Steering the Metal Precursor Location in Pd/Zeotype Catalysts and its Implications for Catalysis

Supporting Materials

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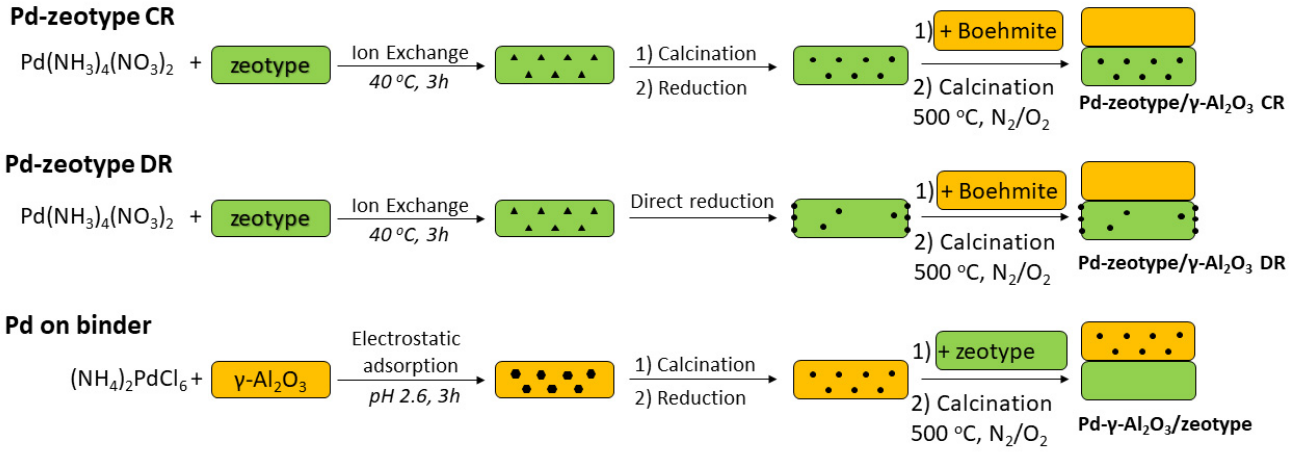

Figure S1. Schematic overview of catalyst synthesis.

Table S1. Number of acid sites as determined using NH_3-TPD and FT-IR using pyridine (Py) as probe molecule.

Material	NH_3-TPD (mmol/g)			Py-FT-IR (mmol/g)	
	Weak	Medium/Strong	Total	BAS	LAS
SAPO-11	0.17	0.22	0.40	0.082	0.021
ZSM-22	0.20	0.28	0.48	0.081	0.016
γ-Al_2O_3	-	-	0.46	0	0.226
SAPO-11/γ-Al_2O_3	0.08	0.27	0.35	0.020	0.096
ZSM-22/γ-Al_2O_3	0.14	0.35	0.49	0.025	0.086
Pd-γ-Al_2O_3/SAPO-11	0.08	0.29	0.37	0.015	0.112
Pd-SAPO-11/γ-Al_2O_3 DR	0.08	0.26	0.34	n.d.	n.d.
Pd-SAPO-11/γ-Al_2O_3 CR	0.07	0.25	0.32	0.018	0.117
Pd-γ-Al_2O_3/ZSM-22	0.17	0.37	0.53	0.023	0.149
Pd-ZSM-22/γ-Al_2O_3 DR	0.14	0.35	0.49	n.d.	n.d.
Pd-ZSM-22/γ-Al_2O_3 CR	0.15	0.33	0.48	0.019	0.108

Table S2. Palladium loading, palladium nanoparticle properties and acid properties of each catalyst.

Catalyst	Pd weight loading[a] (wt%)	Pd size, d_{Pd} (nm)	D[c]	n_{Pd}[d]	n_a[e]	n_{Pd}/n_a
Pd-γ-Al_2O_3/SAPO-11	0.49	2.0 ± 0.4	56	0.026	0.29	0.088
Pd-SAPO-11/γ-Al_2O_3 DR	0.45	2.3 ± 0.9	48	0.020	0.26	0.079
Pd-SAPO-11/γ-Al_2O_3 CR	0.41	1.7 ± 0.4	65	0.025	0.25	0.101
Pd-γ-Al_2O_3/ZSM-22	0.50	2.0 ± 0.4	56	0.024	0.37	0.064
Pd-ZSM-22/γ-Al_2O_3 DR	0.44	1.9 ± 0.4	59	0.024	0.35	0.069
Pd-ZSM-22/γ-Al_2O_3 CR	0.41	2.1 ± 0.4	53	0.020	0.33	0.062

[a]By inductively coupled plasma optical emission spectroscopy on digested samples.
[b]Number average particle size by measurement Pd nanoparticle diameter of at least 400 particles in STEM images.
[c]Dispersion of Pd nanoparticles using Dispersion = $1.112/d_{Pd}$
[d]Calculated based on the ICP weight loading of Pd and the dispersion.
[e]By deconvolution of NH_3-TPD profiles and integration of the peak at higher temperatures (T ≥ 200 °C for SAPO-11 and T ≥ 300 °C for ZSM-22).

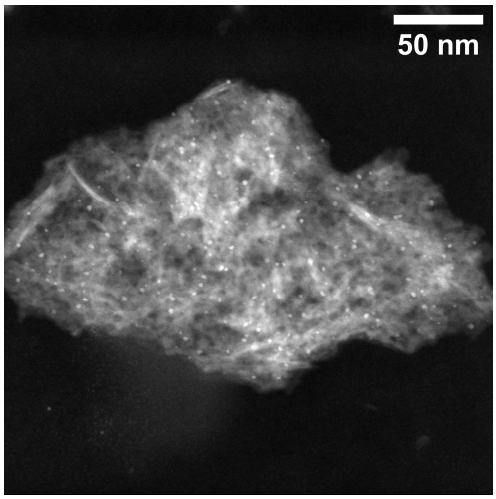

Figure S2. HAADF-STEM image of Pd/γ-Al_2O_3 before mixing with a zeotype material.

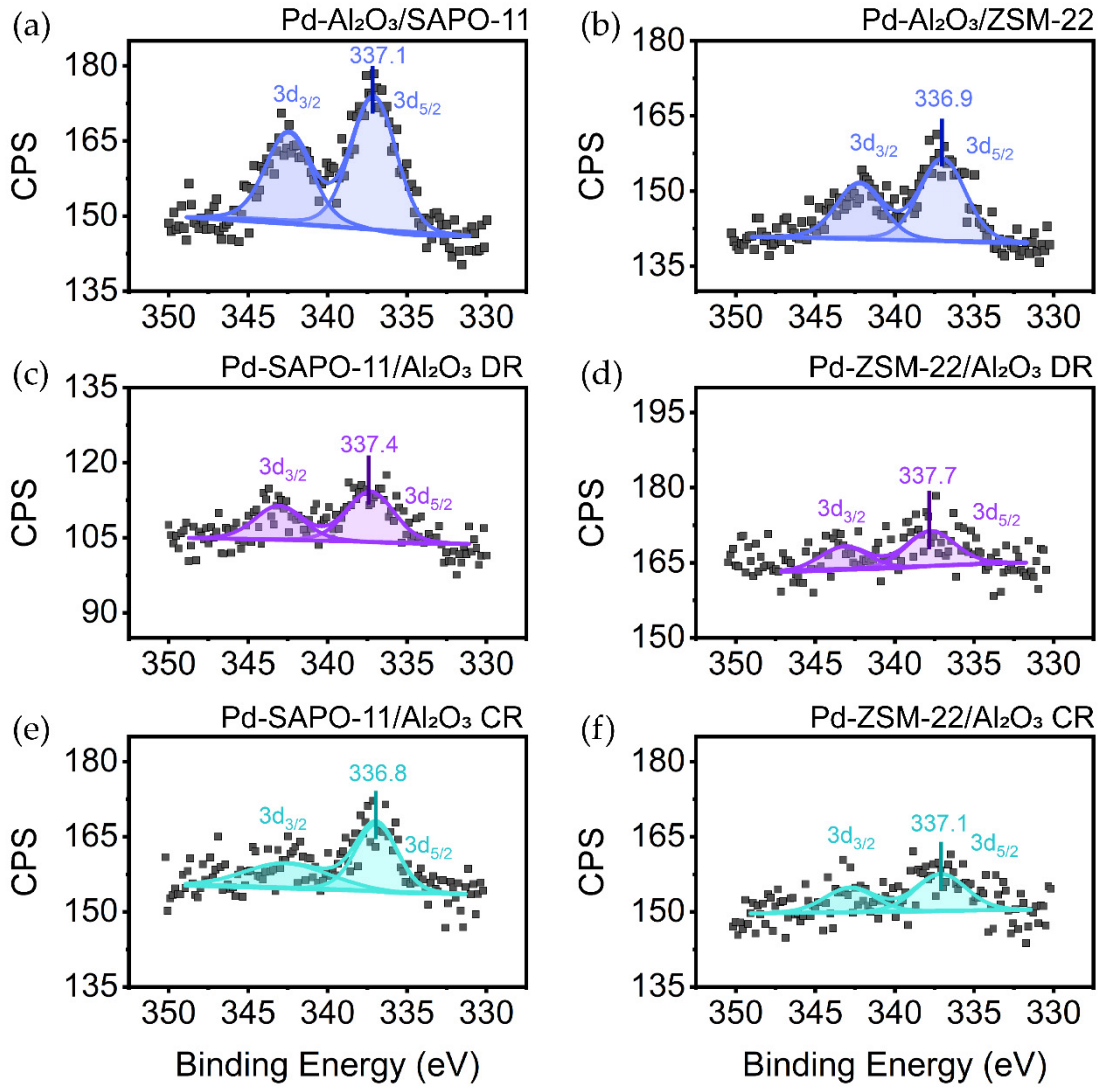

Figure S3. XPS spectra of Pd in all catalysts.

Table S3. Results of N_2 physisorption on samples without γ-alumina.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	S_{micro} (m^2/g) Dubinin-Astakhov	$S_{Langmuir}$ (m^2/g)
SAPO-11	134	56	78	0.17	0.024	119	147
0.5Pd-SAPO-11 CR	122	58	64	0.16	0.024	108	129
1Pd-SAPO-11 DR	131	68	64	0.16	0.028	125	142
ZSM-22	126	70	56	0.19	0.029	170	136
0.5Pd-ZSM-22 CR	138	83	55	0.32	0.033	132	144
0.9Pd-ZSM-22 DR	174	93	83	0.22	0.040	170	194

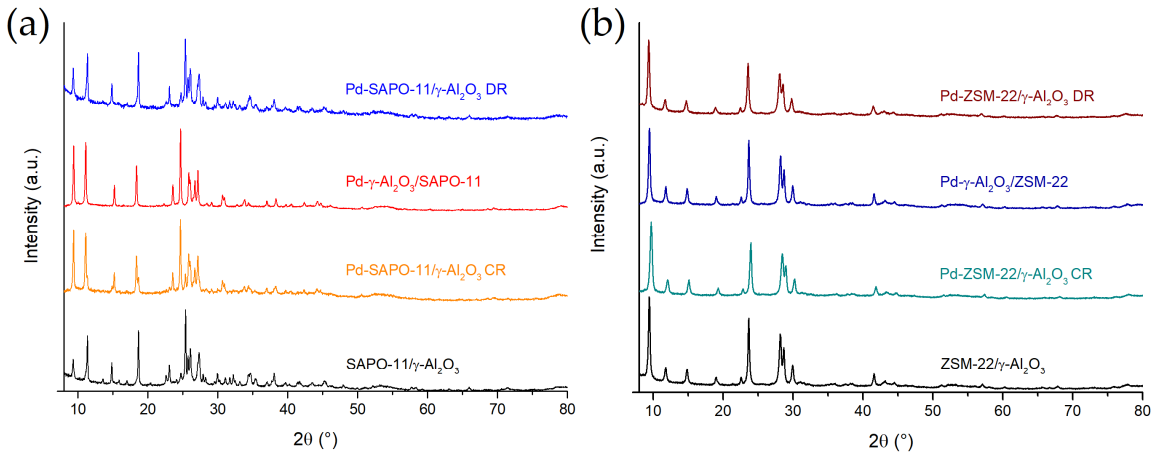

Figure S4. XRD patterns of (a) SAPO-11 based catalysts and (b) ZSM-22 based catalysts each catalyst and zeotype/alumina composite materials.

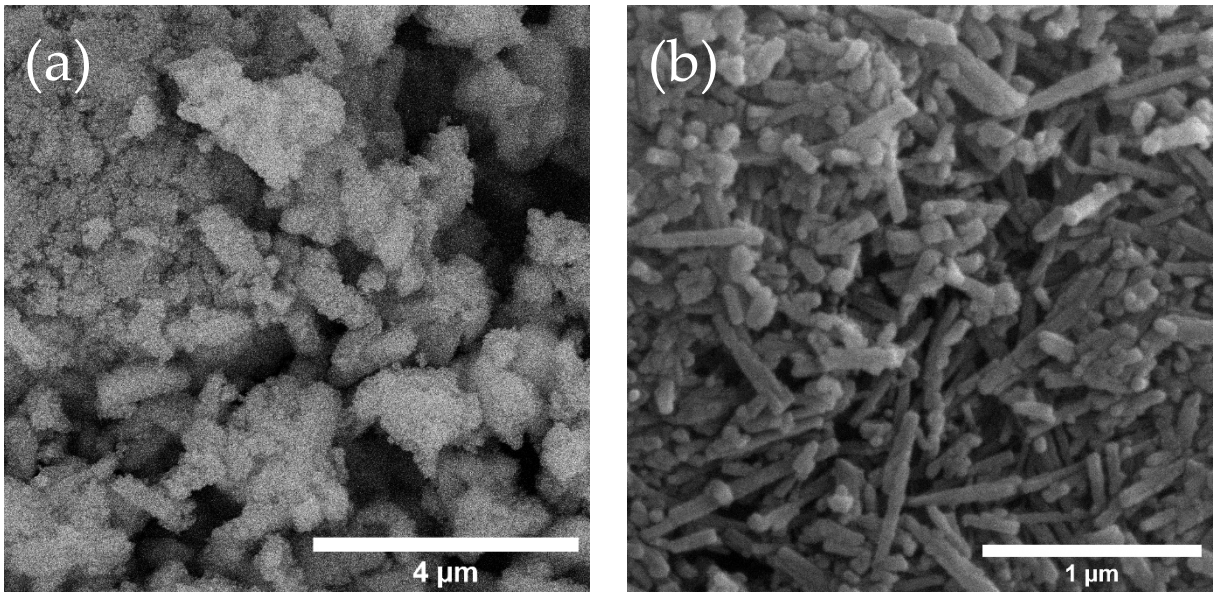

Figure S5. SEM images of as-received (a) SAPO-11 and (b) ZSM-22. As can be seen in (a) the SAPO-11 sample contains both the typical cuboid SAPO-11 crystals, as well as a less crystalline component (top right). In (b) the needle-like shape of ZSM-22 is evident.

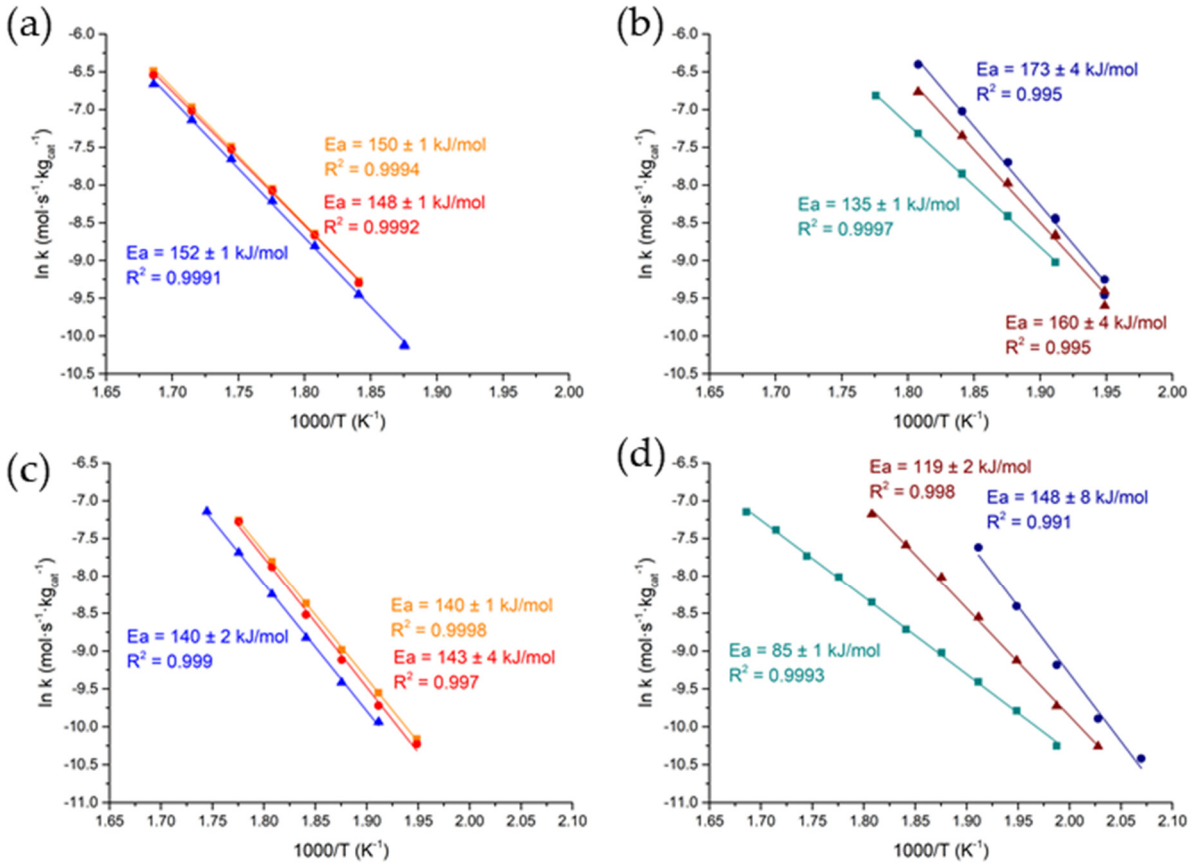

Figure S6. Arrhenius plots of (a) *n*-heptane conversion over SAPO-11 based catalysts, (b) *n*-heptane conversion over ZSM-22 based catalysts, (c) *n*-hexadecane conversion over SAPO-11 based catalysts and (d) *n*-hexadecane conversion over ZSM-22 based catalysts. The catalysts are depicted as follows: Pd-SAPO-11/γ-Al_2O_3 (CR) (orange squares), Pd-γ-Al_2O_3/SAPO-11 (red circles), Pd-SAPO-11/γ-Al_2O_3 (DR) (blue triangles), Pd-ZSM-22/γ-Al_2O_3 (CR) (dark cyan squares), Pd-γ-Al_2O_3/ZSM-22 (dark blue circles) and Pd-ZSM-22/γ-Al_2O_3 (DR) (brown triangles). The plots are based on measurements below 20 % conversion. Reaction conditions of *n*-heptane conversion: P = 10 bar, H_2/*n*-heptane = 10 : 1 (mol/mol), WHSV = 2.4 $g_{n\text{-}C7} \cdot g_{cat}^{-1} \cdot h^{-1}$. Reaction conditions of *n*-hexadecane conversion: P = 5 bar, H_2/*n*-heptane = 10 : 1 (mol/mol), WHSV = 2.9 $g_{n\text{-}C16} \cdot g_{cat}^{-1} \cdot h^{-1}$.