

## Supporting Information

### Catalytic selective hydrogenation of acetic acid to acetaldehyde over the surface of the iron shell on Pd-Fe alloy nanoparticles

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Table S1 Results obtained by hydrogenation of acetic acid under various reaction conditions on 28wt% Pd/Fe<sub>2</sub>O<sub>3</sub>.

React. Pres. (MPa.)	React. Temp. (K)	Contact Time (sec)	H <sub>2</sub> /AC Feed mol ratio	Time on Stream (h)	AD Yield (%)	AC Conv. (%)	AD Sel. (%)	EtOH Sel. (%)	AT Sel. (%)	CO <sub>2</sub> Sel. (%)	CO+HC Sel. (%)
0.1	588	0.25	5	10	25.8	36.3	71	3.3	14.9	8.8	1.4
0.1	588	0.25	5	125	24.3	30	80.9	6.1	7	4	1.5
0.5	588	0.25	5	150	34.0	55	61.8	21.9	5.9	3.4	4.1
0.5	588	0.25	7	25	35.5	65.6	54.1	29.7	5.5	1.9	1.6
0.5	588	0.25	7	200	35.6	60.4	58.9	27.4	4	1.5	2.2
0.5	588	0.125	7	75	35.0	51.4	68.1	23.3	2.9	1.2	1.6
0.5	603	0.25	7	50	32.8	73.4	44.7	33.7	6.8	2.6	2.9

Table S2 Conversion, yield, and selectivity in hydrogenation of acetic acid (reaction time 24 h).

Catalyst	AC Conv.(%)	AD Yield(%)	Selectivity(%)								
			AD	EtOH	AT	AE	ACT	CH <sub>4</sub>	CO <sub>2</sub>	Others	
2wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	50.9	30.1	59.2	22.1	9.6	0.7	2.2	1.0	3.0	2.1	
28wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	65.6	35.5	54.1	29.7	5.5	1.3	5.0	0.7	1.9	1.9	
44wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	72.9	33.8	46.3	32.0	7.7	2.4	5.9	0.8	2.9	2.1	
54wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	58.9	38.2	64.9	24.3	5.4	1.2	0.9	0.2	2.0	1.2	

AC, acetic acid; AD, acetaldehyde; EtOH, ethanol; AT, acetone; AE, ethyl acetate; ACT, diethyl acetal formed from acetaldehyde and ethanol.

Table S3 Conversion, yield, and selectivity in hydrogenation of acetic acid (reaction time 200 h).

Catalyst	AC Conv.(%)	AD Yield(%)	Selectivity(%)								
			AD	EtOH	AT	AE	ACT	CH <sub>4</sub>	CO <sub>2</sub>	Others	
2wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	28.0	18.9	67.5	20.9	2.5	1.9	1.3	1.8	0.8	3.4	
28wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	60.4	35.5	58.8	27.4	4.0	1.1	4.5	0.9	1.5	1.8	
44wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	69.4	37.7	54.4	29.0	4.4	1.3	5.4	0.8	2.8	2.0	
54wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	61.9	29.8	48.1	40.3	3.1	2.0	2.9	0.5	1.1	2.0	

AC, acetic acid; AD, acetaldehyde; EtOH, ethanol; AT, acetone; AE, ethyl acetate; ACT, diethyl acetal formed from acetaldehyde and ethanol.

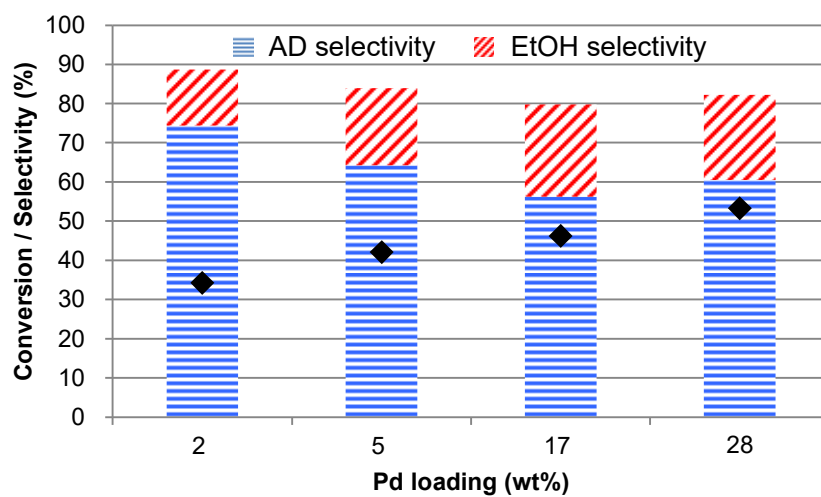


Figure S1 Conversion (◆) and selectivity in hydrogenation of acetic acid after 100 h. Reaction conditions: catalyst weight, 1.0 g; AC flow rate, 0.107 ml min<sup>-1</sup>; H<sub>2</sub> flow rate, 12.57 L h<sup>-1</sup>; contact time, 0.25 sec; reaction temperature, 588 K ; reaction pressure, 0.5 MPa. AC, acetic acid ; AD, acetaldehyde ; EtOH, ethanol.

Table S4 Elemental analysis (C/H/N) results of used catalysts after the reactions for 200 h.

Catalyst	C / Fe <sub>2</sub> O <sub>3</sub> (wt.%)
2wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	9.5
28wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	4.0
44wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	1.8

Table S5 CO pulse adsorption results of the catalysts and BET surface area.

Catalyst	Amount adsorbed (cm <sup>3</sup> g <sup>-1</sup> )	metal dispersion (%)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
2wt%Pt/Al <sub>2</sub> O <sub>3</sub>	0.766	33.32	-
28wt%Pd/Fe <sub>2</sub> O <sub>3</sub>	0.034	0.058	39

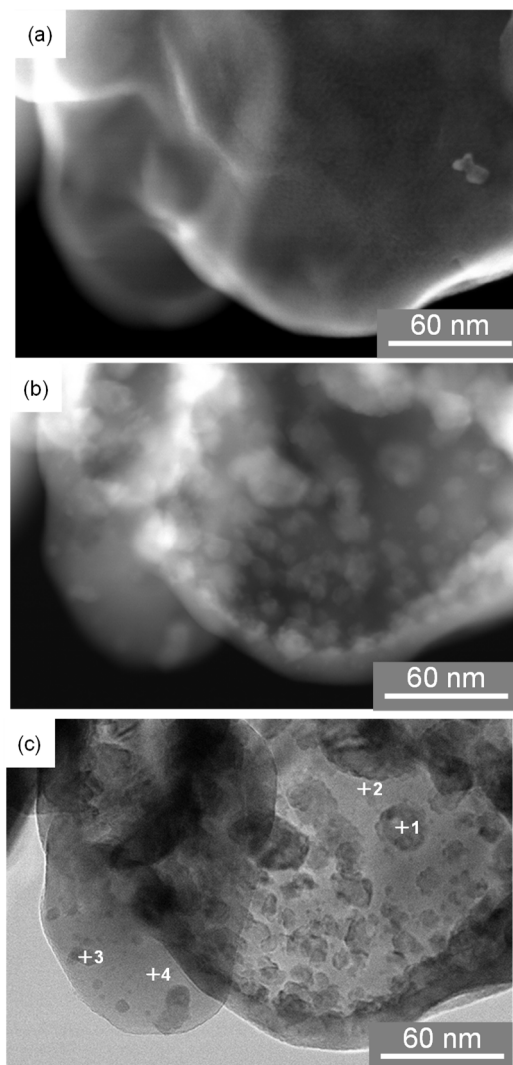


Figure S2 STEM images of as-synthesized 28wt% Pd/Fe<sub>2</sub>O<sub>3</sub>. (a) secondary electron image, (b) reflected electron image, (c) transmission electron image.

Table S6 STEM-EDX analysis results of as-synthesized 28wt%Pd/Fe<sub>2</sub>O<sub>3</sub>.

Point	O-K (wt%)	Fe-K (wt%)	Pd-K (wt%)
1	10.4	51.7	37.9
2	12.2	72.2	15.5
3	1.7	60.6	37.7
4	1.5	87.1	11.4

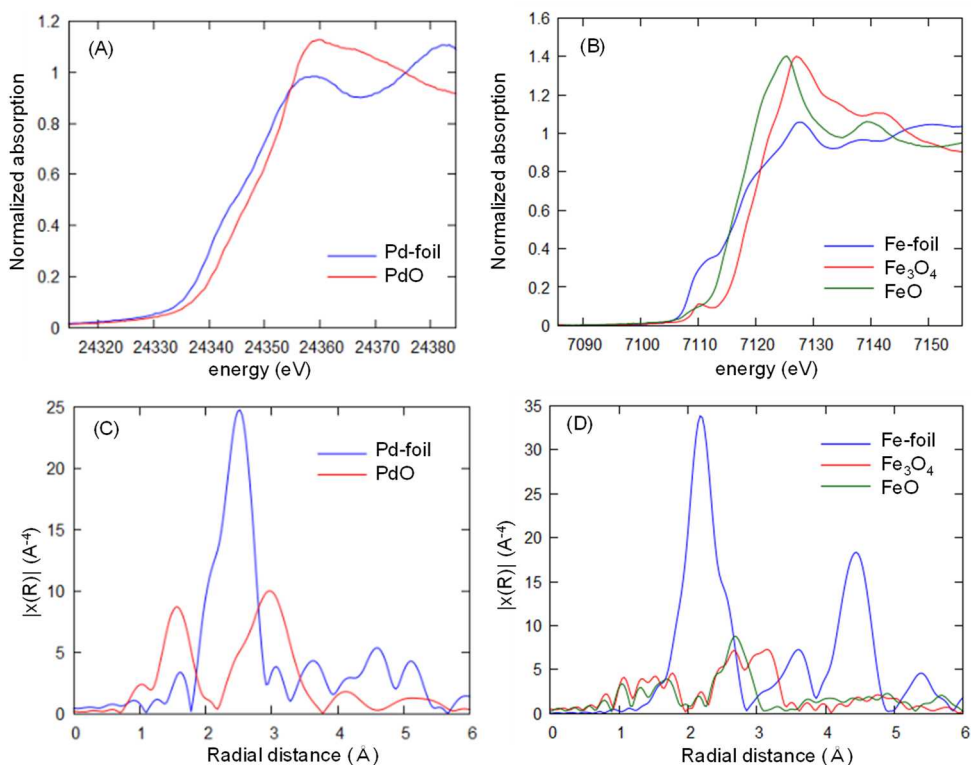


Figure S3 XANES spectra and Fourier transformations of EXAFS spectra for Pd K-edge (A and C) Fe K-edge (B and D) of standard samples. The  $k$  range of Fourier transformation for EXAFS spectrum was 3.0-12.0.

Table S7 Curve fitting analysis of the reduced 28 wt% Pd/Fe<sub>2</sub>O<sub>3</sub> catalyst.

	Ab-Sc	CN	R/Å	dE/eV	DW/Å <sup>-1</sup>
Pd/Fe <sub>2</sub> O <sub>3</sub> <sup>a)</sup>	Pd-Fe	2.7	2.60	1.56	0.008
	Pd-Pd	4.9	2.68	-4.15	0.016
Pd metal	Pd-Pd	12.0	2.74	0.01	0.006

a) The catalyst was reduced under H<sub>2</sub> flow at 573 K for 90 min. The curve fitting was performed using the spectra shown in Fig. 5(C-b).

Analysis conditions: Pd/Fe<sub>2</sub>O<sub>3</sub>  $\Delta k = 3.0-12.0$ ,  $\Delta R = 1.3-2.9$ ,  $S_0^2 = 1.0$ ; Pd metal  $\Delta k = 3.0-12.0$ ,  $\Delta R = 1.8-2.9$ ,  $S_0^2 = 0.83$ .

CN: coordination number, R: atomic distance, dE: edge shift, DW: Debye-Waller factor.