Supplementary Data

Insights into the selective hydrogenation of cinnamaldehyde on low–loading Pd based catalysts

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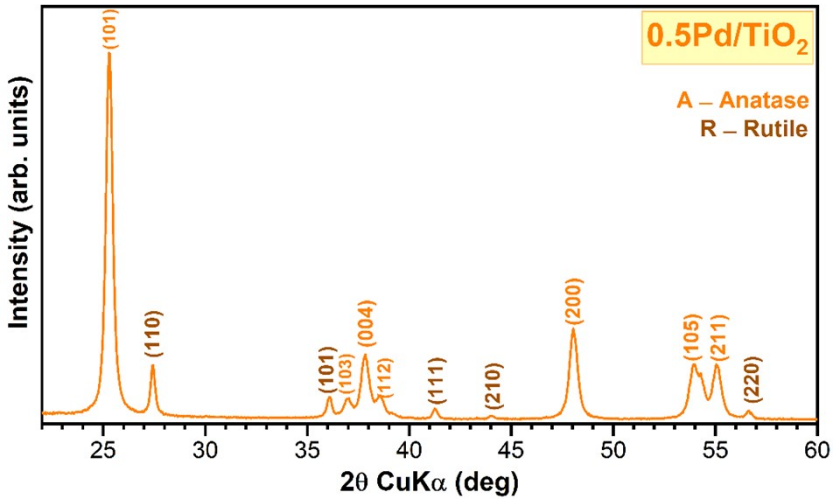


Figure S1. XRD pattern for 0.5Pd/TiO_2 based material.

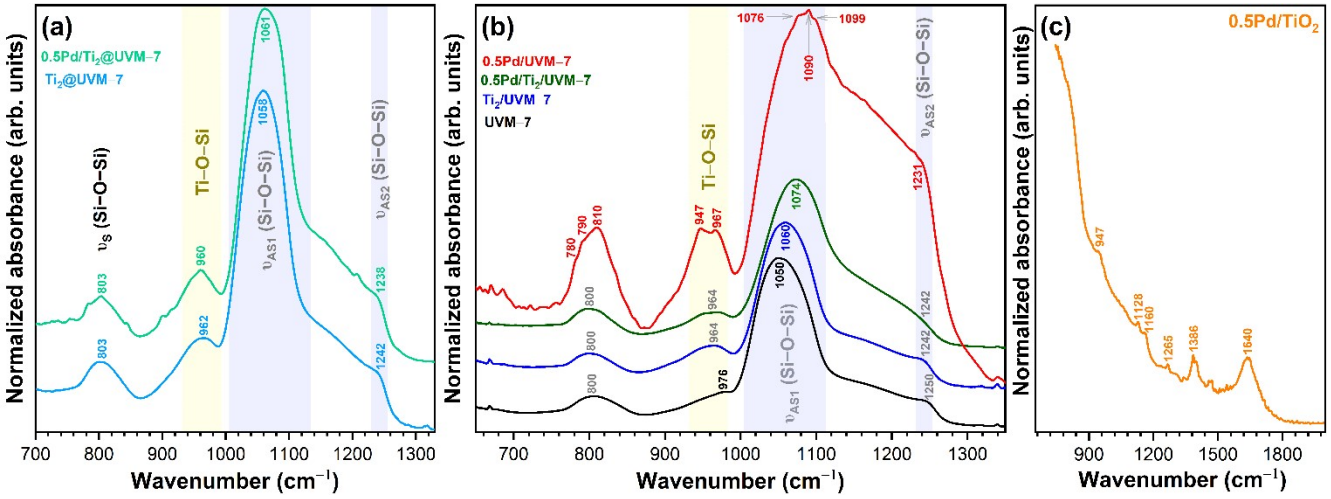


*Figure S2. ATR–FTIR spectra for the **a)** Ti_2@UVM–7, **b)** Ti_2/UVM–7 based materials and **c)** 0.5Pd/TiO_2 based material.*

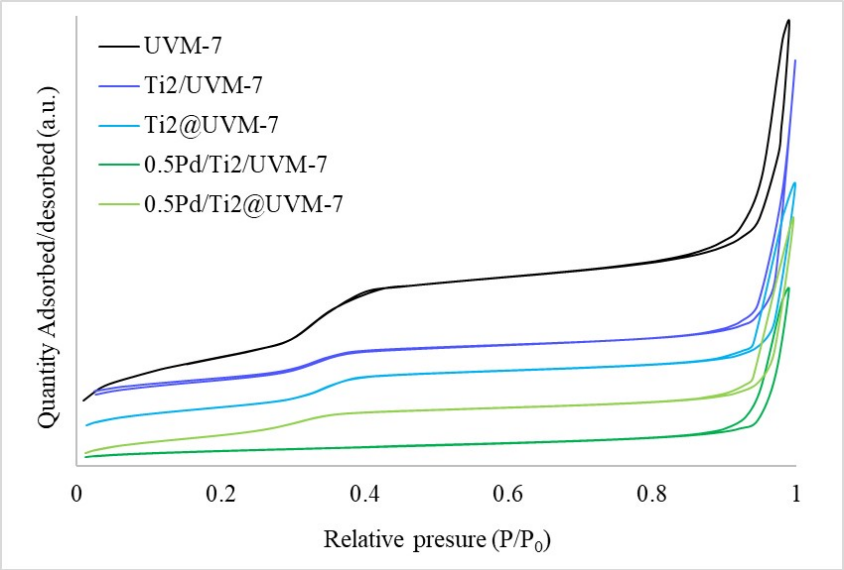


Figure S3. N_2 adsorption−desorption isotherms of the UVM−7 investigated catalysts.

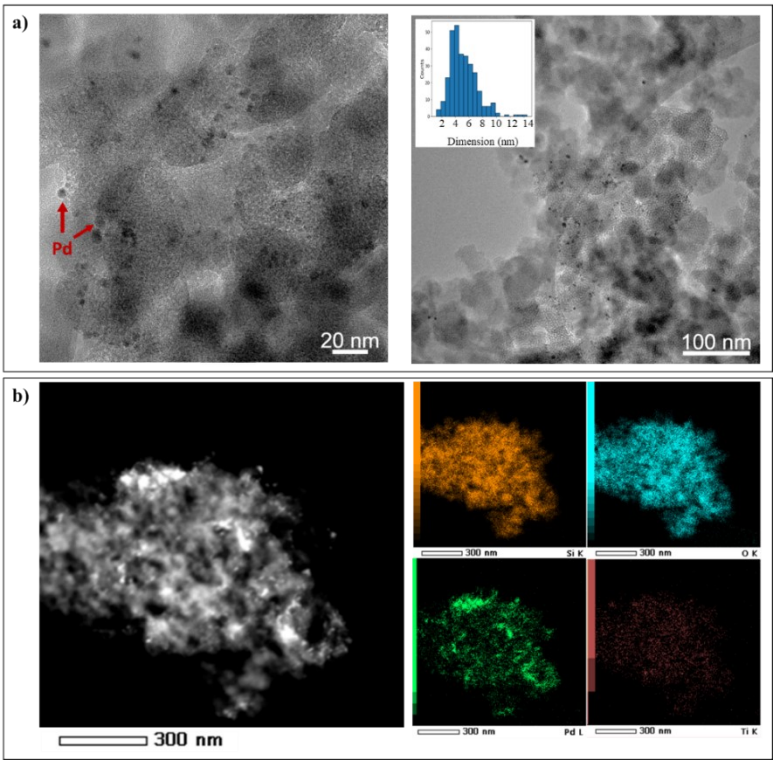


*Figure S4. **a)** TEM images taken at various magnifications of the sample 0.5 Pd/Ti_2@UVM−7 and the histogram showing the size distribution of the Pd nanoparticles and **b)** STEM dark field images and EDX mapping of the 0.5Pd/Ti_2@UVM−7 showing the elemental distribution of Si, O, Pd, Ti.*

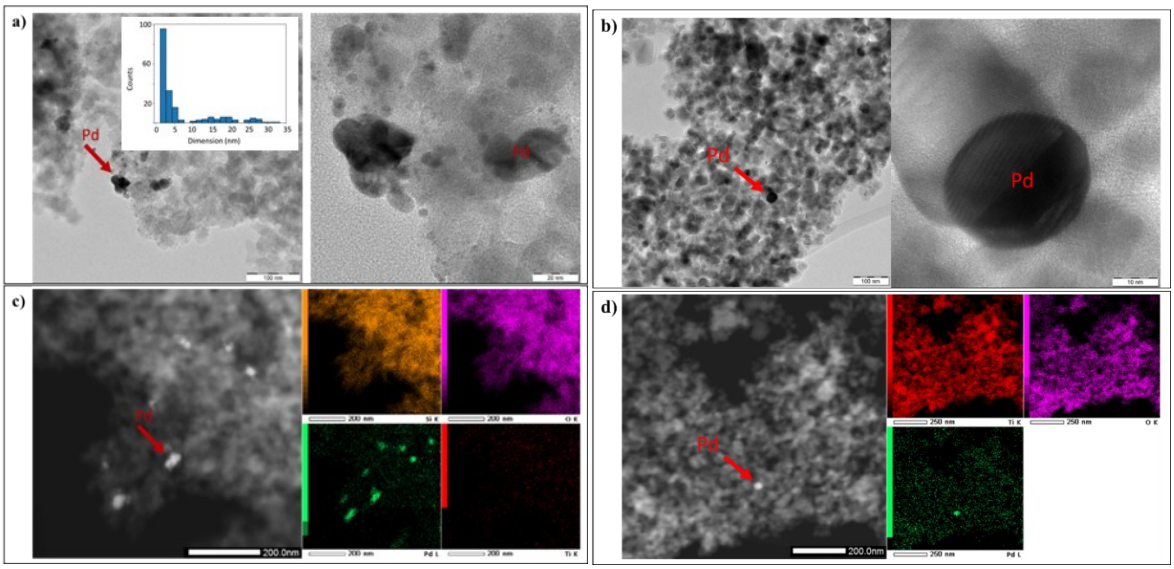


Figure S5. TEM images taken at various magnifications of the sample ***a)*** *0.5 Pd/UVM−7 and* ***b)*** *0.5Pd/TiO_2; STEM dark field images and EDX mapping of the sample* ***c)*** *0.5Pd/UVM−7 and* ***d)*** *0.5Pd/TiO_2 showing the elemental distribution of Si, O, Pd and Ti.*

Table S1. Pd crystallite size determined from XRD and TEM.

Entry	Material	Pd crystallite size * (nm)	Pd crystallite size # (nm)
1	0.5 Pd/Ti_2@UVM7	8	1-14 (average 5.4)
2	0.5Pd/Ti_2/UVM7	u.d.l.	<2
3	0.5Pd/UVM-7	u.d.l.	1-33 (average 6.9)
4	0.5Pd/TiO_2	u.d.l.	u.d.l. (30 – rarely)

u.d.l.= under detection limit; *noble metal crystal size as calculated from XRD; #particle size values as measured from TEM images.

Table S2. ***EDX chemical composition determined from SEM analysis.***

Entry	Material	Chemical element (Atom %)				Si/Ti[a)]	Si/Ti[b)]
		O	Si	Ti	Pd		
1	Ti_2@UVM−7	73.9	25.5	0.6	-	70	42.0
2	0.5Pd/Ti_2@UVM−7	74.6	24.5	0.7	0.2	70	35.0
3	UVM−7	73.7	26.3	-	-	-	-
4	Ti_2/UVM−7	73.9	25.7	0.4	-	67	64.0
5	0.5Pd/Ti_2/UVM−7	71.7	27.6	0.5	0.2	67	55.2
6	0.5Pd/UVM−7	56.0	43.5	-	0.5	-	-
7	0.5Pd/TiO_2	29.0	70.3	-	0.7	-	-

[a)] Si/Ti atomic ratio in the mother liquor (as added into the preparation step);

[b)] Si/Ti atomic ratio obtained from EDX measurements.

Table S3. Surface elemental composition as determined from XPS.

Entry	Material	Chemical element (Atom %)			
		O	Si	Ti	Pd
1	Ti_2@UVM−7	71.90	27.90	0.20	-
2	0.5Pd/Ti_2@UVM−7	70.93	28.72	0.31	0.04
3	Ti_2/UVM−7	71.40	28.30	0.30	-
4	0.5Pd/Ti_2/UVM7	70.05	29.70	0.17	0.08

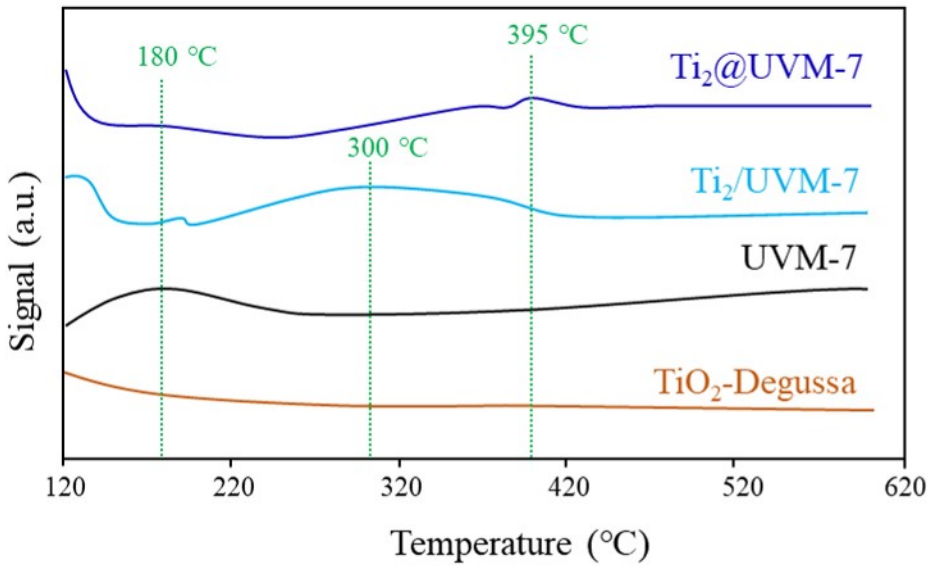


Figure S6. NH_3−Temperature programmed desorption measured for the investigated supports.

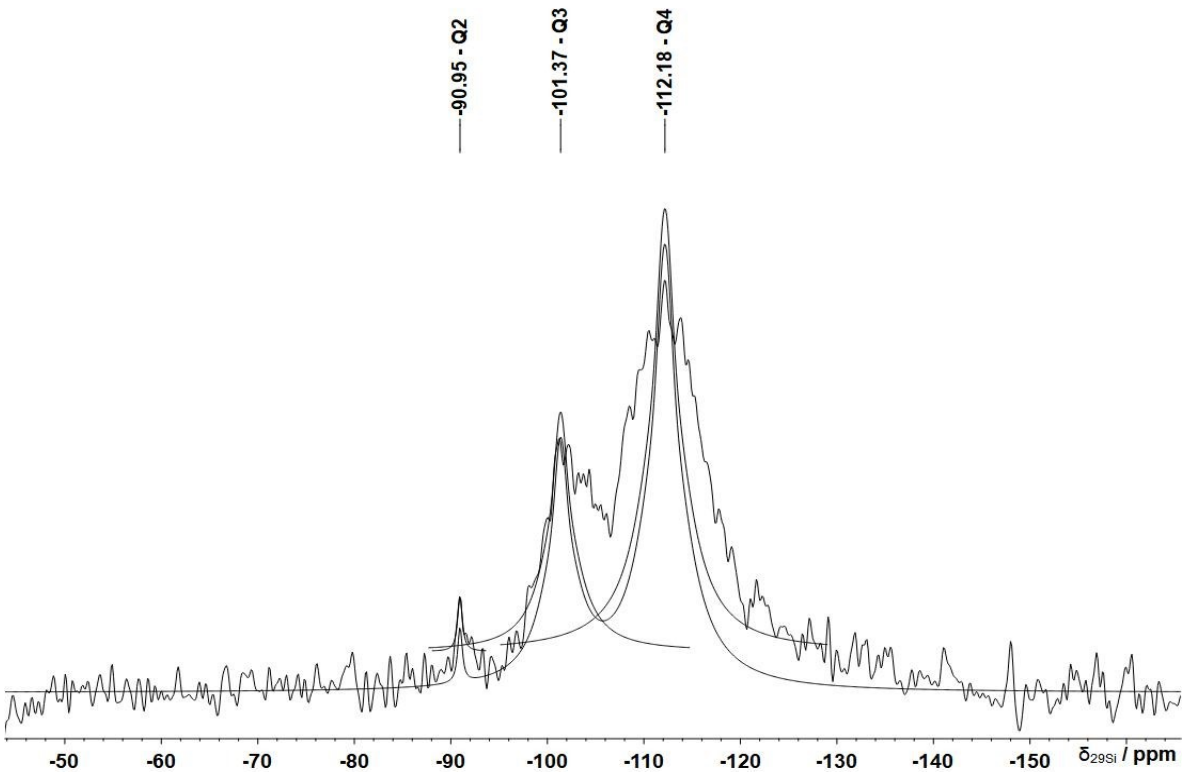


Figure S7. ^{29}Si MAS NMR spectra of UVM-7

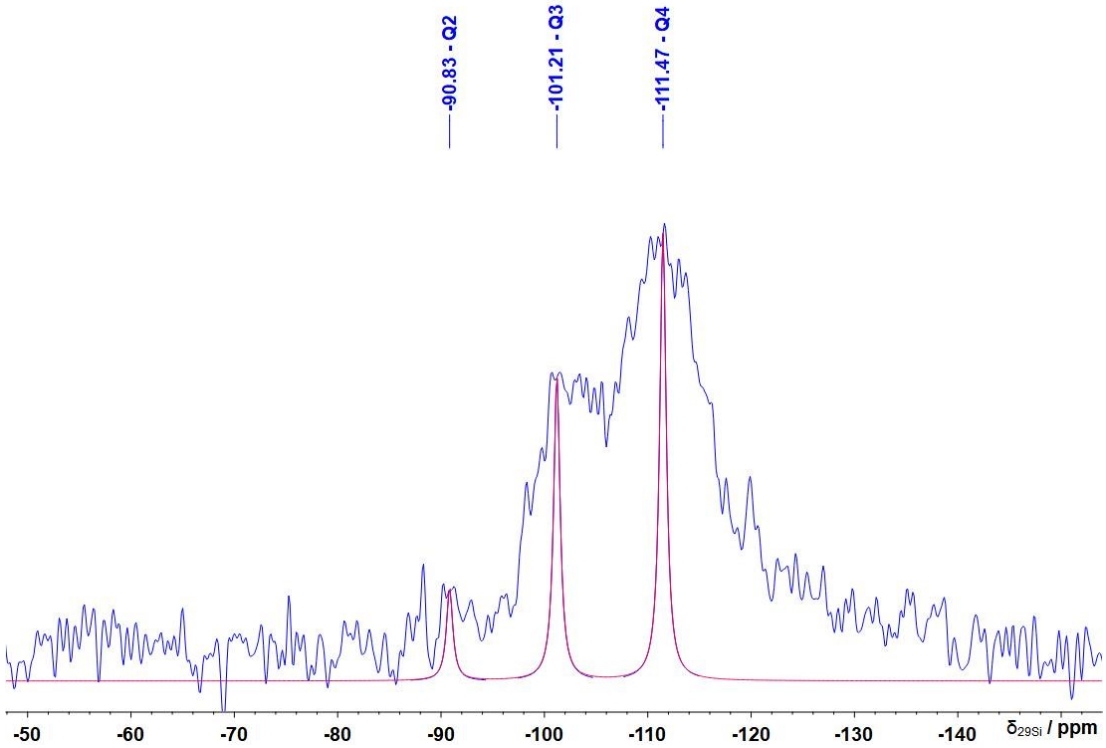


Figure S8. ^{29}Si MAS NMR spectra of Ti_2/UVM-7

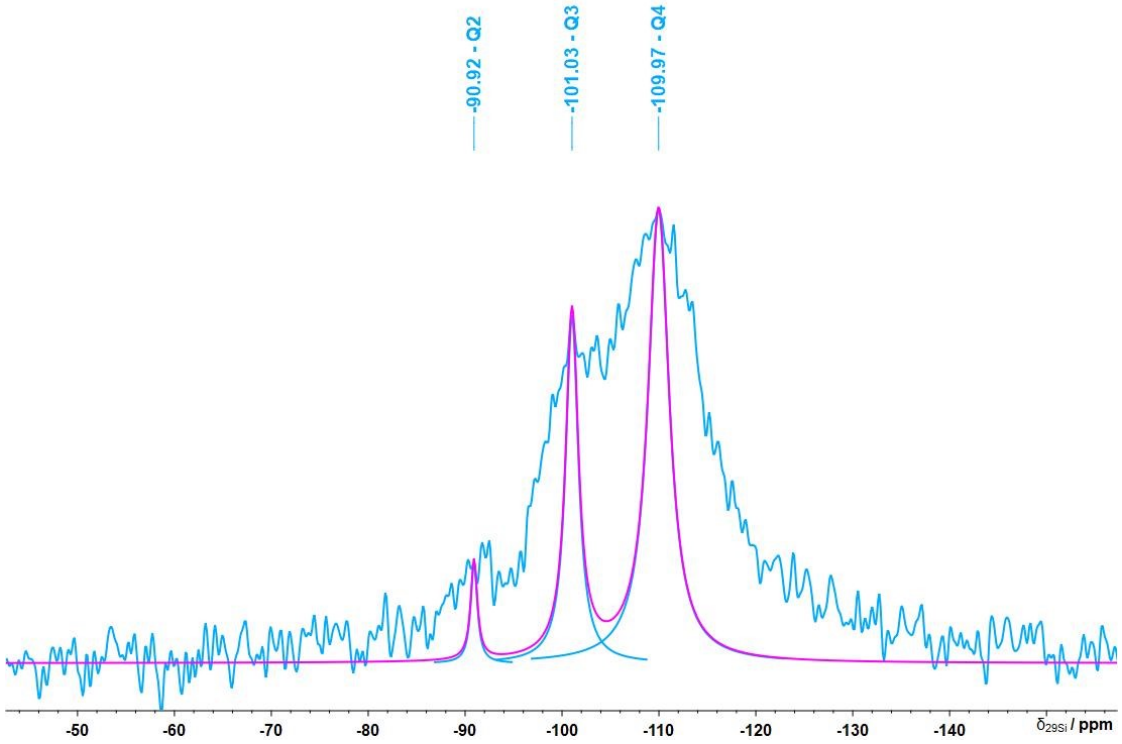


Figure S9. ^{29}Si MAS NMR spectra of Ti_2@UVM-7

Table S4. Comparative Q4 chemical shifts

Sample	Q^4 Chemical shift (δ, ppm)	Observed Δδ (vs UVM-7)
UVM-7	-112.18	-
Ti2 /UVM-7	-111.47	+ 0.71
Ti2@UVM-7	-109.97	+ 2.21

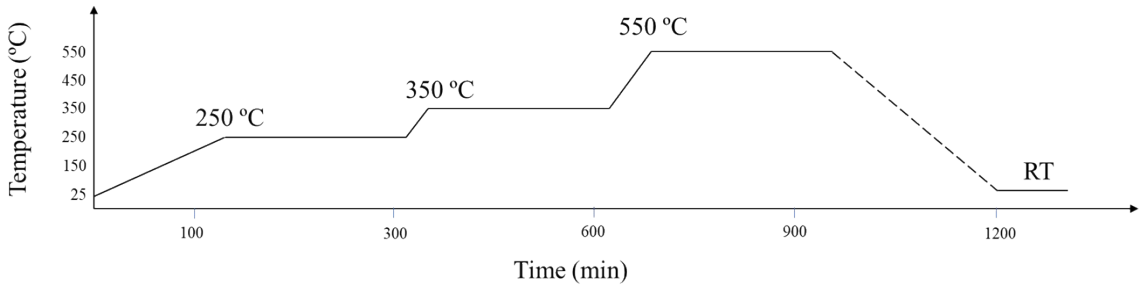
Table S5. Blank and support reaction tests.

Entry	**Catalyst**	**Reaction time (h)**	**Conv. (%)**	**Selectivity (%)**			
			CAL	HCAL	HCOL	HCDA	CDA
1	–	24	**14**	0	0	0	**100**
2	UVM−7	24	**26**	0	0	0	**100**
3	Ti_2@UVM−7	24	**31**	0	0	0	**100**
4	Ti_2/UVM−7	24	**28**	0	0	0	**100**

Table S6. Reaction time influence on the performances of the investigated catalysts with 0.5%Pd.

Entry	Catalyst	Reaction time (h)	Conv. (%)	Selectivity (%)				
			CAL	HCAL	HCOL	HCDA	CDA	COL
1	**0.5Pd/Ti_2@UVM−7**	1	**37**	74	0	0	26	-
2		2	**100**	75	0	25	0	-
3		4	**100**	50	0	50	0	-
4		6	**100**	70	0	30	0	-
5		8	**100**	68	2	30	0	-
7		12	**100**	54	4	42	0	-
8		24	**100**	49	6	45	0	-
9	**0.5Pd/Ti_2/UVM−7**	0.16	**100**	98.8	0	1.2	0	-
10		0.5	**100**	98.7	0	1.3	0	-
11		1	**100**	98.1	0	1.9	0	-
12		2	**100**	96	0	4	0	-
13		4	**100**	94	0	6	0	-
14		8	**100**	90	0	10	0	-
15		24	**100**	73	3	24	0	-
16	**0.5Pd/TiO_2**	0.16	**22**	85	1	3	11	0
17		0.5	**75**	89	1	8	2	0
18		1	**94**	83	2	14	1	0
19		2	**97**	79	2.4	18	0.6	0
20		4	**100**	67	4	29	0	3
21		24	**100**	24	42	31	0	3
22	**0.5Pd/UVM−7**	0.16	**93**	98	<1	1	0	0
23		0.5	**97**	94	<1	2	0	3
24		1	**100**	92.5	<1	2.5	0	4
25		2	**100**	92	<1	3	0	4
26		4	**100**	87	1	8	0	4
27		24	**100**	60	20	16	0	4

Reaction conditions: 0.1 mmoles of CAL, 10 mg of catalyst, 5 mL of ethanol, 140 °C, 25 atm H_2 pressure.



Scheme S1. Calcination heating ramp used for Ti_2@UVM−7 and UVM-7.