Electronic Supplementary Material (ESI) for CrystEngComm

Post-synthetic Incorporation of Nickel into CPO-27(Mg) to give Materials with Enhanced Permanent Porosity

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S1 Reported activation procedures for CPO-27/MOF-74 materials

Table S1: Various activation procedures reported in the literature

Divalent metal	Adsorption		Synthesis	Activation	Pre-adsorption treatment	Ref.
	CO_2 298K / 0.1 bar (mmol g^{-1})	N_2 77K (m^2 g^{-1}/ mmol g^{-1})				
Mg	5.68	1542 / 18.2	THF/water	513 K / 48 h, 393 K / 1 h	MeOH exchange (7×7 days)	1
Mg	5.9	1495	DMF/EtOH/ water	523 K / 5 h	MeOH exchange (4×2 d), stored under vac or inert gas	2
Mg	5.68	--	DMF/EtOH/ water	523 K / 6 h	MeOH exchange (4 × 2 d)	3
Mg	5.5	/ 16.5	DMF/EtOH/ water	Soaking DMF, MeOH, soak DMF(heating), MeOH exchange (6 × 36 h), 353 K/24h under vac		4
Mg	4.59	--	DMF/EtOH/ water	hot DMF decanted, immediate MeOH exchange (2×), MeOH exchange (4 × 2 d), dried 303-313 K, 523 K vac 10 h, stored under N_2 atmosphere		5
Ni	4.09	1218 / 13.6	THF/water	473 K/19 h, 383 K / 1 h	--	1
Ni	--	1083	THF/water	373 K / 20 h	--	6
Ni	--	1242 / 13.6	THF/water	?	?	7
Ni mod	1.1	46.7	THF/water	353 K / 12 h	--	8
Ni	3.1	921	THF/water	323 K / vac in N_2-flow	EtOH exchange (6 × 8 d)	9
Ni	3.1	1147	THF/water	523 K / 15 h vac or He	--	10
Ni	4.09	1070	DMF/EtOH/ Water	523 K / 5 h	MeOH exchange (4 × 2 d), Stored under vac. or inert gas	2
Ni	2.72	--	THF/water		Hot mother liquor decanted, MeOH exchanged (4 × 2 d), dried RT, 523 K vac 5 h, stored in N_2 atmos.	5
Co	2.95	1080	DMF/EtOH/ water	523 K / 5 h	MeOH exchange (4 × 2 d), Stored under vac. or inert gas	2
Co	2.59	--	DMF/EtOH/ water	Hot mother liquor decanted, MeOH exchanged (4 × 2 d), dried RT, 523 K vac 5 h, stored under N_2 atmosphere		5
Zn	1.31	816	DMF/water	543 K	Hot mother liquor decanted, rinsed DMF, MeOH exchanged (3 × 6 d)	1

S2 Metal salts and acids used in the modification step

Table S2.1: Amounts of metal salts and acids used for modification, related to magnesium nitrate used in the first step, showing mixture of nickel acetate and nickel chloride

Amounts and Species used in post-modification			
% $Ni(OAc)_2$	% $NiCl_2$	% Acid	Acid
10	0	10	Trimesic acid
10	0	10	H_3PO_3
10	0	10	*cbIm*
10	0	10	*cpmp*
10	20	10	*cpmp*
10	40	10	*cpmp*
10	60	10	*cpmp*

S3 X-ray Photoelectron Spectroscopy (XPS)

Typical example of XPS spectra of Mg, Ni and P for a modified material, showing spectral fitting.

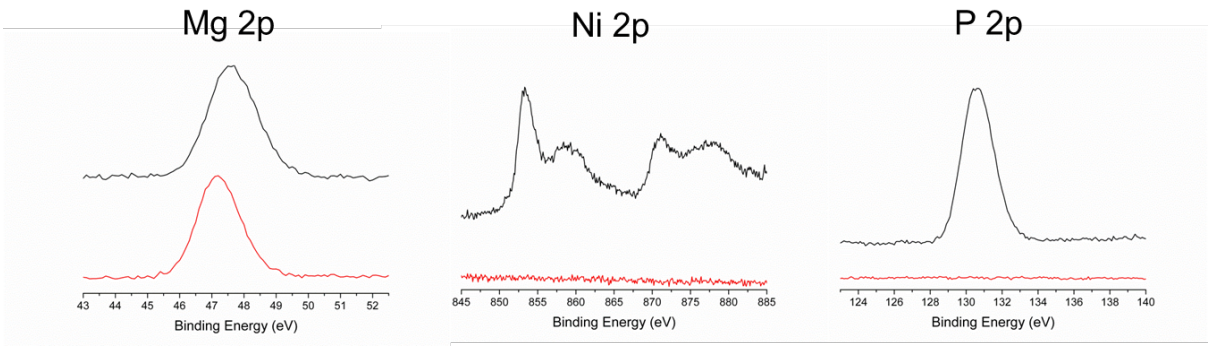

Figure S3.1 XPS spectra of unmodified (red) and with 10 % nickel and H_3PO_3 modified CPO-27(Mg) (black).

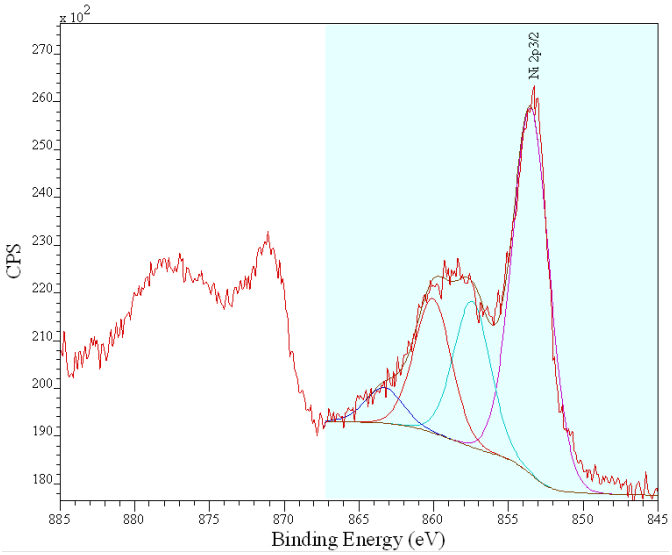

Figure S3.2 XPS spectra of 10 % nickel and H_3PO_3 modified CPO-27(Mg) with applied fitting parameters in Ni $2p_{3/2}$ region.[11]

S4 Laboratory Powder X-Ray Diffraction

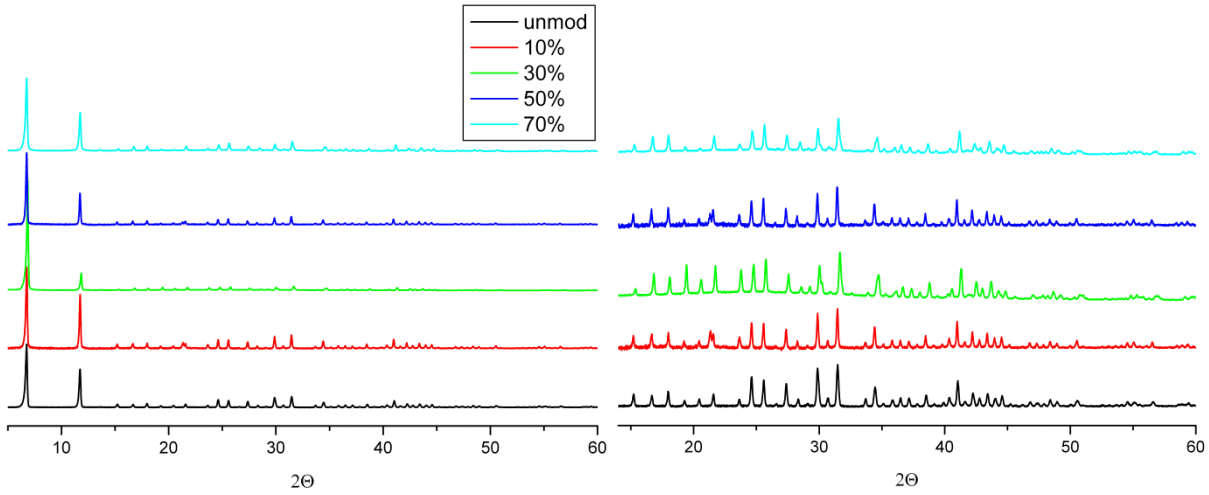

Figure S4.1 PXRD of unmodified CPO-27 (Mg) and with various amounts of *cpmp* and Ni^{2+}(aq) modified material. Powder patterns were collected after activation at 373 K followed by 523 K and adsorption experiments.

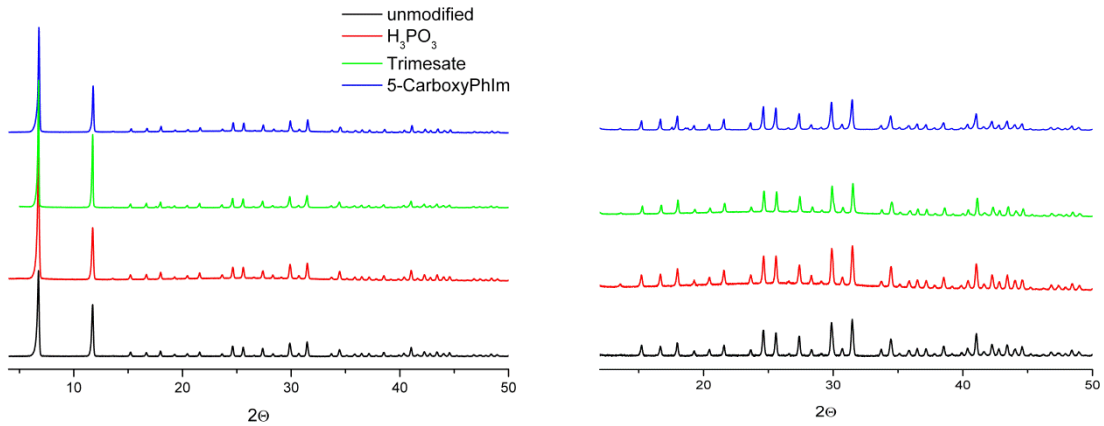

Figure S4.2 PXRD of unmodified CPO-27(Mg) and also CPO-27(Mg) modified with 10% nickel acetate and different acids.

S5 Porosity - Nitrogen Adsorption (77 K)

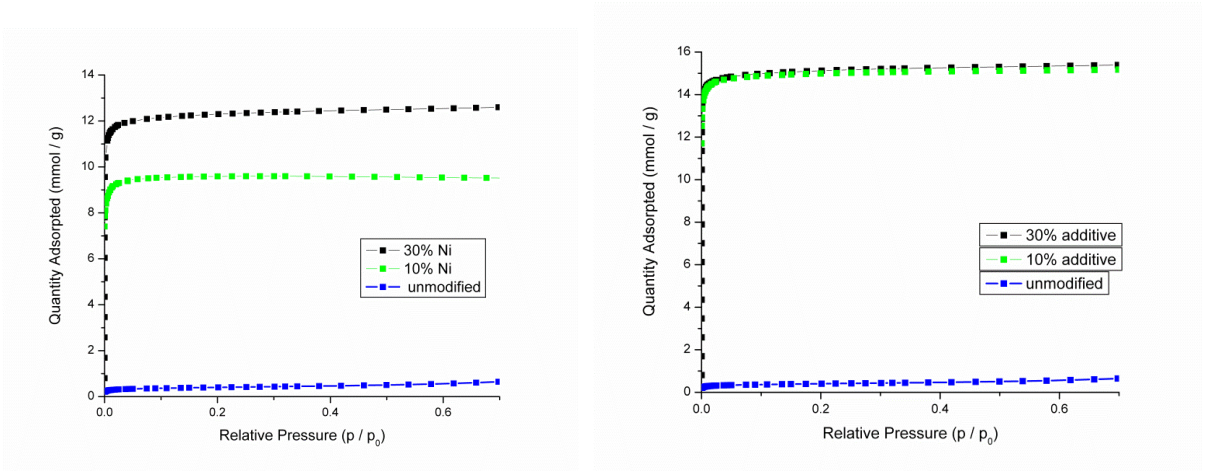

Figure S5.1 (Left) N_2 adsorption (77K) of CPO-27(Mg) and material modified with 10% and 30% of nickel acetate and 10% *cpmp* after samples were activated at 373K followed by 523K. (Right) N_2 adsorption (77K) of CPO-27(Mg) and material modified with 10% and 30% of nickel acetate and 10% *cpmp* where samples have been activated for a second time at 373K followed by 523K.

S6 Product Yield vs. Amount of Incorporated Ni

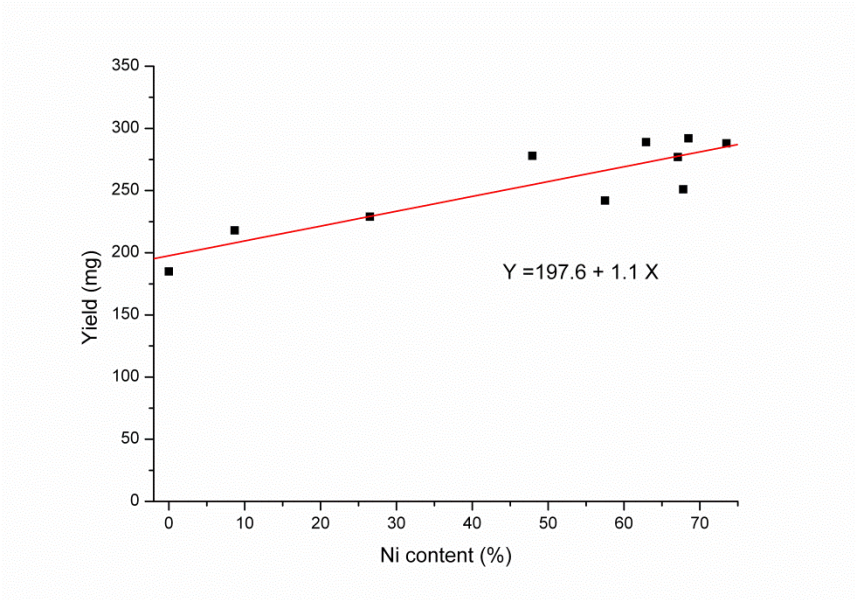

Figure S6.1 Yield (mg) vs. Ni content (%) observed by EDX analysis of nickel and *cpmp* modified CPO-27(Mg) materials, all with the same starting amounts and conditions in the first synthesis step (see paper for details).

S7 Structure refinement of CPO-27(Mg) modified with 70 mol% Ni

Table S7.1 Structural Parameters (Fractional Atomic coordinates, Fractional Occupancies and Displacement Parameters) (*R* -3, a = 25.87358(13) Å, c = 6.79917(4) Å)

Atom	x	y	z	Frac.	U_{iso} / Å^2
Mg	0.36114(9)	0.31559(9)	0.02428(24)	0.354(4)	0.007
Ni	0.36114(9)	0.31559(9)	0.02428(24)	0.646(4)	0.007
C(1)	0.4074(4)	0.4203(4)	0.7376(12)	1	0.004(1)
C(2)	0.4570(5)	0.4649(5)	0.8763(15)	1	0.004(1)
C(3)	0.4994(5)	0.5157(5)	0.7946(12)	1	0.004(1)
C(4)	0.4555(4)	0.4456(4)	0.0696(17)	1	0.004(1)
O(1)	0.40614(25)	0.43738(24)	0.5635(8)	1	0.005(1)
O(2)	0.36701(24)	0.36892(23)	0.7989(7)	1	0.005(1)
O(3)	0.58386(23)	0.60751(22)	0.8369(8)	1	0.005(1)

Occupancies of Mg and Ni constrained to sum to 1.

U_{iso} values of each element type refined as the same value.

S8 SEM Images of CPO-27(Mg,Ni) after modification steps of different duration

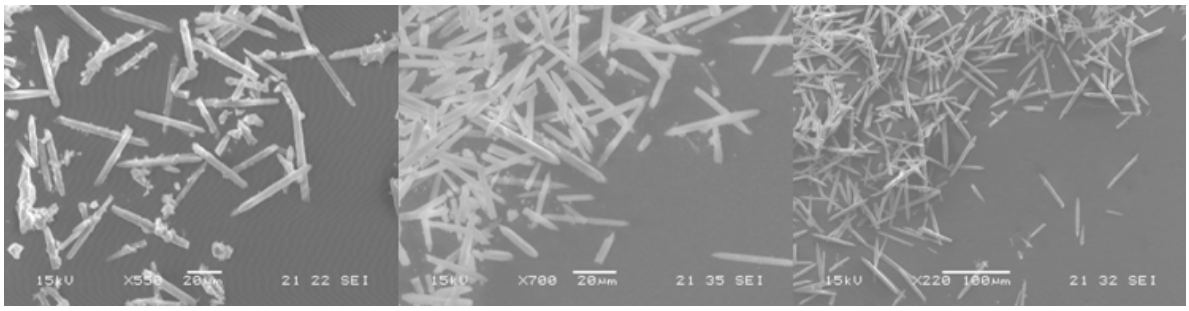

Figure S8.1 SEM images of CPO-27(Mg) modified with 70% Ni^{2+} and 10% *cpmp* recorded after different second step reaction times. 1 hour (left), 8 hours (middle), 3 days(right).

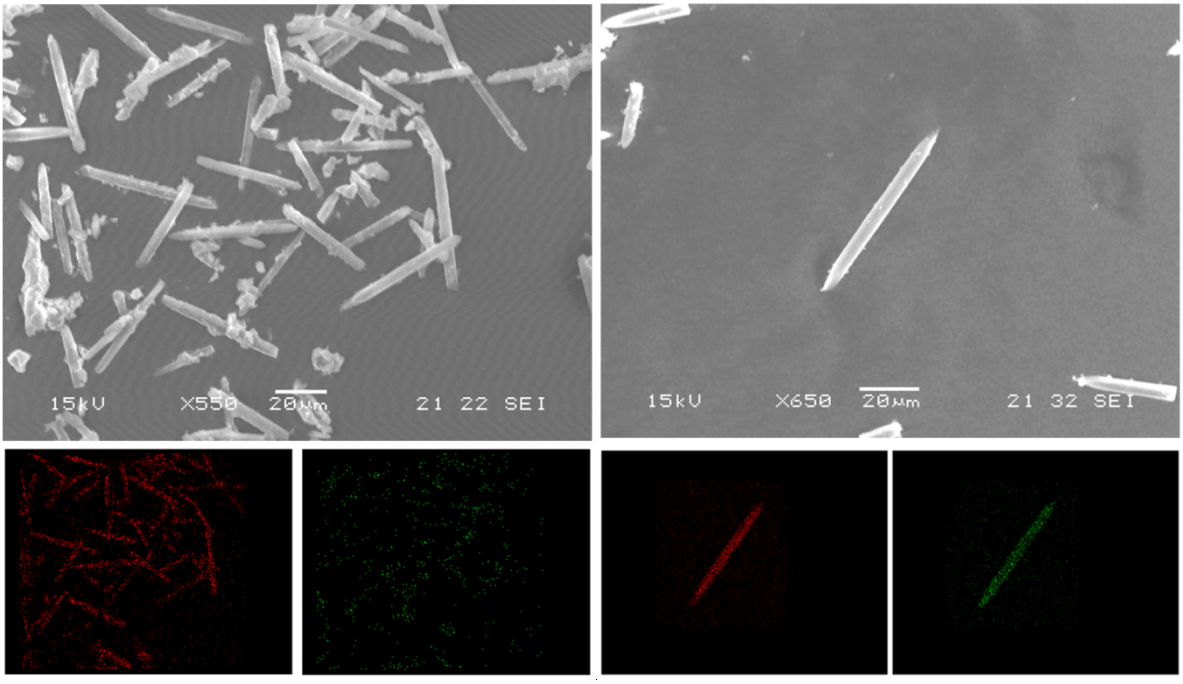

Figure S8.2 Elemental maps of CPO-27(Mg) modified with 70% Ni^{2+} and 10% *cpmp* recorded after different second step reaction times. 1 hour (left), 3 days(right). (Mg Ka, red; Ni Ka, green)

S9 Repeated Carbon Dioxide Adsorption Measurements (298 K)

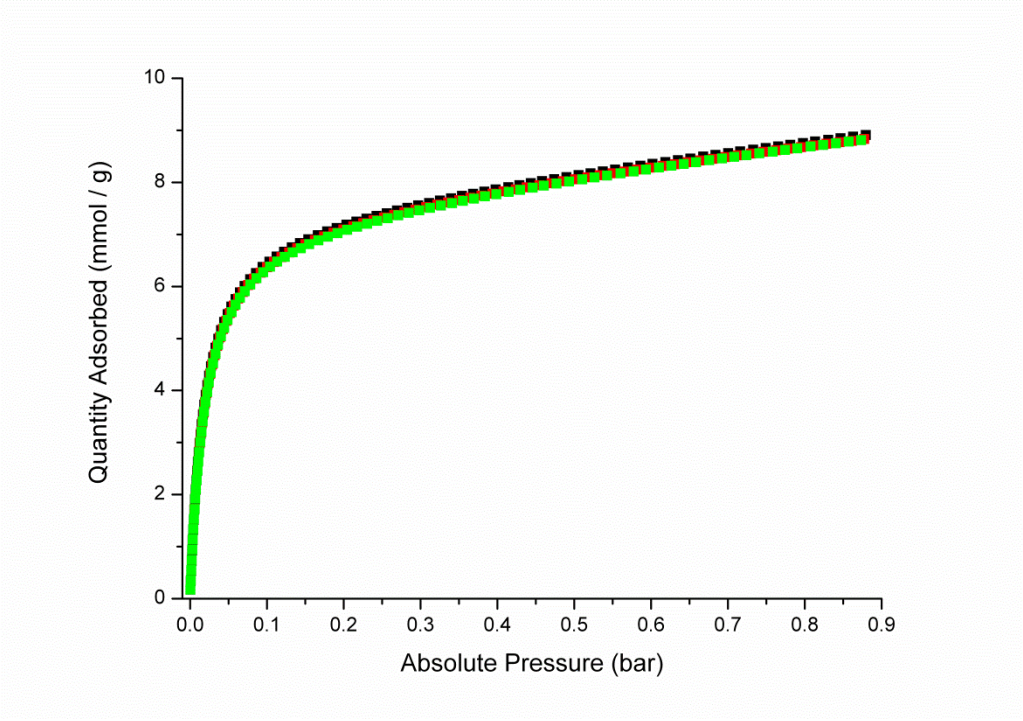

Figure S9.1: Repeated CO_2 adsorption (298 K) of CPO-27(Mg) modified with 10% nickel acetate and 10% *cblm*. The same batch has been activated at 373 K followed by 553 K and measured 3 times. First (green), second (red), third (black).

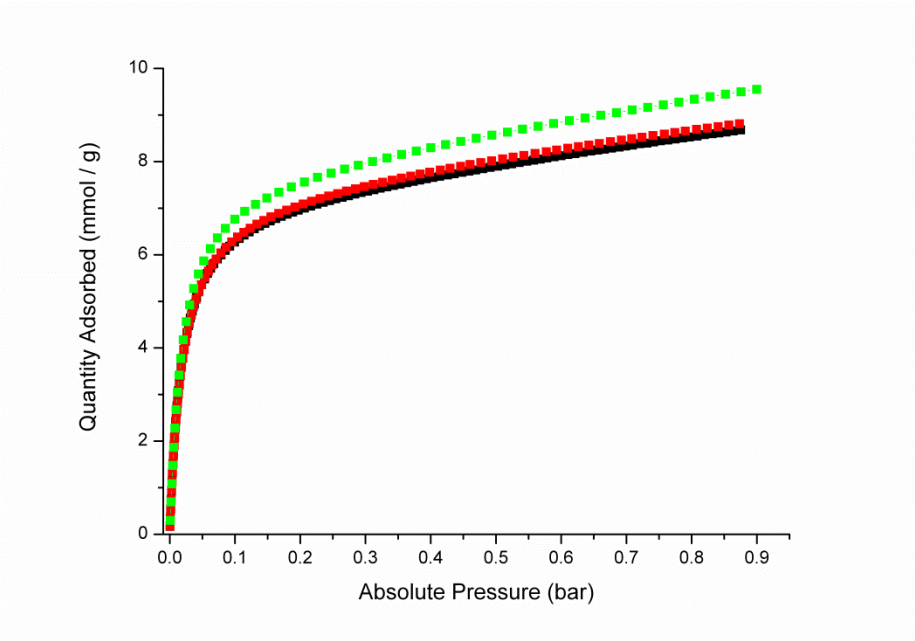

Figure S9.2: Repeated CO_2 adsorption (298 K) of CPO-27(Mg) modified with 10% nickel acetate and 10% *cblm*. Samples were obtained as described in experimental part from 3 different syntheses and have been activated at 373K followed by 553 K before measurement.

S10 References

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