Electronic Supplementary Information

The electronic structure and surface properties of mechanochemically synthesised $LaMnO_3$ during *in situ* N_2O decomposition

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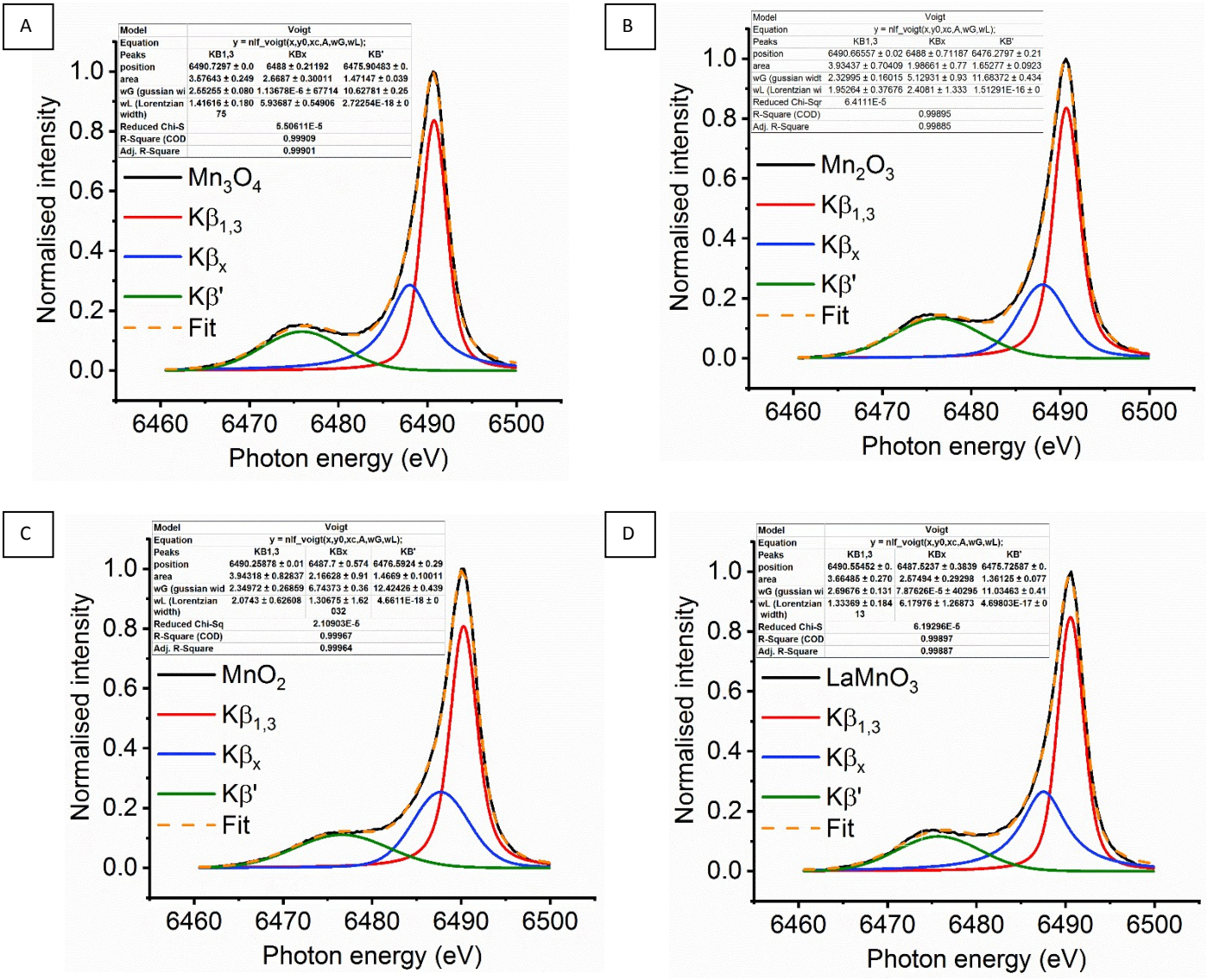
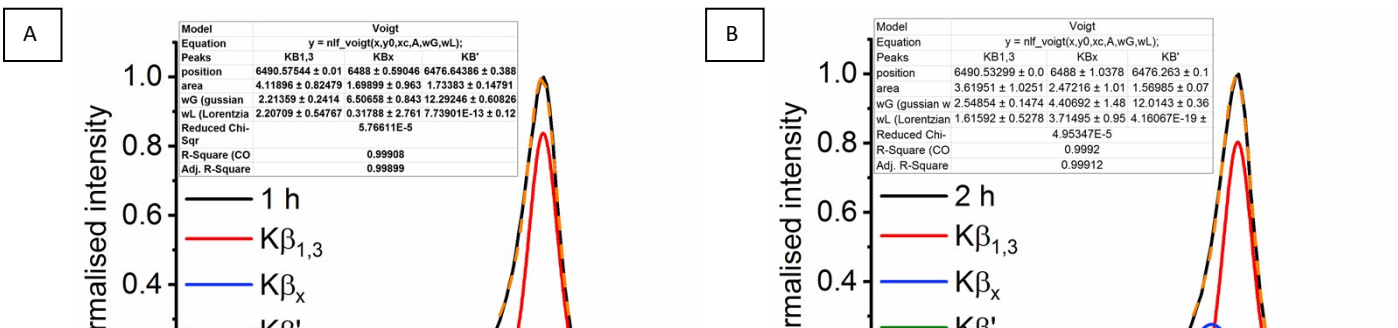


Figure S1: Mn Kβ mainlines fitted using three symmetric Voigt curves ($K\beta_{1,3}$, Kβ' and $K\beta_x$) for Mn reference materials **(A)** Mn_3O_4 **(B)** Mn_2O_3 **(C)** MnO_2 compared to **(D)** sol-gel synthesised $LaMnO_3$



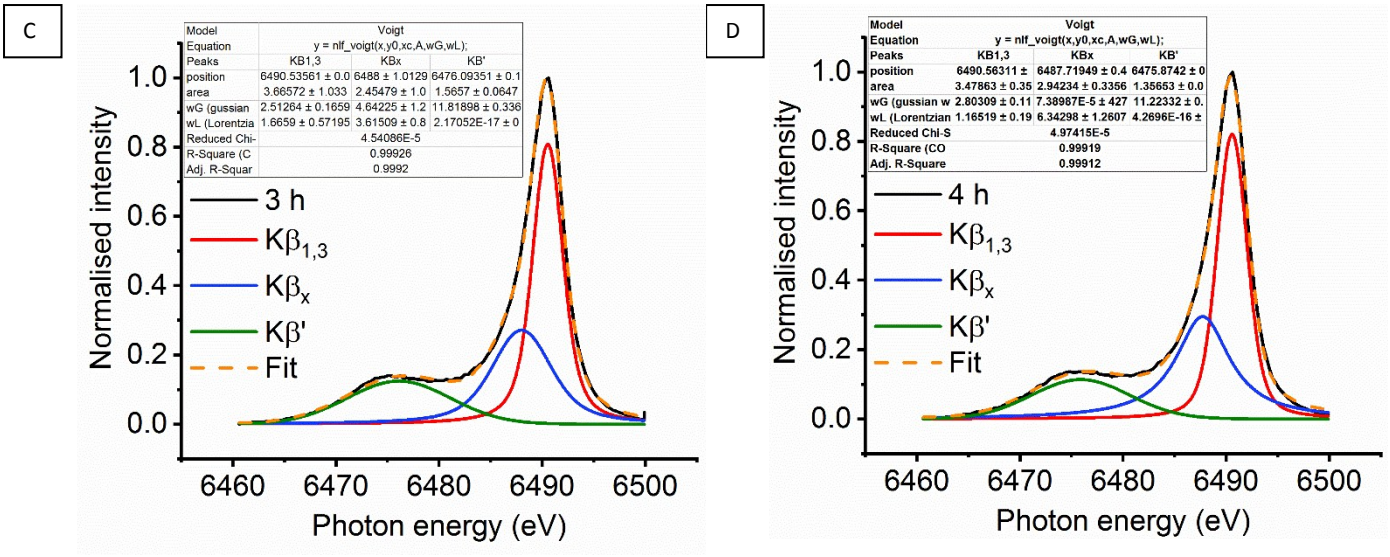


Figure S2: Mn Kβ mainline fitted using three symmetric Voigt curves ($K\beta_{1,3}$, Kβ' and $K\beta_x$) during the mechanochemical synthesis of $LaMnO_3$ after **(A)** 1 h **(B)** 2h **(C)** 3 h and **(D)** 4 h

Table S1: EXAFS fitting parameters for the Mn K-edge for spectra collected after 4 h of milling in air and inert (argon) conditions for the mechanochemical synthesis of $LaMnO_3$ compared to precursor Mn_2O_3 and sol-gel synthesised $LaMnO_3$. Fitting parameters: $S_0^2 = 0.7$ determined by a Mn foil standard; Fit range $3 < k > 11$, $1.2 < R > 3.85$. [a]CN fixed to known structures and the number of scattering paths reduced in order to minimise fitting parameters [b]All refined CN are within 10% error margin

Sample	Bond (Abs-Sc)	CN	E0 (eV)	σ2	R / Å
[a]Mn_2O_3	Mn-O1	4.0	-5.7(2)	0.007(1)	1.92(2)
	Mn-O2	2.0		0.011(6)	2.27(3)
	Mn-Mn1	6.0		0.0070(8)	3.10(2)
	Mn-Mn2	6.0		0.012(3)	3.57(3)
[b]Air milled $LaMnO_3$	Mn-O	5.0(1)	-8.5(4)	0.0054(3)	1.90(2)
	Mn-La1	5.9(5)		0.014(1)	3.24(1)
	Mn-La2	2.0(1)		0.0043(3)	3.37(1)
[b]Argon milled $LaMnO_3$	Mn-O	4.9(1)	-9.6(2)	0.0062(1)	1.90(1)
	Mn-La2	6.0(1)		0.010(1)	3.30(1)
	Mn-La1	2.0(1)		0.0050(1)	3.13(2)
[a]Sol-gel $LaMnO_3$	Mn-O	6.0	-2.7(4)	0.0058(5)	1.93(4)
	Mn-La2	6.0		0.0071(6)	3.34(6)
	Mn-La3	2.0		0.0020(9)	3.70(9)

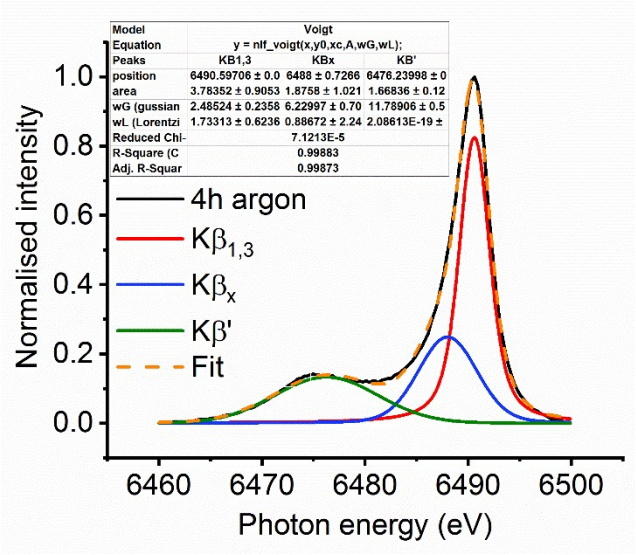


Figure S3: Mn Kβ mainline fitted using three symmetric Voigt curves ($Kβ_{1,3}$, Kβ' and $Kβ_x$) for mechanochemically synthesised $LaMnO_3$ in an argon environment

Table S2: Surface Atomic percentage ratios of both 3 and 4 h milled $LaMnO_3$ compared to sol-gel synthesised sample

	Sol-gel	Air	Argon
La : Mn	1.1 : 1	1.2 : 1	1.7 : 1
O : La	1 : 0.2	1 : 0.2	1 : 0.2
O : Mn	1 : 0.2	1 : 0.2	1 : 0.1

Table S3: Mn3*s* and La3*d* splitting energies for $LaMnO_3$ synthesised by sol-gel and mechanochemistry under different environments

	Sol-gel	Air	Argon
Mn3*s* splitting (eV)	4.8	4.9	5.0
La3*d* splitting (eV)	4.5	4.6	3.7

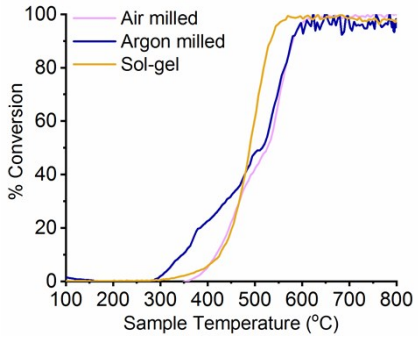


Figure S4: Repeat catalytic activity testing of deN_2O for $LaMnO_3$ prepared by milling in air and argon compared to a sol-gel prepared perovskite

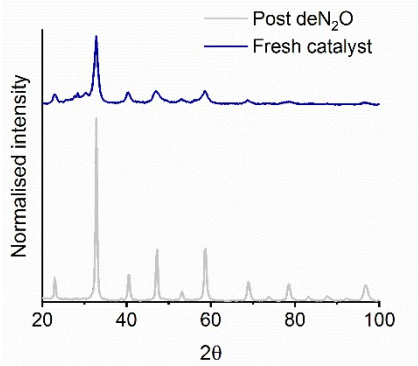


Figure S5: XRD patterns of $LaMnO_3$ mechanochemically synthesised in an argon atmosphere before and after deN_2O

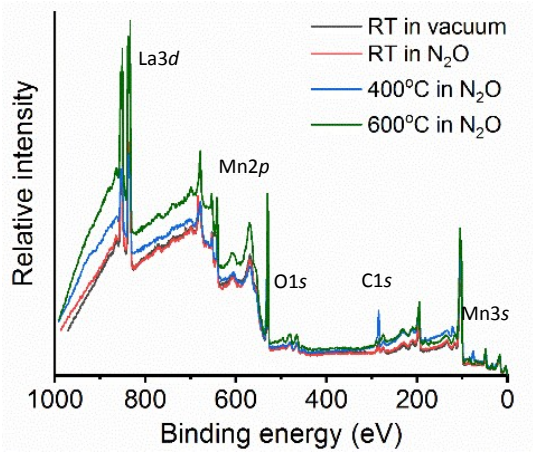


Figure S6: Survey scan at 1200 eV to calibrate correct binding energies for La3*d,* Mn3s, Mn2*p* and O1*s* for the argon milled catalyst at room temperature (RT) in vacuum, RT under a N_2O atmosphere and after heating at 400˚C and 600˚C

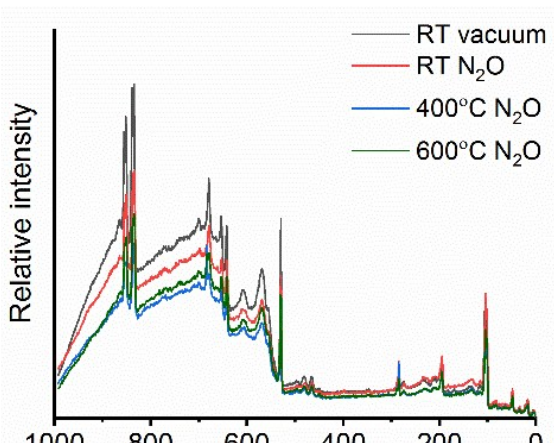


Figure S7: Survey scan at 1200 eV to calibrate correct binding energies for La3*d,* Mn3s, Mn2*p* and O1*s* for the air milled catalyst at room temperature (RT) in vacuum, RT under a N_2O atmosphere and after heating at 400˚C and 600˚C

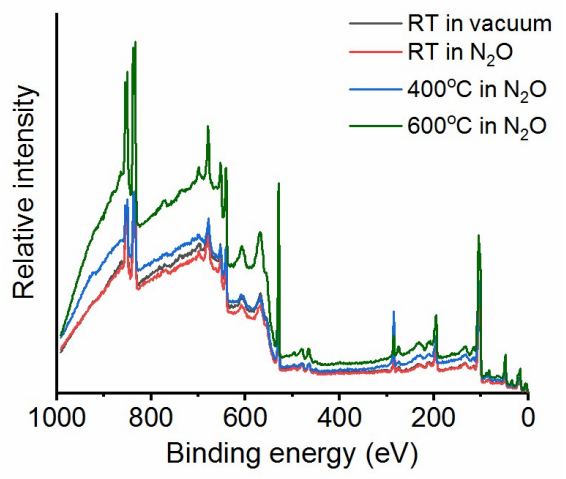


Figure S8: Survey scan at 1200 eV to calibrate correct binding energies for La3*d,* Mn3s, Mn2*p* and O1*s* for the sol-gel synthesised catalyst at room temperature (RT) in vacuum, RT under a N_2O atmosphere and after heating at 400˚C and 600˚C

Table S4: NAP-XPS deconvoluted peak positions and areas during *in situ* deN_2O of the air milled catalyst at Mn2*p*, Mn3*s*, La3*d* and O1*s* regions

		RT vacuum	RT in N_2O	400 ˚C in N_2O	600 ˚C in N_2O
Mn2*p*	**Peak 1**	641.6, 37671	641.8, 50225	641.3, 71126	641.5, 86067
	Peak 2	643.7, 27363	644.3, 19745	643.2, 58775	653.5, 67777
	Peak 3	653.2, 16135	653.6, 26975	652.9, 32281	653.2, 34134
	Peak 4	655.2, 10737	656.3, 2412	655.0, 35168	654.8, 36277
	Spin coupling	11.7	11.9	11.7	11.8
	Ratio Mn(III):Mn(IV)	1.4	2.5	1.2	1.3
Mn3*s*	**Peak 1**	83.6	83.7	83.3	83.0
	Peak 2	88.6	88.7	88.6	88.3
	Satellite	92.0	91.9	92.3	92.3
	Splitting	5.0	5.1	5.3	5.3
La3*d*	**Peak 1**	834.0	834.1	834.95	834.6
	Peak 2	838.2	838.1	839.44	839.22
	Peak 3	850.9	836.4	837.23	837.05
	Peak 4	855.0	851.0	851.8	851.5
	Peak 5	853.0	855.0	856.29	855.97
	Peak 6	836.2	853.4	854.21	853.91
	$La3d_{5/2}$ splitting	4.1	4.0	4.5	4.6
	Spin coupling	16.8	16.9	16.8	16.9
O1*s*	**Peak 1**	529.2, 15913	529.2, 22031	529.4, 46689	530.2, 34509
	Peak 2	531.1, 20980	531.0, 32303	531.4, 34064	531.3, 37535
	Peak 3	533.3, 1540	533.1, 4718	533.9, 1349	533.4, 1516
	Peak 4	-	-	-	-

Table S5: NAP-XPS deconvoluted peak positions and areas during *in situ* deN_2O of the sol-gel catalyst at Mn2*p*, Mn3*s*, La3*d* and O1*s* regions

		RT vacuum	RT in N_2O	400 ˚C in N_2O	600 ˚C in N_2O
Mn2p	**Peak 1**	641.6, 42127	641.4, 15869	641.3, 54139	641.3, 113016
	Peak 2	643.7, 14016	643.5, 15941	643.5, 40711	643.6, 67138
	Peak 3	653.3, 19832	653.4, 7762	653.1, 22587	653.0, 46964
	Peak 4	655.2, 6549	655.5, 3353	654.9, 17644	655.2, 35191
	Spin coupling	11.7	12.0	11.7	11.8
	Ratio Mn(III):Mn(IV)	3.0	1.0	1.3	1.7
Mn3s	**Peak 1**	-	83.33	83.08	83.11
	Peak 2	-	88.47	88.42	88.57
	Satellite	-	-	-	-
	Splitting	-	5.1	5.3	5.5
La3d	**Peak 1**	833.94	833.89	833.87	834.1
	Peak 2	838.1	838.08	838.19	838.44
	Peak 3	836.14	836.05	835.68	835.94
	Peak 4	850.77	850.68	850.73	850.95
	Peak 5	854.96	854.8	855.06	855.27
	Peak 6	852.97	852.73	852.6	852.79
	La3d5/2 splitting	4.2	4.2	4.3	4.3
	Spin coupling	16.8	16.8	16.9	16.9
O1s	**Peak 1**	529.2, 10246	529.2, 6013	529.4, 30261	529.7, 66906
	Peak 2	531.0, 12478	531.3, 7440	531.3, 23633	531.2, 52792
	Peak 3	533.9, 1454	533.1, 2975	533.6, 3188	533.7, 1942
	Peak 4	-	-	-	-

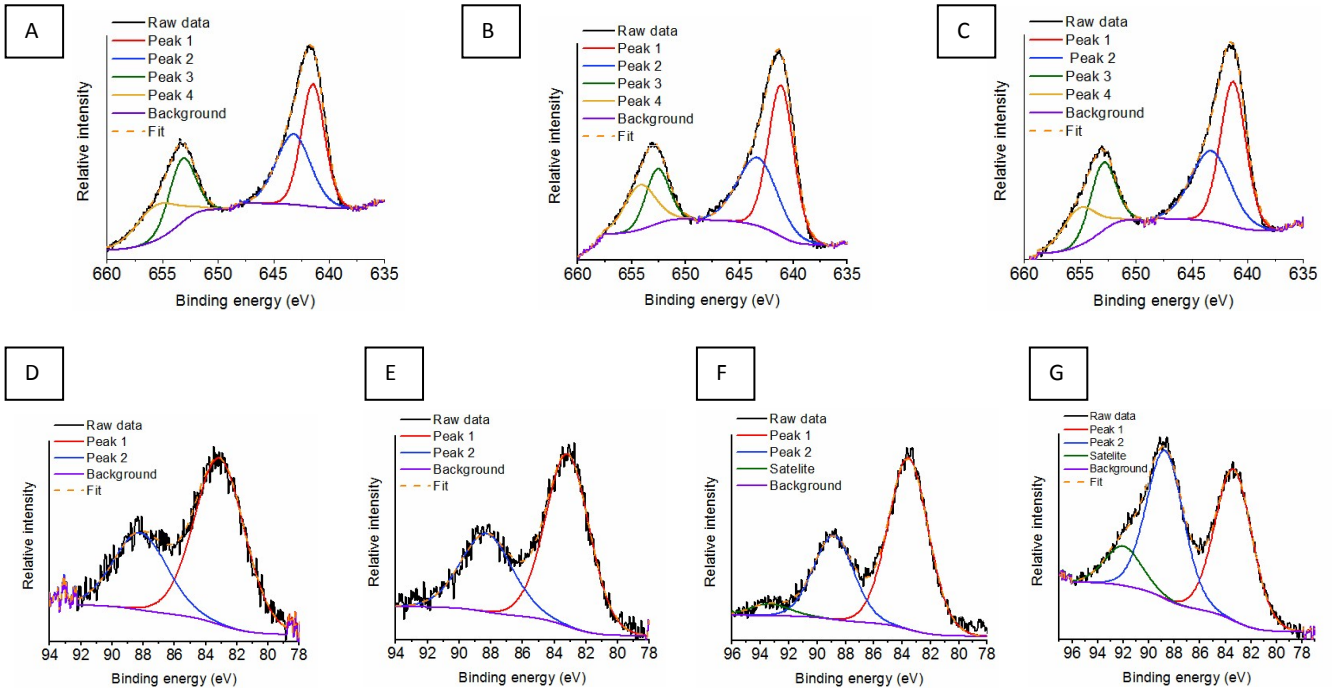


Figure S9: NAP-XPS performed on the argon milled catalyst at the Mn2*p* region at **(A-C)** RT under a N_2O atmosphere and then heated to 400˚C and 600˚C and at the Mn3*s* region **(D-G)** at RT in vacuum, RT under a N_2O atmosphere and then heated to 400˚C and 600˚C, respectively

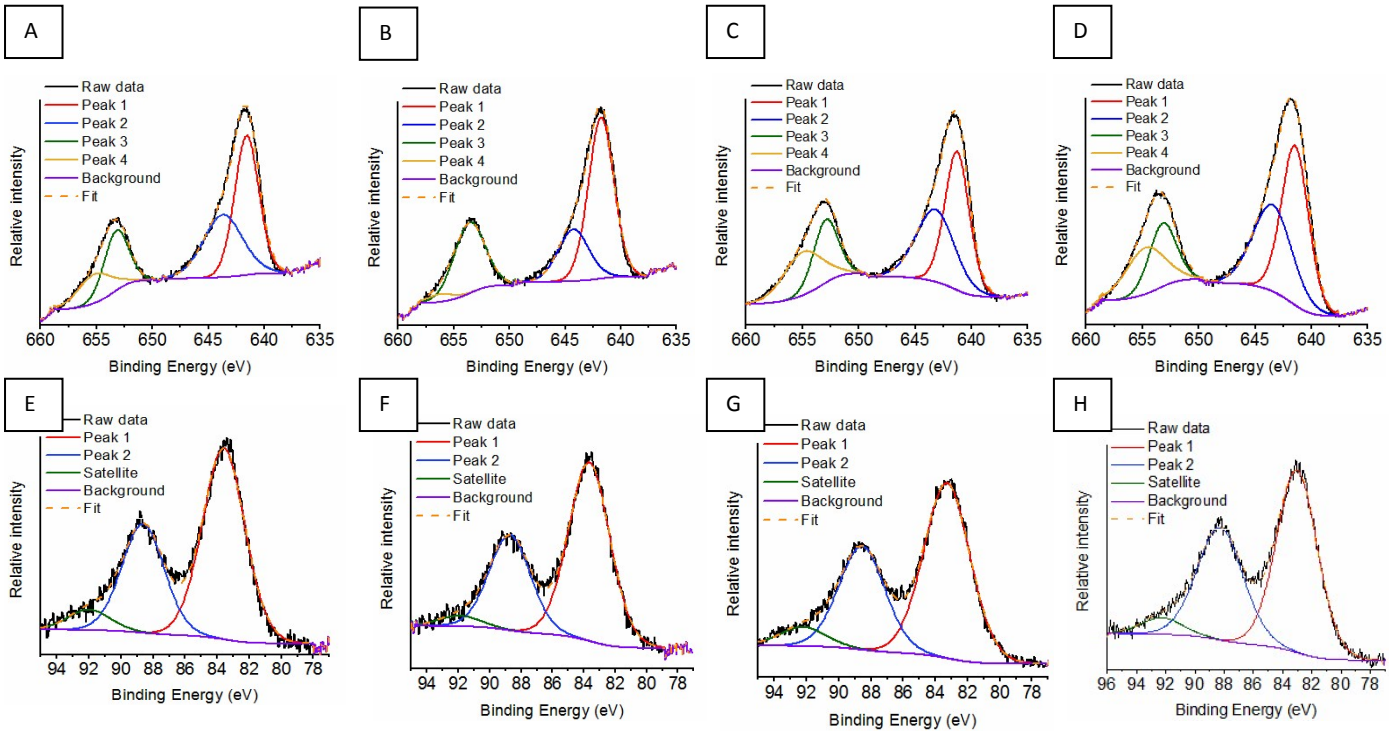


Figure S10: NAP-XPS performed on the air milled catalyst at the **(A-D)** Mn2*p* region and **(E-H)** Mn3*s* region at RT in vacuum, RT under a N_2O atmosphere and then heated to 400˚C and 600˚C, respectively

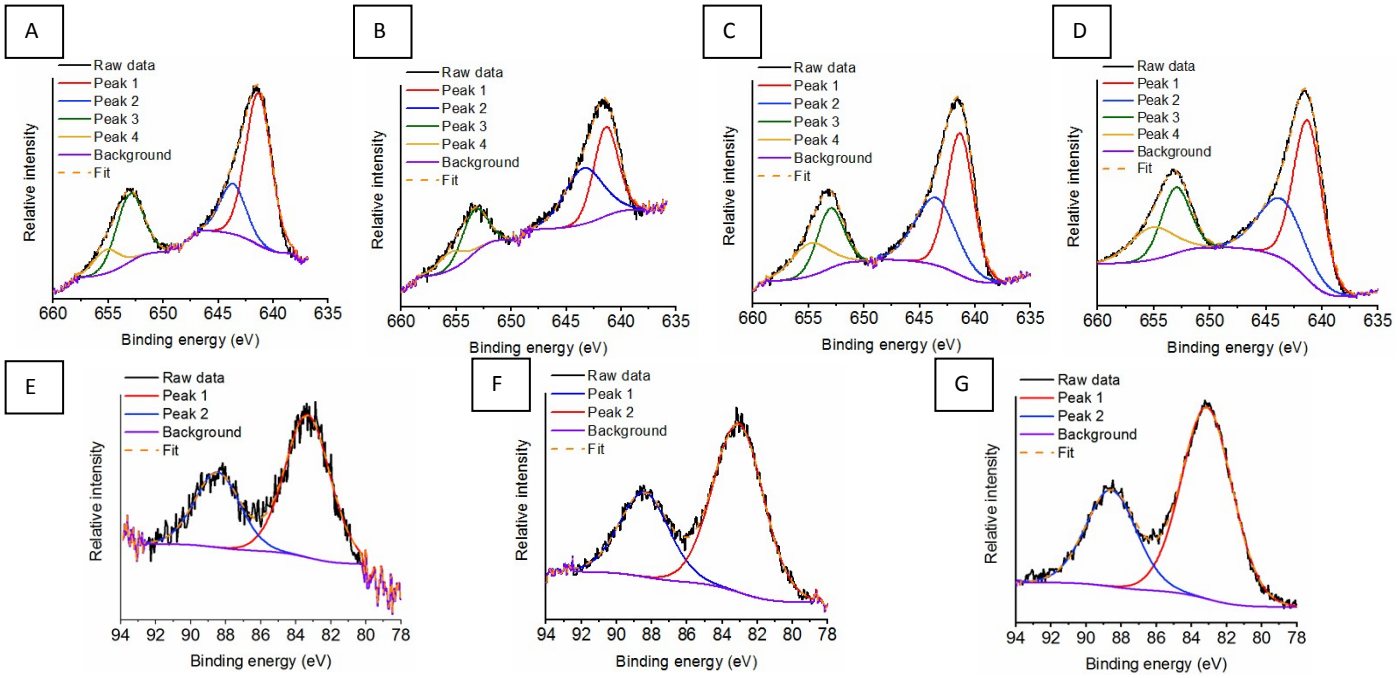


Figure S11: (A-D) Mn2*p* region RT in vacuum, RT under a N_2O atmosphere and then heated to 400˚C and 600˚C and **(E-G)** Mn3*s* for the sol-gel synthesised catalyst at RT under a N_2O atmosphere and then heated to 400˚C and 600˚C

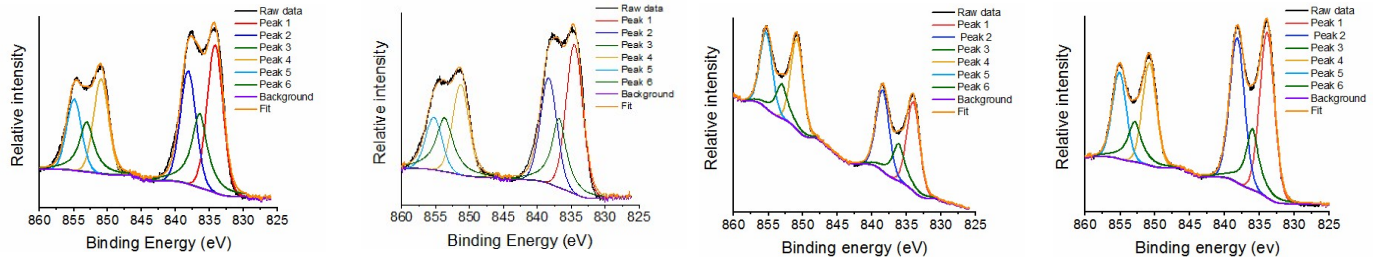


Figure 12 (A-D) La3*d* region for the argon milled catalyst at RT in vacuum, RT under a N_2O atmosphere and then heated to 400˚C and 600˚C

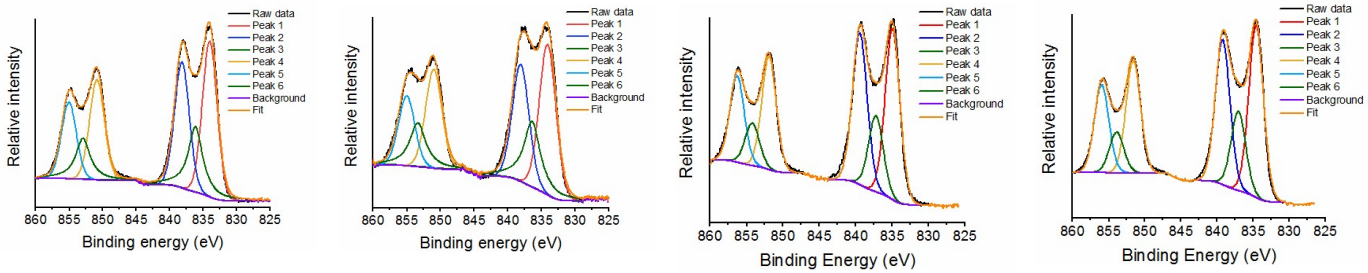


Figure S13: La3*d* region for the air milled catalyst at **(A)** RT in vacuum, **(B)** RT under a N_2O atmosphere and then heated to **(C)** 400˚C and **(D)** 600˚C

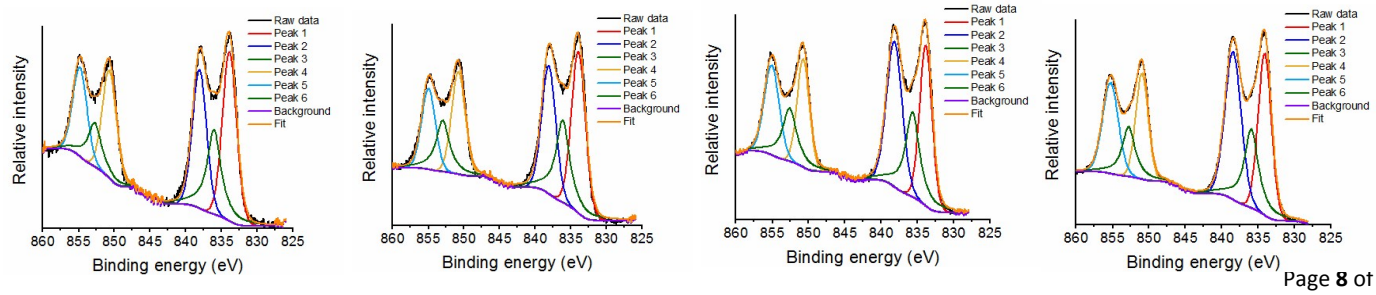


Figure S14: La3*d* region for the sol-gel synthesised catalyst at **(A)** RT in vacuum, **(B)** RT under a N_2O atmosphere and then heated to **(C)** 400˚C and **(D)** 600˚C

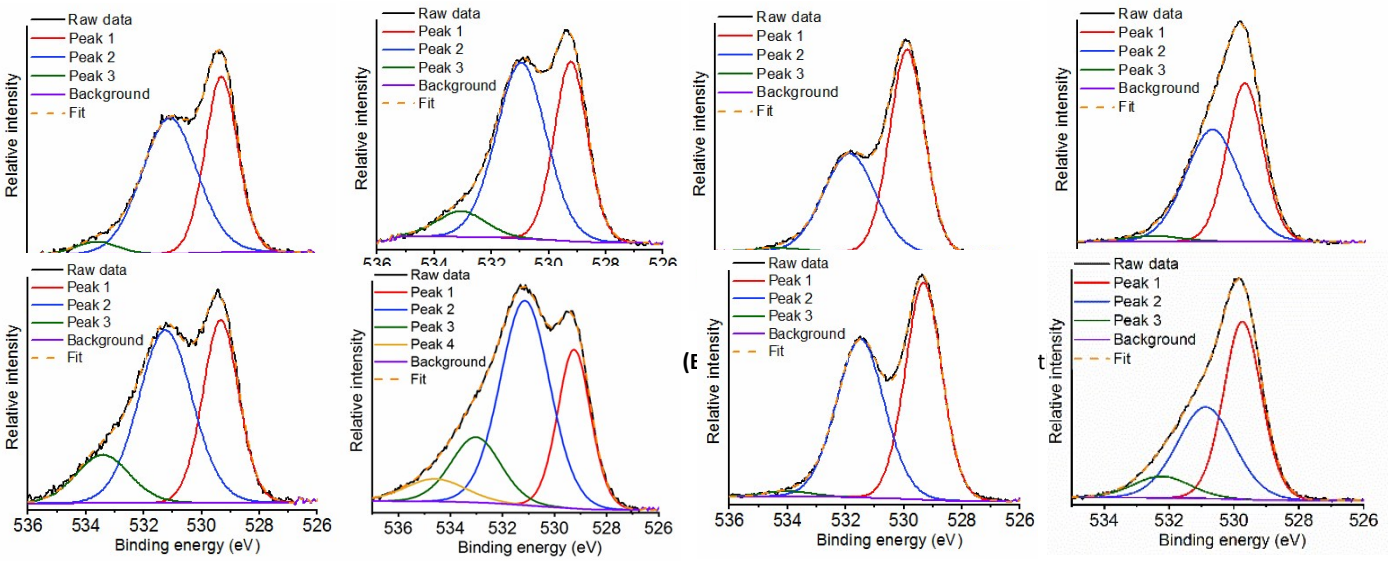


Figure S15: (A-D) O1*s* region for the argon milled catalyst at RT in vacuum, RT under a N_2O atmosphere and then heated to 400˚C and 600˚C

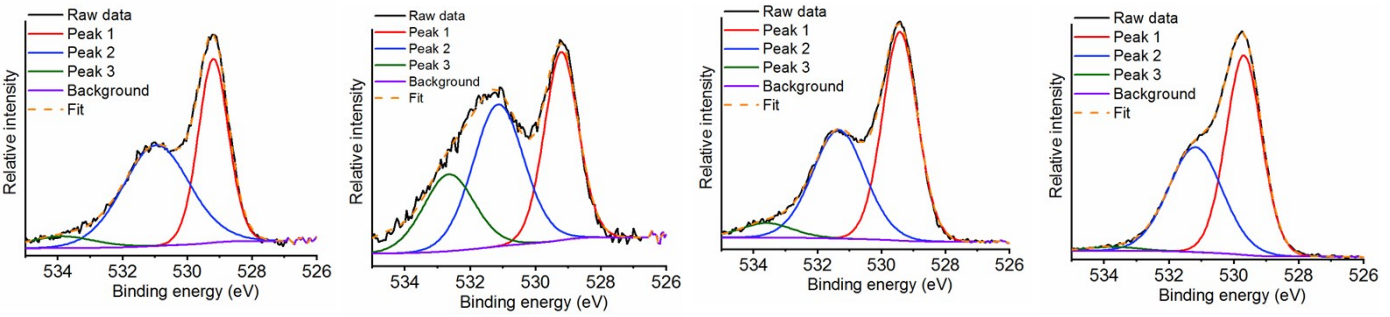


Figure S17: O1*s* region for the sol-gel synthesised catalyst at **(A)** RT in vacuum, **(B)** RT under a N_2O atmosphere and then heated to **(C)** 400˚C and **(D)** 600˚C