Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

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Peculiarities of high-pressure hydrogen adsorption on Pt catalyzed Cu-BTC metal-organic framework

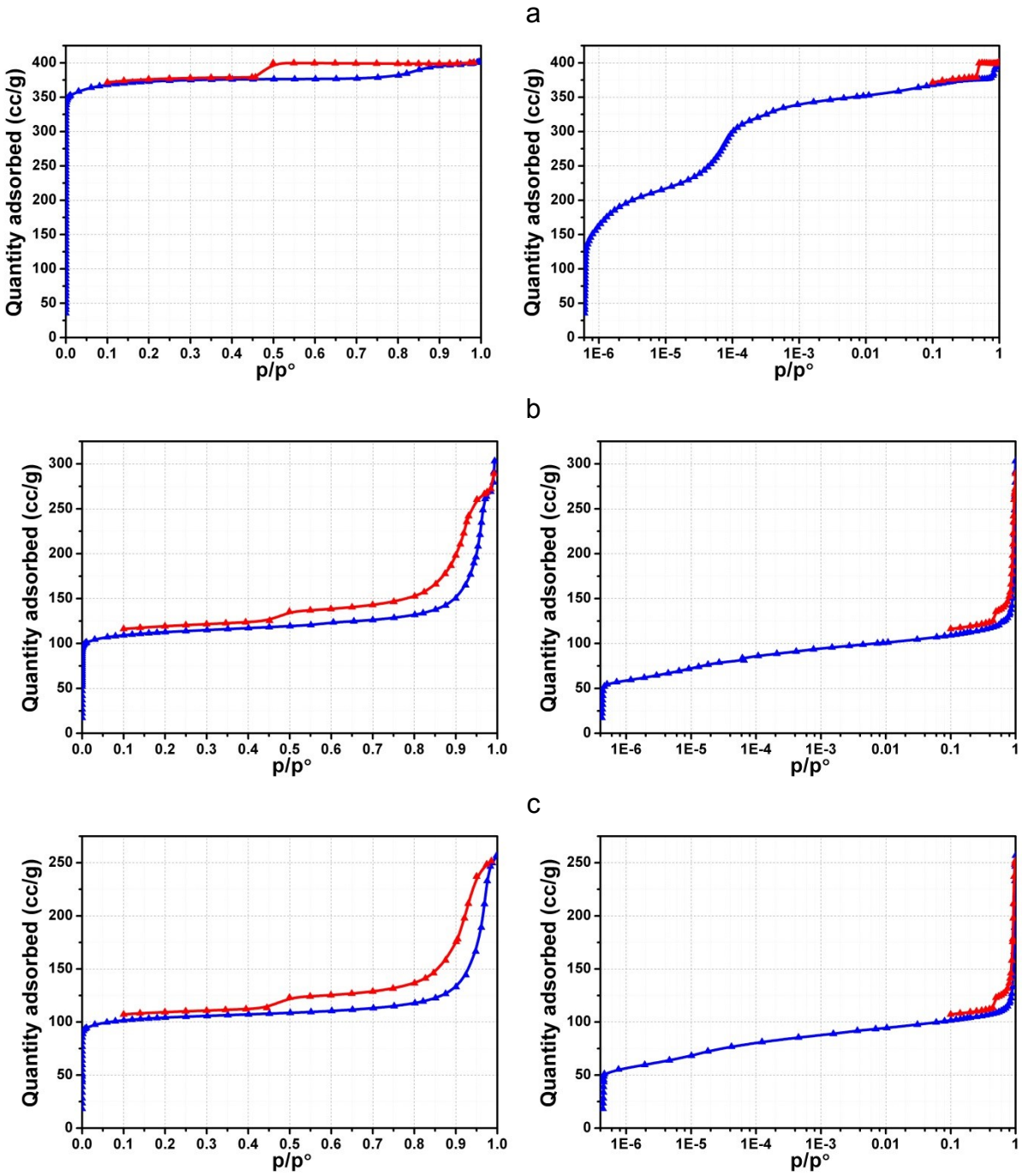

Figure SI1. Experimental low temperature nitrogen adsorption/desorption isotherms for ***Cu-BTC+Pt/C+Glu*** mixture: as-prepared (a), after carbonization (b), and after first hydrogenation (c).

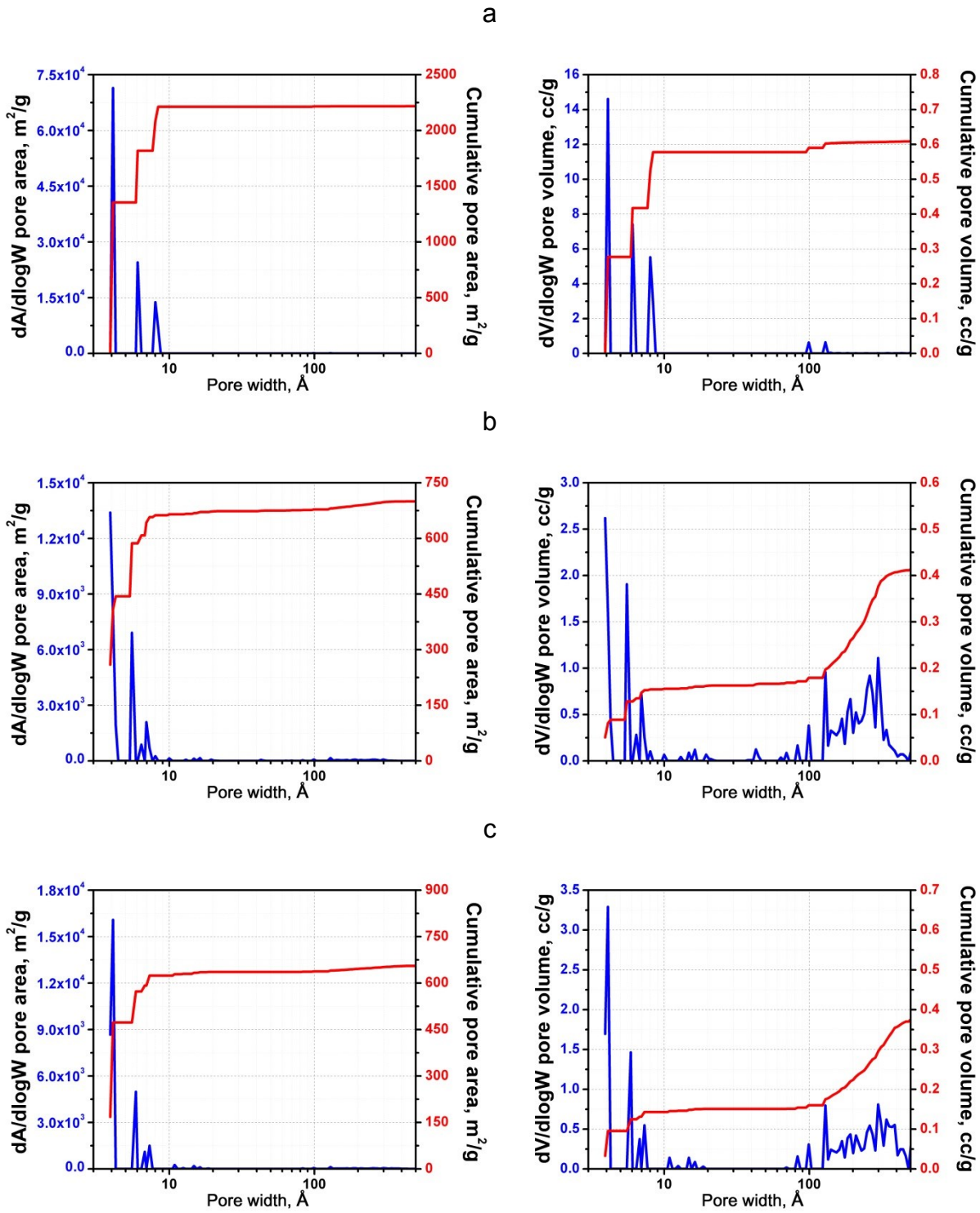

Figure SI2. Pore size distribution, cumulative pore area, and cumulative pore volume for ***Cu-BTC+Pt/C+Glu*** mixture: as-prepared (a), after carbonization (b), and after first hydrogenation (c).

Table SI1. Refined structure parameters of the studied materials from XRD data.

Sample	a (Å)	b (Å)	V(Å^3)	Space group	GOF	Rp	wRp
Cu-BTC	26.314(2)	-	18221	$Fm\bar{3}m$	1.13	2.71	3.68
Cu-BTC-milled	26.318(8)	-	18230	$Fm\bar{3}m$	1.35	3.02	4.16
Cu-BTC+Pt/C	26.310(19)	-	18213	$Fm\bar{3}m$	1.39	3.74	4.54
Cu-BTC+Pt/C+Glu	26.41(3)	-	18413	$Fm\bar{3}m$	1.87	4.31	5.96
Cu-BTC+Pt/C-b	26.563(13)	28.298(19)	19968	P4/mmm	2.73	5.68	7.65
Cu-BTC+Pt/C-b+H_2	26.20(3)	26.39 (4)	18120	P4/mmm	2.86	6.01	7.98

Table SI2. Specific surface area and pore volume evaluated from nitrogen adsorption by BET theory and NLDFT approach.

Sample	BET theory		2D-NLDFT-HS		
	p/p^0 range	Surface area, m^2/g	Cumulative surface area, m^2/g	Cumulative pore volume, cm^3/g	RMSD, cm^3/g
Initial mixture **Cu-BTC+Pt/C+Glu**	0 – 0.011	1517	2005	0.57	4.88
After carbonization **Cu BTC+Pt/C-b**	0 – 0.030	440	640	0.40	0.68
After carbonization and hydrogenation **Cu-BTC+Pt/C-b+H_2**	0 – 0.031	390	613	0.37	0.64

EPR experiment details

The EPR spectra of the samples were modeled as the sum of the spectra of complexes with spins 1/2 and 1 with different spin Hamiltonian parameters:

$$\hat{H} = \beta(g_x S_x H_x + g_y S_y H_y + g_z H_z S_z) + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2)$$

where S = 1/2, 1 - full complex spin; S_x, S_y, S_z – projections of the full spin on the x, y, z axis, respectively; D, E – components of the subtle interaction tensor (for S = 1); g_x, g_y, g_z – components of g-tensor; H – applied magnetic field.

Parameters D and E, components of g-tensor and relative concentrations of complexes are given in the Table S2. The Figures S2-S5 represent the experimental spectra in comparison with the simulated ones.

Table SI3. Spin Hamiltonian parameters

№	S	№	C %	g_x	g_y	g_z	D(cm^{-1})	E(cm^{-1})
Cu-BTC	1	1	16	2.03	2.15	2.32	0.4219	0.1292
	1/2	1	84	2.15	2.16	2.21	0.0	0.0
Cu-BTC+Pt/C	1	1	83	2.03	2.15	2.32	0.4209	0.1292
	1/2	1	17	2.15	2.15	2.19	0.0	0.0
Cu-BTC+Pt/C-b+H_2	1	1	24	2.06	2.13	2.29	0.4256	0.1235
		2	47	2.08	2.20	2.40	0.0692	0.0037
	1/2	1	29	2.10	2.07	2.32	0.0	0.0
Cu-BTC+Pt/C-b	1	1	29	2.06	2.13	2.29	0.4116	0.1122
		2	57	2.08	2.20	2.40	0.0702	0.0047
	1/2	1	14	2.09	2.06	2.32	0	0

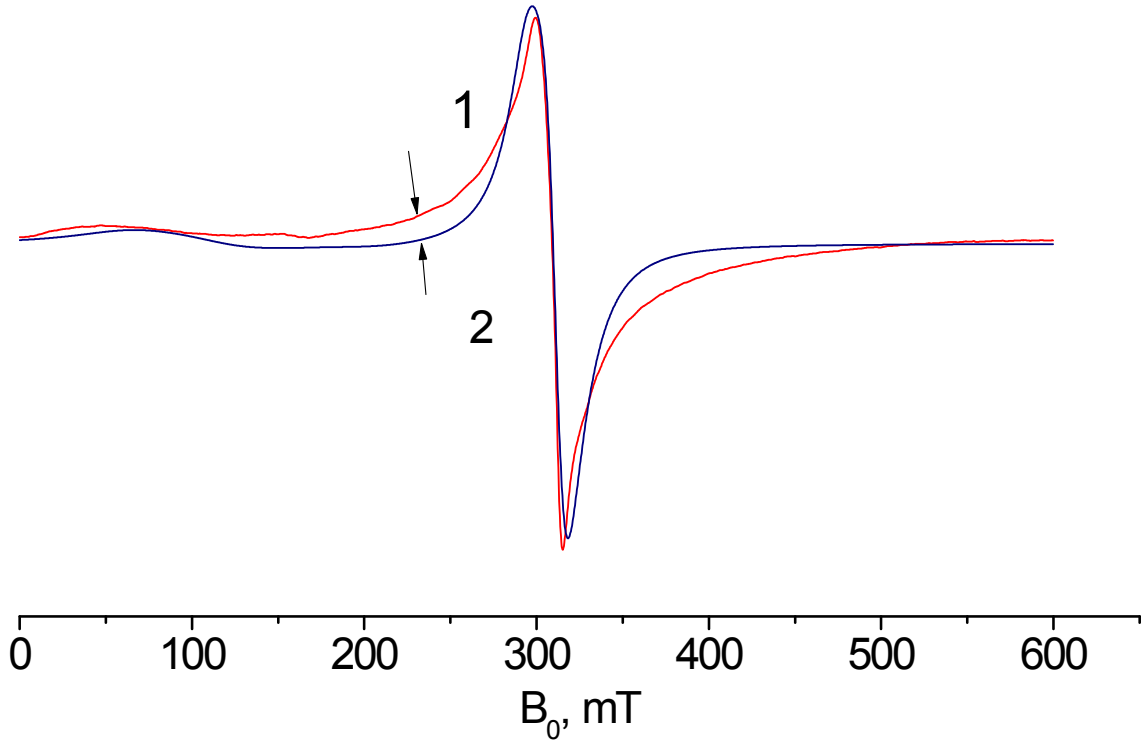

Fig. SI3. EPR spectrum of the pristine Cu-BTC; 1- experimental, 2 - simulated.

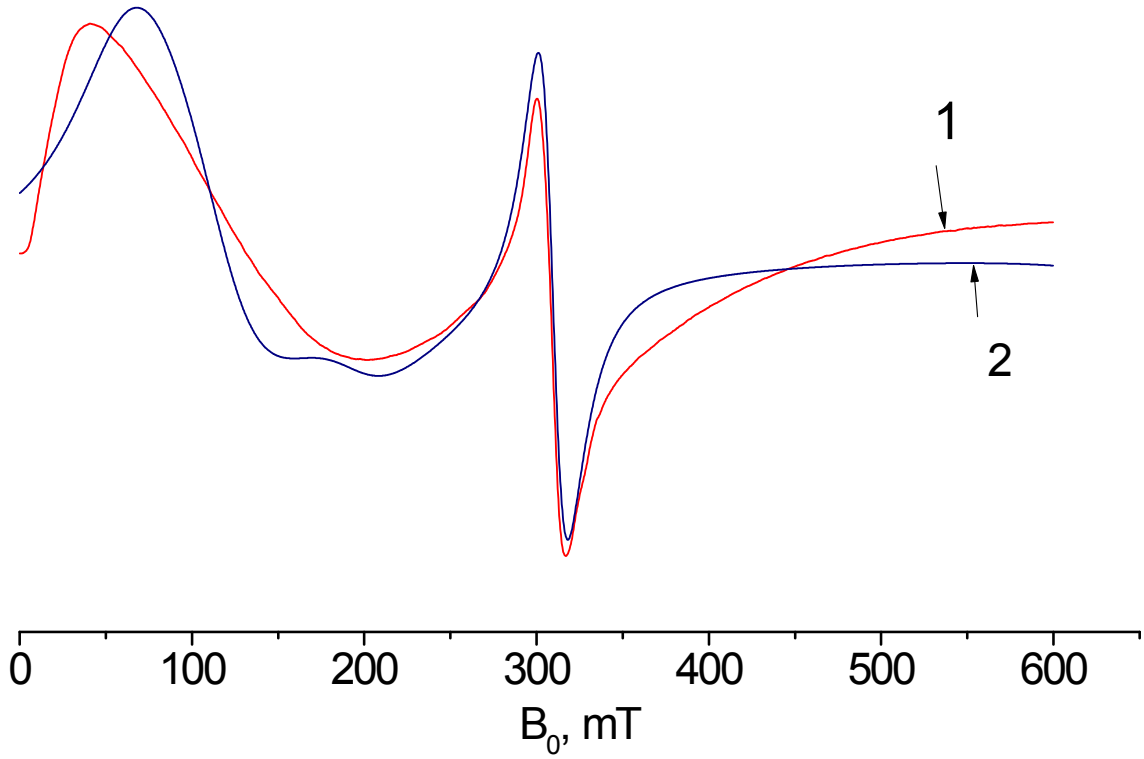

Fig. SI4. EPR spectrum of Cu-BTC+Pt/C; 1- experimental, 2 - simulated.

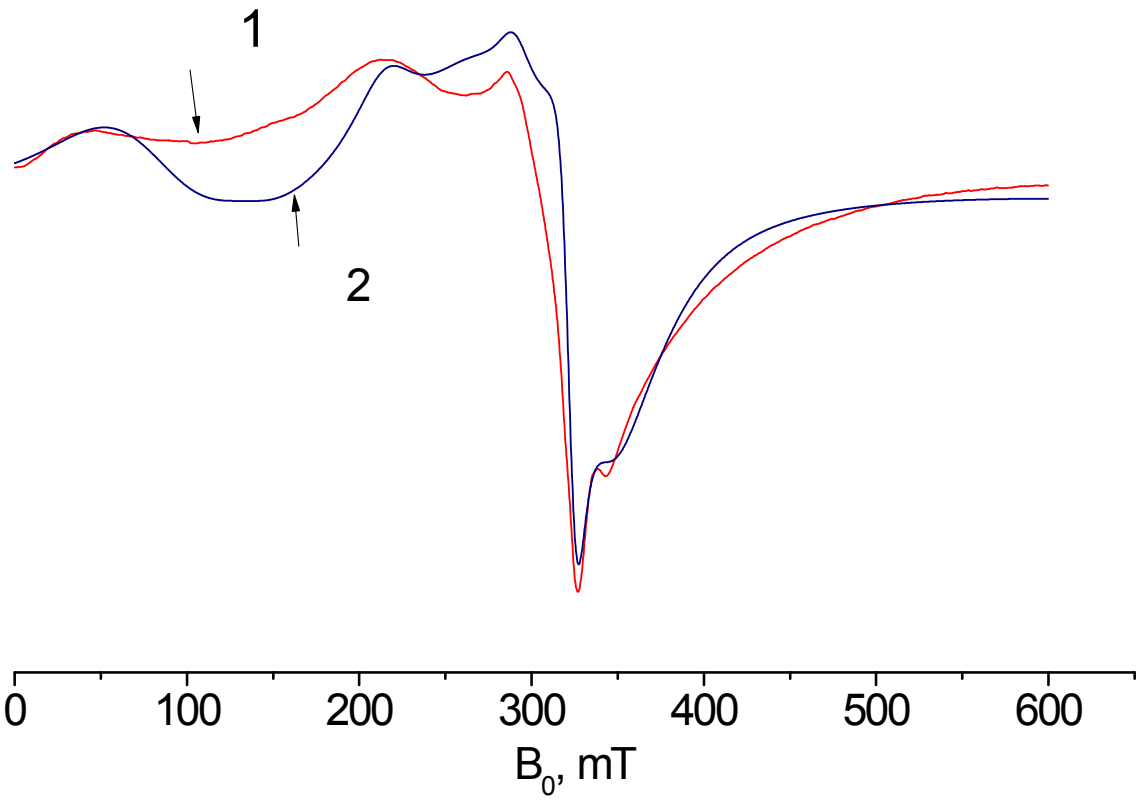

Fig. SI5. EPR spectrum of Cu-BTC+Pt/C-b; 1- experimental, 2 - simulated.

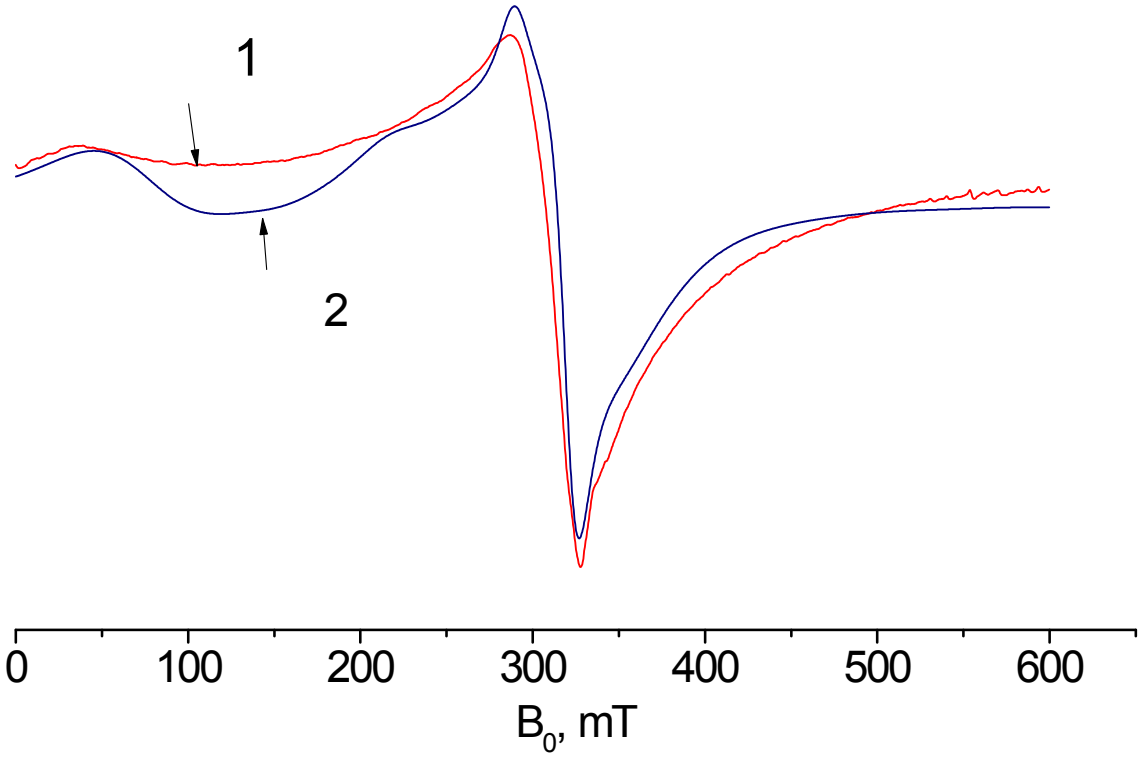

Fig. SI6. EPR spectrum of Cu-BTC+Pt/C-b+H_2; 1- experimental, 2 - simulated.

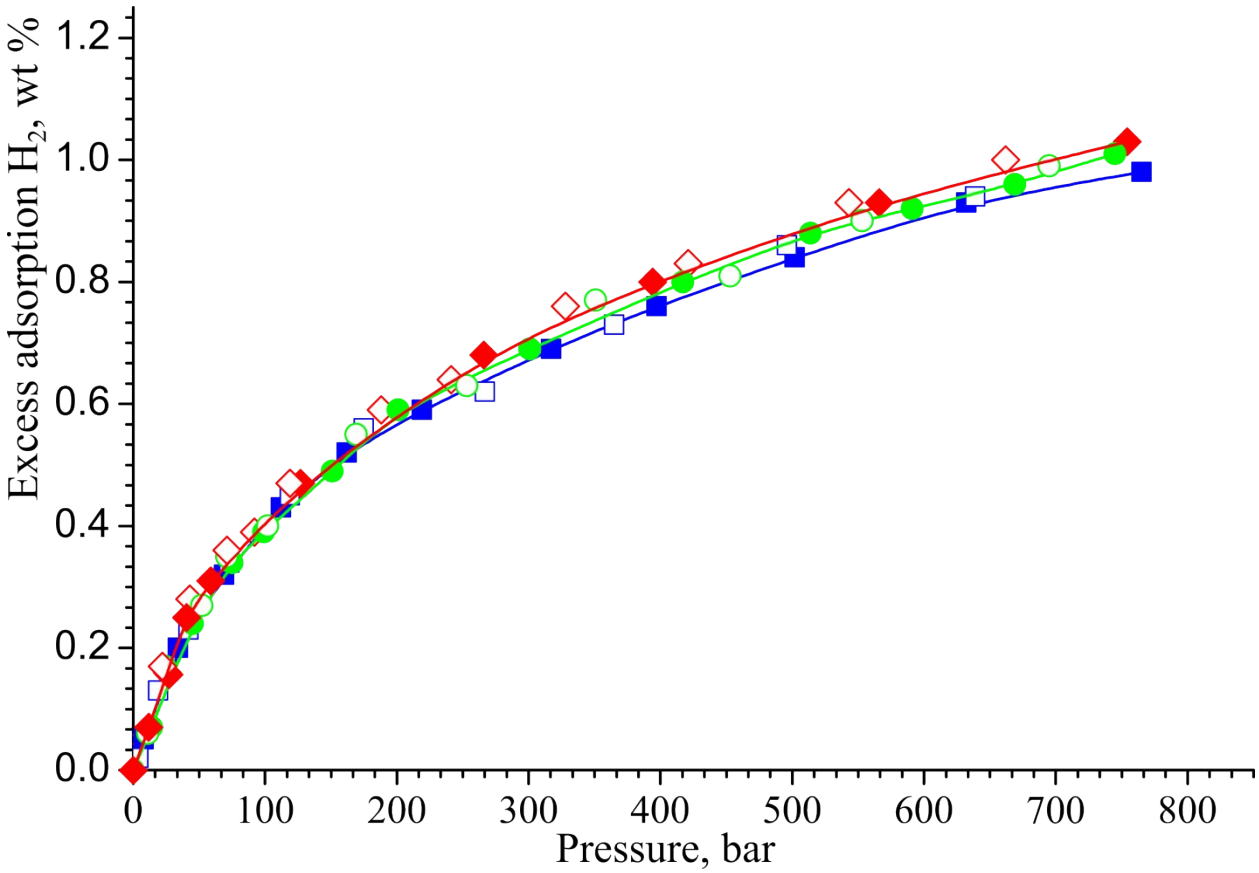

Fig. SI7. Hydrogen adsorption (close symbols) and desorption (open symbols) isotherms on Cu−BTC+Pt/C-b at 293 K; 2nd (♦), 3rd (■), 4th (●) cycles