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Supporting Information

Enhancing the Matching of Acid/Metal Balance by Engineering an Extra Si-Al Framework Outside Pd/HBeta Catalyst Towards Benzene Hydroalkylation

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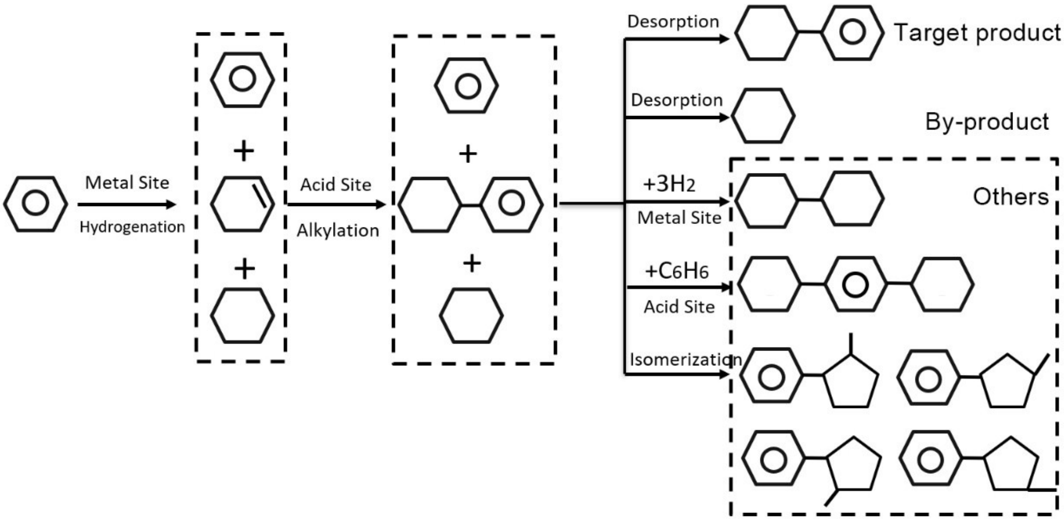
Reaction network

As the reaction network illustrated in Scheme 1, it is found that Pd/HBeta can catalyze the hydroalkylation of benzene while distinct reaction products might be obtained. In this reaction, benzene adsorbed both on the metal and acid site, hydrogenation to cyclohexene (CHE) and cyclohexane (CHA) at metal site. Meanwhile, some of the CHE desorbed from the metal site to acid site, which allowed benzene to react with CHE to form the target product cyclohexylbenzene (CHB). Moreover, CHB can continue to alkylate at the acid site to form dicyclohexylbenzene (DCHB) and continue to hydrogenate at the metal site to form bicyclohexyl. In addition, benzene and CHE can also isomerized on HBeta zeolite to form methylcyclopentylbenzene and its isomers.



Scheme S1 Reaction network for the hydroalkylation of benzene.

Quantitative analysis

The units of conversion and selectivity are mol %. The details of GCMS data converted to mol % are as follows:

$$\text{Benzene Conversion (\%)} = \left(1 - \frac{A_{BZ}}{f_{BZ}}\right) \times 100\%$$

""

$$CHB\ Selectivity\ (\%) = \frac{2 \cdot \frac{A_{CHB}}{f_{CHB}} \cdot \rho_{CHB}}{M_{CHB}} \Bigg/ \frac{\left(1 - \frac{A_{BZ}}{f_{BZ}}\right) \cdot \rho_{BZ}}{M_{BZ}} \times 100\%$$

""

""$$CHB\ formation\ rate\ (mmol{\cdot}g^{-1}{\cdot}h^{-1}) = \frac{M_{max}}{M_{Cat} \times T_{max}} \times 100\%$$

Here, A_{BZ} and A_{CHB} refer to peak area of benzene and CHB in 1.0 µL products, respectively; f_{BZ} refers to the peak area of 1.0 µL standard benzene, and f_{CHB} refers to the peak area of 1.0 µL standard CHB. M_{BZ} and M_{CHB} are the relative molecular mass of benzene and CHB, respectively; ρ_{BZ} and ρ_{CHB} are the density of benzene and CHB, respectively. Here, M_{cat} refers to the mass of catalyst, M_{max} refers to the maximum mass of CHB formation, and T_{max} is the time to reach this yield.

Preparation of catalysts

Synthesis of Pd@HBeta(0.2) with mean size at 2.8 nm. The as-prepared Pd@Na-Beta was ion exchanged with 1.0 M NH_4Cl solution three times, dried at 80 °C overnight, calcined in flowing air at 500 °C for 4 h, and finally reduced in 10 vol.% H_2/N_2 at 400 °C for 2 h to produce the Pd@H-Beta sample with 2.8 nm Pd NPs size. Then, the reduced catalyst is stored in the vacuum environment until the process of catalytic activity test.

Synthesis of Pd/HBeta(0.2) with mean size at 2.0 and 2.9 nm. 555.5 mg of PVP was added to the 50 mL of aqueous $PdCl_2$ solution (1.0 $g\cdot L^{-1}$). After stirring at 0 °C for 5.0 h, 15 mL $NaBH_4$ aqueous solution (0.1 M) was added. After stirring for another 2 h, the mixture containing nanoparticles was dialyzed for 2 days to remove unnecessary ions. The pH was adjusted to 10 by adding 0.5 M NaOH aqueous solution with stirring, the samples were obtained by centrifuging, washing with a large excess of water, drying at 80 °C ,calcining at 350 °C in air for 4.0 h, reducing at 300 °C in 10 vol. % H_2/N_2 for 2 h. the Pd/HBeta(0.2) with Pd nanoparticle size at 1.6-3.6 nm with mean size at 2.0 nm. By calcining the Pd/HBeta(0.2) in flowing nitrogen at 400 and 450 °C for 3 h, the Pd/HBeta samples with larger Pd nanoparticles (mean sizes at about 2.9 nm) were obtained.

Synthesis of Pd@HBeta(L2) catalysts with two framework layers. The encapsulated gel (Si/Al= 13.0) with the composition $11Na_2O/Al_2O_3/26SiO_2/270H_2O$ was prepared by mixing 0.64 g of $NaAlO_2$, 1.12 g of NaOH, 13.6 g of H_2O and 4.0 g fumed silica. After stirring (150 $rpm\cdot min^{-1}$) for 12.0 h at room temperature, 0.2g as-prepared Pd/HBeta(4.0) precursor was then added directly into the encapsulated gel, which was stirred for 6 h. Finally, the synthesis gel was transferred into a hydrothermal reactor. After hydrothermal treatment at 120 °C for 96 h. The sample was collected by centrifugation, washing with deionized water and drying at vacuum oven (at 60 °C). The obtained product was denoted as Pd@Na-Beta(L2). Then, The as-prepared Pd@Na-Beta(L2) was ion exchanged with 1.0 M NH_4Cl solution three times, dried at 80 °C overnight, calcined in flowing air at 400 °C for 6 h, and finally reduced in 10 vol.% H_2/N_2 at 315 °C for 3.0 h to derive the Pd@HBeta(L2) sample. Then, the reduced catalyst is stored in the vacuum environment until the process of catalytic activity test.

Figures and Tables

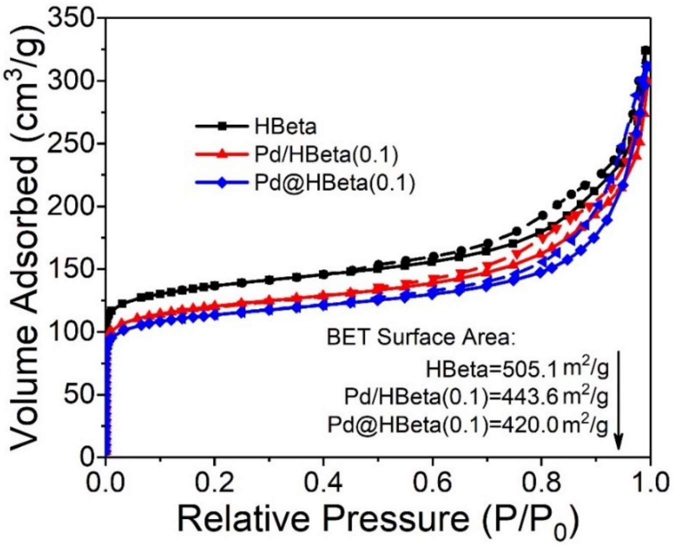


Figure S1 N_2 adsorption-desorption isotherms of samples

Note: The N_2 adsorption-desorption isotherms displayed in Figure S1. The curves of the samples belong to type I in the IUPAC classification. The existence of hysteretic loops indicates that there are mesopores in these catalysts. The curves present a sharp knee at low relative pressures, indicating that micropores are abundant in these materials.

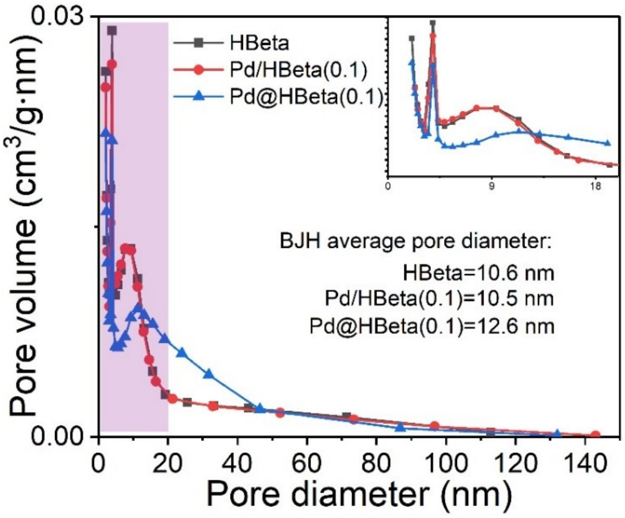


Figure S2 Pore size distribution of samples.

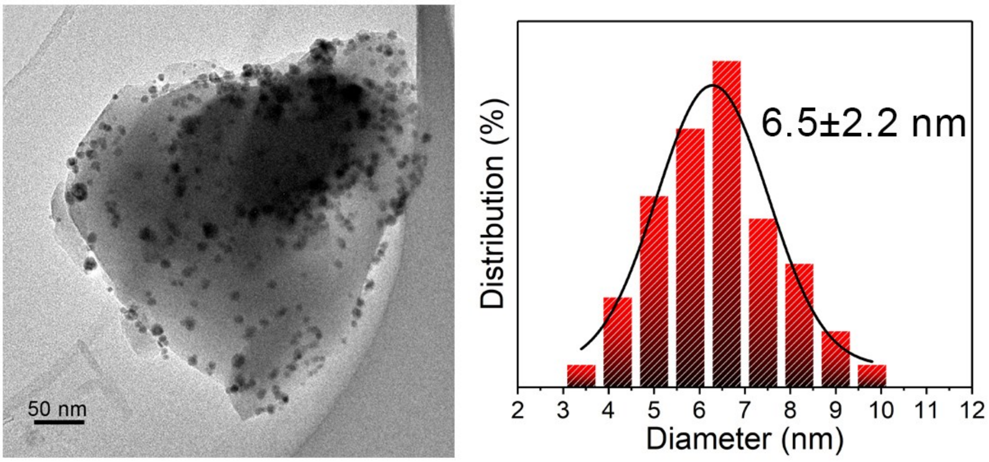


Figure S3 TEM images of Precursor Pd/HBeta(4.0).

Note: Pd@HBeta(0.2) catalyst was obtained by 96 hours hydrothermal treatment of Pd/HBeta(4.0) with Si-Al gel.

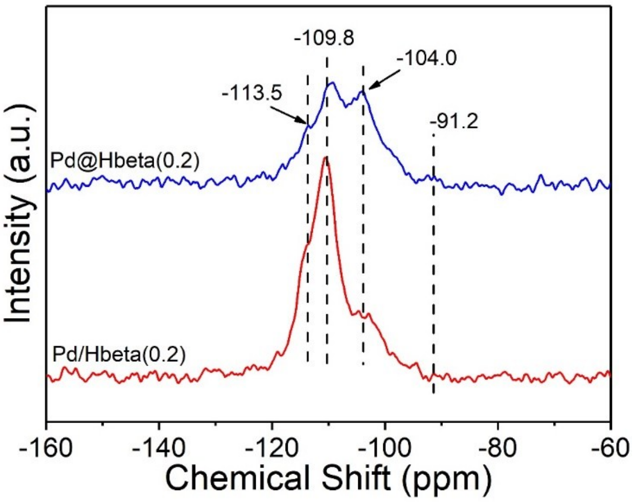


Figure S4 ^{29}Si MAS NMR spectra of Pd@HBeta and Pd/HBeta.

Note: The peak at 91.2 ppm is assigned to three Al atoms around the Si atom, and the peak at 103.9 ppm is regarded as one Al atom around one Si atom. As for the peaks at 109.2 and 113.5 ppm indicate that no Al atom around the Si atom. The intensity ratio of peaks at 103.9 and 109.2 ppm in Pd@HBeta catalysts ($I_{109.8}/I_{104.0}$= 1.2) is different with that in Pd/HBeta catalysts ($I_{109.8}/I_{104.0}$= 1.6). This suggests that the chemical environment of Si atom was altered after coating an extra Si-Al framework.

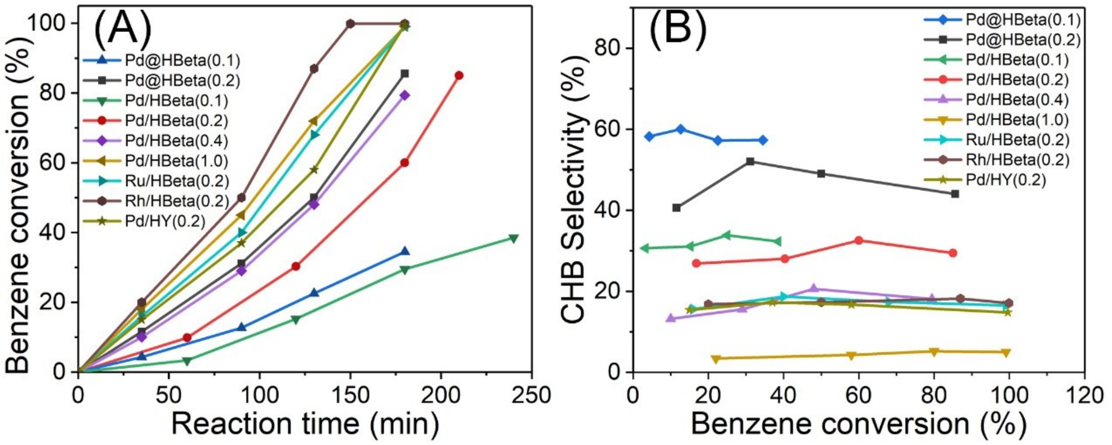


Figure S5 Plots of the (A) conversion of the benzene versus the reaction time. (B) CHB selectivity versus the benzene conversion over various catalysts. Reaction condition: 1.0 g of catalysts, 280.5 mmol of benzene, 4.0 MPa H_2, T= 200 °C, t= 180 min, and a stirring rate of 800 rpm·min^{-1}.

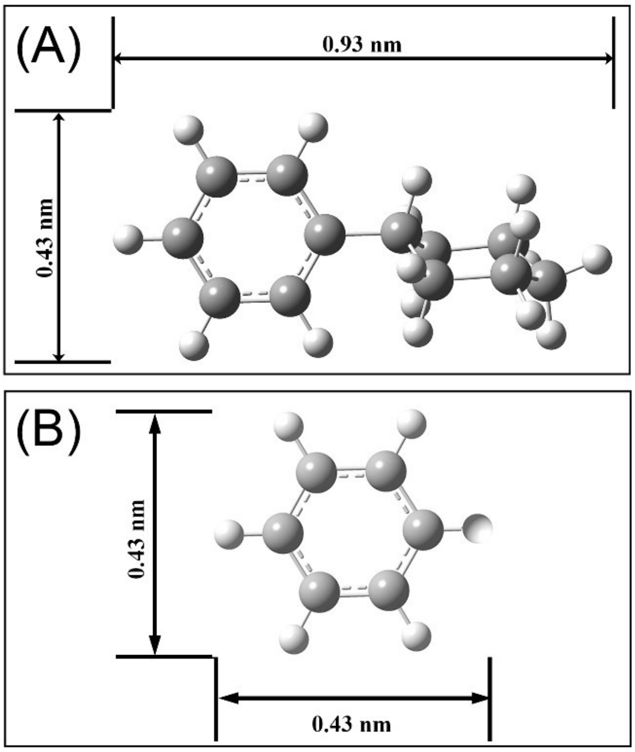


Figure S6 Scientific back up for molecule diameter for (A) CHB and (B) benzene.

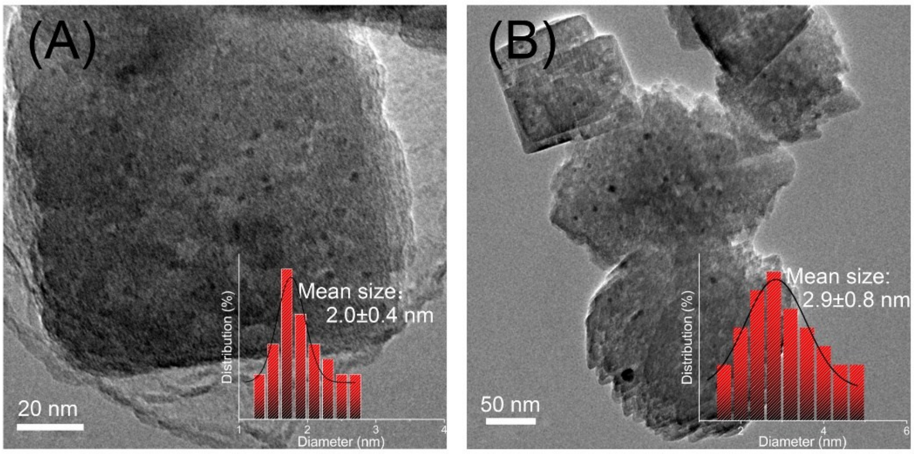


Figure S7 TEM images of Pd/HBeta catalysts with (A)2.0 nm (B)2.9 nm metal particle size

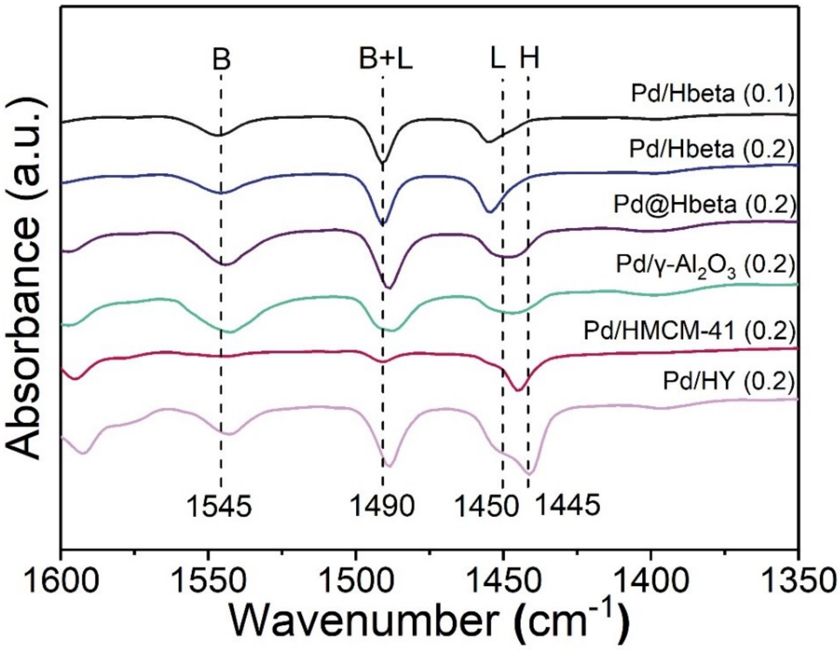


Figure S8 Py-IR images of all samples.

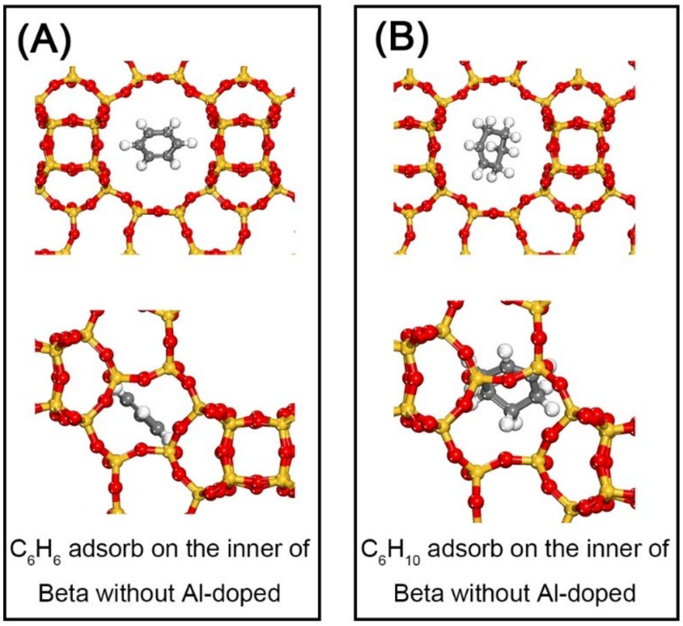


Figure S9 the models for C_6H_6 and C_6H_{10} adsorb on the inner of Beta zeolite without Al-doped.

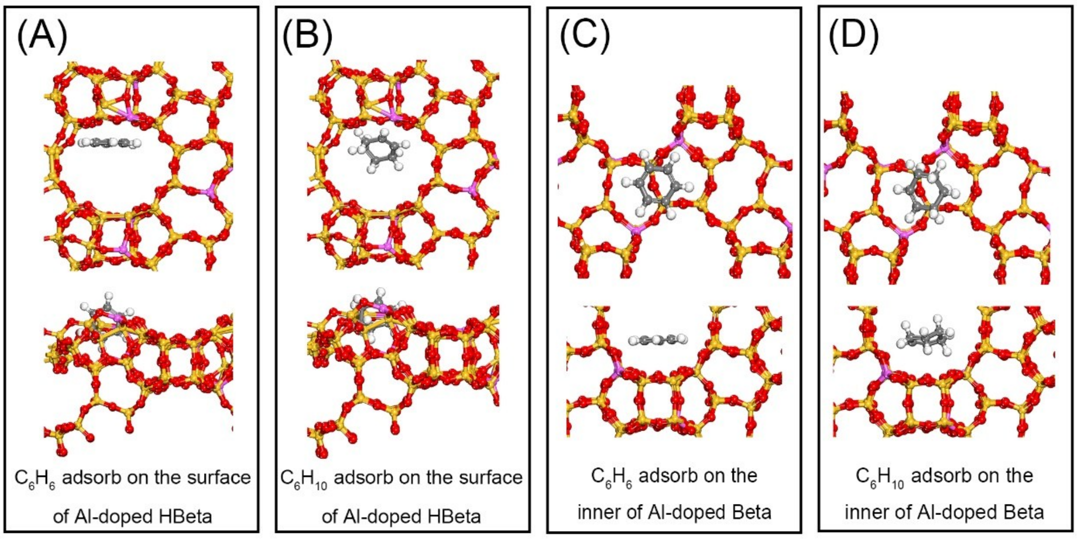


Figure S10 the models for (A, B) C_6H_6 and C_6H_{10} adsorb on the surface of Beta zeolite with Al-doped (Al-Beta). (C, D) C_6H_6 and C_6H_{10} adsorb on the inner of Al-Beta.

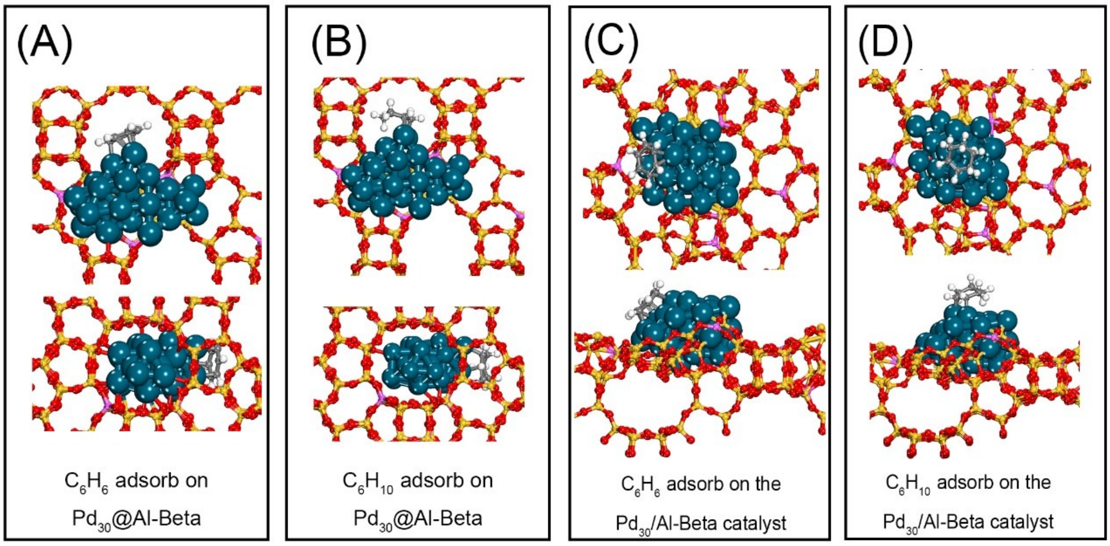


Figure S11 the models for (A, B) C_6H_6 and C_6H_{10} adsorb on the Pd_{30}/Al-Beta catalyst. (C, D) C_6H_6 and C_6H_{10} adsorb on the Pd_{30}@Al-Beta catalyst.

Table S1 Catalytic performances influenced by various SiO_2/Al_2O_3 ratio.

Catalysts	SiO_2/Al_2O_3 Ratio	Conversion (%)	Selectivity(%)			Yields
			CHA	CHB	Others	CHB(%)
Pd/HBeta(0.2)	25	60.1	64.5	30.5	4.8	18.3
	50	55.3	70.3	26.7	2.6	14.8
	80	37.5	75.8	22.8	1.3	8.5
	150	18.4	78.2	21.3	0.5	3.9
	300	7.6	81.3	18.4	0.3	1.4

Reaction conditions: 1.0 g of Pd/HBeta(0.2-300) catalyst, 280.5 mmol of benzene, 4.0 MPa H_2, T= 200 °C, t= 180 min, and a stirring rate of 800 rpm·min^{-1}.

Table S2 Catalytic performance for different metal particle size in Pd@HBeta(0.2) and Pd/HBeta(0.2) catalysts.

Catalysts	ICP metal content wt.%	Pd NPs Size	Conversion (%)	Selectivity (%)		
				CHA	CHB	Others
Pd@HBeta	0.19	~2.0 nm	85.6	49.8	44	6.2
	0.19	~2.8 nm	84.4	44.3	46.2	9.4
Pd/HBeta	0.20	~2.0 nm	89.3	92.4	5.8	1.4
	0.21	~2.9 nm	82.5	84.8	11.5	3.5
	0.20	~5.8nm	85.0	68.0	25.1	6.9

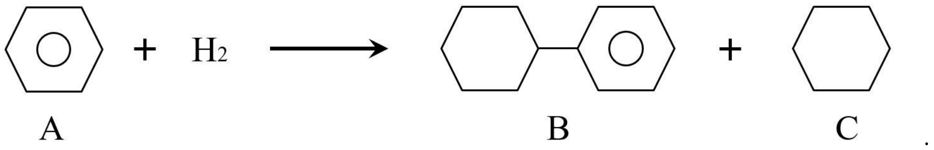
Reaction conditions: 1.0 g of Pd/HBeta(0.2-300) catalyst, 280.5 mmol of benzene, 4.0 MPa H_2, T= 200 °C, t= 180 min, and a stirring rate of 800 rpm·min^{-1}.

Table S3 Catalytic performances influenced by the thickness of HBeta layer.

Catalysts	Hydrothermal number	Preparation mass[a]	Conversion (%)	Selectivity (%)		
				CHA	CHB	Others
Pd/HBeta(L0)	0	0.2 g	85.0	68	25.1	6.9
Pd@HBeta(L1)	1	4.1 g	85.6	49.8	44	6.2
Pd@HBeta(L2)	2	7.9 g	81.5	54.4	30.6	14.9

Reaction condition: 1.0 g of Pd/HBeta(0.2) catalyst, 280.5 mmol of benzene, 4.0 MPa H_2, T= 200 °C, and a stirring rate of 800 rpm·min^{-1}. [a] Preparation mass means the mass weight of the catalysts after centrifuge, calcined 400 °C in the air and reduced at 315 °C in 10 vol.% H_2/N_2 for 3 h.

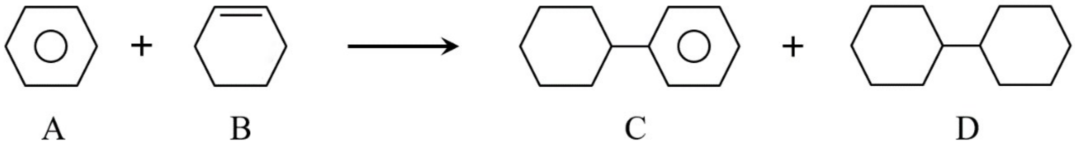
Table S4 Benzene hydroalkylation over Pd/HBeta(0.2-300) catalyst.



Catalyst	Reaction time min	Conversion of A %	Yields of B %	Yields of C %	Carbon balance
Pd/HBeta (0.2-300)	35	1.32	0.16	1.15	≥99.5
	90	5.33	0.9	4.40	
	180	7.6	1.4	6.17	

Reaction conditions: 1.0 g of Pd/HBeta(0.2-300) catalyst, 280.5 mmol of benzene, 4.0 MPa H_2, T= 200 °C, t= 180 min, and a stirring rate of 800 rpm·min^{-1}.

Table S5 Alkylation of benzene and cyclohexene over HBeta zeolite.



Catalyst	Reaction time min	Conversion of B %	Yields of C %	Yields of D %	A/B Volume ratio
HBeta (Si/Al~12.5)	35	7.32	1.89	1.72	1
	90	40.35	6.58	5.34	
	180	68.84	14.46	11.77	

Reaction conditions: 1.0 g of HBeta catalysts, 25 mL benzene, 25ml cyclohexene, 4.0 MPa N_2, T= 200 °C, t= 180 min, and a stirring rate of 800 rpm·min^{-1}.

Note: this reaction confirms that the alkylation active sites exist in HBeta zeolite.