Supporting Information

A Pt/TiH_2 Catalyst for Ionic Hydrogenation via Stored Hydrides in the Presence of Gaseous H_2

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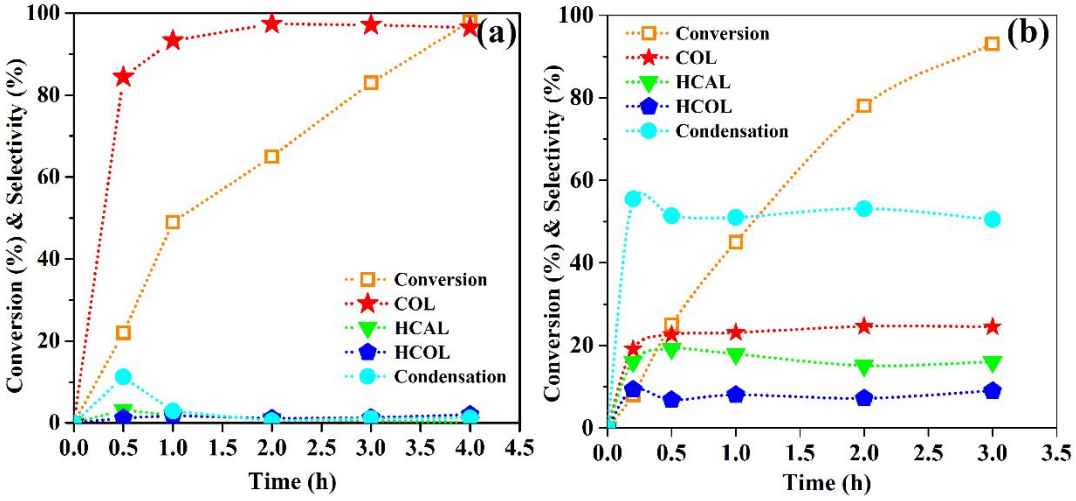

Figure S1. Time–Conversion/Selectivity profiles of hydrogenation of CAL over (1.0%Pt/TiH_2)-150H_2 (a) and (1.0%Pt/TiO_2)-150H_2 (b). Reaction conditions: 50 mg catalyst, 1 mmol CAL, 5 mL isopropanol, 100 ºC, 4 MPa H_2.

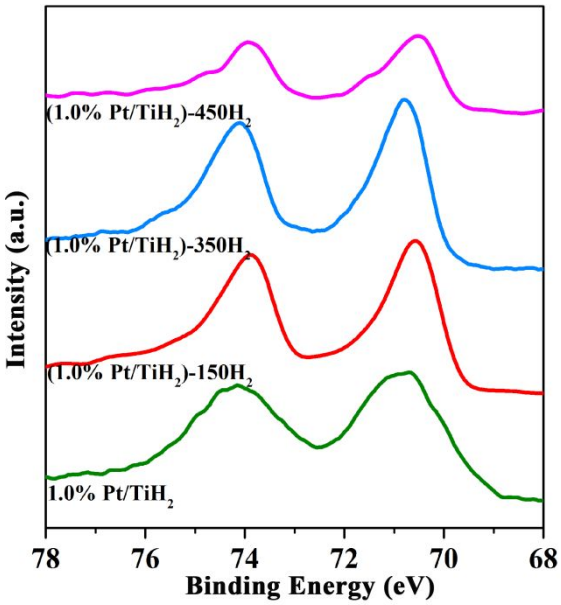

Figure S2. Pt 4f XPS profiles of 1.0%Pt/TiH_2 catalyst and 1.0%Pt/TiH_2 ones reduced at different temperatures. The Pt $4f_{7/2}$ binding energy is 70.9, 70.7, 70.8, and 70.6 eV for the 1.0%Pt/TiH_2 catalyst and 1.0%Pt/TiH_2 ones reduced at 100 ºC, 350 ºC, and 450 ºC, respectively.

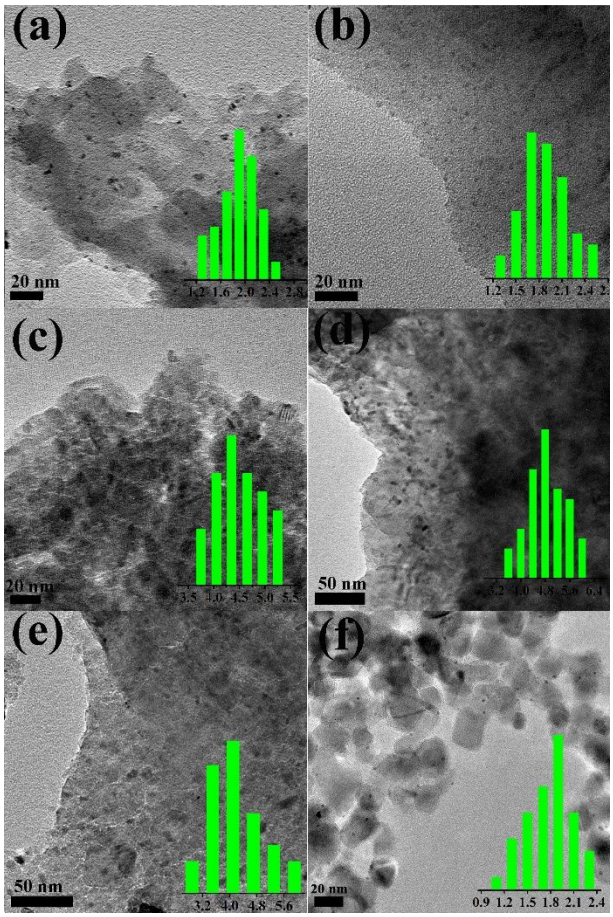

Figure S3. TEM images of (1.0%Pt/TiH_2) (a), (1.0%Pt/TiH_2)-150H_2 (b), (1.0%Pt/TiH_2)-350H_2 (c), (1.0%Pt/TiH_2)-450H_2 (d), (5.0%Pt/TiH_2)-150H_2 (e), and (1.0%Pt/TiO_2)-150H_2 (f)

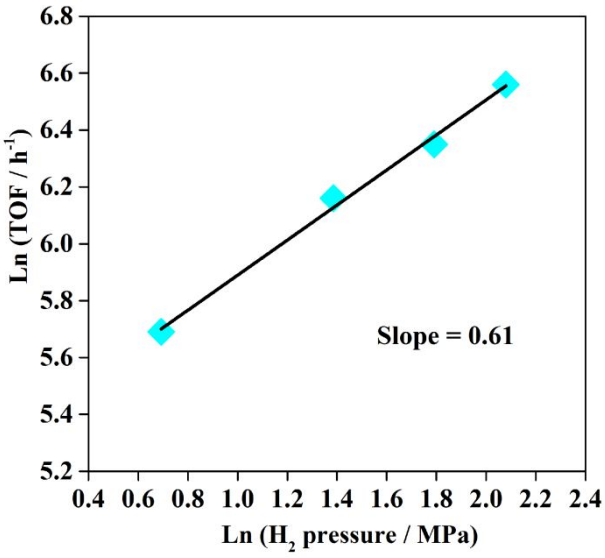

Figure S4. H_2 pressure dependence in hydrogenation of CAL over (Pt/TiO_2)-150H_2. Reaction conditions: 25 mg catalyst, 1 mmol CAL, 5 mL isopropanol, 100 ºC, 2, 4, 6, and 8 MPa H_2 pressure. The TOF was calculated at the conversion values of 6%, 8%, 8% and 9% at different H_2 pressures.

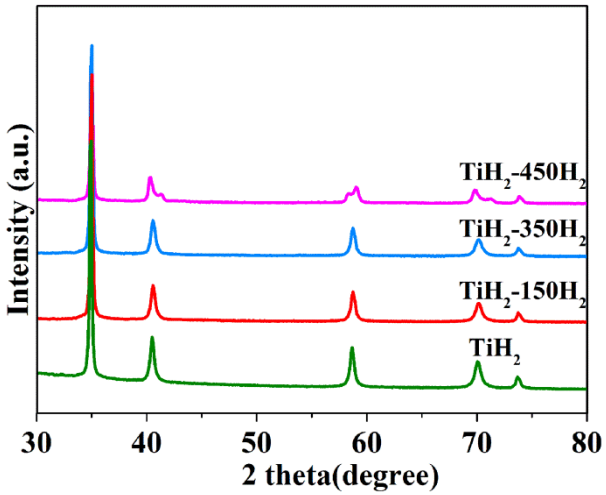

Figure S5. XRD profiles of TiH_2 reduced at different temperatures. The diffraction peaks at 2θ= 35.0, 40.6, 58.8, 70.2 and 73.8º are indexed to the (111), (200), (220), (311), and (222) planes of cubic $TiH_{1.92}$, respectively. (JCPDF: 25-0982).

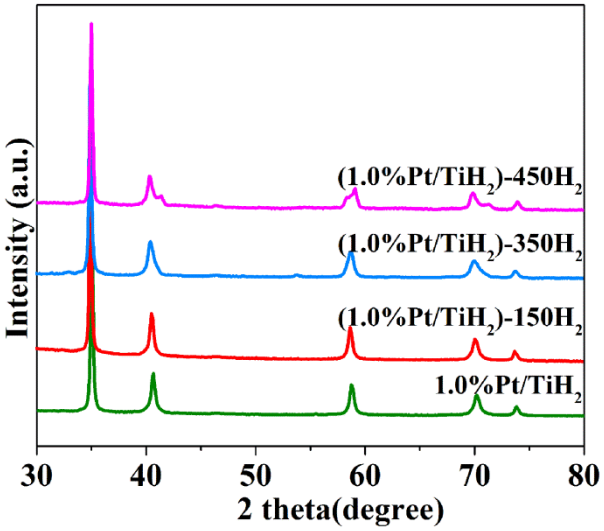

Figure S6. XRD profiles of TiH_2 reduced at different temperatures. The diffraction peaks at 2θ= 35.0, 40.6, 58.8, 70.2 and 73.8º are indexed to the (111), (200), (220), (311), and (222) planes of cubic $TiH_{1.92}$, respectively. (JCPDF: 25-0982).

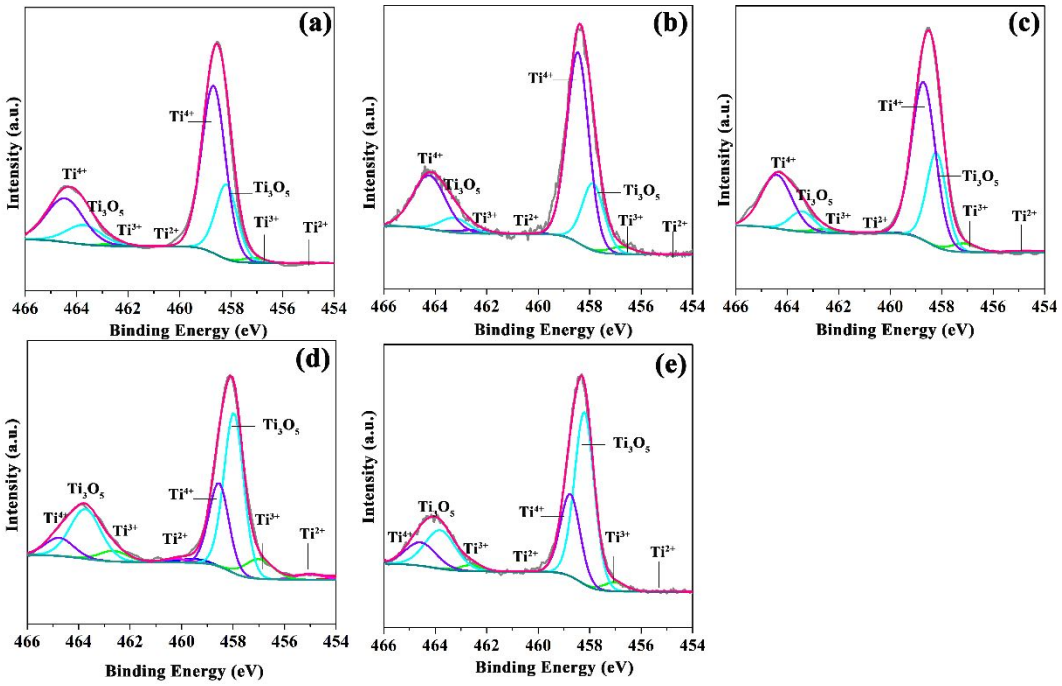

Figure S7. Ti 2p XPS of TiH_2 (a), 1.0%Pt/TiH_2 (b), and (1.0%Pt/TiH_2)-150H_2 before (c) and after sputtering by Ar in 3 nm (d), and (1.0%Pt/TiH_2)-450H_2 (e)

Table S1. Results of CAL Hydrogenation over Pt/TiH_2 catalysts with different Pt loadings.

Entry	Catalyst	Time(h)	Conversion (%)	Selectivity (%)			
				COL	HCAL	HCOL	Others [a]
1	$(0.1\%Pt/TiH_2)$-$150H_2$ [b]	3	84	92	1	4	3
2	$(1.0\%Pt/TiH_2)$-$150H_2$	3	83	97	1	1	1
3	$(5.0\%Pt/TiH_2)$-$150H_2$	6	75	95	1	2	2

Reaction conditions: 50 mg catalyst, 1 mmol CAL, 5 mL isopropanol, 100 ºC, 4 MPa H_2.

a. Condensation products from CAL and isopropanol.

b. 500 mg catalyst.

Table S2. Degree of metal dispersion and average diameter of metal particles for the various Pt/TiH_2 catalysts reduced by H_2 or D_2.

Entry	Catalyst	D_{Pt} (%) [a]	d_{Pt} (nm) [b]
1	$1.0\%Pt/TiH_2$	50	2.1
2	$(1.0\%Pt/TiH_2)$-$150H_2$	52	2.0
3	$(1.0\%Pt/TiH_2)$-$150D_2$	52	2.0
4	$(1.0\%Pt/TiH_2)$-$350H_2$	26	4.4
5	$(1.0\%Pt/TiH_2)$-$450H_2$	22	5.1
6	$(0.1\%Pt/TiH_2)$-$150H_2$	98	1.0
7	$(5.0\%Pt/TiH_2)$-$150H_2$	28	4.0
8	$(Pt/(TiH_2$-$150H_2))$-$150H_2$	53	2.1
9	$(Pt/(TiH_2$-$450H_2))$-$150H_2$	58	1.9
10	$(1\%Pt/TiO_2)$-$150H_2$	66	1.8
11	$(1\%Pt/TiO_2)$-$450H_2$	63	1.9

a. Degree of Pt dispersion determined by CO pulse adsorption.

b. Average diameter of the Pt particles determined by CO pulse adsorption.

Table S3. Results of CAL hydrogenation with 1%Pt/TiH_2 catalysts using H_2 and D_2 for CAL hydrogenation and catalyst reduction.

Entry	Catalyst	Conversion (%)	Time (h)	Reaction gas	TOF (h^{-1})[a]
1	(1.0%Pt/TiH_2)-150H_2	8	0.3	H_2	400
2		10	1	D_2	150
3	(1.0%Pt/TiH_2)-150D_2	8	0.25	H_2	480
4		7	0.25	D_2	420

Reaction conditions: 25 mg catalyst, 1 mmol CAL, 5 mL isopropanol, 100 ºC, 4 MPa H_2 or D_2.

TOF= moles of CAL reacted per moles of exposed Pt species (from CO chemisorption) per 1 h.

Table S4. Assignment of in situ DRIFT absorption bands observed in Figure 6.

Entry	Peak position(cm^{-1})	Vibration mode	Reference
1	1123-1250 cm^{-1}	H in-plane bending of phenyl	1
2	1320 cm^{-1}	bending mode of –CH=O	2
3	1618 cm^{-1}	stretching of C=C in –CH=CH–	2a
4	1449, 1492, 1600 cm^{-1}	C=C stretching of phenyl ring	3
5	1625 cm^{-1}	stretching of C=C in –CH=CH–	3a, 4
6	1673-1681 cm^{-1}	stretching vibration of -C=O	3a, 4

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