

## Supporting Information

### **Tuning Electronic Structure of Pd by Surface Configuration of Al<sub>2</sub>O<sub>3</sub> for Hydrogenation Reactions**

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Table S3 The proportions of OH groups in the XPS spectra of Al 2p and O 1s.

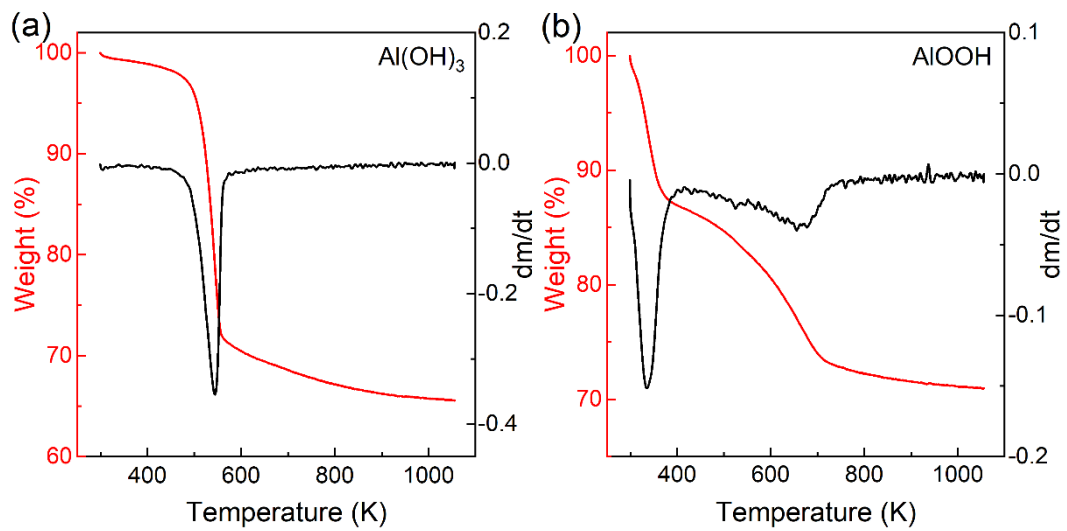


Figure S1 TG-DTA curves of (a) Al(OH)<sub>3</sub> and (b) AlOOH in air flow.

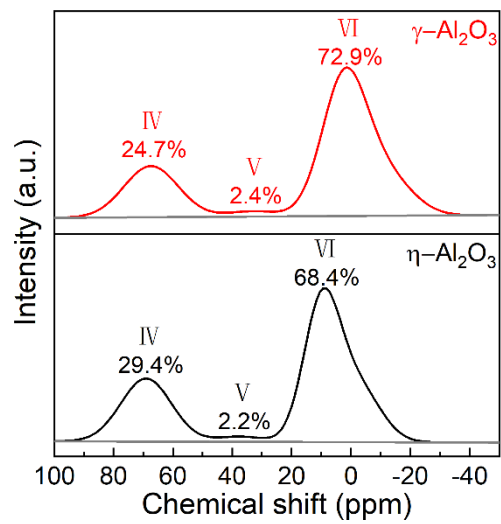


Figure S2  $^{27}\text{Al}$  MAS NMR of  $\gamma\text{-Al}_2\text{O}_3$  and  $\eta\text{-Al}_2\text{O}_3$ .

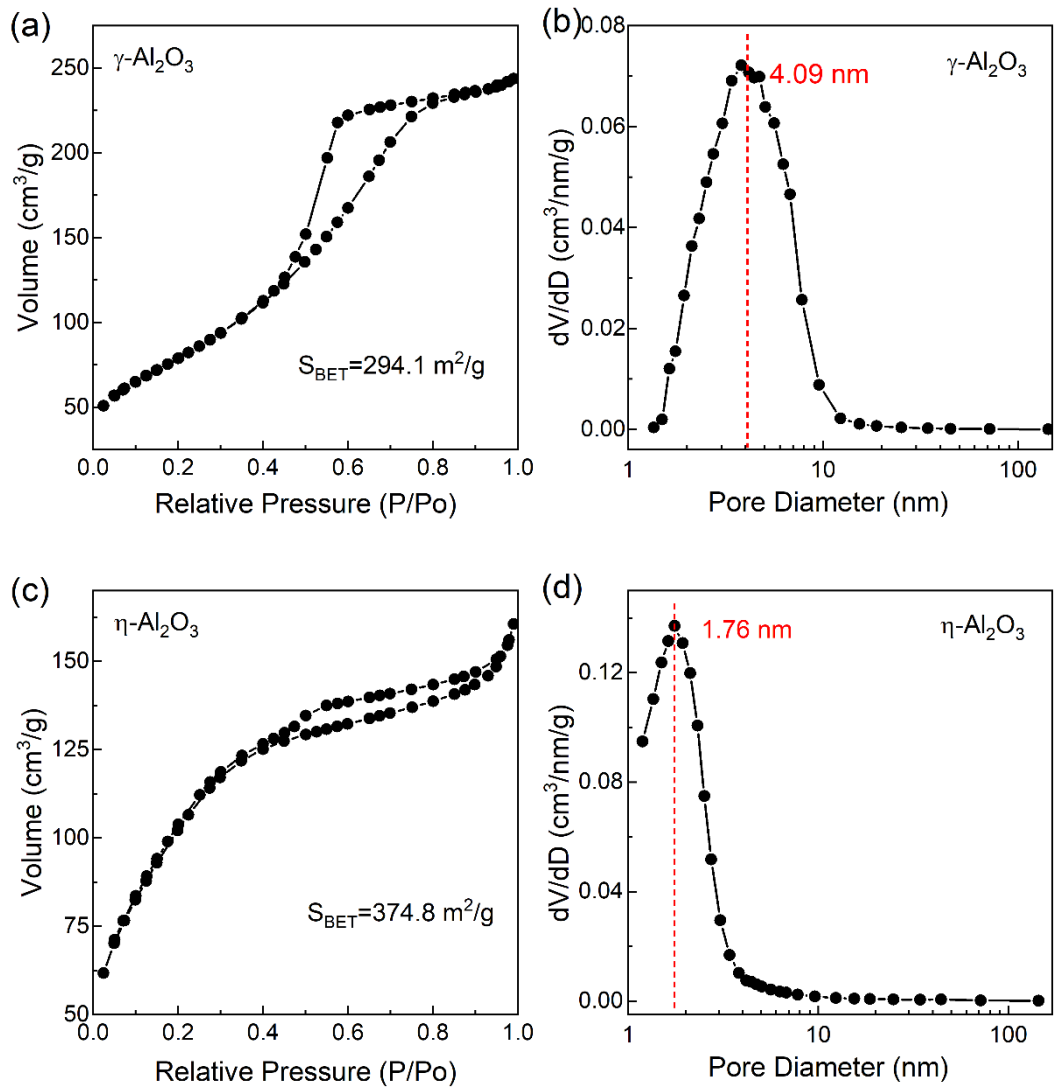


Figure S3 N<sub>2</sub> sorption isotherm and pore size distributions of  $\gamma\text{-Al}_2\text{O}_3$  (a and b) and  $\eta\text{-Al}_2\text{O}_3$  (c and d).

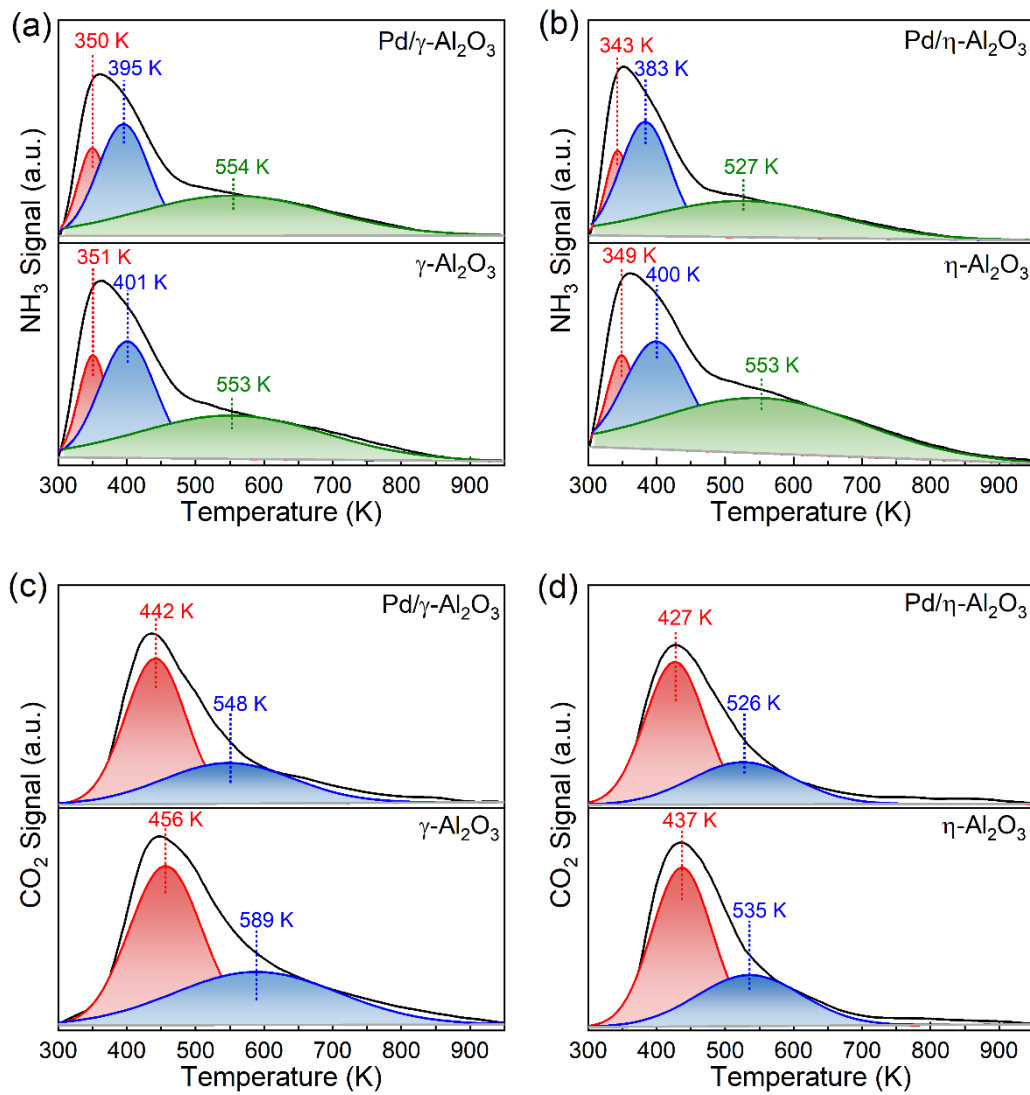


Figure S4 TPD profiles of supports and Pd supported catalysts: (a) and (b)  $\text{NH}_3$ , (c) and (d)  $\text{CO}_2$ .

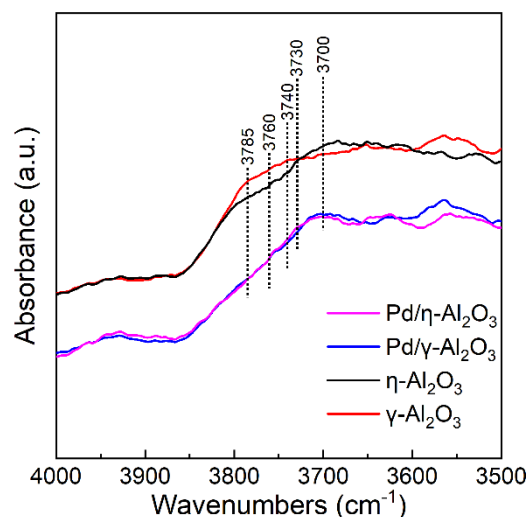


Figure S5 FT-IR spectra of OH groups on the surfaces of supports and catalysts.

There are five types of OH stretching vibrations within the frequency range of 3700-3800  $\text{cm}^{-1}$ .<sup>1-3</sup> The band at 3785  $\text{cm}^{-1}$  corresponds to a terminal OH group coordinated with an octahedral  $\text{Al}^{3+}$  ion, while the band at 3760  $\text{cm}^{-1}$  corresponds to a terminal OH group coordinated with a tetrahedral  $\text{Al}^{3+}$  ion. The band at 3740  $\text{cm}^{-1}$  is assigned to a bridging OH group that links two octahedral  $\text{Al}^{3+}$  ions. The three OH configurations are more abundant on  $\gamma\text{-Al}_2\text{O}_3$  and act as the sites accepting H-bonds. The bands at 3730  $\text{cm}^{-1}$  and 3700  $\text{cm}^{-1}$  are attributed to the stretching vibrations of a bridging OH group, which links an octahedral and a tetrahedral  $\text{Al}^{3+}$  ions, as well as a OH group coordinated to three  $\text{Al}^{3+}$  ions in octahedral interstices. The two types of OH configurations, which serve as H-bond donors, are more abundant on  $\eta\text{-Al}_2\text{O}_3$ . Loading Pd onto the supports results in a decrease in the intensity of OH vibration bands, and the similar spectra between Pd/ $\gamma\text{-Al}_2\text{O}_3$  and Pd/ $\eta\text{-Al}_2\text{O}_3$  eliminate the influence of OH groups on the catalytic performance in the hydrogenation reactions.

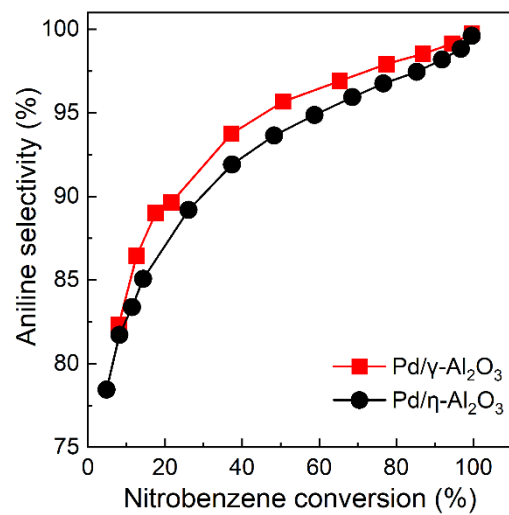


Figure S6 Selectivity of nitrobenzene hydrogenation of Pd/γ-Al<sub>2</sub>O<sub>3</sub> and Pd/η-Al<sub>2</sub>O<sub>3</sub>.



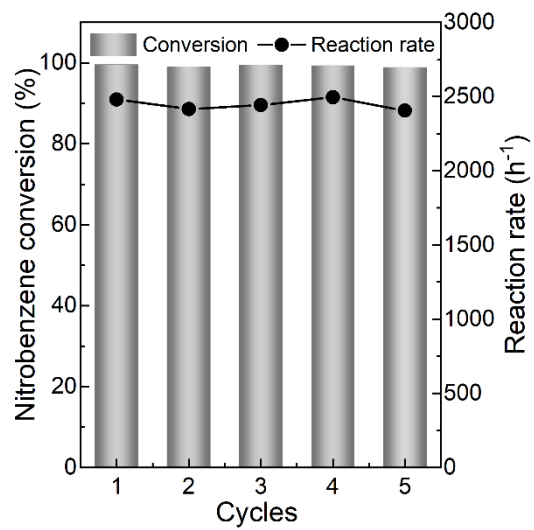


Figure S7 Recycling stability of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the hydrogenation of nitrobenzene.

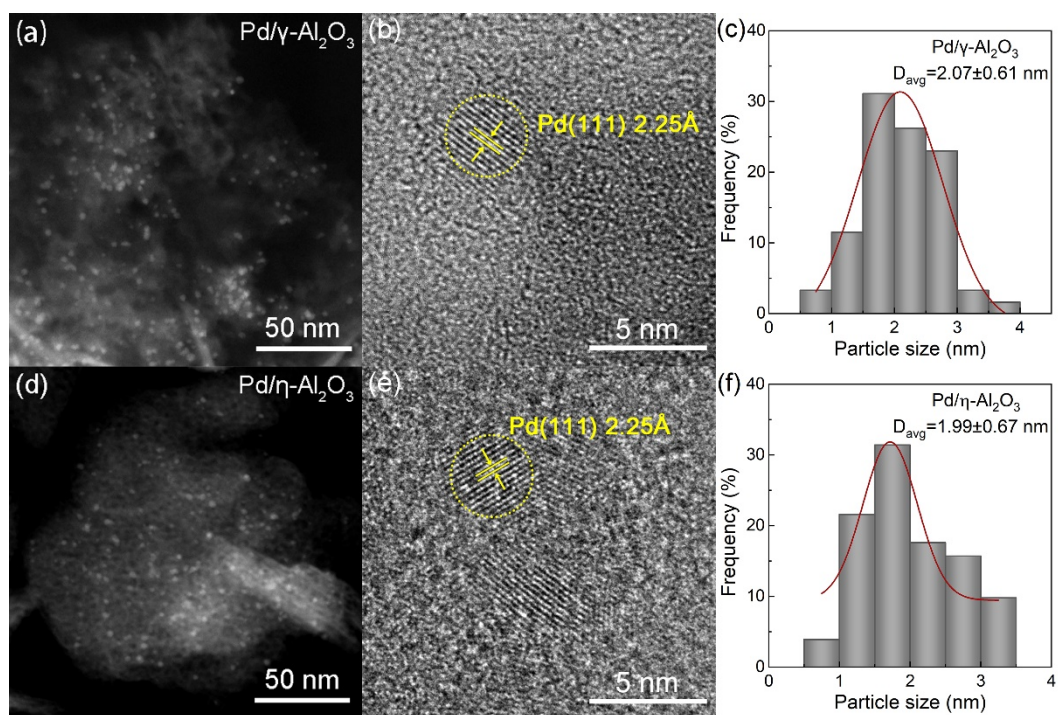


Figure S8 DF-STEM images, HR-TEM images and Pd size histograms of the used Pd/γ-Al<sub>2</sub>O<sub>3</sub> (a, b, c) and Pd/η-Al<sub>2</sub>O<sub>3</sub> (d, e, f) after the hydrogenation of nitrobenzene.

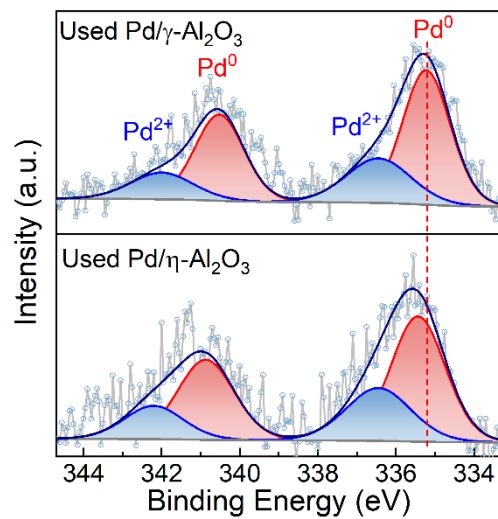


Figure S9 XPS spectra of the used catalysts after the hydrogenation of nitrobenzene.

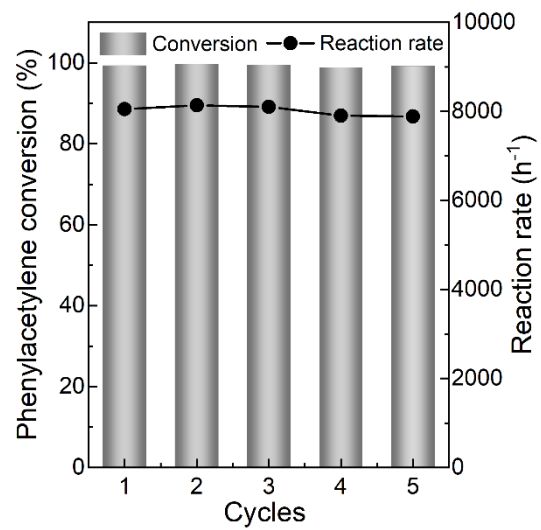


Figure S10 Recycling stability of Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> in the hydrogenation of phenylacetylene.

Table S1 Possible configuration and net charge on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\eta$ -Al<sub>2</sub>O<sub>3</sub>.<sup>2</sup>

Acid sites			Basic sites		
Configuration	Net charge	Acid strength	Configuration	Net charge	Basic strength
Al <sup>VI</sup> -OH-Al <sup>VI a</sup>	0	Weak	Al <sup>IV</sup> -OH	-1/4	Weak
Al <sup>VI</sup> -OH-Al <sup>IV b</sup>	+1/4	Weak	Al <sup>VI</sup> -OH	-1/2	Weak
Al <sup>VI</sup> -OH-Al <sup>VI b</sup> Al <sup>VI</sup>	+1/2	Moderate	Al <sup>VI</sup> -O-Al <sup>IV b</sup>	-3/4	Strong
Al <sup>VI</sup> -□	+1/2	Moderate	Al <sup>VI</sup> -O-Al <sup>VI a</sup>	-1	Strong
Al <sup>IV</sup> -□ <sup>b</sup>	+3/4	Strong			

<sup>a</sup> More abundant for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

<sup>b</sup> More abundant for  $\eta$ -Al<sub>2</sub>O<sub>3</sub>

Table S2 Acidity and basicity of supports and Pd supported catalysts.

Samples	Acidity ( $\mu\text{mol NH}_3/\text{g}$ )			Basicity ( $\mu\text{mol CO}_2/\text{g}$ )		
	Total	Weak	Strong	Total	Weak	Medium
$\gamma\text{-Al}_2\text{O}_3$	200	89	111	471	268	203
Pd/ $\gamma\text{-Al}_2\text{O}_3$	187	81	106	344	215	129
$\eta\text{-Al}_2\text{O}_3$	247	96	151	357	228	129
Pd/ $\eta\text{-Al}_2\text{O}_3$	172	80	92	309	204	105

Table S3 The proportions of OH groups in the XPS spectra of Al 2p and O 1s.

	Al 2p	O 1s
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	28.5%	34.5%
Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	17.5%	27.3%
$\eta$ -Al <sub>2</sub> O <sub>3</sub>	25.1%	27.5%
Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	19.3%	23.8%

## References

- 1 H. Knözinger and P. Ratnasamy, *Catal. Rev. Sci. Eng.*, 1978, **17**, 31–70.
- 2 P.O. Scokart and P.G. Rouxhet, *J. Colloid Interface Sci.*, 1982, **86**, 96–104.
- 3 H. Knozinger, *Studies in Surface Science and Catalysis*, 1985, **20**, 111–125.