Supporting Information

Designed Catalysts of Pt Nanoparticles Supported on Macroporous Oxides for Selective Isomerization of *N*-hexane

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Experimental Section

Synthesis of macroporous Al_2O_3, TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2. Macroporous oxides were prepared by using polystyrene beads. The polystyrene beads were synthesized through emulsifier-free emulsion polymerization.[1] Briefly, 14 g of styrene monomer and 0.7 g of divinylbenzene as a crosslinker were washed with 0.1 M NaOH solution and then with DI water to remove inhibitors, in which each washing was repeated for 4 times, respectively. The mixture of styrene and divinylbenzene was stirred in 140 mL of DI water at 70 ^oC and purged by flowing Ar for 1 h, then potassium persulfate (0.03 g dissolved in water) as an initiator was added for the polymerization. After reacting at 70 ^oC for 12 h, the polystyrene beads with an average diameter of 500 nm were collected by washing with methanol and water and following centrifugation.

For the preparation of macroporous aluminas,[2] 4.0 g of Pluronic P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$ triblock copolymer, EO = ethylene oxide, PO = propylene oxide, Mw = ~ 5,800) was dissolved in 40 mL of anhydrous ethanol for 4 h. Separately, 8.16 g of aluminum isopropoxide (40 mmol, Sigma-Aldrich, >98%) was dissolved in 6.4 mL of 68-70 wt% nitric acid and 20 mL of anhydrous ethanol under vigorous stirring. After dissolved completely, the precursor solution was added dropwise into the P123 solution. For macroporous Nb_2O_5 and Ta_2O_5, 30 mmol of niobium chloride (Sigma-Aldrich, 99%) or tantalum chloride (Sigma-Aldrich, >99%) in 30 ml ethanol was added to 3 g of P123 and 30 ml of ethanol. For macroporous TiO_2 and ZrO_2, 20 mmol of titanium isopropoxide (Sigma-Aldrich, 97%) or zirconium isopropoxide (in 70 wt% in 1-propanol, Sigma-Aldrich) was added to P123 dissolved in ethanol and HCl. The combined solution was stirred for 5 h and 4 g of the dried polystyrene beads was added. The solvent of the mixture was evaporated at 60 °C for 48 h. The resulting flakes were calcined in a furnace at 700 °C for 6 h (for Al_2O_3, 900 °C for 10 h) in air. After calcinations, highly crystalline macroporous Al_2O_3, TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2 with an average pore size of 300 nm were obtained. When the oxides were prepared with the same recipe described above without the polystyrene beads, mesoporous oxides with an average pore size of ca.10 nm were synthesized as well.

Synthesis of 1.7, 2.7, and 5.5 nm sized Pt nanoparticles. The synthesis of poly(vinylpyrrolidone) (PVP)-capped spherical Pt nanoparticles with the size of 1.5 – 6 nm was carried out by following reported literature methods with modifications.[3,4] For 1.7 nm Pt nanoparticles, 0.1 g of NaOH was dissolved in ethylene glycol (5 mL, 0.5 M) and the solution was added to an ethylene glycol solution (5 mL) containing $H_2PtCl_6 \cdot xH_2O$ (0.08 g, 0.2 mmol, Sigma-Aldrich, >99.9%). The mixture was heated to 160 ^{o}C and held at that temperature for 2 h under a N_2 atmosphere. The resulting nanoparticles were precipitated with 2 ml of 2 M HCl and re-dispersed in ethanol with 0.1 g of PVP (Sigma-Aldrich, *M*w = 55,000). In order to synthesize 2.7 nm Pt nanoparticles, mixed precursors of 4 mg of $H_2PtCl_6 \cdot xH_2O$ (0.01 mmol) and 0.016 g of $Pt(acac)_2$ (0.04 mmol, Sigma-Aldrich, 97%), and 0.1 g of PVP were added to 10 ml of ethylene glycol in a 50 ml three-necked flask. The solution was heated to 50 °C and evacuated at this temperature for 20 min to remove water and oxygen under vigorous magnetic stirring. The flask was then heated to 200 °C and maintained at this temperature for 10 min under Ar atmosphere. The solution was then cooled to room temperature and an excess of acetone was poured into the solution to form a cloudy black suspension. The Pt nanoparticles were precipitated by centrifugation and re-dispersed in ethanol. 5.5 nm Pt nanoparticles were synthesized by using 0.02 g of $Pt(acac)_2$, 0.1 g of PVP, and 10 ml of diethyleneglycol (Aldrich, >99%) at 245°C for 1 h.

Preparation of Pt nanoparticle catalysts supported onto macroporous oxides. The desired amount of a macroporous oxide was added to Pt nanoparticles dispersion and sonicated for 2 h at room temperature. The brown precipitates were collected by centrifugation. In order to remove PVP surfactants, the catalysts were washed with acetone and ethanol, then calcined at 360 ^{o}C for 6 h in air.

Characterization. Structural characterizations of Pt nanoparticles were analyzed using a Hitachi H-7650 transmission electron microscope (TEM) operated at 120 kV. Pt particle sizes were measured by TEM and the average particle sizes and their histograms were determined by counting 300 particles on TEM images. XRD patterns were measured on a Bruker D8 GADDS diffractometer using Co Kα radiation (1.79 Å). Nitrogen physisorption data was obtained on a Micromeritics ASAP 2020. Elemental analyses by inductively coupled plasma atomic emission spectroscopy (ICP-OES) were conducted using a Perkin Elmer optical emission spectrometer, Optima 7000 DV. Before a measurement of ICP-OES, calibration was conducted by using platinum standard (Fluka, TraceCERT 1000 mg L^{-1}) as a certified reference material (CRM).

Catalytic reaction. *N*-hexane isomerization was conducted over supported Pt nanoparticle catalysts in a stainless steel tubular plug-flow reactor. Reaction products were analyzed using an HP 5890 Series II GC equipped with a 10 m dimethylpolysiloxane (HP-1) capillary column in line with a flame ionization detector (FID). 0.5 – 0.7 g of catalysts were diluted by quartz and loaded in the reactor bed. The catalyst pre-treatment consisted of a reduction in a flow of 50 vol.% mixture of H_2 and N_2 at 20 sccm total flow rate. The reduction treatment was performed under ambient pressure at 260 ^{o}C for 2 h. The heating/cooling rate during catalyst reduction treatment was kept at 1 ^{o}C/min. *N*-hexane isomerization was conducted with 140 Torr *n*-hexane and 620 Torr H_2 in the temperature range of 240 – 360 ^{o}C. *N*-hexane (≥ 99%, Aldrich) vapor was carried to the reactor using a syringe pump. Each temperature was maintained for 1 h in the reactor for steady-state environment. The catalytic measurements were taken in the steady state under isothermal conditions. We kept the reaction in a kinetic region by having the total conversion below 10 % to avoid any mass and heat transfer limitations. Furthermore, the catalysts checked positive for the Madon-Boudart criterion.

APXPS and XRD measurements. All synchrotron-based X-ray studies were conducted in the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. For APXPS[5] and XRD[6] under catalytically relevant reaction conditions, Pt/oxide catalysts were pressed into a thin pellet (ca. 200μm) and heated to 150°C under He for XRD or in vacuum for APXPS. APXPS measurement was carried out by dosing 100 mTorr (0.13 mbar) H_2 or O_2 at 360 ^oC in beamline 9.3.2 and XPS data were analyzed using CasaXPS software. *In situ* XRD study was conducted in the purpose-built flow cell, described elsewhere,[7] under 50 sccm flow of 20 vol. % (150 Torr) H_2 in Ar at 360 ^oC in beamline 12.2.2. The diffraction experiment was carried out in the transmission geometry using 25 keV photons. Sample-to-detector distance was calibrated by using LaB_6 standard.

FT-IR measurement of oxides adsorbed by pyridine. For FT-IR measurement, all the macroporous oxides were pressed into a thin wafer after grinding with KBr (25.5 mg cm^{-2}, 25 wt% of oxides in KBr). Each thin wafer was placed in glass IR-cell equipped with CaF_2 windows. Before the measurement, each sample was degassed at 500^{o}C for 2 h in a vacuum and cooled to room temperature in an IR-cell. Then, the degassed macroporous oxides were oxidized at 350^{o}C for 1 h in O_2. For the measurement of acidity, pyridine was used as an organic base probe molecule.[8,9] Pyridine was adsorbed on the degassed samples at room temperature, and the weakly physisorbed pyridine was desorbed at 150^{o}C for 1 h in a vacuum. After cooling to room temperature, IR spectra were collected using an FT-IR spectrometer (Thermo electron corporation Nicolet 6700) with 160 scans and 2 cm^{-1} resolution in the 4000 – 400 cm^{-1} range.[8-13]

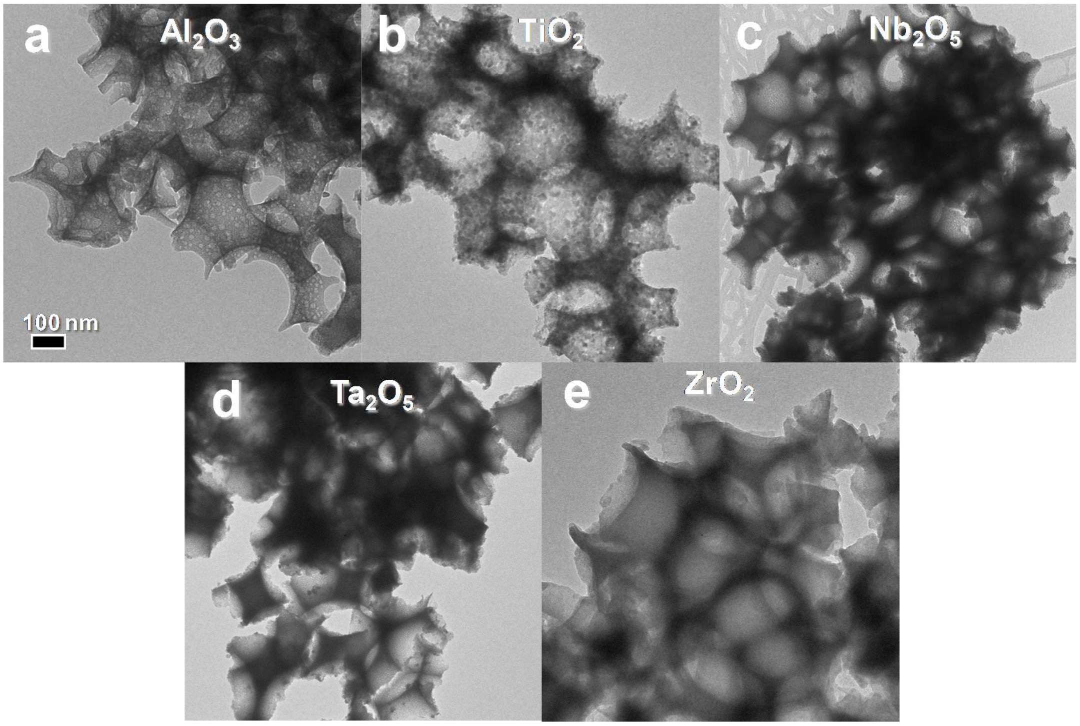


Figure S1. TEM images of macroporous oxides synthesized through the templating method by using polystyrene beads: (a) Al_2O_3, (b) TiO_2, (c) Nb_2O_5, (d) Ta_2O_5, and (e) ZrO_2.

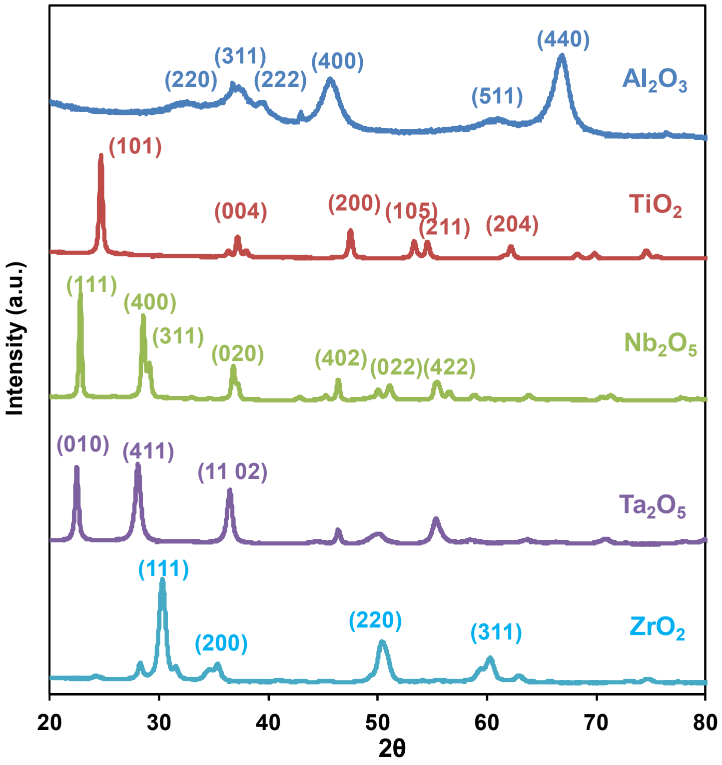


Figure S2. XRD Pattern of macroporous oxides of Al_2O_3, TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2.

Macroporous Materials	**Surface Area (m^2/g)**	**Pore Volume (cc/g)**	**Mesopore Size (nm)**
Al_2O_3	117.8	0.263	8.9
TiO_2	13.3	0.041	11.8
Nb_2O_5	102.9	0.098	3.8
Ta_2O_5	96.7	0.068	2.8
ZrO_2	19.2	0.047	9.7

Table S1. BET surface areas, pore volumes, and average pore sizes of macroporous oxides.

Catalysts	Pt Sizes (nm)	Pt loading (wt%)	TOF (S^{-1})	Selectivity (%)			
				Isomerization	Cyclization	Cracking	Aromatization
Pt/SiO_2	2.7	0.87	0.013	47.94	25.55	16.39	10.12
Pt/Al_2O_3	2.7	0.34	0.011	46.97	23.04	21.41	8.58
Pt/TiO_2	2.7	0.65	0.034	75.32	13.80	8.28	2.60
Pt/ZrO_2	2.7	0.44	0.025	35.35	24.20	28.21	12.24
Pt/Nb_2O_5	1.7	1.00	0.028	91.22	0.06	8.49	0.23
	2.7	0.44	0.023	93.22	1.43	4.12	1.23
	5.5	0.60	0.022	97.91	0.00	2.09	0.00
Pt/Ta_2O_5	1.7	1.00	0.032	84.63	5.96	6.74	2.68
	2.7	0.29	0.030	92.07	0.00	6.30	1.63
	5.5	0.60	0.024	97.18	0.00	1.27	1.55

Table S2. Supported catalysts details and corresponding catalytic turnover frequencies and selectivities in *n*-hexane isomerization at 360 °C in 140 Torr *n*-hexane and 620 Torr H_2.
(We also carried out the reaction over Pt supported mesoporous Al_2O_3 and TiO_2. However there is no distinct activity and selectivity changes between mesoporous and macroporous oxides, demonstrating there is no pore size effect of the support in this reaction.)

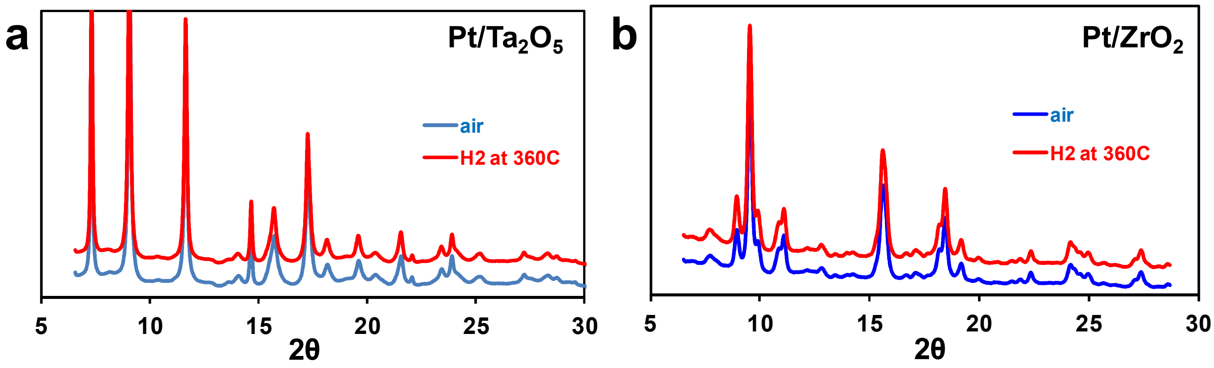
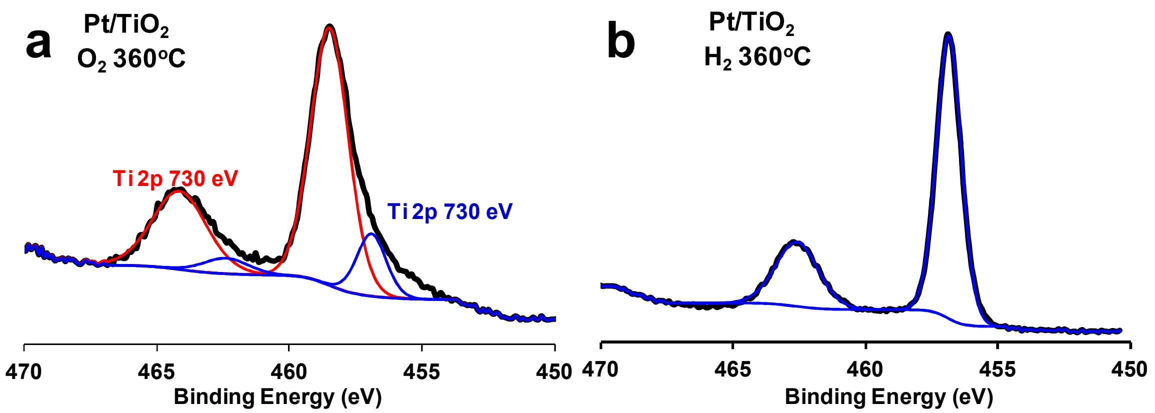
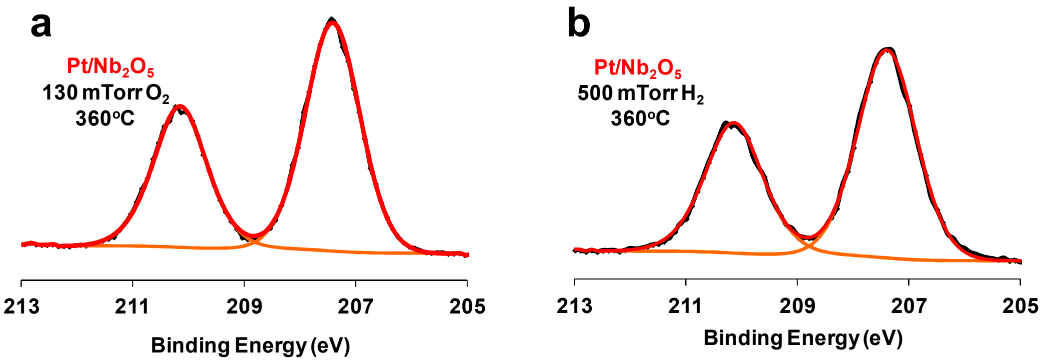


Figure S3. X-ray diffraction patterns of (a) Pt/Ta_2O_5 and (b) Pt/ZrO_2 catalysts obtained in 150 Torr of H_2 at 360°C and room temperature in air.



		BE (eV)[14]	ΔE	FWHM
O_2 360°C	TiO_x	456.9	5.5	1.3
	TiO_2	458.5	5.6	1.7
H_2 360°C	TiO_x	456.9	5.6	1.1
	TiO_2	-	-	-

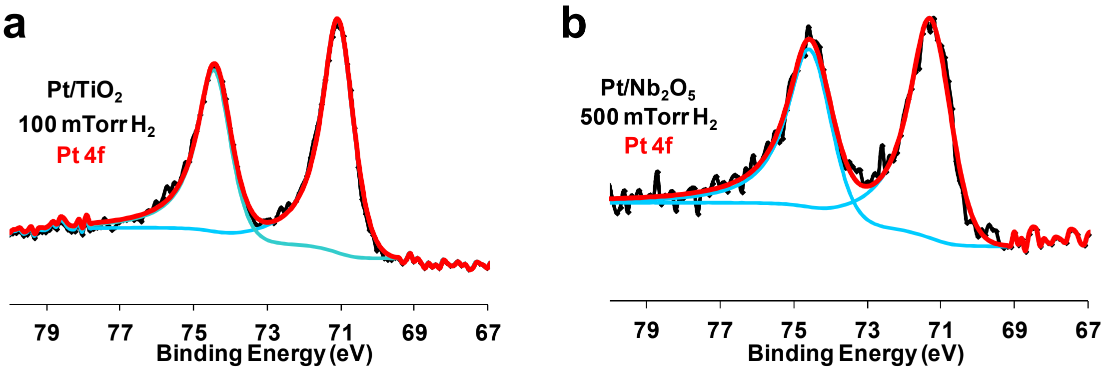
Figure S4. APXPS spectra of Pt/TiO_2 in (a) O_2 and (b) H_2 at 360°C, respectively.



Conditions	Assignment	BE (eV)[15]	ΔE[a]	FWHM
130 mTorr O_2 360°C	Nb_2O_5	207.4	2.7	1.2
500 mTorr H_2 360°C	Nb_2O_5	207.4	2.7	1.2

Figure S5. APXPS spectra of Nb4d core levels in Pt/Nb_2O_5 in (a) 130 mTorr O_2 and (b) 500 mTorr H_2 at 360°C.

[a] refined spin-orbit coupling constant.



Conditions	Assignment	BE (eV)	ΔE	FWHM
100 mTorr H_2 360°C	Pt	71.1	3.4	1.0
500 mTorr H_2 360°C	Pt	71.1	3.3	1.3

Figure S6. APXPS spectra of Pt4f in (a) Pt/TiO_2 under 100 mTorr H_2 and (b) Pt/Nb_2O_5 under 500 mTorr H_2 at 360°C.

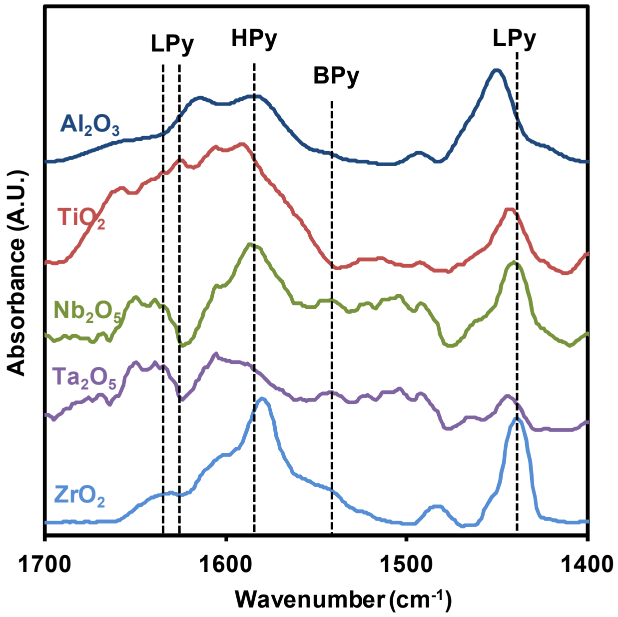


Figure S7. FT-IR spectra of pyridine adsorbed on macroporous oxides of Al_2O_3, TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2. Lewis (LPy) and Brönsted (BPy) acidic sites, and H-bonded pyridine (HPy) were indicated.[8-13]

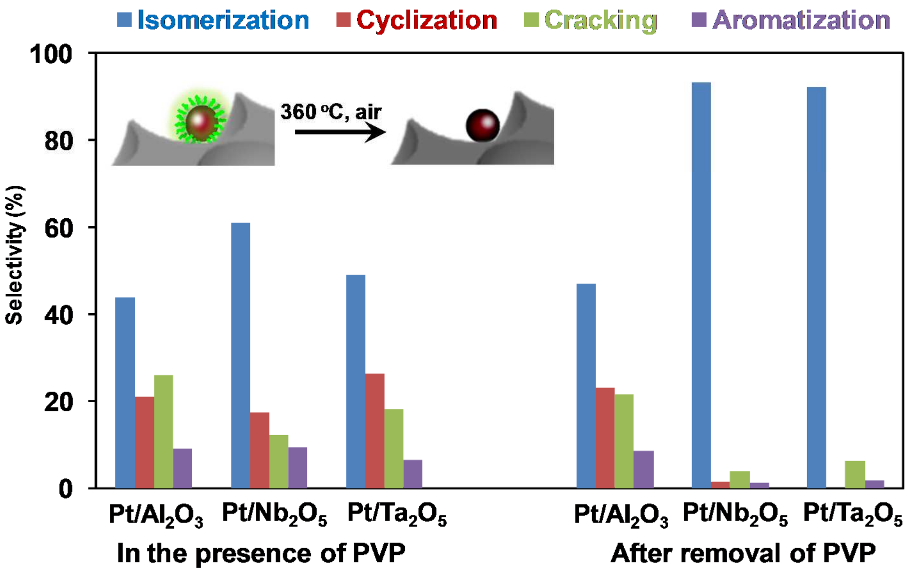


Figure S8. Product selectivity in *n*-hexane isomerization over Pt/Al_2O_3, Pt/Nb_2O_5, and Pt/Ta_2O_5 catalysts before and after removal of organic capping molecules.

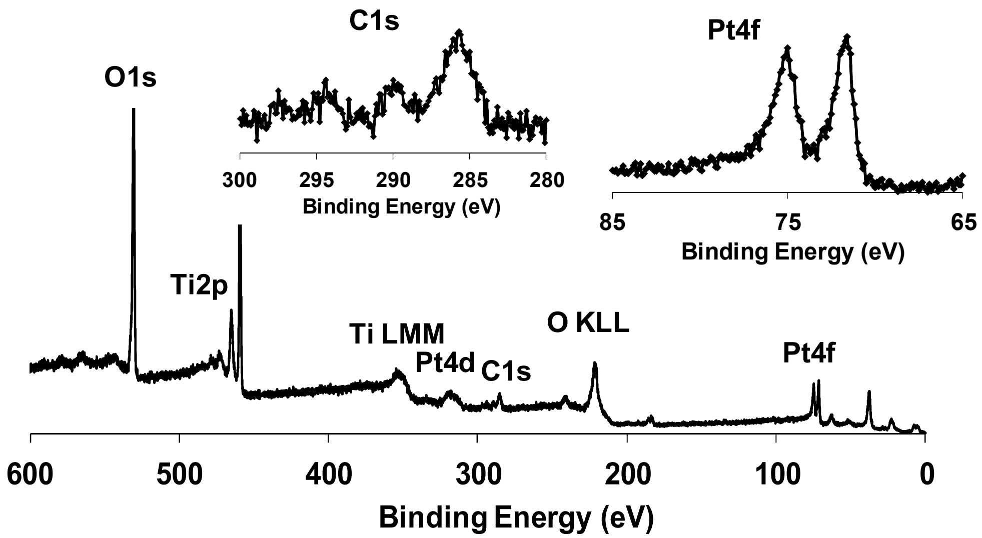


Figure S9. XPS spectra of Pt/TiO_2 collected using 730 eV photon energy in 100 mTorr H_2 at 360°C. By the relative sensitivity factors, 1:3 of Pt:C ratio was obtained.

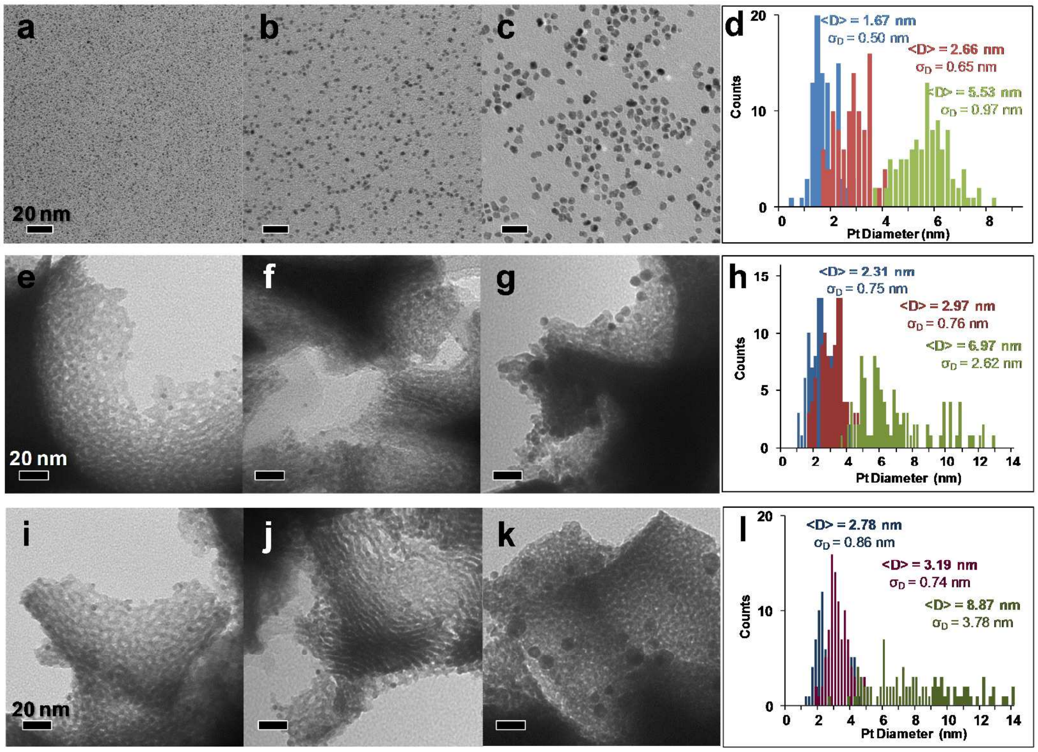


Figure S10. TEM images of (a-c) as-synthesized PVP-capped Pt nanoparticles with an average diameter of 1.7, 2.7, and 5.5 nm, (e-g) Pt nanoparticle-supported on Ta_2O_5 (Pt/Ta_2O_5) catalysts after removal of PVP by calcinations at 360 °C for 2 h in air, (i-k) Pt/Ta_2O_5 catalysts after *n*-hexane isomerization at 360 °C. The corresponding particle size distribution histograms of (d) Pt nanoparticles and (h,l) Pt/Ta_2O_5 catalysts are provided at the end of the raw.

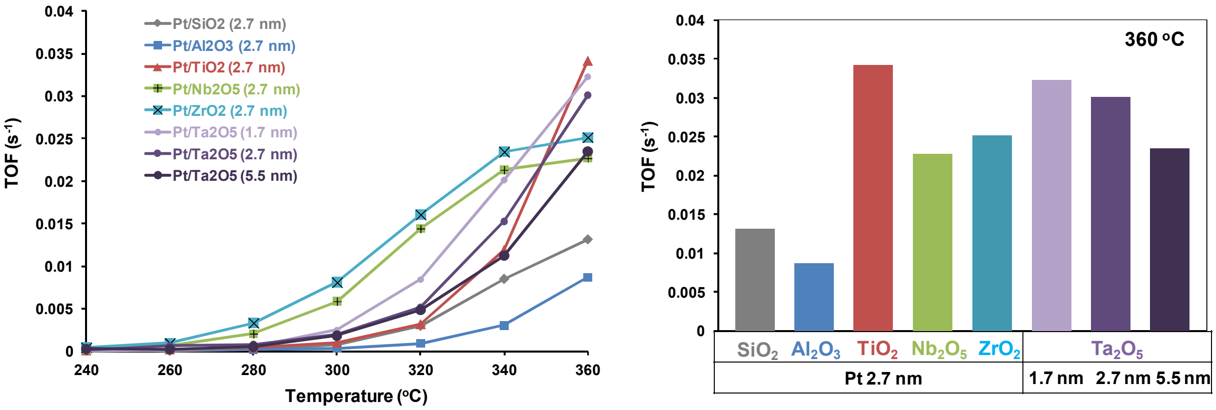


Figure S11. Temperature-dependent turnover frequencies (TOFs) over Pt nanoparticle-supported oxide catalysts in *n*-hexane isomerization over the temperature range of 240 – 360 °C in 140 Torr *n*-hexane and 620 Torr H_2. TOFs were calculated by normalizing the number of available surface Pt atoms based on size arguments in TEM.

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