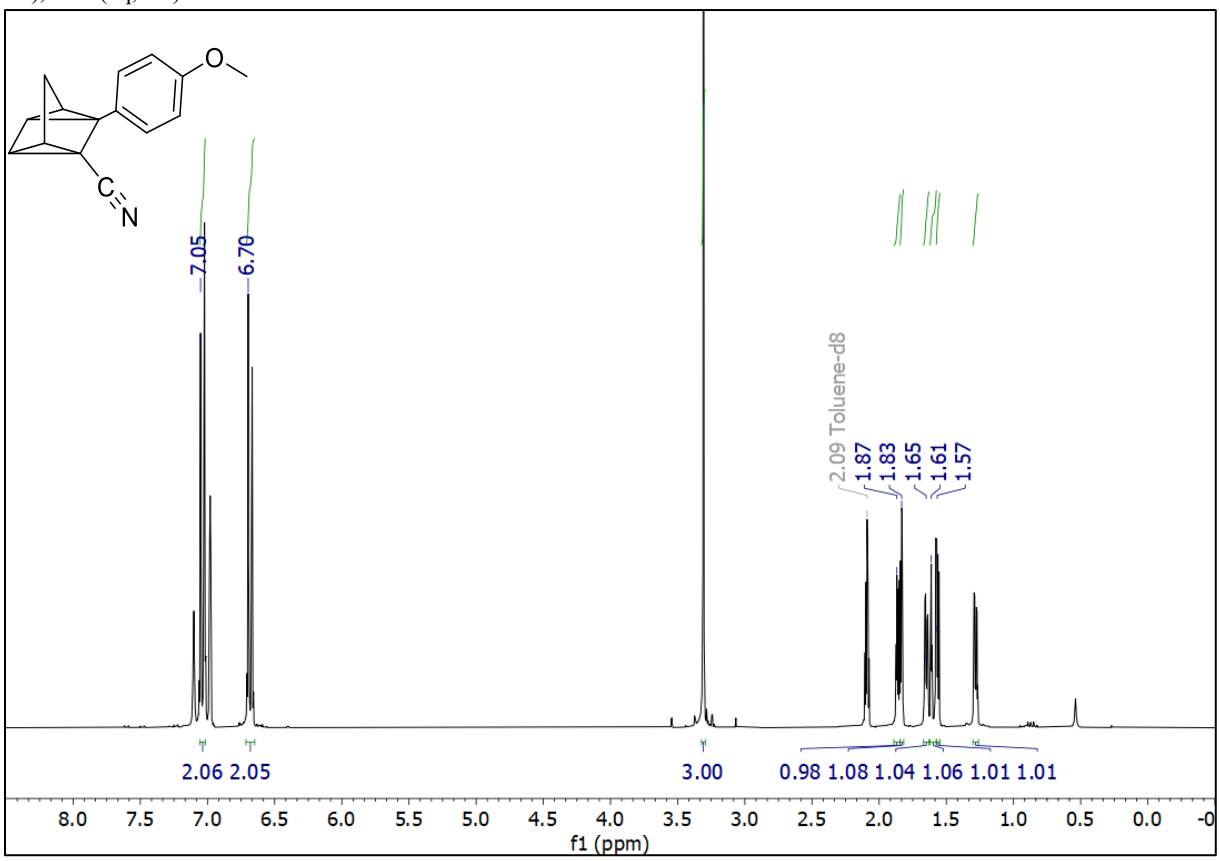


Figure S 3 ^{1}H NMR 300 MHz spectrum of QC1 in Toluene-d8.

UV-Vis Spectroscopy

UV-Vis measurements were recorded using a Shimadzu UV-3600 spectrophotometer. Standard 1 cm length path quartz cuvettes were used. Firstly, a calibration curve was constructed with different NBD1 solutions in the working range of the instrument where the signals were observed properly without saturation (10^{-4} to 10^{-5} M order). The value of absorbance used for the construction of the curve is measured at λ=340nm, due to the overlap of QC1 and NBD1 at the maximum absorbance of NBD1 (λ=326nm). Dilutions of a stock solution of 1mg/mL of NBD1 were used to prepare the different points of the curve.

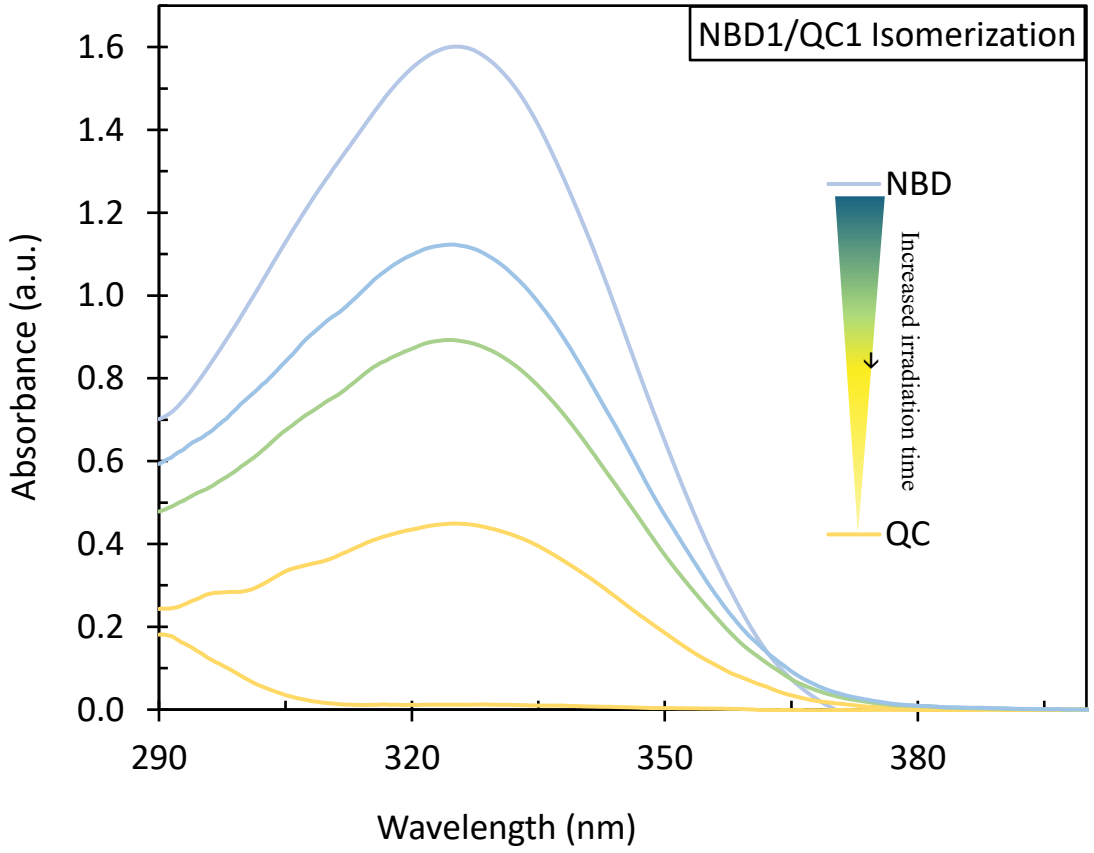


Figure S 4 UV-Vis of NBD1 irradiated at different times until full isomerization into QC1 is achieved. Samples were prepared in toluene. From top to bottom (t = 0 min, 2 min, 6 min, 10 min, 15 min).

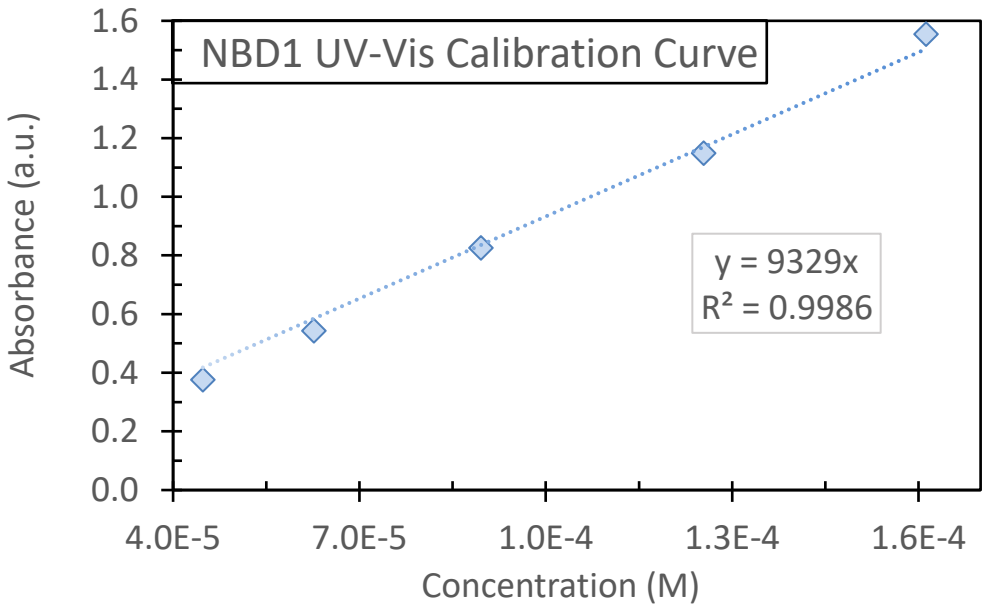


Figure S 5 UV-Vis calibration curve of NBD1 in toluene. Values of absorbance are measured at λ=340nm.

Method 1 – Catalyst testing

Catalytic measures were taken three times. There is an error margin in the measurements, particularly for longer durations, each measurement was typically repeated three times yielding results with an estimated margin of error within 3%. Linear fit of the ln[QC1] *vs*. time shows that this is a first-order reaction.

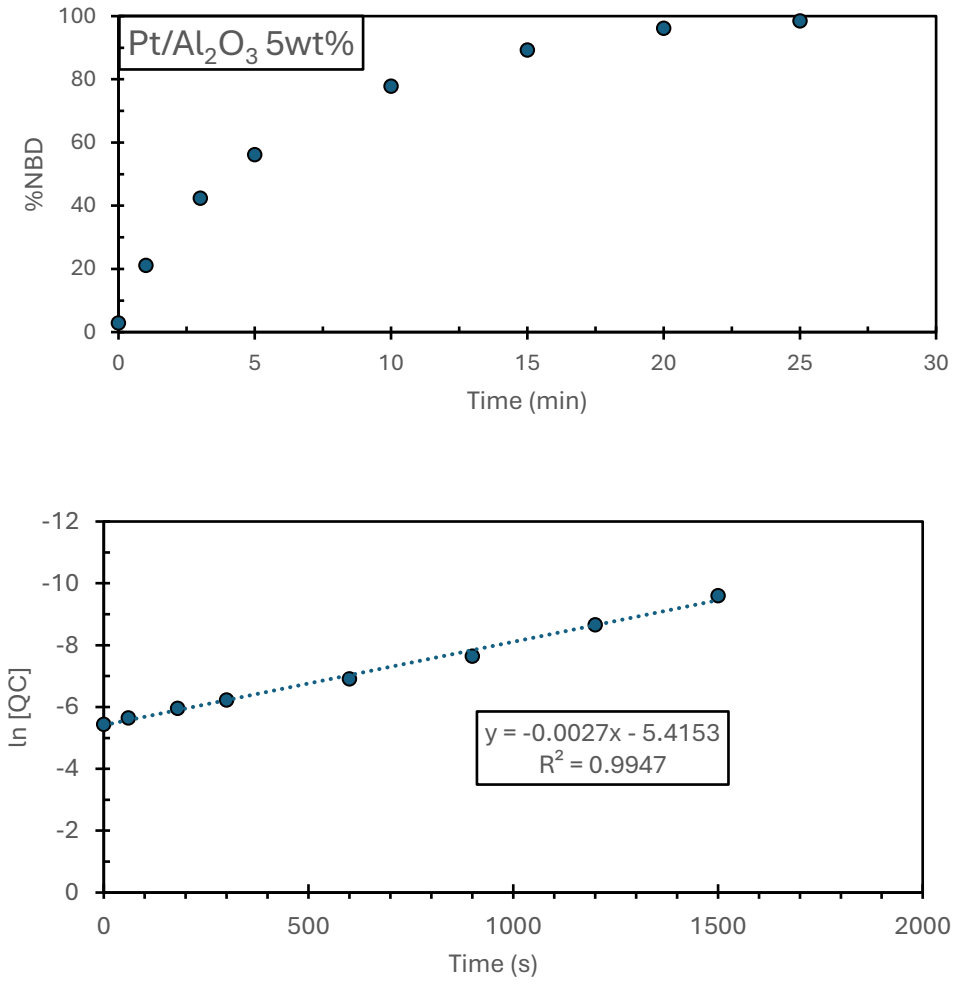


Figure S 6 Pt/Al_2O_3 5 wt% Conversion over time (Top). Catalytic reaction rate calculation (Bottom).

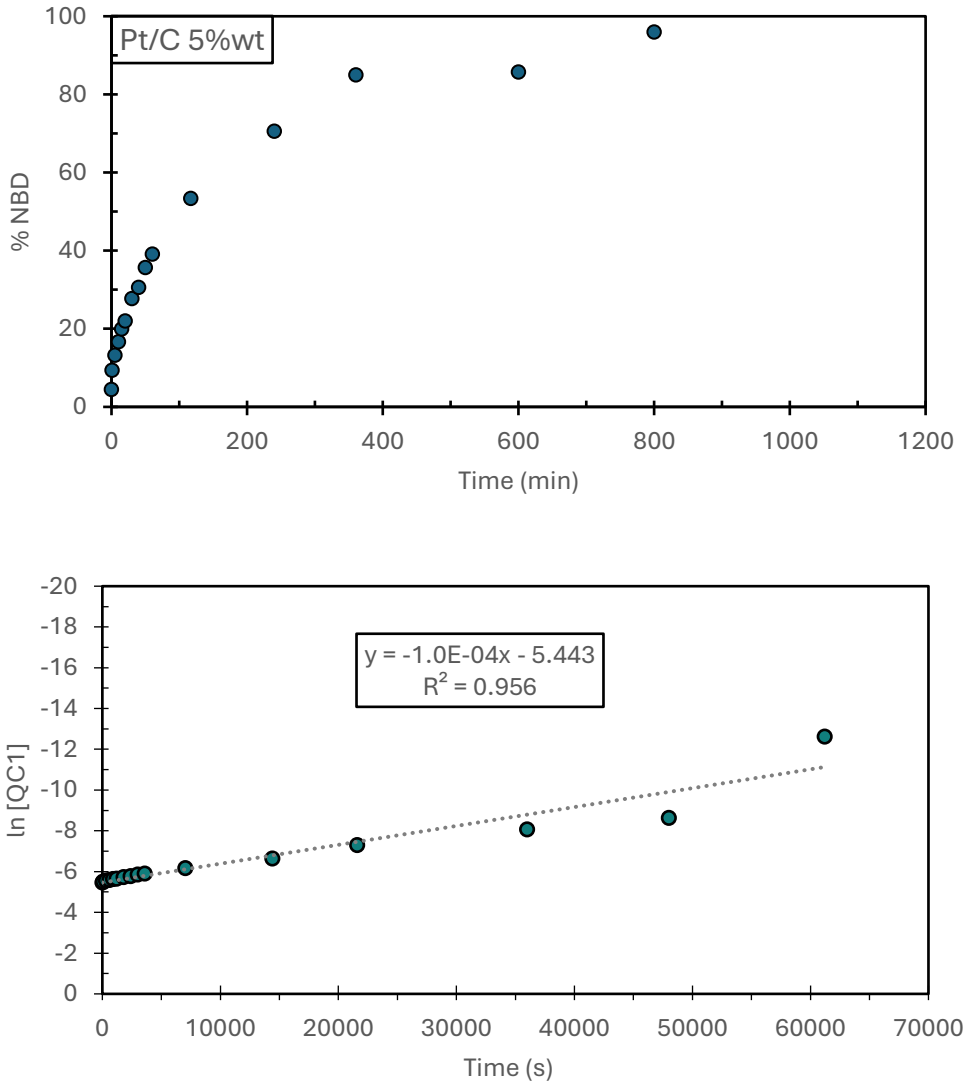


Figure S 7 Pt/C 5 wt% Conversion over time (Top). Catalytic reaction rate calculation (Bottom).

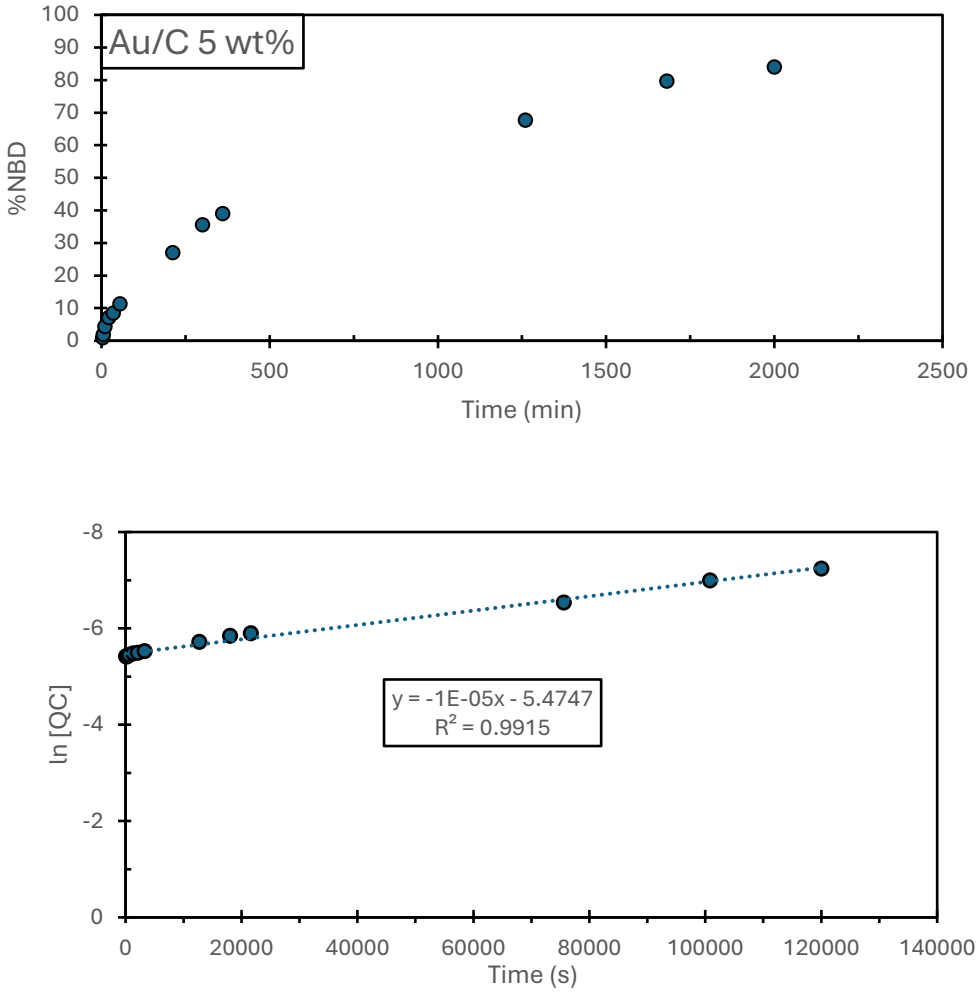


Figure S 8 Au/C 5 wt% Conversion over time (Top). Catalytic reaction rate calculation (Bottom).

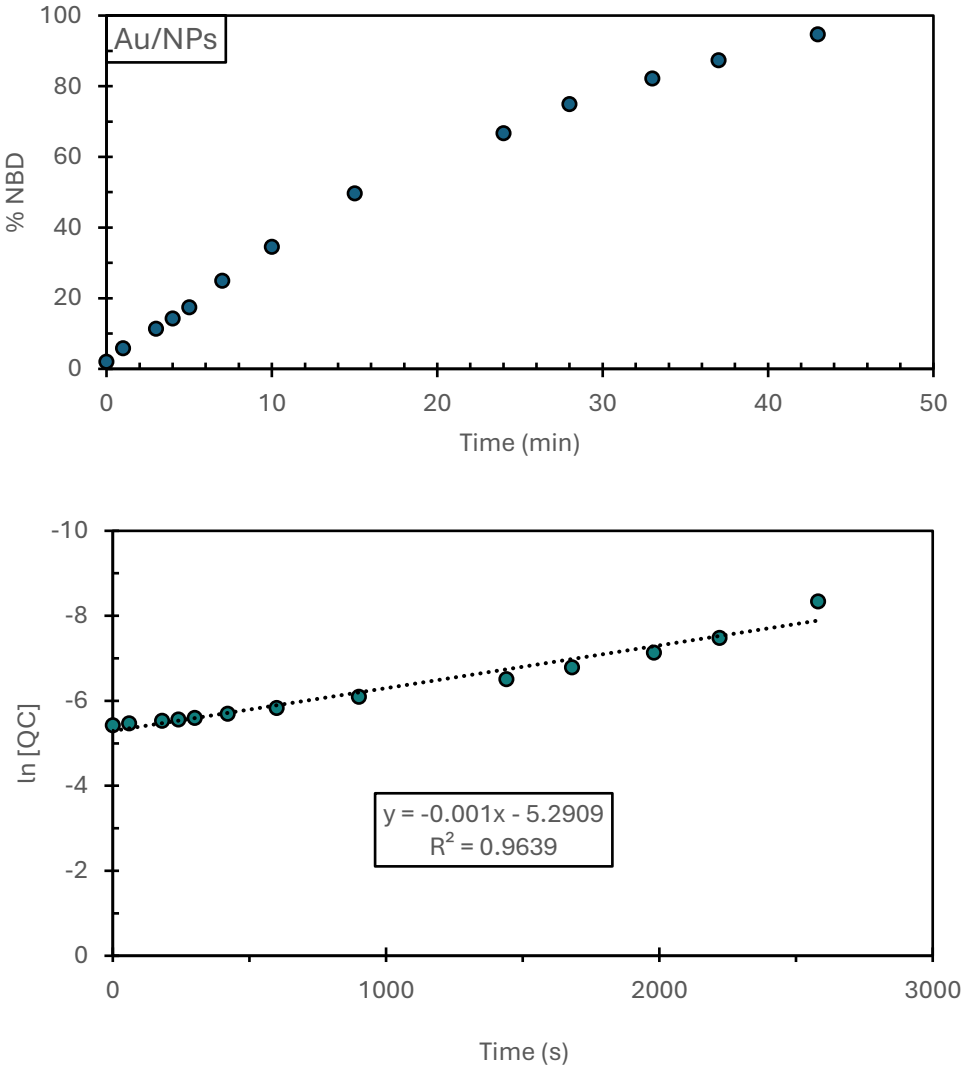


Figure S 9 Au/NPs <5 nm Conversion over time (Top). Catalytic reaction rate calculation (Bottom).

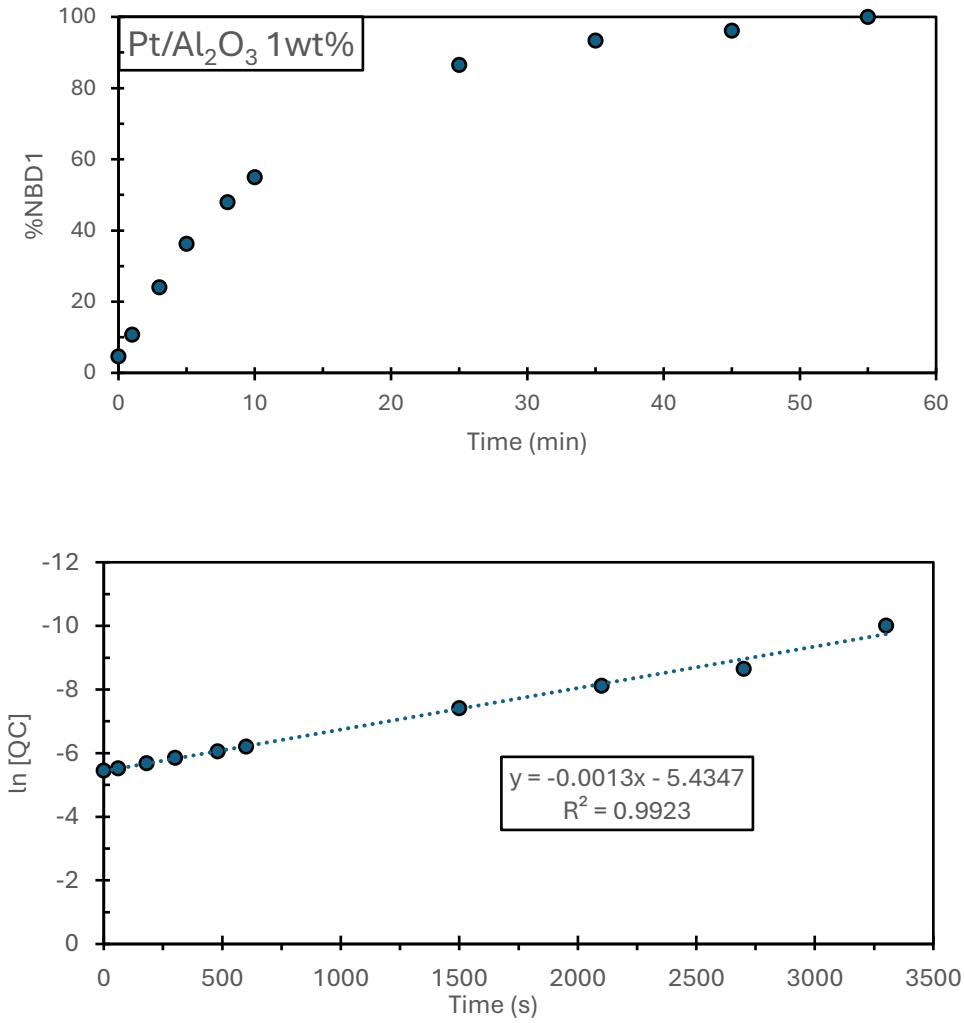


Figure S 10 Pt/Al_2O_3 1 wt% Conversion over time (Top). Catalytic reaction rate calculation (Bottom).

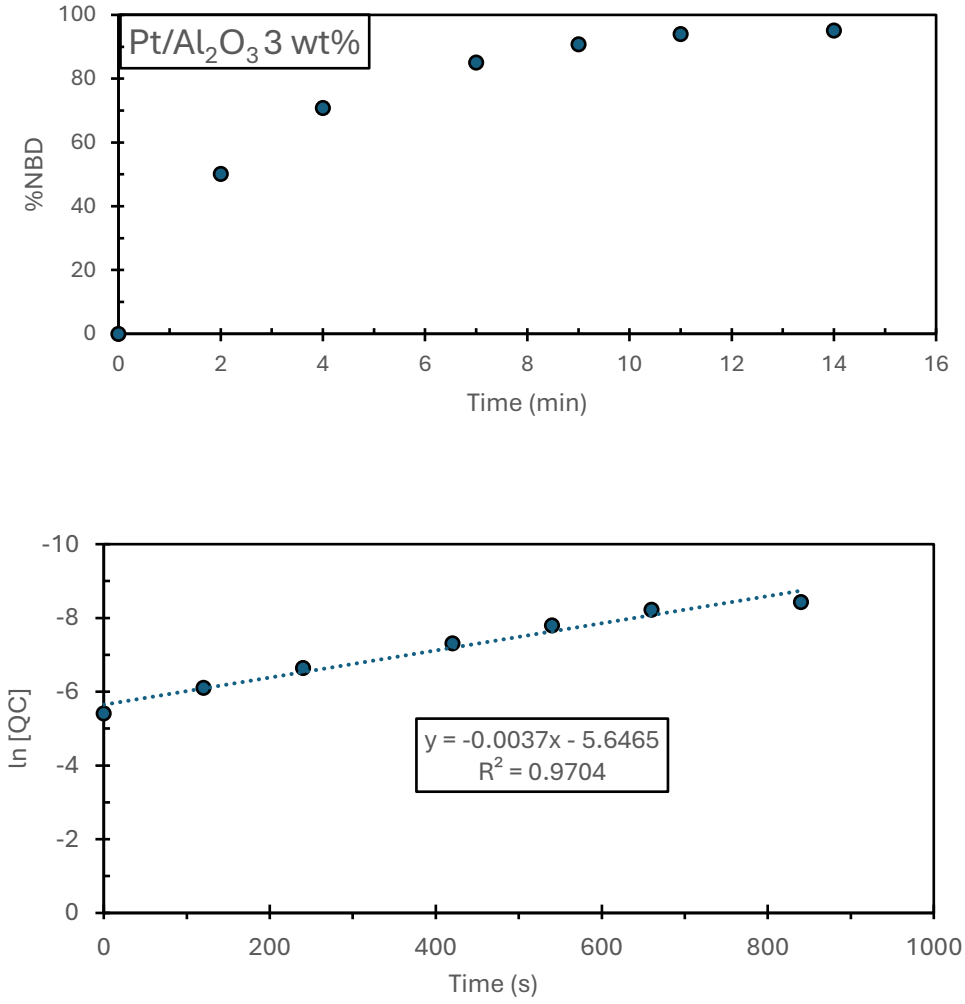


Figure S 11 Pt/Al_2O_3 3 wt% Conversion over time (Top). Catalytic reaction rate calculation (Bottom).

Method 2 – Calibration curve

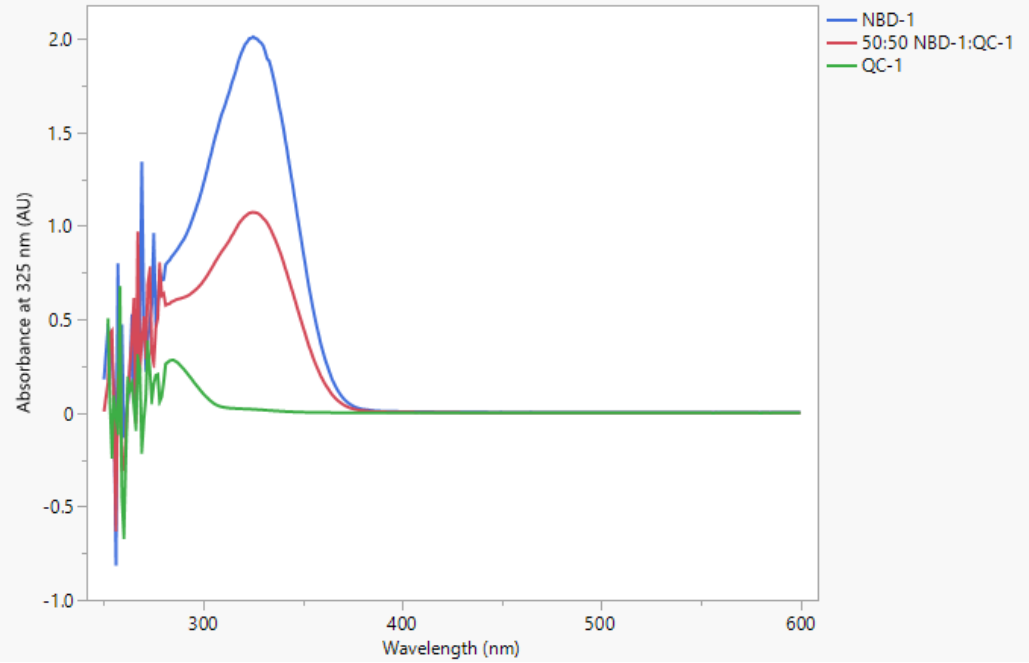


Figure S 12 UV-Vis spectra of NBD-1 solution, QC-1 solution and a 50:50 mix of both compounds.

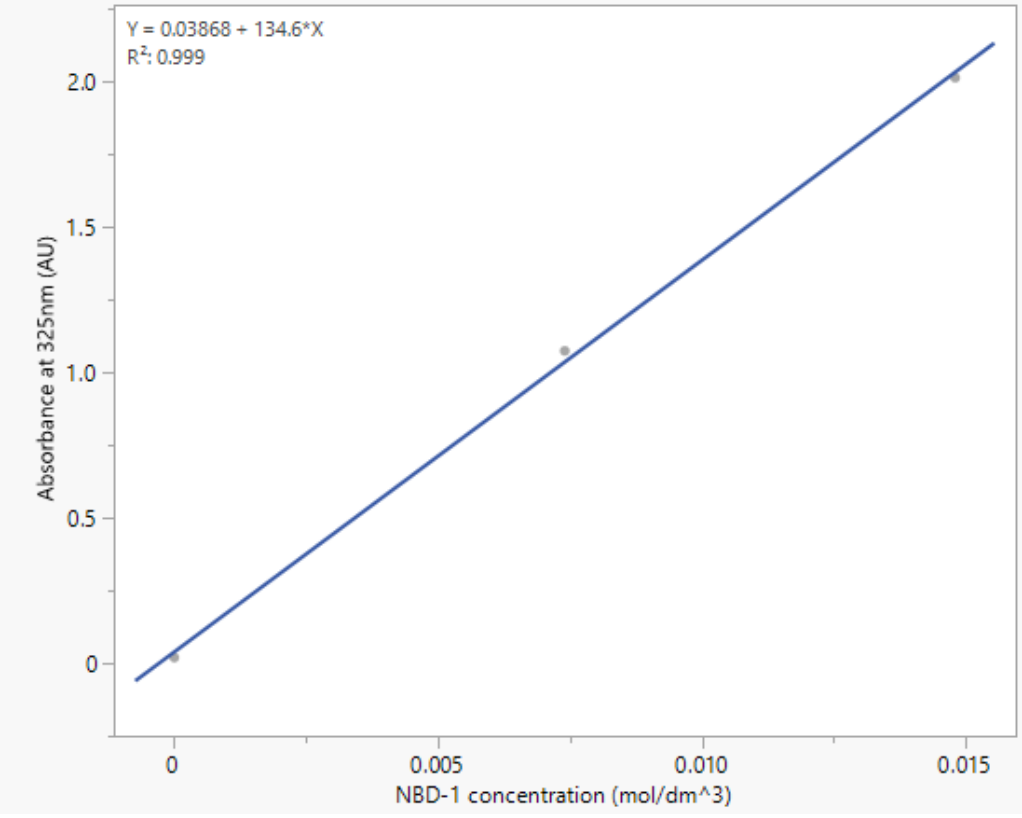


Figure S 13 Calibration curve of NBD-1 concentration vs UV-Vis absorbance at 325 nm.

Nitrogen isotherms

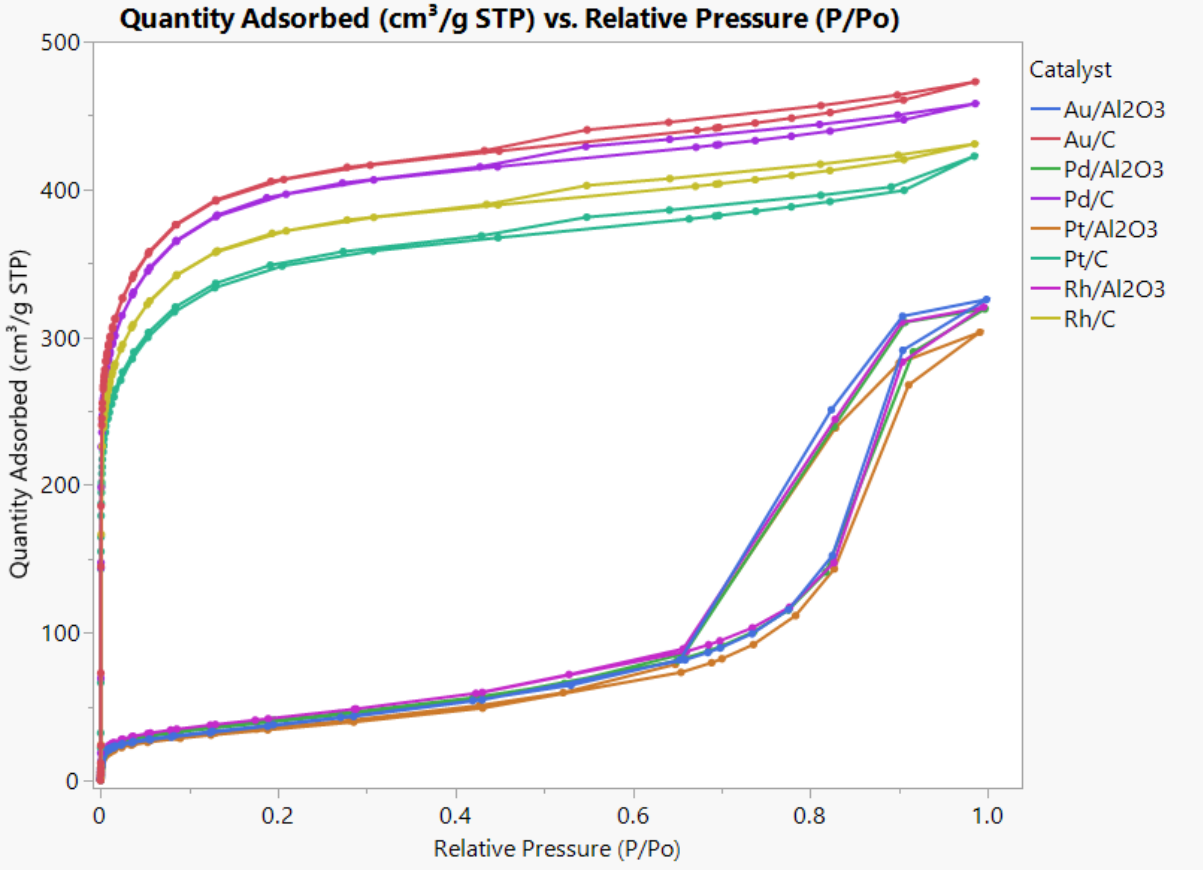


Figure S 14 N_2 sorption isotherms for the 5 wt% loading catalysts.

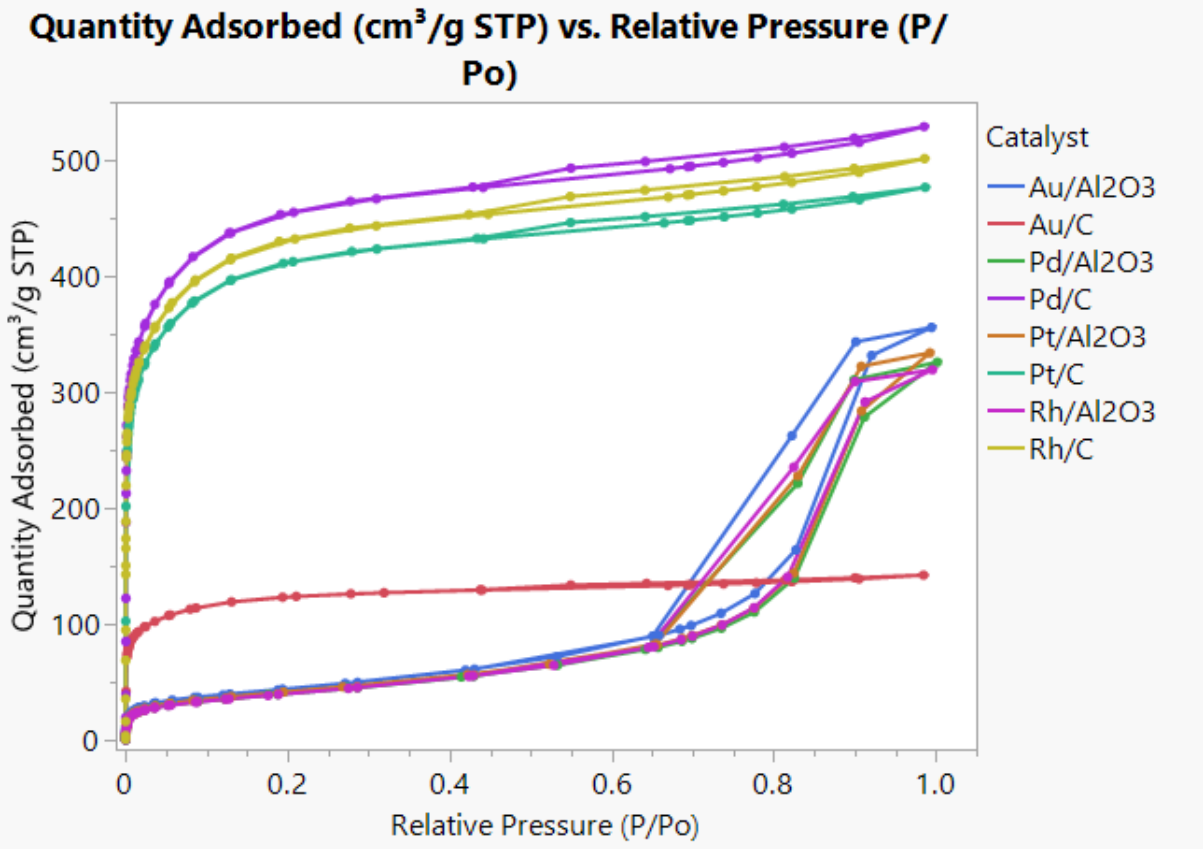
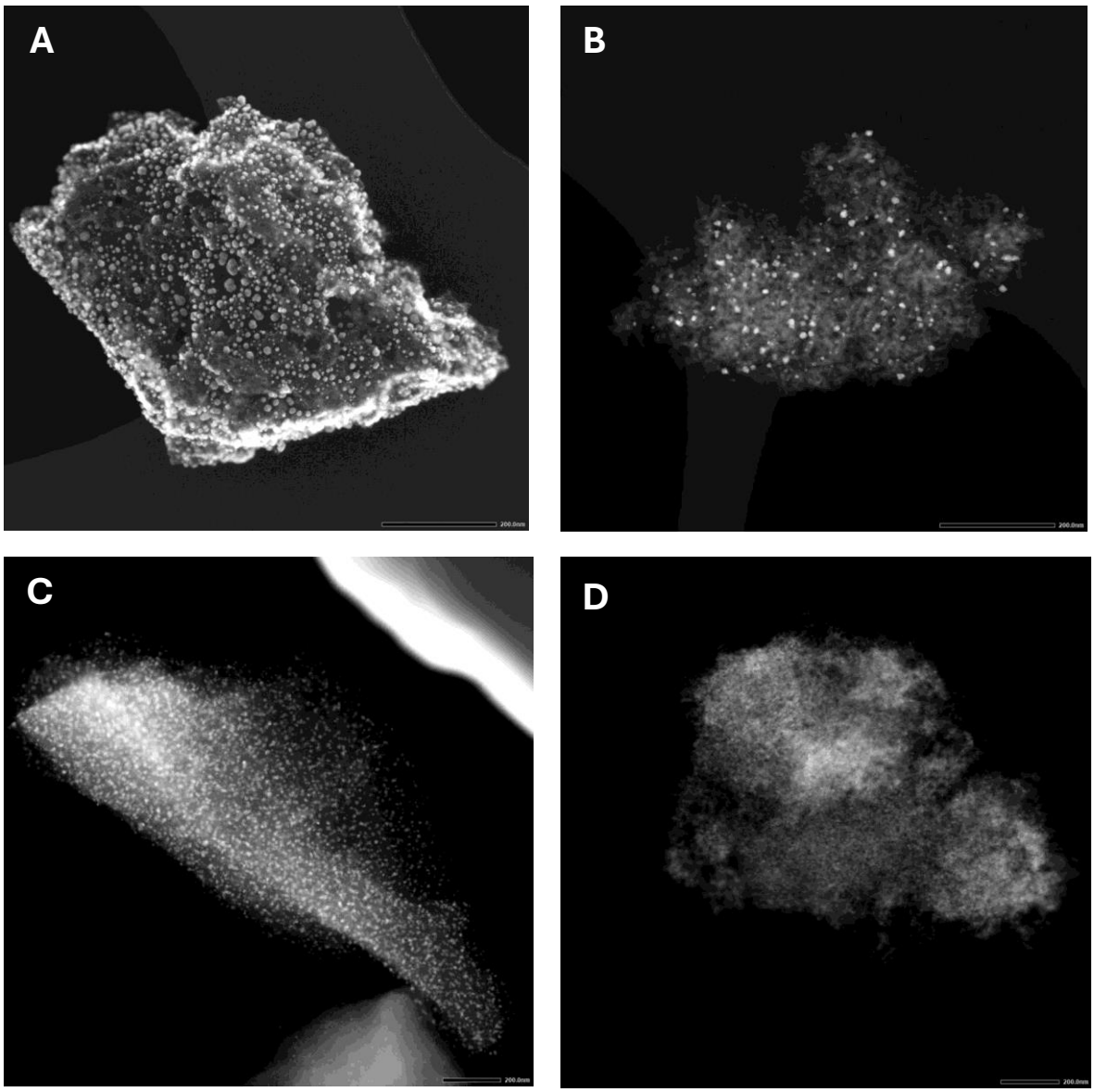


Figure S 15 N2 sorption isotherms for the 0.1 wt% loading catalysts.

TEM - 5% loaded catalysts



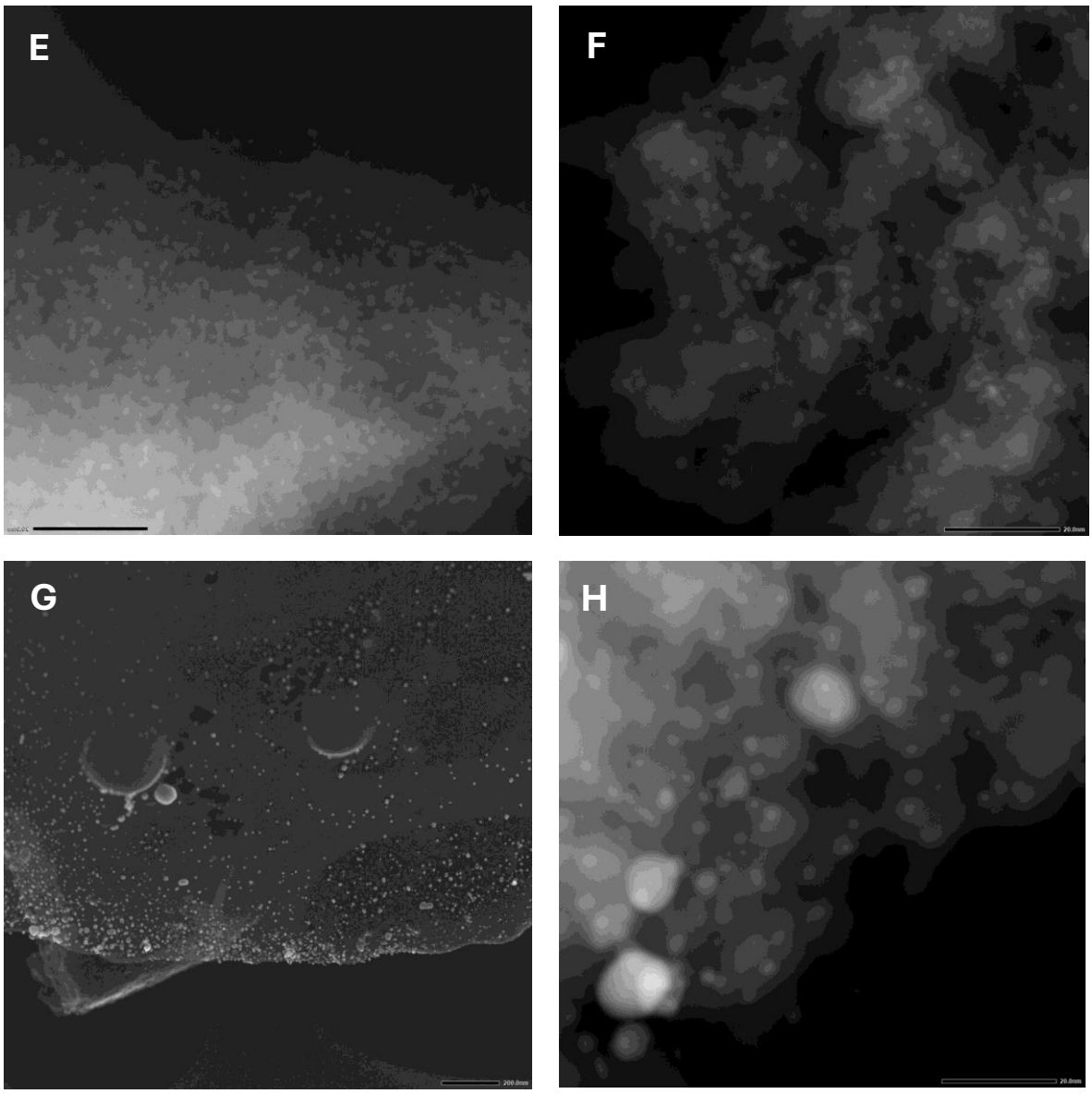


Figure S 16 TEM images of the eight catalysts at 5wt% loading A) Pt/C B) Pt/Al2O3 C) Pd/C D) Pd/Al2O3 E) Rh/C F) Rh/Al2O3 G) Au/C H) Au/Al2O3. Scale bars on each image are 200 µm except for Rh/C, Rh/Al2O3 and Au/Al2O3 where the scale bars are 20 µm.

Particle size distribution - 5% loaded catalysts.

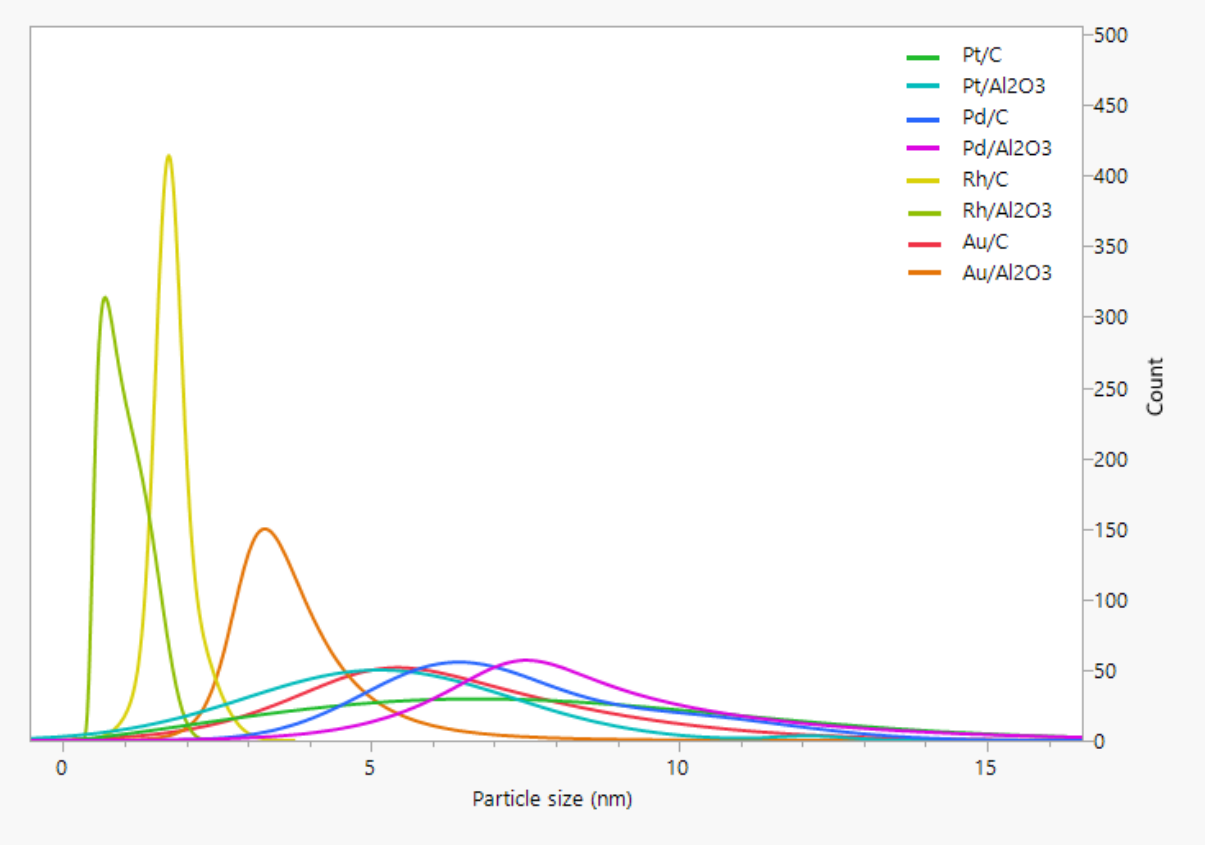


Figure S 17 Particle size distributions for the eight catalysts made at 5 wt% loading.

XPS - 5% loaded catalysts

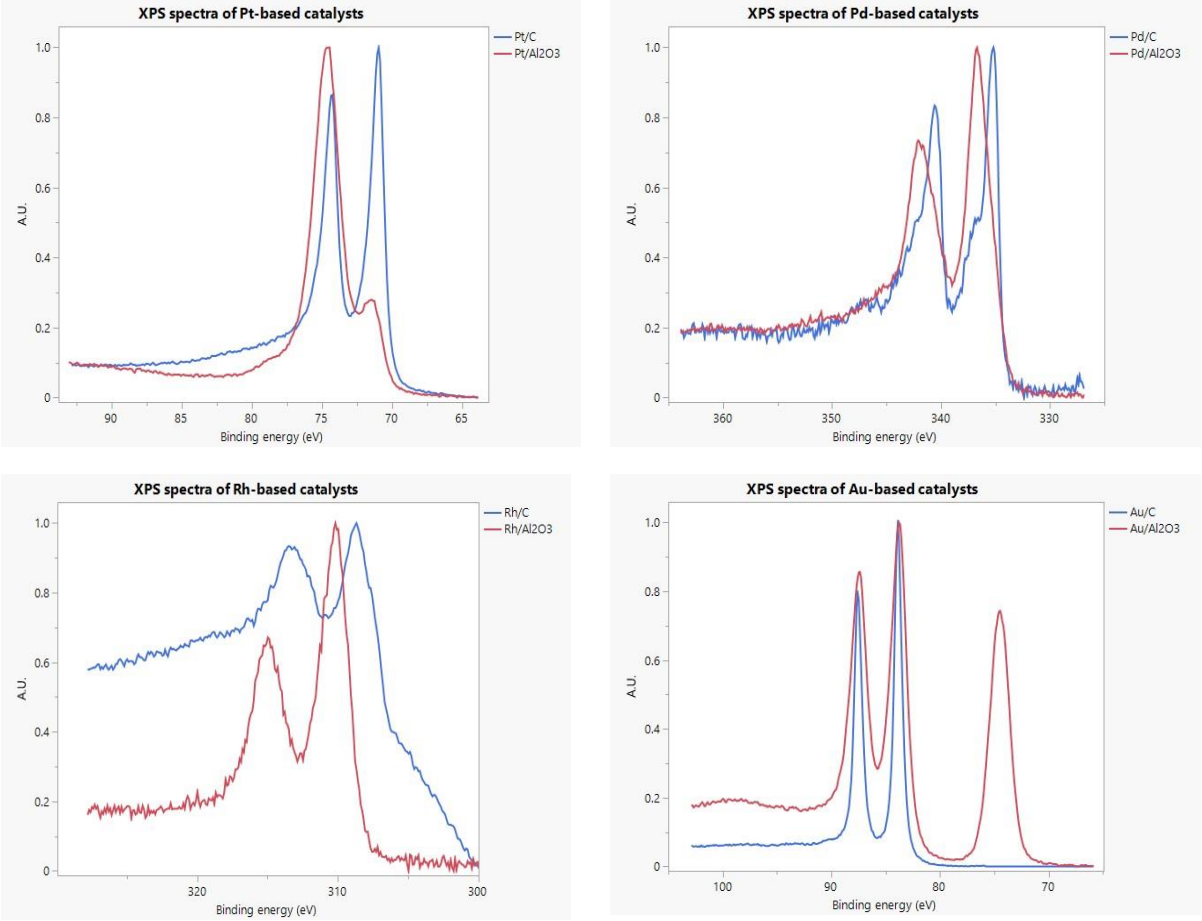
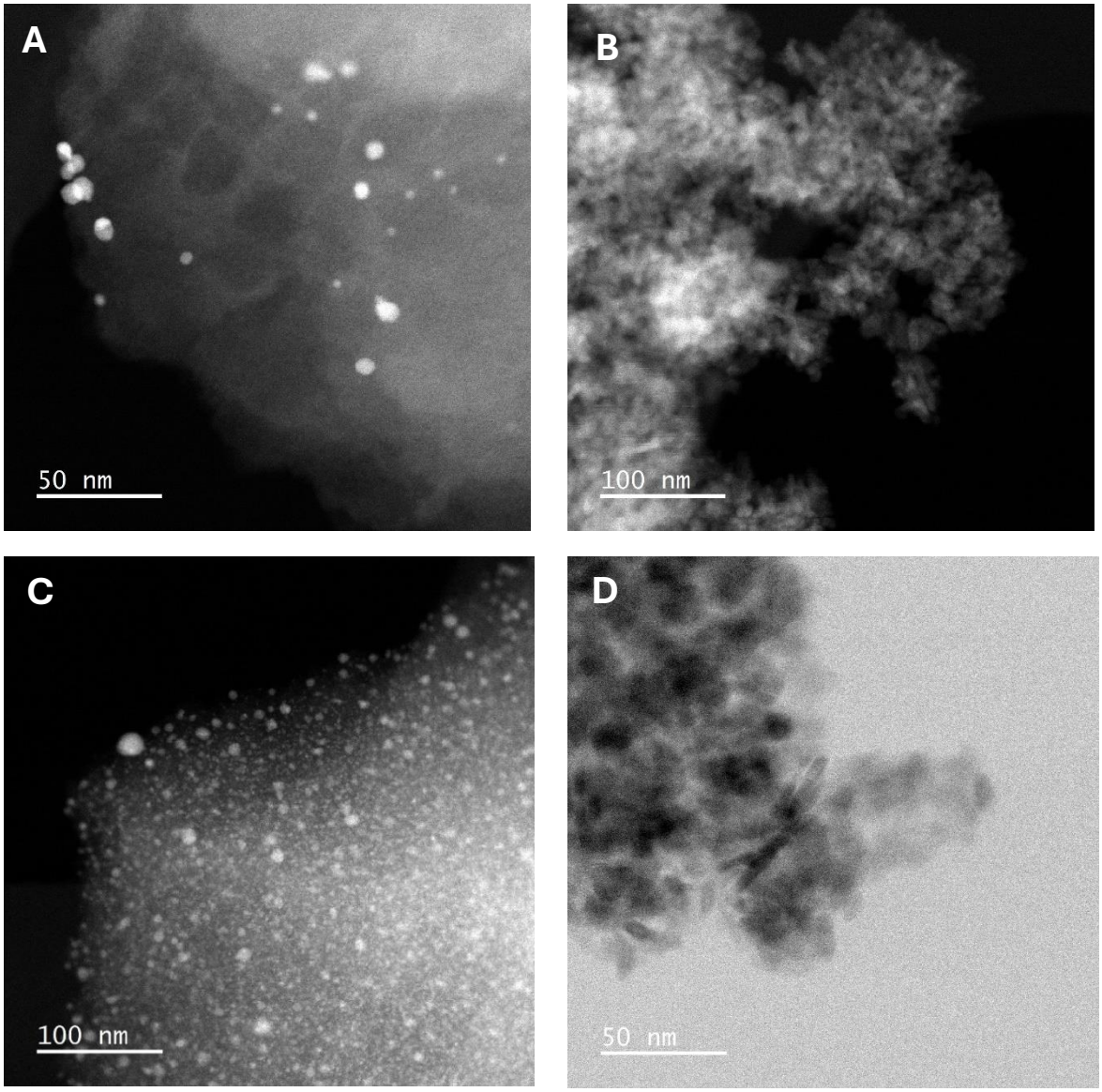


Figure S 18 XPS spectra of Pt-based (top left), Pd-based (top right), Rh-based (bottom left and Au-based (bottom right) catalysts. Carbon-supported catalysts are shown in blue and alumina-based catalysts are shown in red.

TEM - 0.1% loaded catalysts



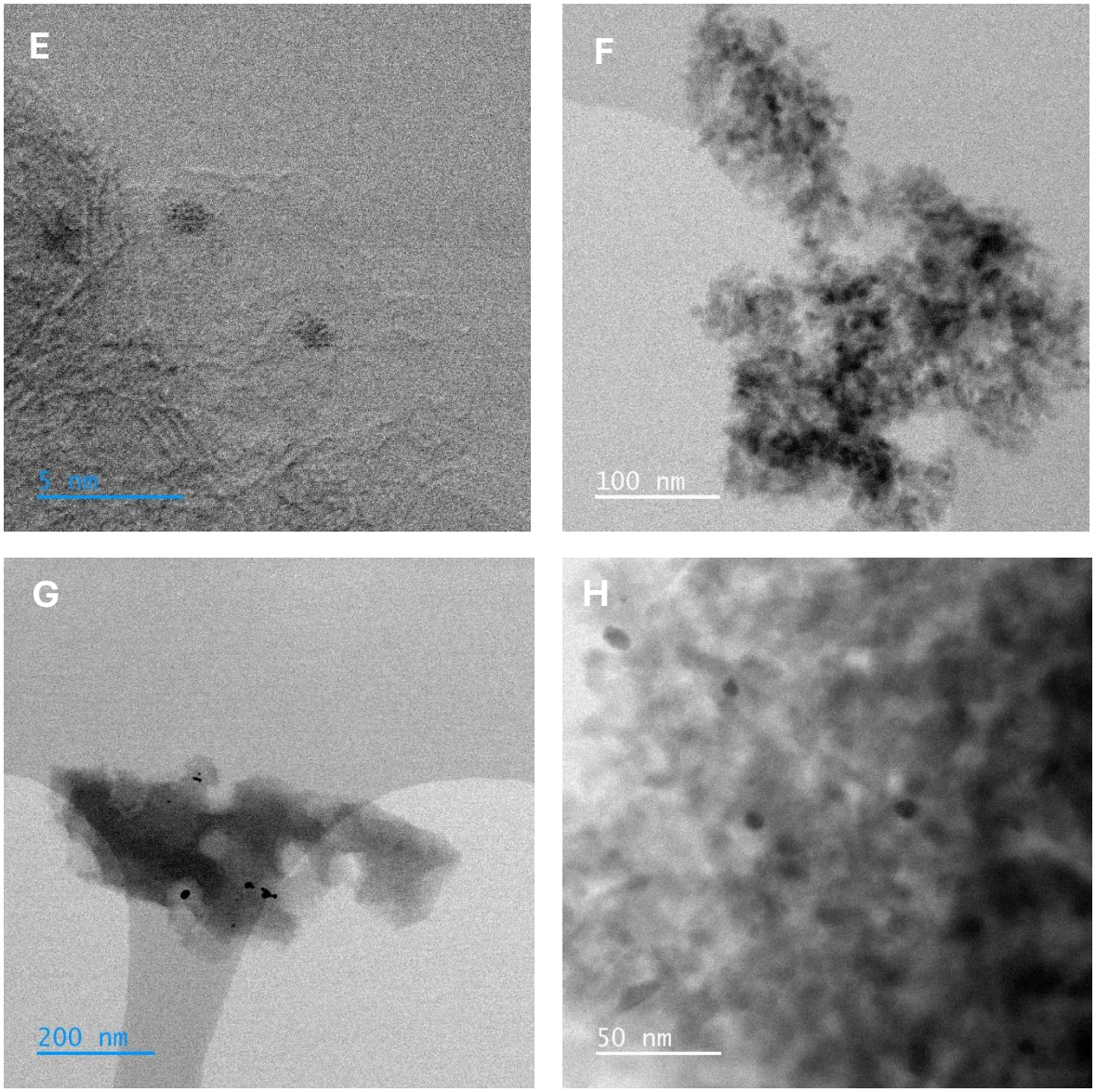


Figure S 19 TEM images of the eight catalysts at 0.1wt% loading A) Pt/C B) Pt/Al_2O_3 C) Pd/C D) Pd/Al_2O_3 E) Rh/C F) Rh/Al_2O_3 G) Au/C H) Au/Al_2O_3

XRD - 0.1% loaded catalysts

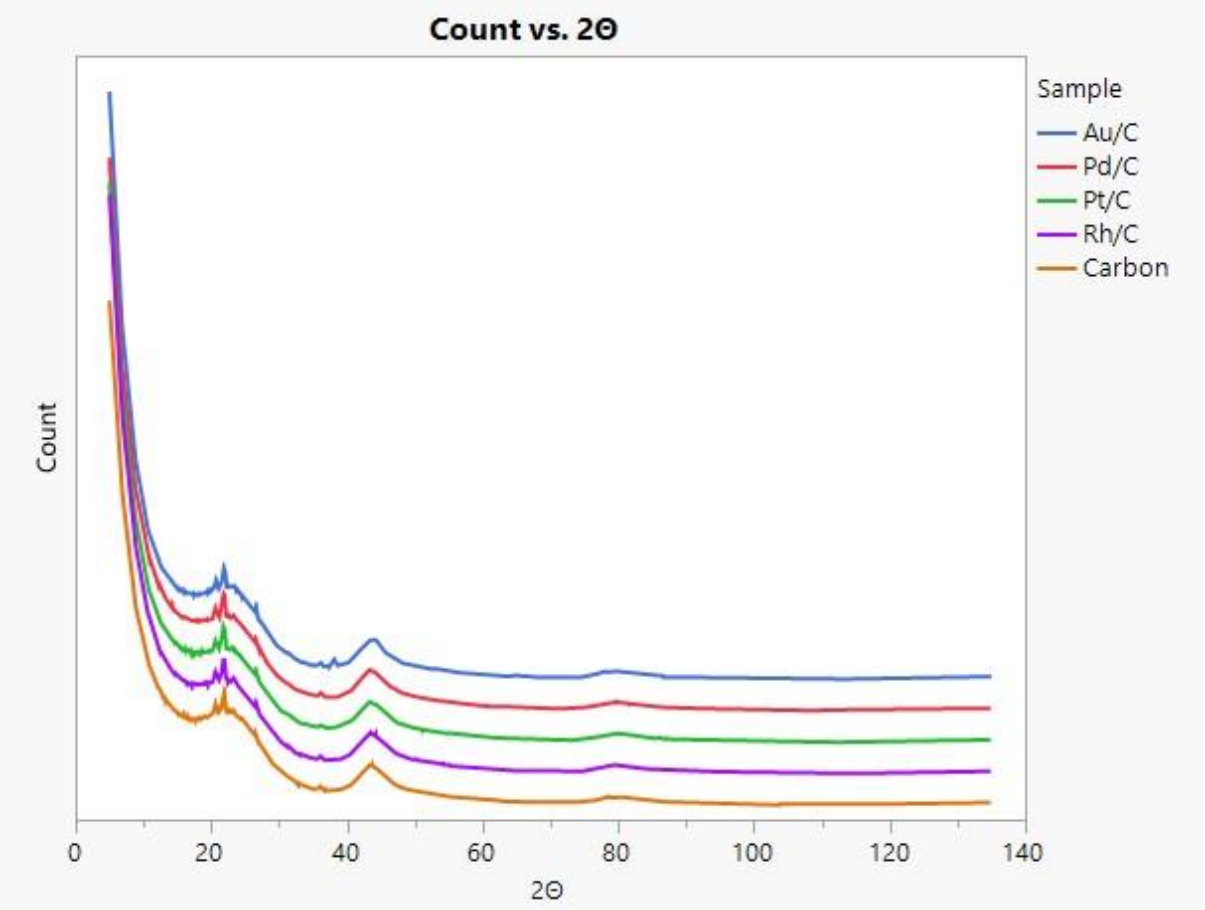


Figure S 20 XRD spectra for the carbon-supported catalysts at 0.1% loading

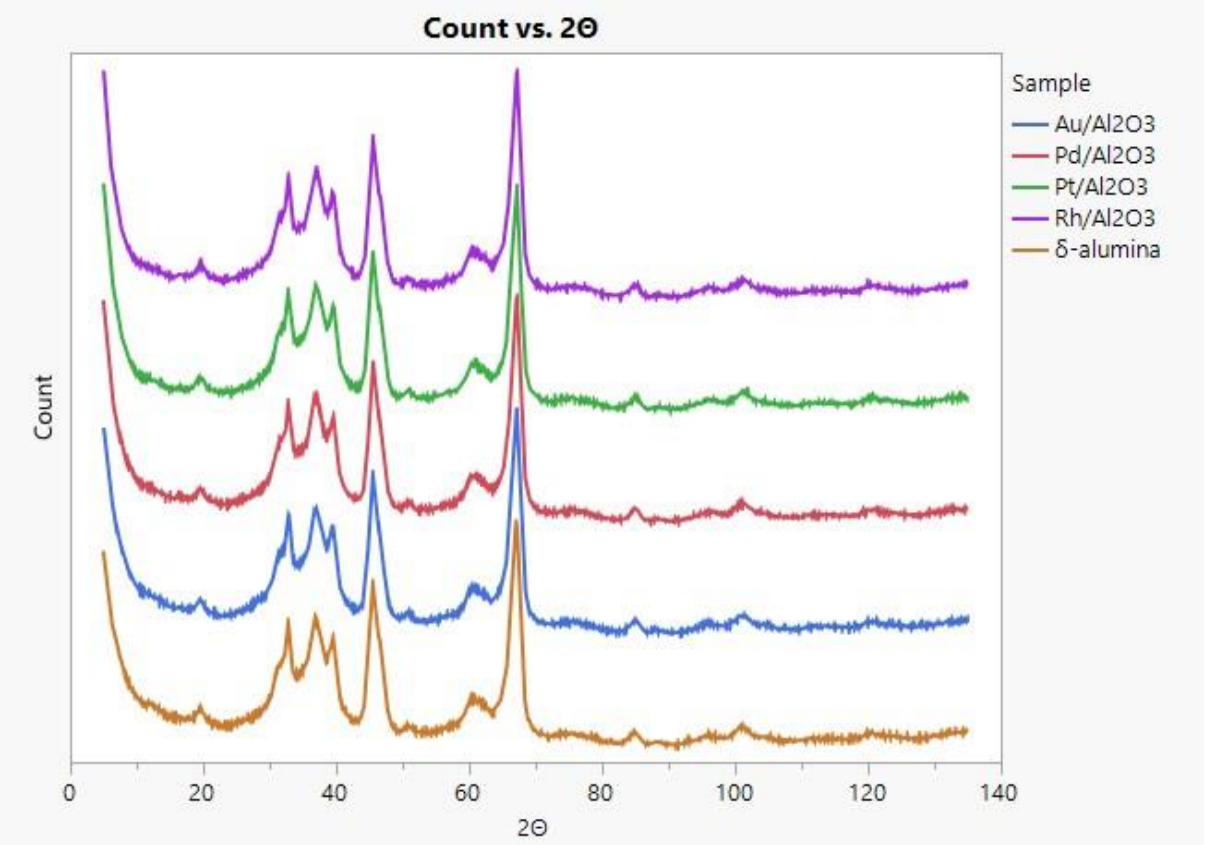


Figure S 21 XRD spectra for the alumina-supported catalysts at 0.1% loading