Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Novel catalytic route for hydrogenation-dehydrogenation of $2LiH+MgB_2$ *via in-situ* formed core-shell Li_xTiO_2 nanoparticles†

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Electronic Supplementary information

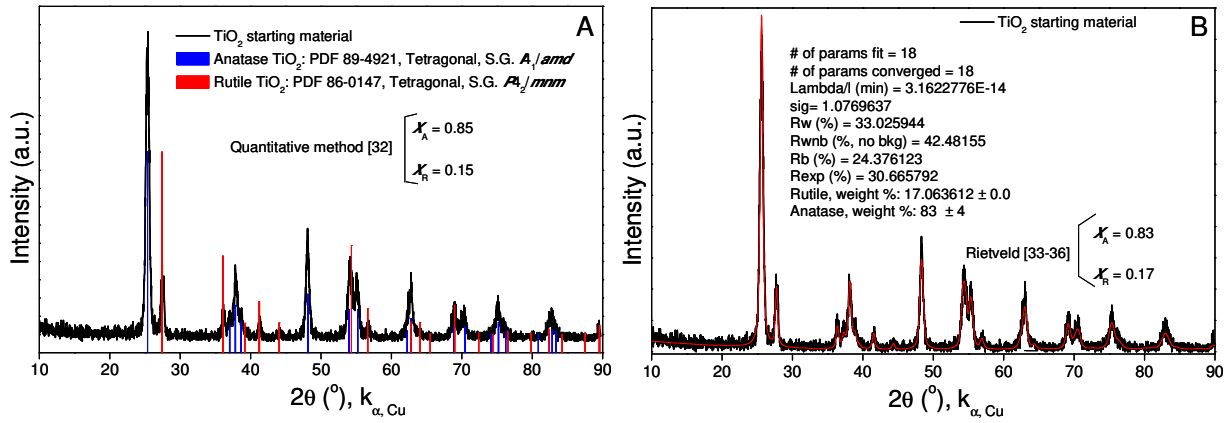


Fig.S1 PXD for as-purchased TiO_2 and weight fractions of anatase and rutile calculated by: **A** quantitative method [32] and **B** Rietveld method.

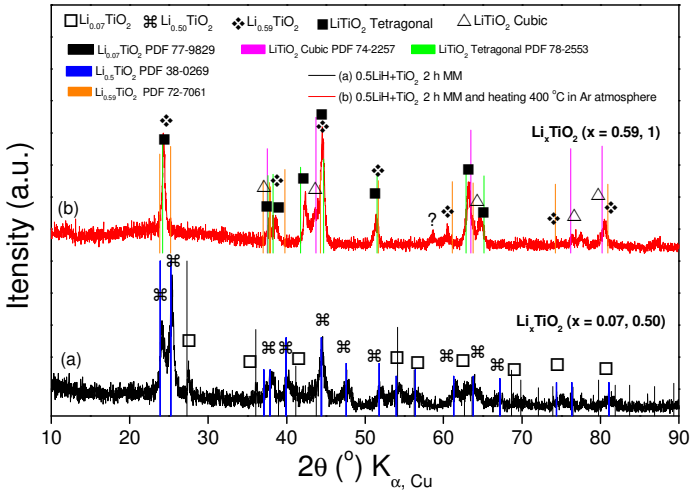


Fig.S2 PXD for $0.5LiH+TiO_2$ (a) after MM and (b) after MM+heating up to 400 °C in Ar atmosphere.

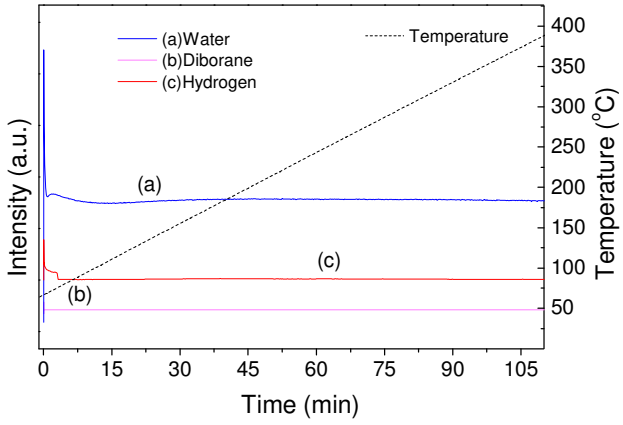


Fig.S3 MS for the 2LM material from about 30 °C to 400 °C.

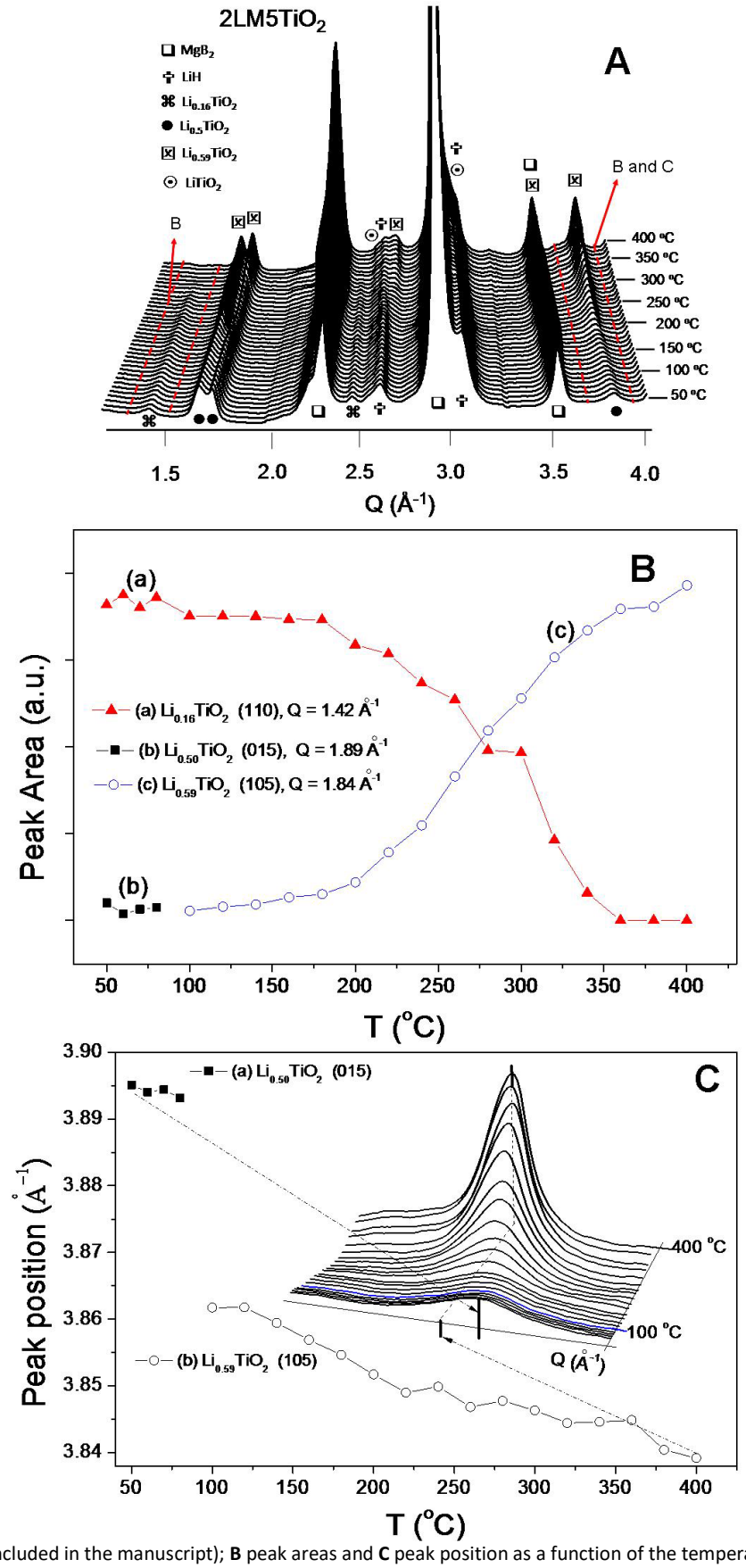


Fig.S4 A *In-situ* SR-PXD (included in the manuscript); **B** peak areas and **C** peak position as a function of the temperature from 50 °C to 400 °C.

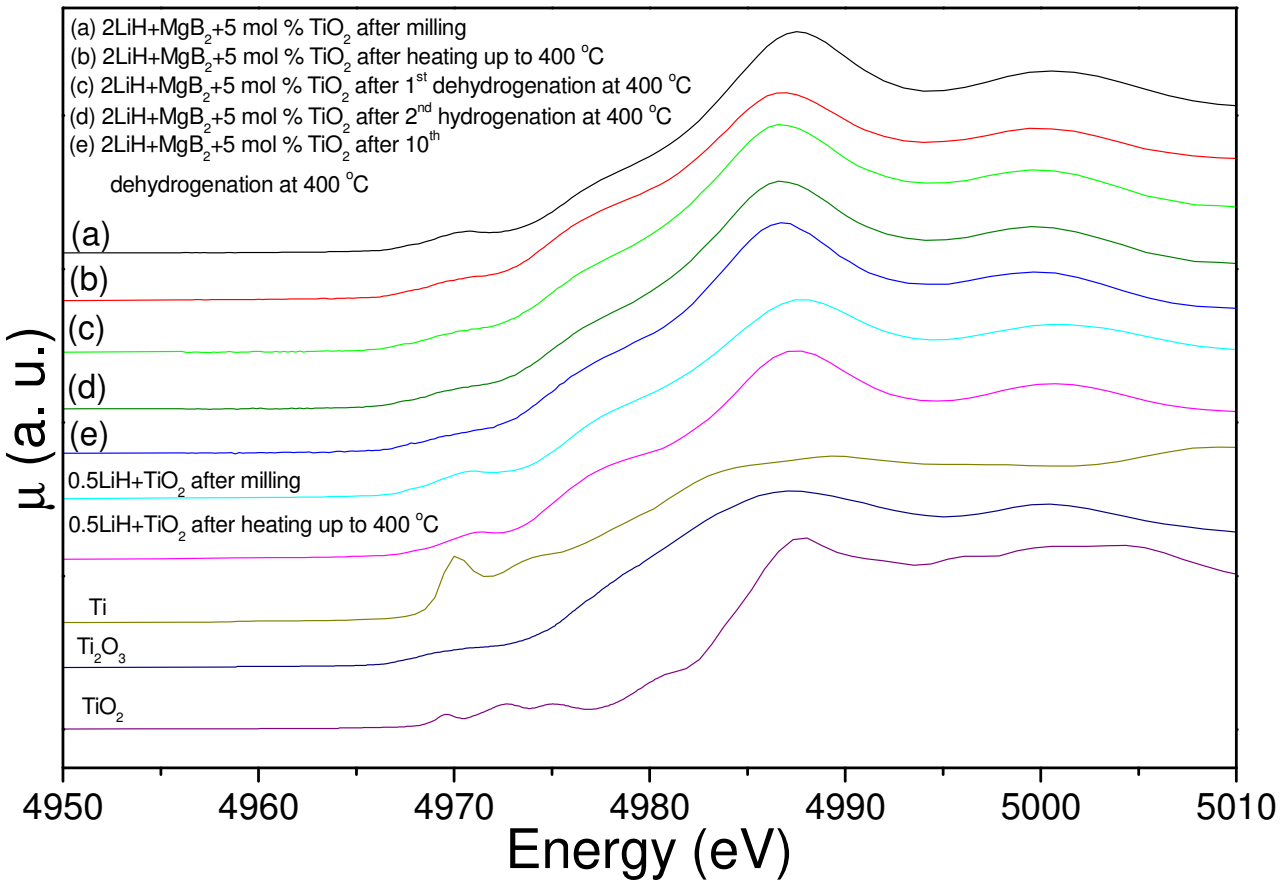


Fig.S5 XANES spectra at the Ti K edge. **Comment:** The references 0.5LiH+TiO_2 after milling and after heating are composed of mixtures of Li_xTiO_2 compounds with x = 0.07, 0.5 and x = 0.59 and 1, respectively (ESI: Fig. S2 PXD of the 0.5LiH+TiO_2 references). All the materials present Ti absorption edge positions similar to Ti_2O_3. However, the shape of the spectrum of Ti_2O_3 differs from those of the 2LM5TiO_2 material at different stages (Fig. S5 (a-e)). It can be noticed that the spectrum of the 2LM5TiO_2 after milling (Fig. S5 (a)) is alike to the one of the reference 0.5LiH+TiO_2 after milling. The spectra of the 2LM5TiO_2 after heating and hydrogen interaction (Fig. S5 (b – e)) are similar to the one of the reference 0.5LiH+TiO_2 after heating.

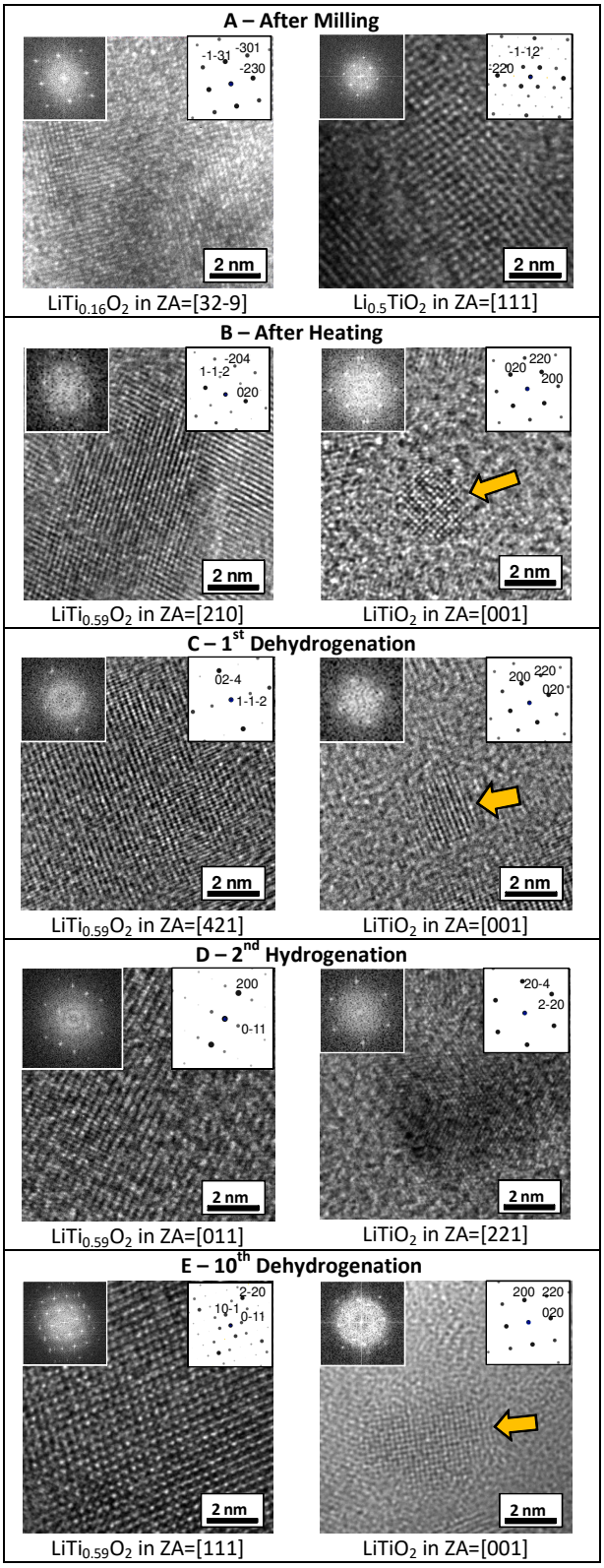


Fig.S6 HR–TEM, FFT and simulation for 2LM5TiO_2: **A** After milling, **B** After heating, **C** After first dehydrogenation, **D** After second hydrogenation and **E** After tenth dehydrogenation. $Li_{0.59}TiO_2$ belongs to the space group *Imma*. $LiTiO_2$ belongs either to the tetragonal crystalographic system, space group: $I4_1/amd$ or cubic system, space group $Fm\text{-}3m$. It is not possible to distinguish to which system the $LiTiO_2$ belongs to, since for [001] zone axis condition both structures are practically identical.

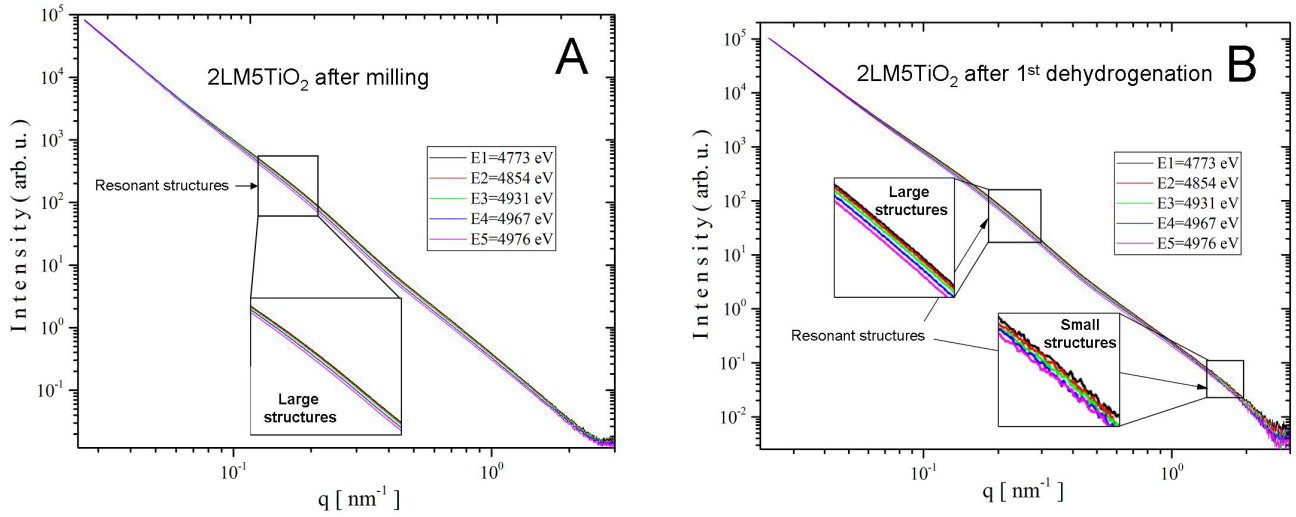


Fig.S7 Scattering curve sets of two ASAXS experiments below the Ti-K absorption edge: **A** after milling and **B** after first dehydrogenation. The energy dependence of the scattering curve shapes identify Ti enrichements or depletions with respect to their environment (resonant structures).

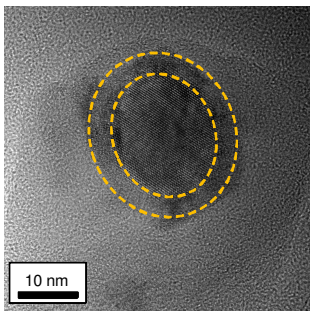
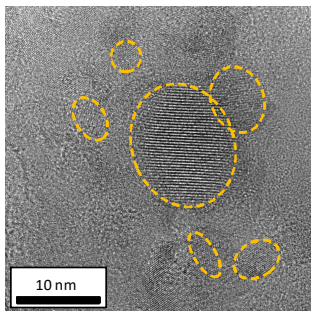
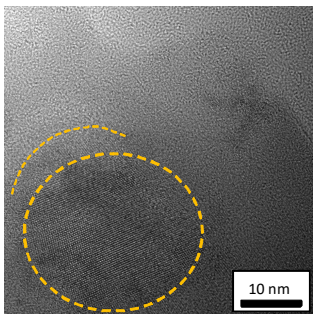
Core-shell Nanoparticles (Complete Image)					
B After Heating		C After 1st Des.		D After 10th Des.	

Fig.S8 HR-TEM for complete core-shell nanoparticles of the Li_xTiO_2 phases corresponding to Fig. 3 of the manuscript: **B** after heating, **C** 1st and **D** 10th dehydrogenation. General FFT was calculated in each case and compared to simulated ring diffraction patterns (DPs).

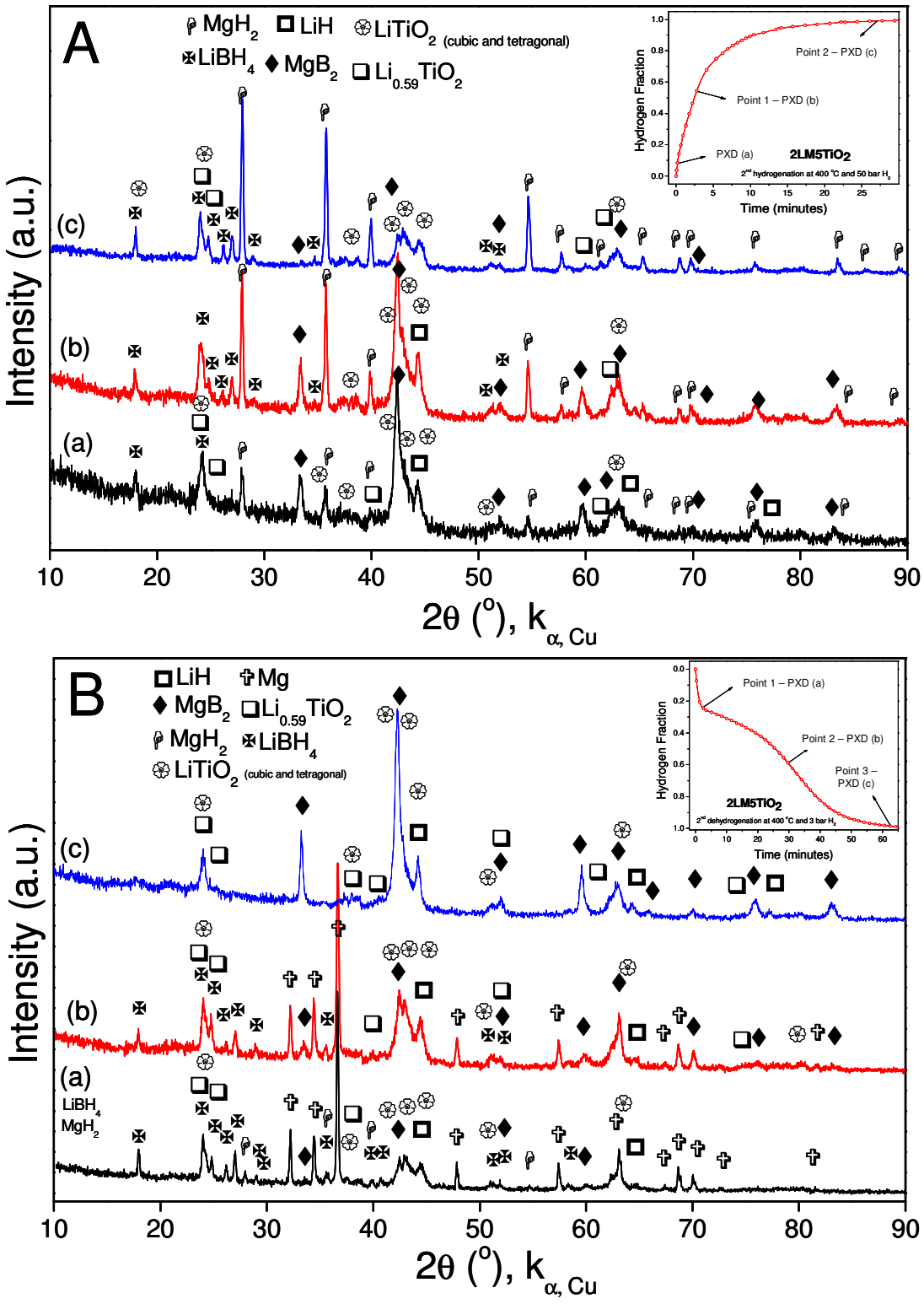


Fig.S9 PXD for $2LM5TiO_2$ during the **A** 2nd hydrogenation at 400 °C under 50 bar H_2 and **B** 2nd dehydrogenation at 400 °C under 3 bar H_2.

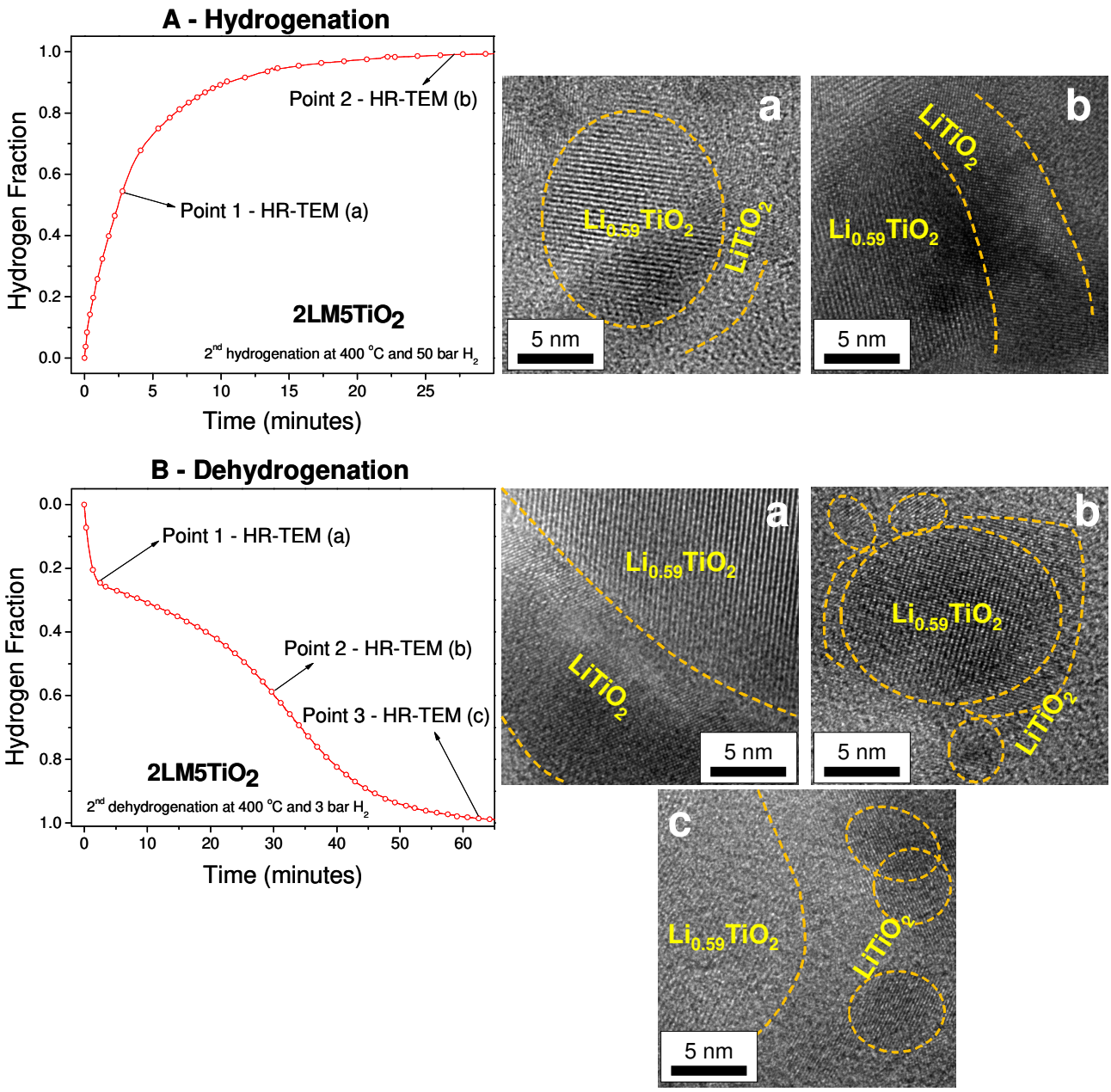


Fig.S10 Additional characterization of the nanosized $LixTiO_2$ phases in $2LM5TiO_2$ material during hydrogenation and dehydrogenation by means of HR-TEM (Fig. 4 of the manuscript).

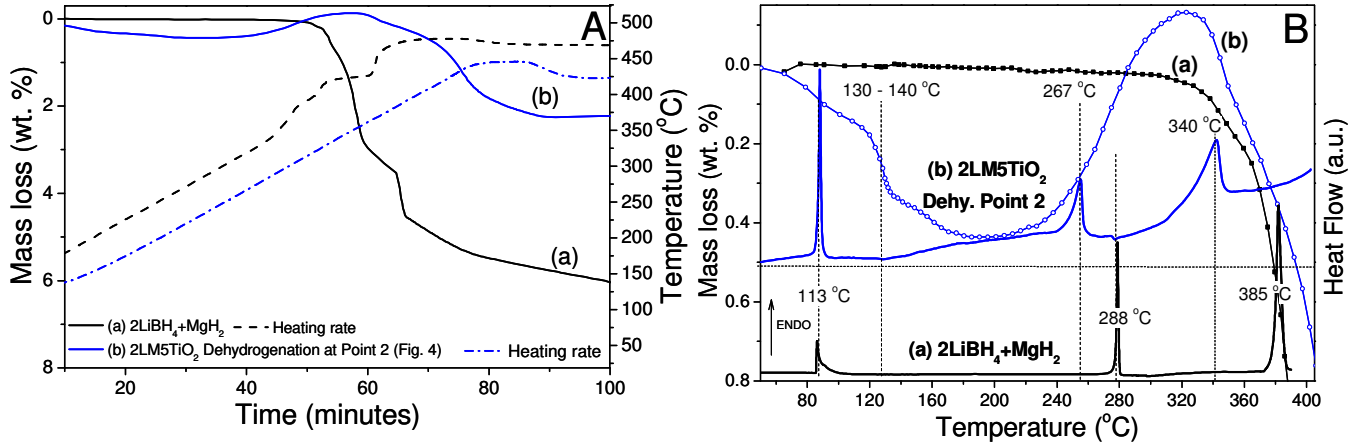


Fig.S11 A TG curves and **B** HP-DSC and TG measurements for (a) $2LiBH_4 + MgH_2$ milled for 2 h in P6 mill device, (b) $2LM5TiO_2$ during the second dehydrogenation at point 2: the sample is composed of free Mg, $LiBH_4$ and the Li_xTiO_2 additive (Fig. 4 of the manuscript). **Comment:** The TG curve (b) presents a mass gain owing to the re-hydrogenation of free Mg (see Fig.S9 PXD B(b)) since the dehydrogenation was performed at 3 bar of hydrogen overpressure and at 250 °C the equilibrium pressure for hydrogenation is about 1 bar. Then as the temperature increases, the formed MgH_2 decomposes.

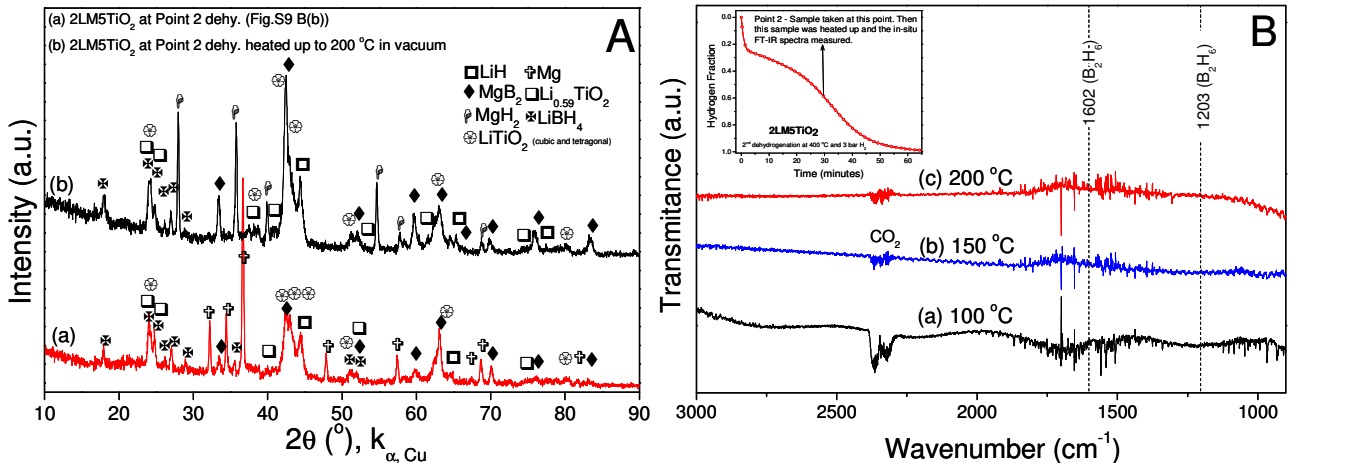


Fig.S12 A PXD of the $2LM5TiO_2$ (a) taken at the second point of the dehydrogenation process (Fig. 4 of the manuscript and Fig.S9 B PXD (b)) and (b) heated up to 200 °C in vacuum atmosphere. **B** FT-IR of gas phases coming from heating up the $2LM5TiO_2$ taken at the second point of the dehydrogenation process (Fig. 4 of the manuscript and Fig.S9 B PXD (b)) at: (a) 100 °C, (b) 150 °C, (c) 200 °C.

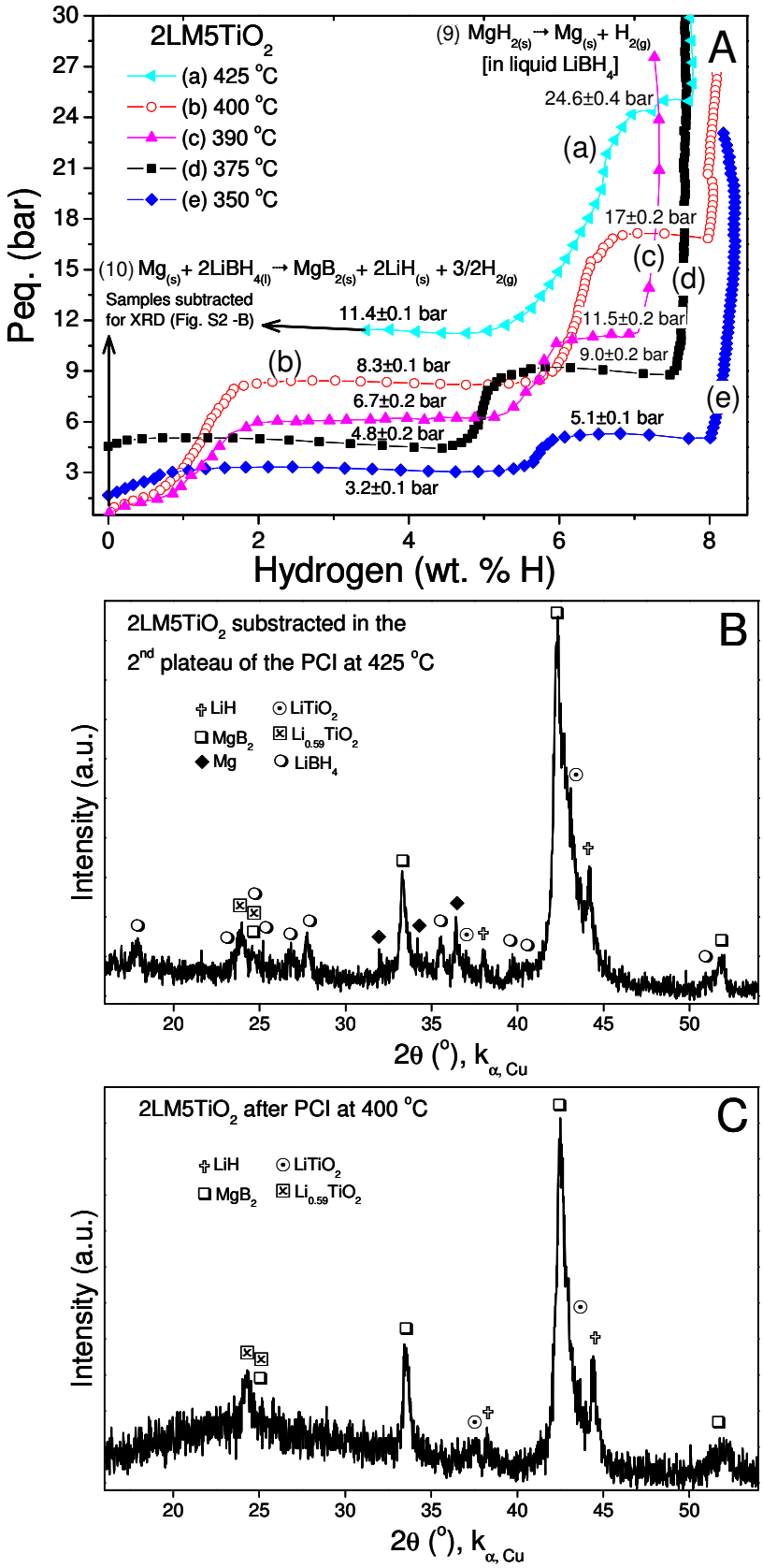


Fig.S13 A Dehydrogenation pressure composition isotherms (PCIs) for 2LM5TiO$_2$. **B** PXD of a sample subtracted during the second plateau of the PCI at 425 °C. **C** PXD of a sample subtracted after the PCI at 400 °C. The dehydrogenation PCIs measurements took between 45 to 57 hours.

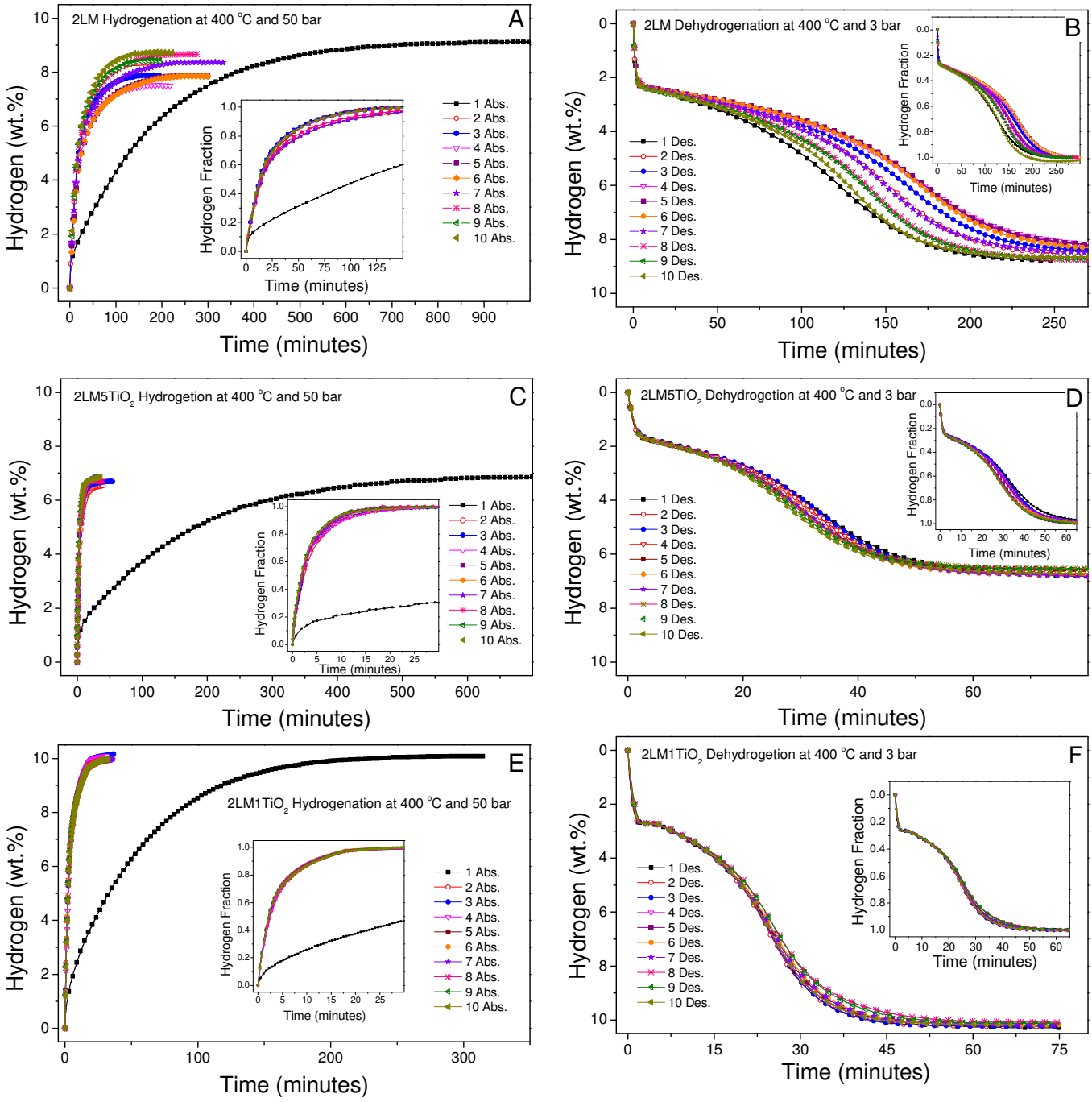


Fig. S14 Kinetic hydrogenation (50 bar) and dehydrogenation (3 bar) behavior at 400 °C for: **A** and **B** 2LM, **C** and **D** 2LM5TiO_2, **E** and **F** 2LM1TiO_2.

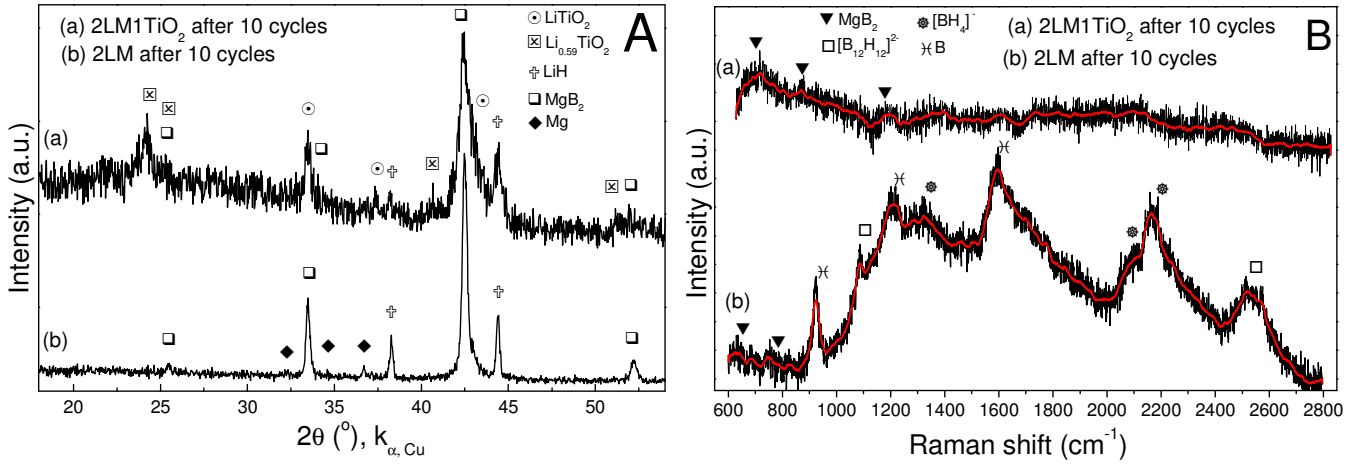
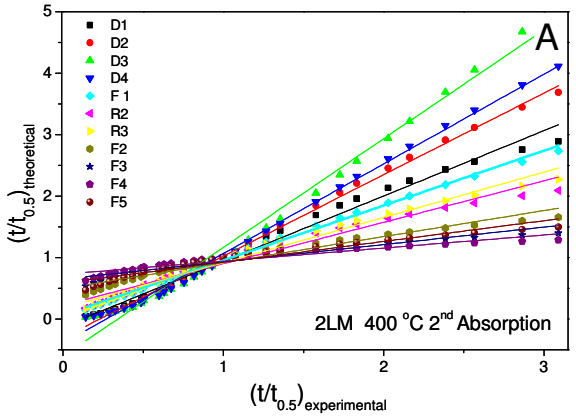
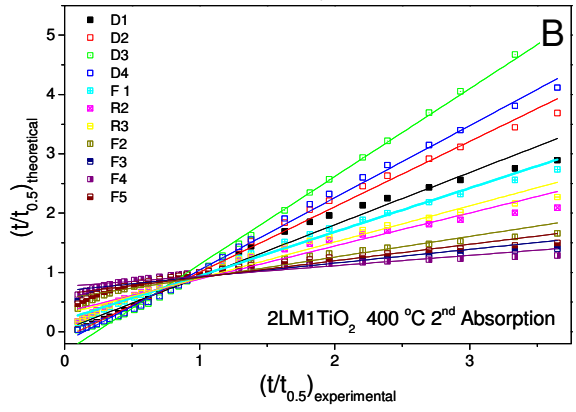


Fig. S15 A PXD and **B** Raman Spectroscopy of dehydrogenated (a) 2LM1TiO_2 and (b) 2LM after 10th absorption-desorption cycles.



Fraction from 0.10 to 0.85	Intercept Value	Intercept Error	Slope Value	Slope Error	Statistics Adj. R-Square
D1 one-dimensional diffusion	-0.12423	0.0305	1.06324	0.02	0.98815
D2 two-dimensional diffusion	-0.30413	0.02126	1.32689	0.02	0.99627
D3 Jander eq. for three dimensional diffusion	-0.60435	0.0542	1.77	0.04	0.98652
D4 Ginstling-Braunshtein eq. for three dimensional diffusion	-0.39393	0.0258	1.4594	0.02	0.99547
F 1 JMA - n = 1	0.06452	0.01185	0.89164	0.01	0.99743
R2 two-dimensional phase	0.22542	0.03004	0.67422	0.02	0.97187
R3 three-dimensional phase boundary	0.17796	0.0252	0.73739	0.02	0.98327
F2 JMA - n = 1/2	0.49416	0.02433	0.42358	0.02	0.95409
F3 JMA - n = 1/3	0.64694	0.02106	0.28264	0.01	0.925
F4 JMA - n = 2/5	0.72812	0.01778	0.21294	0.01	0.90753
F5 JMA - n = 2/5	0.58438	0.02286	0.33853	0.02	0.93757



Fraction from 0.10 to 0.85	Intercept Value	Intercept Error	Slope Value	Slope Error	Statistics Adj. R-Square
D1 one-dimensional diffusion	0.04099	0.03899	0.88147	0.03	0.97691
D2 two-dimensional diffusion	-0.10355	0.0253	1.10476	0.02	0.99371
D3 Jander equation for three dimensional diffusion	-0.34607	0.0309	1.48147	0.02	0.99478
D4 Ginstling-Braunshtein equation for three dimensional diffusion	-0.17595	0.02034	1.21729	0.01	0.99664
F 1 JMA - n = 1	0.20138	0.02138	0.74063	0.01	0.99004
R2 two-dimensional phase boundary	0.33282	0.03558	0.55675	0.02	0.95296
R3 three-dimensional phase boundary	0.29402	0.0319	0.6101	0.02	0.96802
F2 JMA - n = 1/2	0.56258	0.02728	0.34899	0.02	0.93115
F3 JMA - n = 1/3	0.69342	0.02259	0.23217	0.01	0.89713
F4 JMA - n = 2/5	0.76346	0.01875	0.17465	0.01	0.87734
F5 JMA - n = 2/5	0.63965	0.02491	0.27843	0.02	0.91164

Fig. S16 $(t/t0.5)_{experimental}$ vs. $(t/t0.5)_{theoretical}$ plots for **A** 2LM and **B** 2LM1TiO_2 at the 2nd hydrogenation. The method assumes that the most suitable reaction model provides a linear fitting with R^2 close to 1 and a straight line through the origin with a slope of about 1.

f = 1 - (exp(-k*t)^n)			n = 1				Fig. 7 A (a)	
Abs 2LM	k (1/s)	Error	R^2	k^-1 (s)	wt % H	Error	k x hydrogen capacty Abs. (wt. % H.s^-1)	Error
1	0.00607	1.00E-05	0.98584	164.7446458	9.1	0.6	5.524E-02	3.64E-03
2	0.0422	2.50E-04	0.98606	23.69668246	8.3	0.4	3.503E-01	1.69E-02
3	0.04765	3.40E-04	0.9785	20.98635887	7.9	0.4	3.764E-01	1.91E-02
4	0.04438	3.10E-04	0.97862	22.53267237	7.5	0.4	3.329E-01	1.78E-02
5	0.03502	2.80E-04	0.95954	28.55511136	7.8	0.4	2.732E-01	1.40E-02
6	0.03523	2.80E-04	0.95663	28.38489923	7.8	0.4	2.748E-01	1.41E-02
7	0.03597	3.10E-04	0.95262	27.80094523	8.3	0.4	2.986E-01	1.44E-02
8	0.03902	3.30E-04	0.9573	25.62788314	8.7	0.4	3.395E-01	1.56E-02
9	0.045	3.20E-04	0.97585	22.22222222	8.4	0.4	3.780E-01	1.80E-02
10	0.04495	3.10E-04	0.97771	22.24694105	8.7	0.4	3.911E-01	1.80E-02

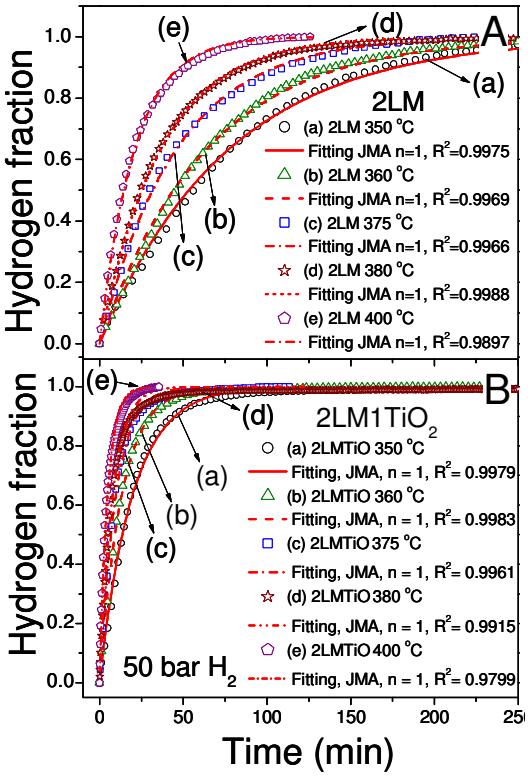
f = 1 - (exp(-k*t)^n)			n = 1				Fig.7 A (b)	
Abs 2LM1TiO2	k (1/s)	Error	R^2	k^-1 (s)	wt % H	Error	k x hydrogen capacty Abs. (wt. % H.s^-1)	Error
1	0.00033	6.62E-07	0.99111	3030.30303	10.1	0.4	3.333E-03	1.320E-04
2	0.00383	3.00E-05	0.97992	261.0966057	9.9	0.3	3.792E-02	1.149E-03
3	0.00411	4.00E-05	0.97292	243.3090024	10.1	0.3	4.151E-02	1.233E-03
4	0.00396	3.00E-05	0.98667	252.5252525	10.1	0.3	4.000E-02	1.188E-03
5	0.00438	4.00E-05	0.97338	228.3105023	10	0.3	4.380E-02	1.314E-03
6	0.00446	5.00E-05	0.97134	224.2152466	9.9	0.3	4.415E-02	1.338E-03
7	0.00435	4.00E-05	0.97087	229.8850575	10	0.3	4.350E-02	1.305E-03
8	0.00421	4.00E-05	0.97146	237.5296912	10	0.3	4.210E-02	1.263E-03
9	0.0042	4.00E-05	0.97034	238.0952381	10	0.3	4.200E-02	1.260E-03
10	0.00412	4.00E-05	0.96802	242.7184466	10	0.3	4.120E-02	1.236E-03

Table S1 Fitting parameters for the JMA model for the hydrogenation kinetic curves during cycling at 400 ^{o}C and 50 bar of H_2: 2LM and 2LM1TiO_2. **Note:** The unit of the rate constant is (1/s). For the sake of clarity in the inset plot of Fig.7 the time axis is expressed in unit of (minutes).

2LM	Fitting	First Step				Second Step			
Cycle	R2	l1	k1 (1/s)	error	n	l2	k2 (1/s)	error	t0 (s)
1	0.9993	0.25	1.28E-02	1.50E-04	1	0.82	4.70E-04	5.90E-07	7100
2	0.99751	0.25	1.34E-02	3.20E-04	1	0.93	3.80E-04	7.62E-07	9300
3	0.99796	0.27	1.07E-02	1.90E-04	1	0.90	3.70E-04	6.81E-07	9900
4	0.99778	0.27	9.20E-03	1.60E-04	1	0.90	3.30E-04	5.99E-07	10400
5	0.9974	0.28	9.61E-03	1.80E-04	1	0.86	3.80E-04	8.04E-07	10300
6	0.99734	0.28	8.86E-03	1.60E-04	1	0.86	3.80E-04	8.33E-07	10300
7	0.99795	0.28	9.83E-03	1.70E-04	1	0.83	4.50E-04	9.19E-07	8900
8	0.99758	0.27	9.63E-03	1.80E-04	1	0.85	4.60E-04	1.02E-06	8300
9	0.99829	0.28	9.44E-03	1.30E-04	1	0.83	4.80E-04	9.20E-07	8200
10	0.99725	0.27	1.01E-02	2.00E-04	1	0.98	4.40E-04	9.71E-07	8200

2LM1TiO2	Fitting	First Step				Second Step			
Cycle	R2	l1	k1 (1/s)	error	n	l2	k2 (1/s)	error	t0 (s)
1	0.99871	0.26	2.43E-02	6.00E-04	1	0.74	3.03E-03	1.00E-05	1430
2	0.99901	0.26	2.36E-02	4.40E-04	1	0.74	3.18E-03	9.83E-06	1420
3	0.99884	0.26	2.17E-02	4.20E-04	1	0.75	3.11E-03	1.00E-05	1440
4	0.99848	0.26	2.13E-02	4.80E-04	1	0.75	3.11E-03	1.00E-05	1440
5	0.99897	0.26	2.10E-02	3.90E-04	1	0.74	3.05E-03	9.35E-06	1450
6	0.99916	0.26	1.87E-02	3.00E-04	1	0.74	2.98E-03	8.30E-06	1465
7	0.99926	0.26	1.85E-02	2.90E-04	1	0.74	2.99E-03	7.70E-06	1450
8	0.99927	0.26	1.79E-02	2.80E-04	1	0.72	2.97E-03	7.82E-06	1470
9	0.99881	0.26	1.84E-02	3.70E-04	1	0.72	2.97E-03	9.97E-06	1480
10	0.99918	0.26	2.10E-02	3.50E-04	1	0.75	3.06E-03	8.37E-06	1440

Table S2 Fitting parameters for the JMA+PT model for the dehydrogenation kinetic curves during cycling at 400 ^{o}C and 3 bar of H_2: 2LM and 2LM1TiO_2. **Note:** The unit of the rate constant and t0 are (1/s) and (s), respectively. For the sake of clarity in the inset plot of Fig. 7 the time axis is expressed in unit of (minutes).

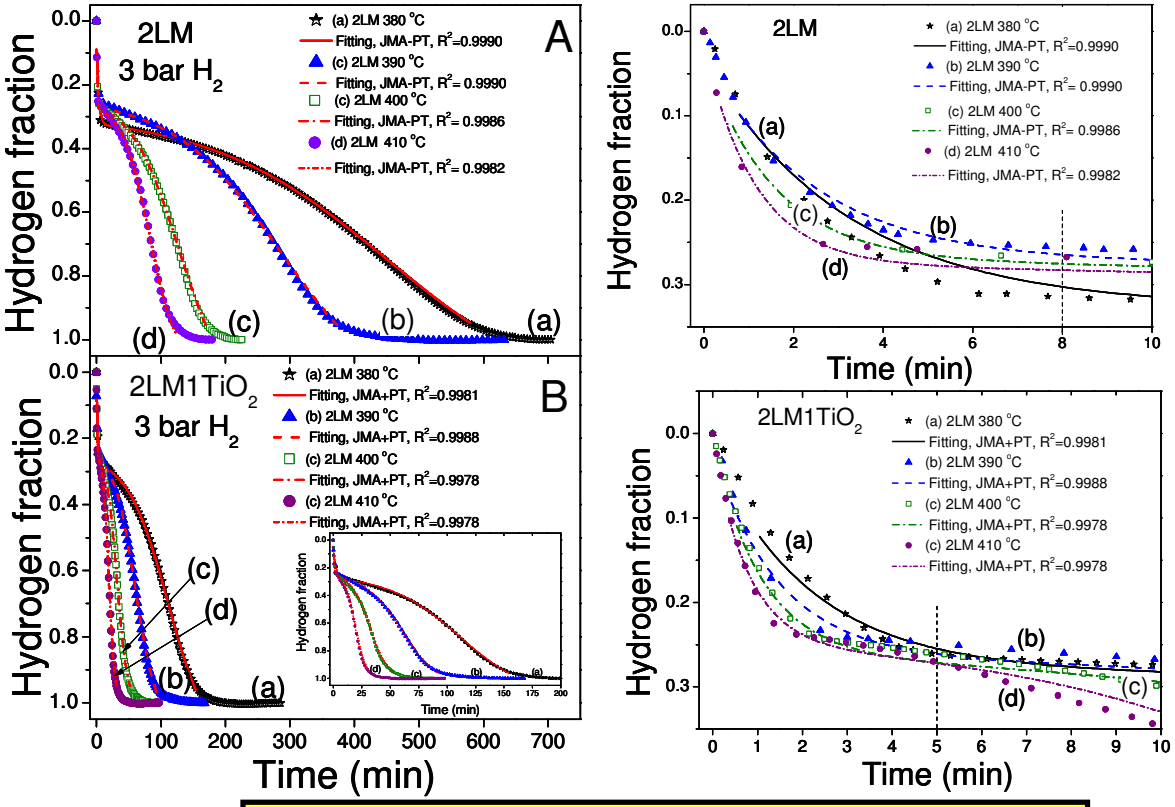


2LM Absorption			
Fitting - JMA, n = 1		Equation: f = 1 - (exp(-k*t)^n)	
T (°C)	k (1/s)	Error	Adj. R-Square
350	0.00022	2.60E-07	0.99757
360	0.00026	2.62E-07	0.99691
375	0.00037	7.51E-07	0.99662
380	0.00046	3.82E-07	0.99885
390	0.00053	1.47E-06	0.99621
400	0.0007	3.49E-06	0.98973

2LM1TiO$_2$ Absorption			
Fitting - JMA, n = 1		Equation: f = 1 - (exp(-k*t)^n)	
T (°C)	k (1/s)	Error	Adj. R-Square
350	0.00098	1.55E-06	0.9979
360	0.00127	3.39E-06	0.9983
375	0.00173	6.89E-06	0.9961
390	0.00304	2.00E-05	0.9848
380	0.00215	8.42E-06	0.9915
400	0.00352	2.00E-05	0.9838

Fig.S17 Hydrogenation curve fitting in the range of temperature between 350 °C and 400 °C for 2LM and 2LMTiO$_2$. **Note:** The unit of the rate constant is (1/s). For the sake of clarity in the Fig. S17 A and B the time axis is expressed in unit of (minutes).

2LM Desorption							
	Fitting	First Step			Second Step		
T (ºC)	R2	l1	k1 (1/s)	n	l2	k2 (1/s)	t0 (s)
380	0.99909	0.29	5.24E-03	1	0.92	1.20E-04	27100
390	0.99907	0.24	6.84E-03	1	0.96	2.00E-04	17035
400	0.99861	0.24	1.08E-02	1	0.94	4.50E-04	7600
410	0.99824	0.26	1.46E-02	1	0.82	8.00E-04	4900



2LMTiO$_2$ Desorption							
	Fitting	First Step			Second Step		
T (ºC)	R2	l1	k1 (1/s)	n	l2	k2 (1/s)	t0 (s)
380	0.99812	0.25	7.67E-03	1	0.89	5.30E-04	6640
390	0.99885	0.24	1.14E-02	1	0.83	1.00E-03	3615
400	0.99788	0.25	1.51E-02	1	0.75	2.13E-03	1900
410	0.99869	0.24	2.11E-02	1	0.76	3.65E-03	1150

Fig.S18 Dehydrogenation curve fitting in the range of temperature between 380 °C and 410 °C for 2LM and 2LMTiO$_2$**. Note:** The unit of the rate constant and t0 are (1/s) and (s), respectively. For the sake of clarity in the Fig. S18 A and B the time axis is expressed in unit of (minutes).

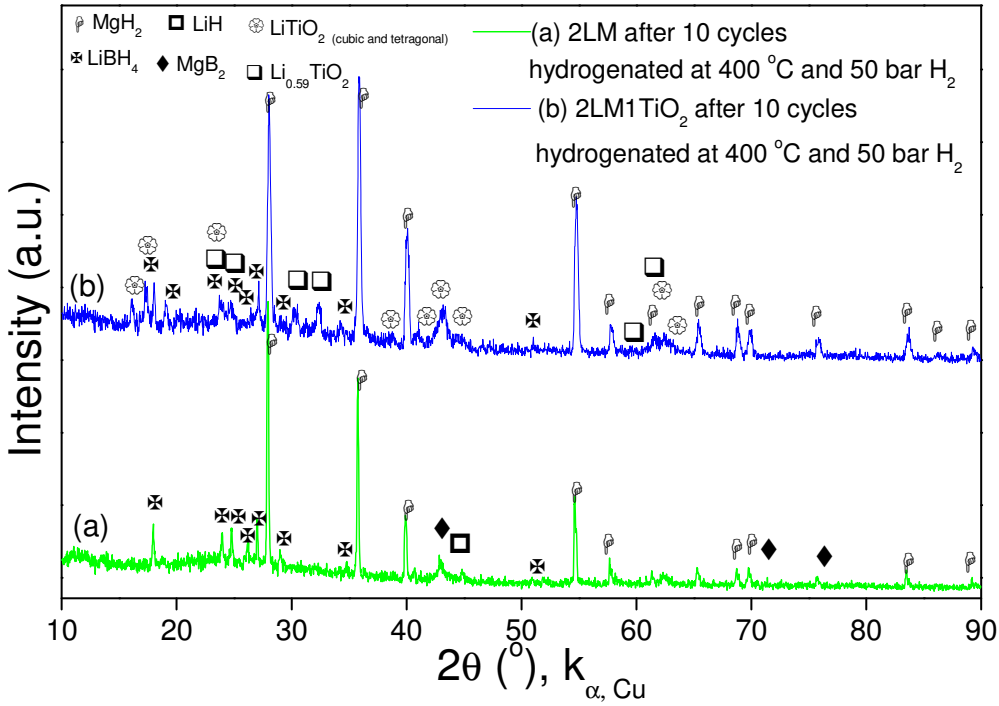


Fig. S19 PXD hydrogenated (a) 2LM and (b) 2LM1TiO_2 after 10th absorption-desorption cycles.