Supplementary information

Mechanochemical defect engineering of HKUST-1 and impact of the resulting defects on carbon dioxide sorption and catalytic cyclopropanation

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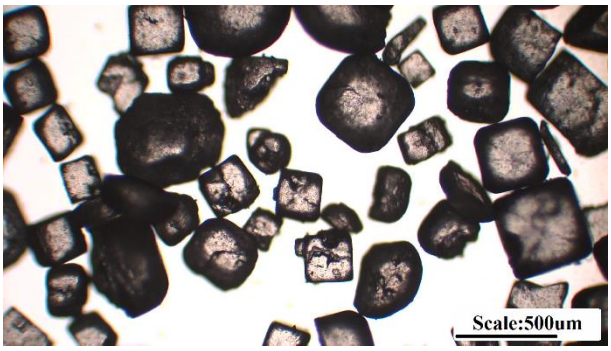
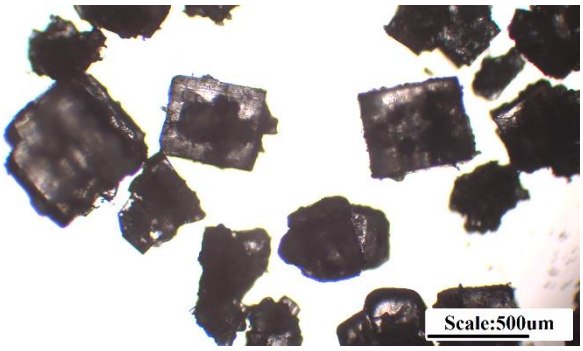
A. Optical microscopy morphological and size characterization of the reactants used for the mechanochemical syntheses and of the HKUST-1 single crystals.

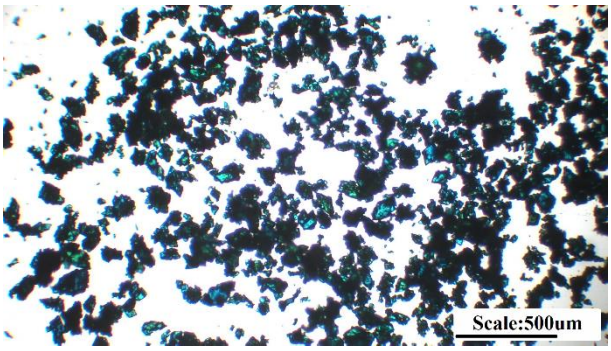
Sodium chloride



Trimesic acid



Copper (II) acetate monohydrate



HKUST-1 single crystals

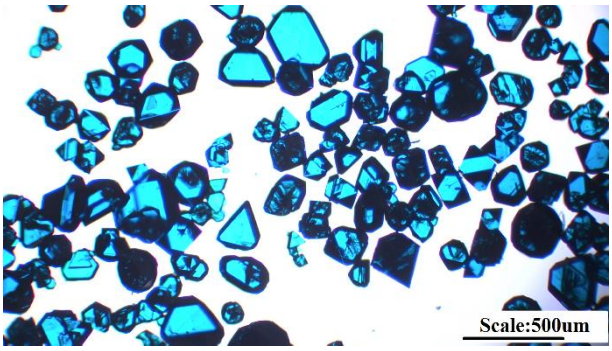


Fig. S1. X-ray powder patterns of the HKUST-1 materials obtained through the different synthesis pathways.

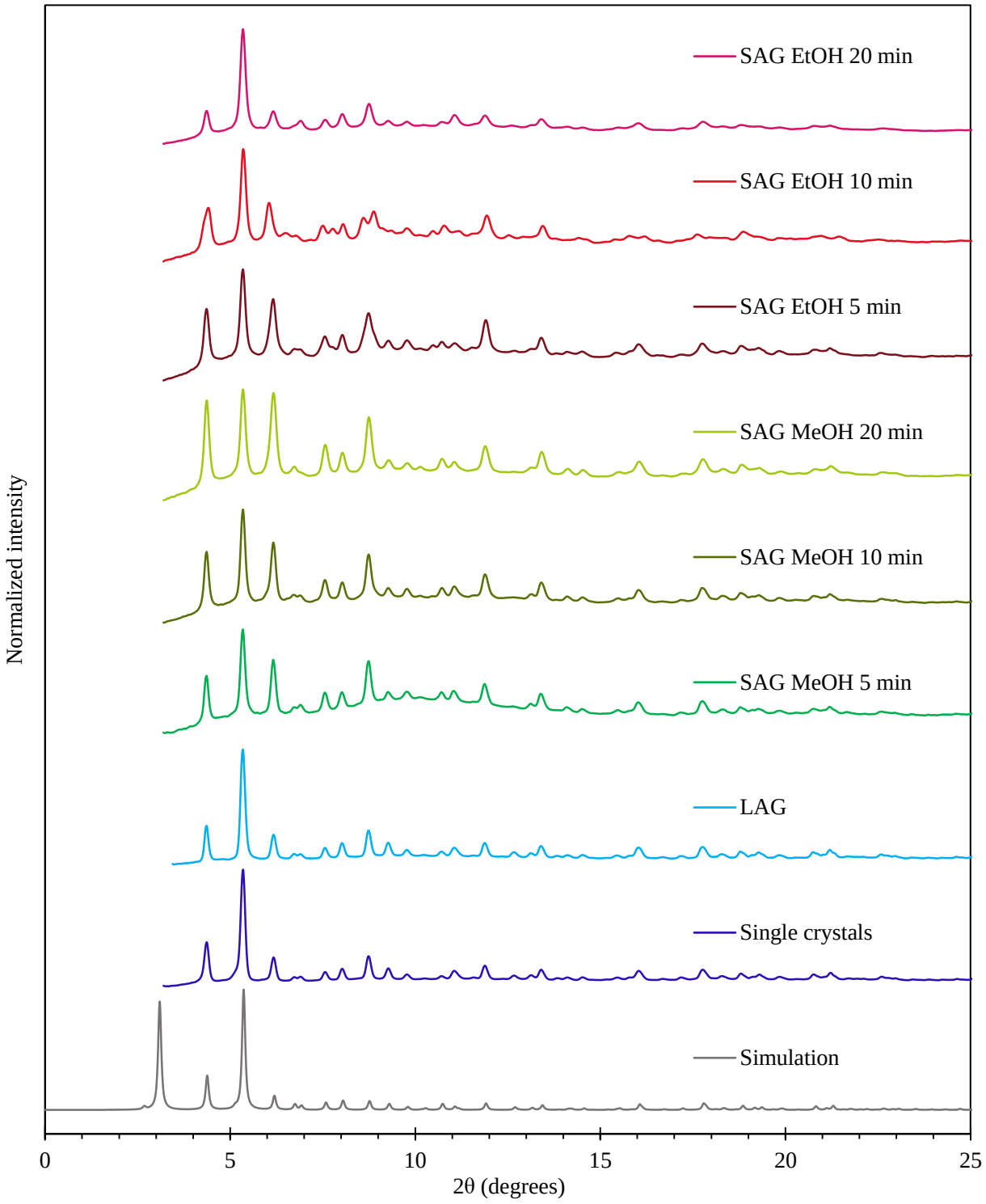


Fig. S2. A. FTIR spectra of copper (II) acetate monohydrate and trimesic acid.

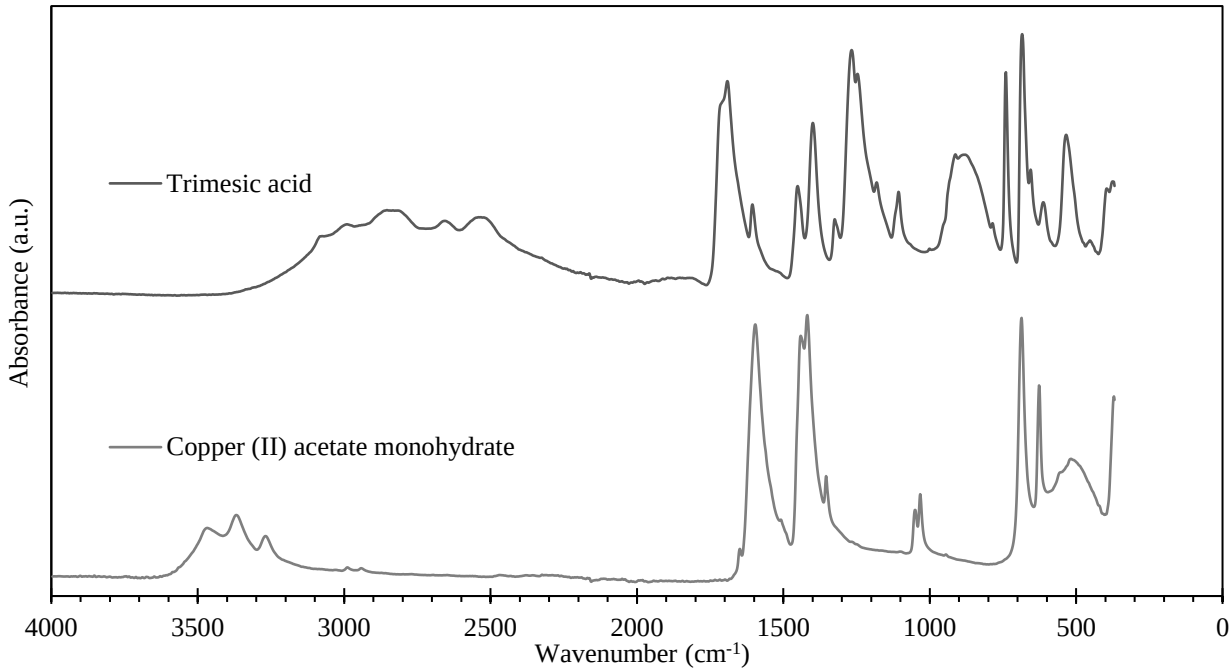


Fig. S2. B. FTIR spectra of as synthesized and activated (150°C, vacuum) samples of HKUST-1 synthesized by LAG. The ν C–O bands of ethanol (arrow) disappear upon activation.

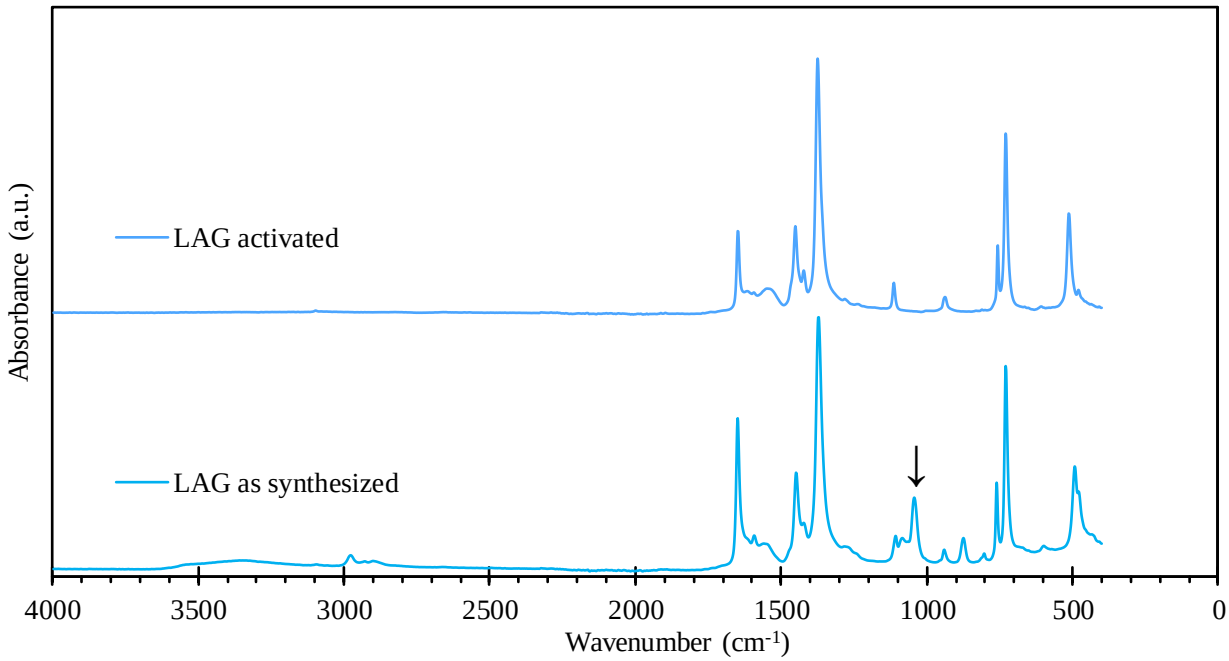


Fig. S2. C. FTIR spectra of activated (150°C, vacuum) HKUST-1 materials.

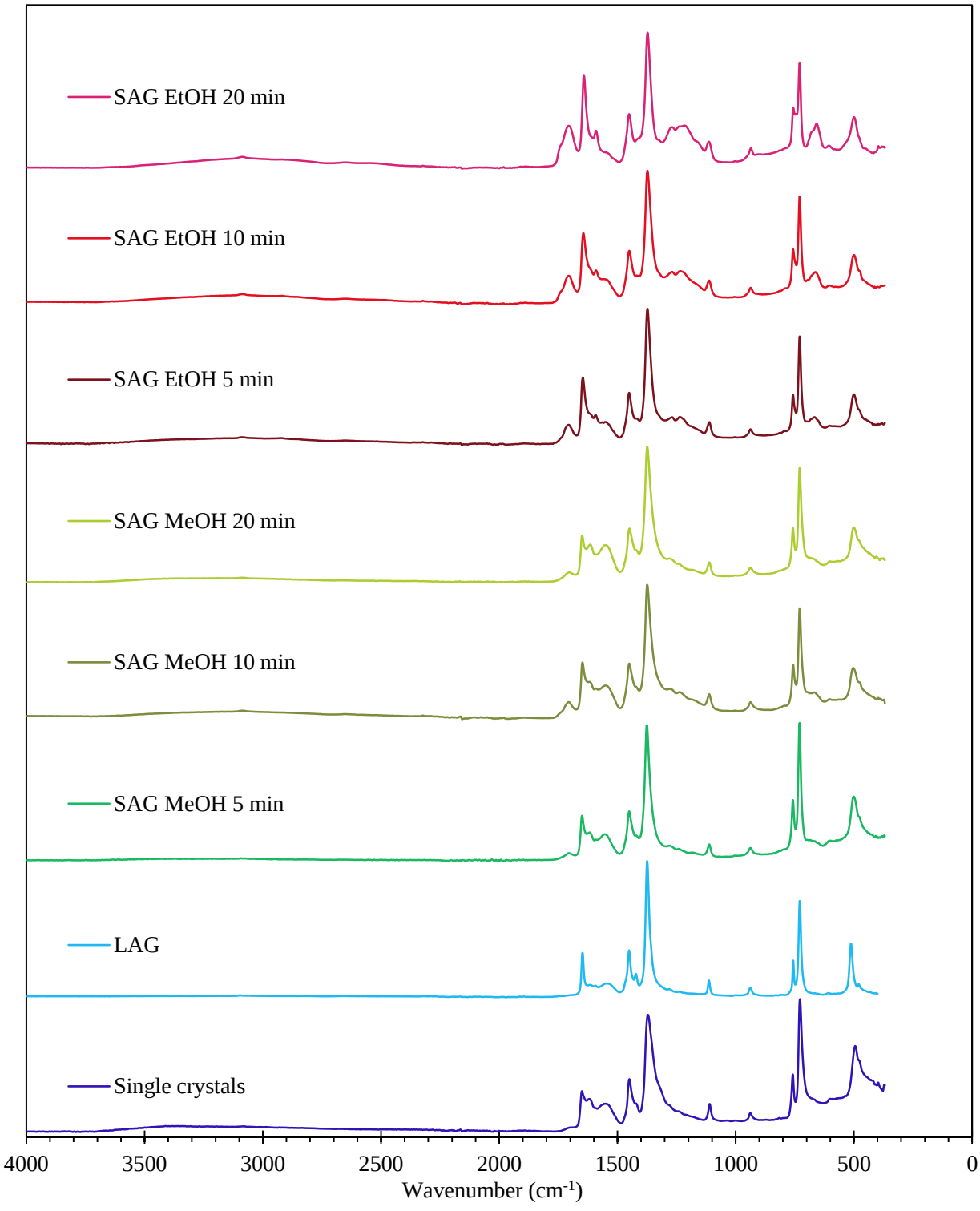


Fig. S3. NH_3 temperature-programmed desorption on HKUST materials prepared by SAG and treated with ethanol in comparison with the sample prepared by LAG.

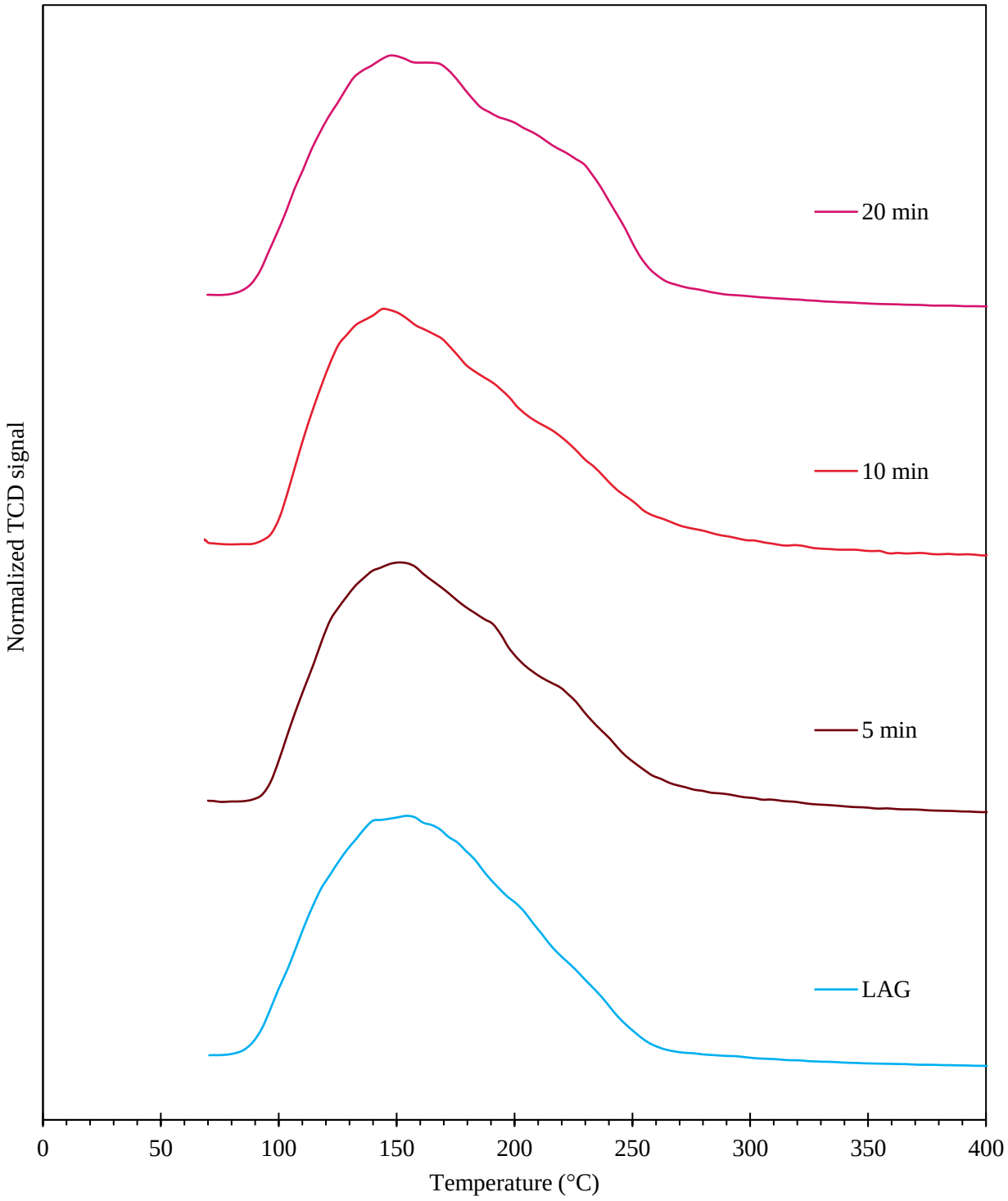


Fig. S4. A1. TGA analyses (under air) of HKUST-1 single crystals (as synthesized and powdered).

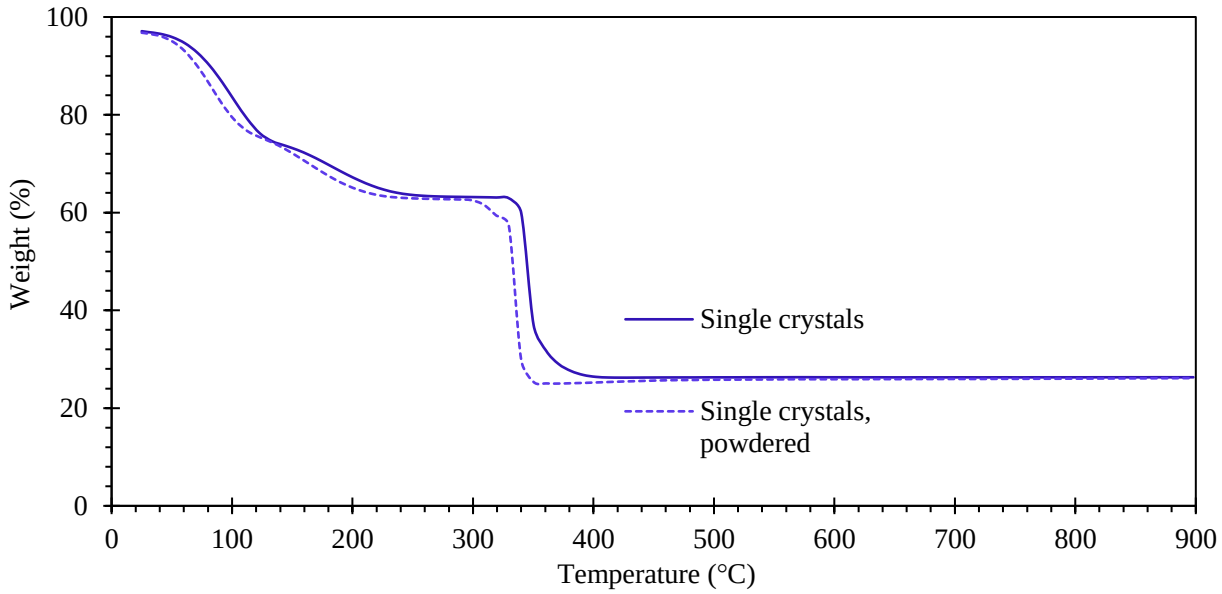


Fig. S4. A2. TGA analysis (under air) of HKUST-1 obtained by LAG.

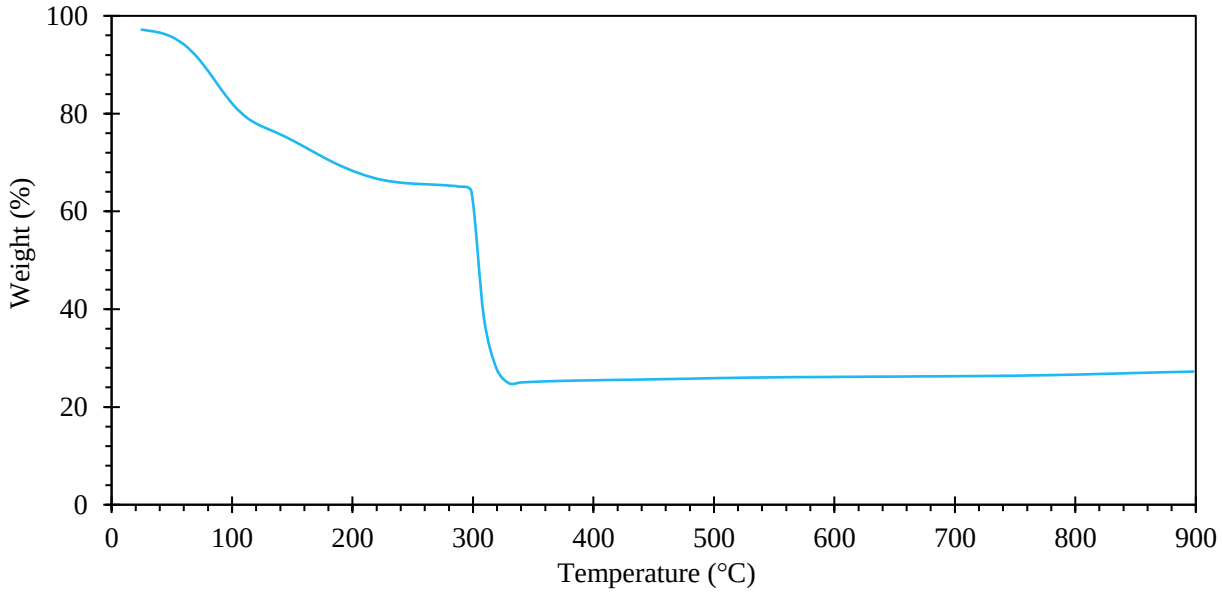


Fig. S4. A3. TGA analysis (under air) of HKUST-1 obtained by SAG (5 min) and treated with MeOH.

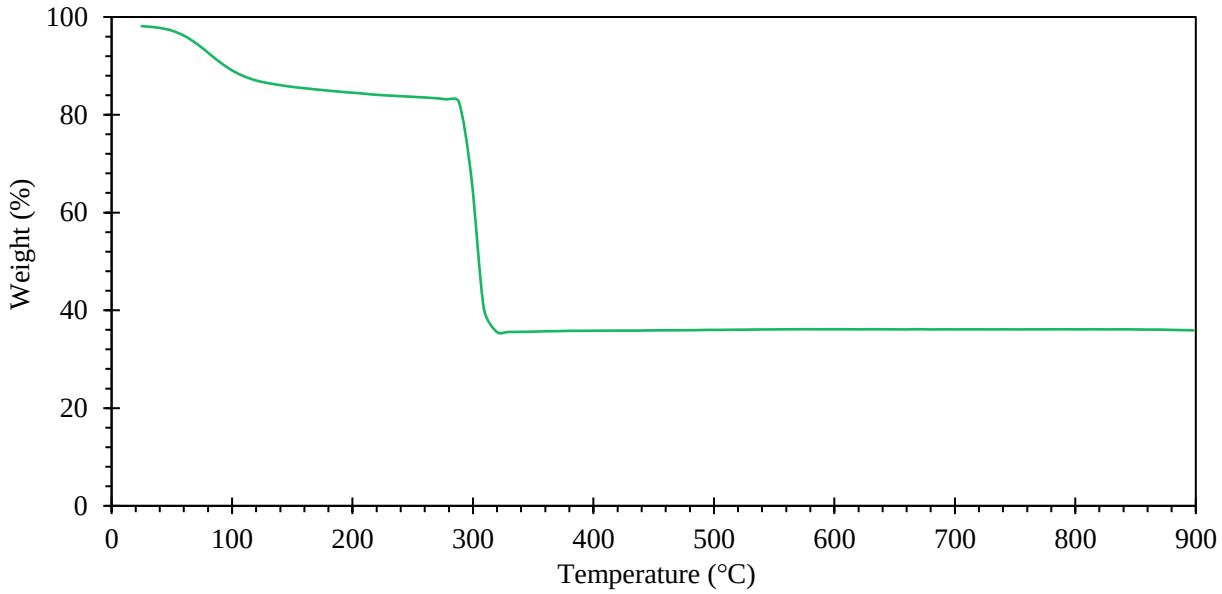


Fig. S4. A4. TGA analysis (under air) of HKUST-1 obtained by SAG (10 min) and treated with MeOH.

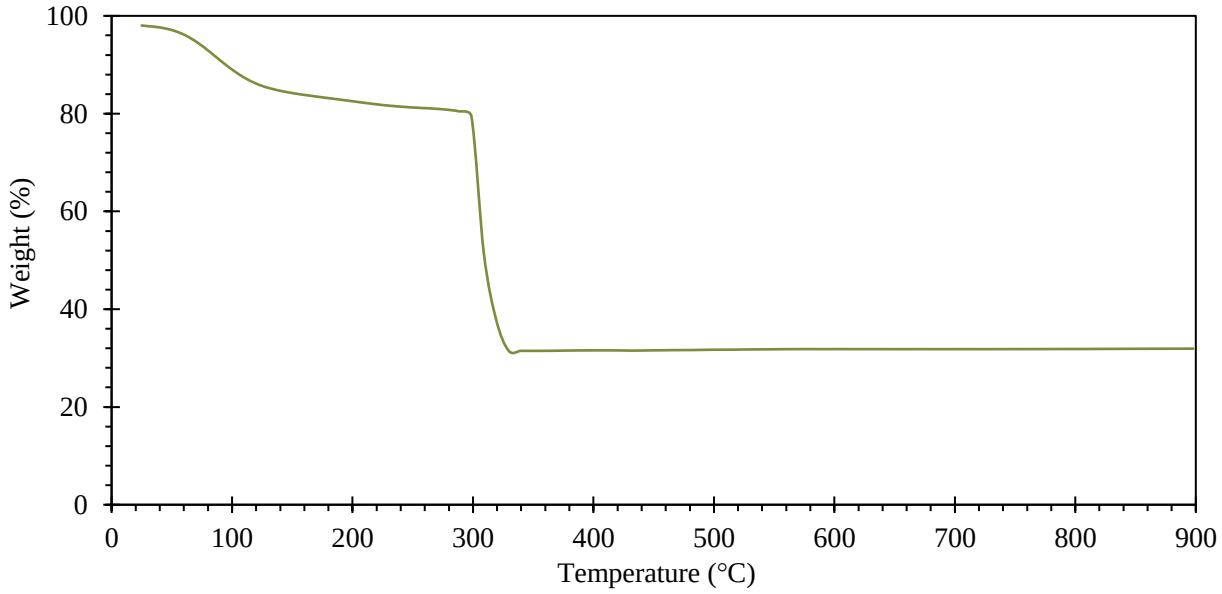


Fig. S4. A5. TGA analysis (under air) of HKUST-1 obtained by SAG (20 min) and treated with MeOH.

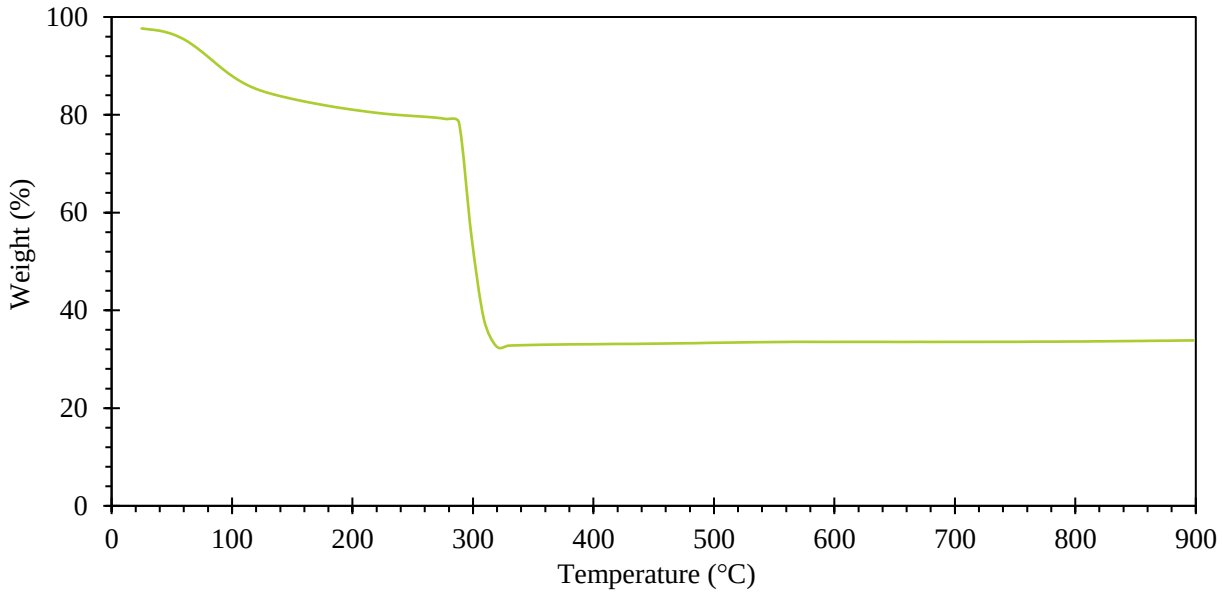


Fig. S4. A6. TGA analysis (under air) of HKUST-1 obtained by SAG (5 min) and treated with EtOH.

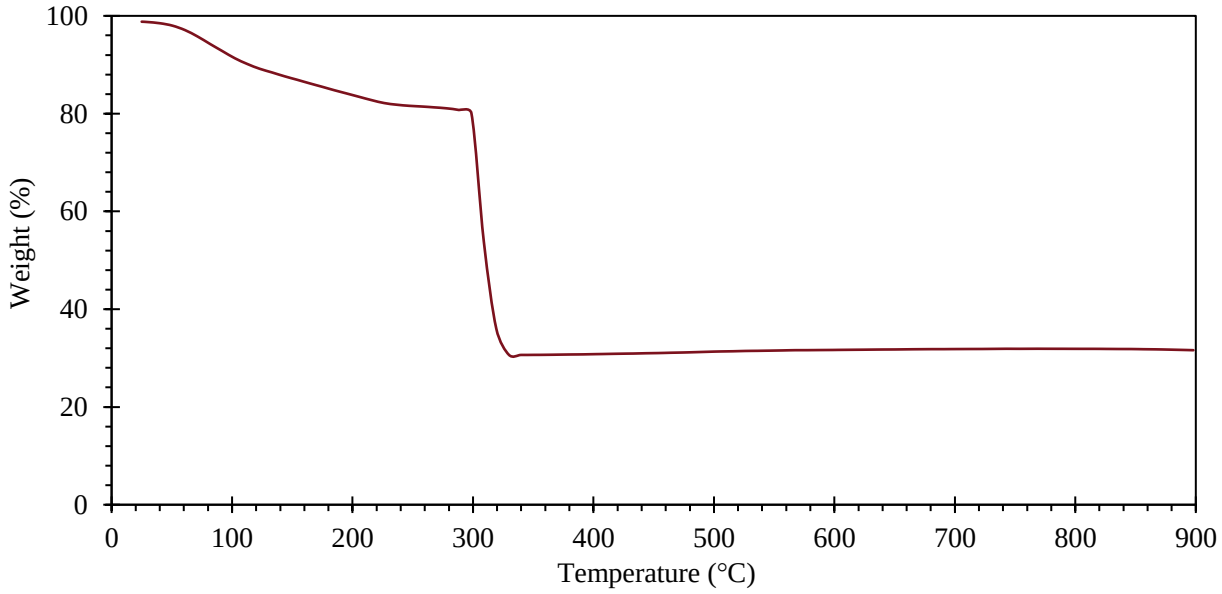


Fig. S4. A7. TGA analysis (under air) of HKUST-1 obtained by SAG (10 min) and treated with EtOH.

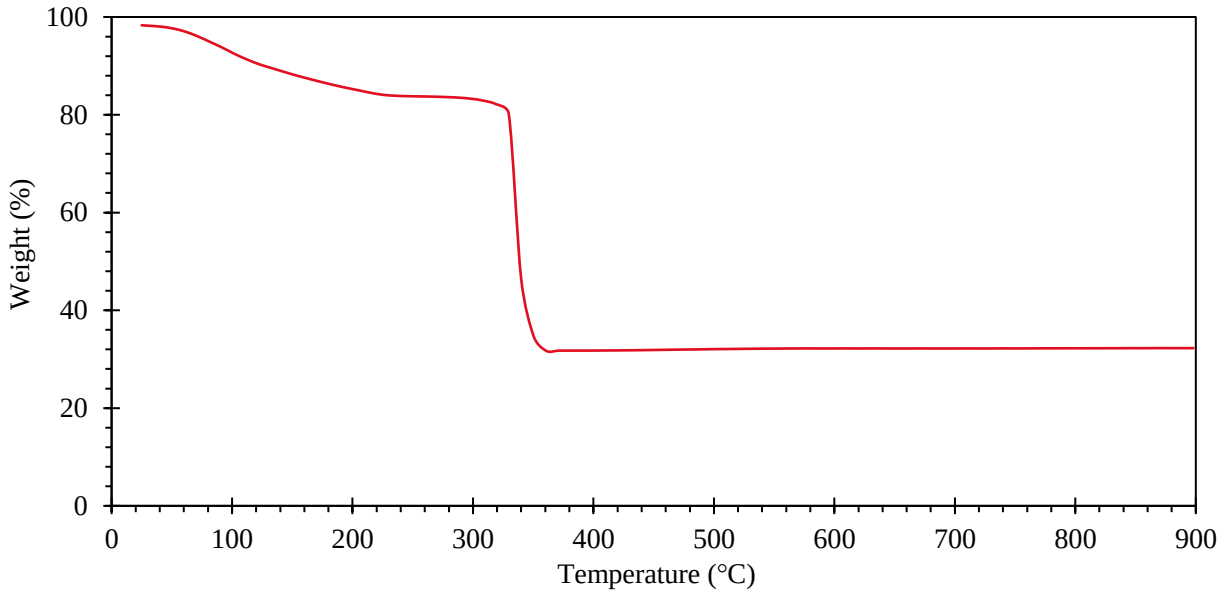


Fig. S4. A8. TGA analysis (under air) of HKUST-1 obtained by SAG (20 min) and treated with EtOH.

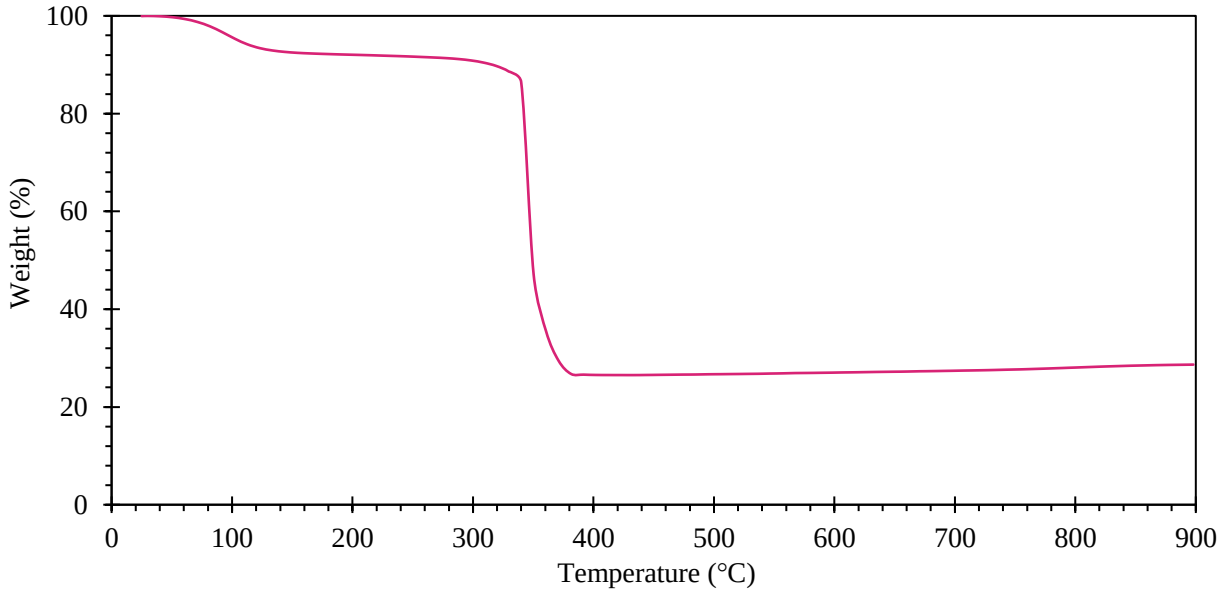


Fig. S4. A9. TGA analysis (under air) of trimesic acid.

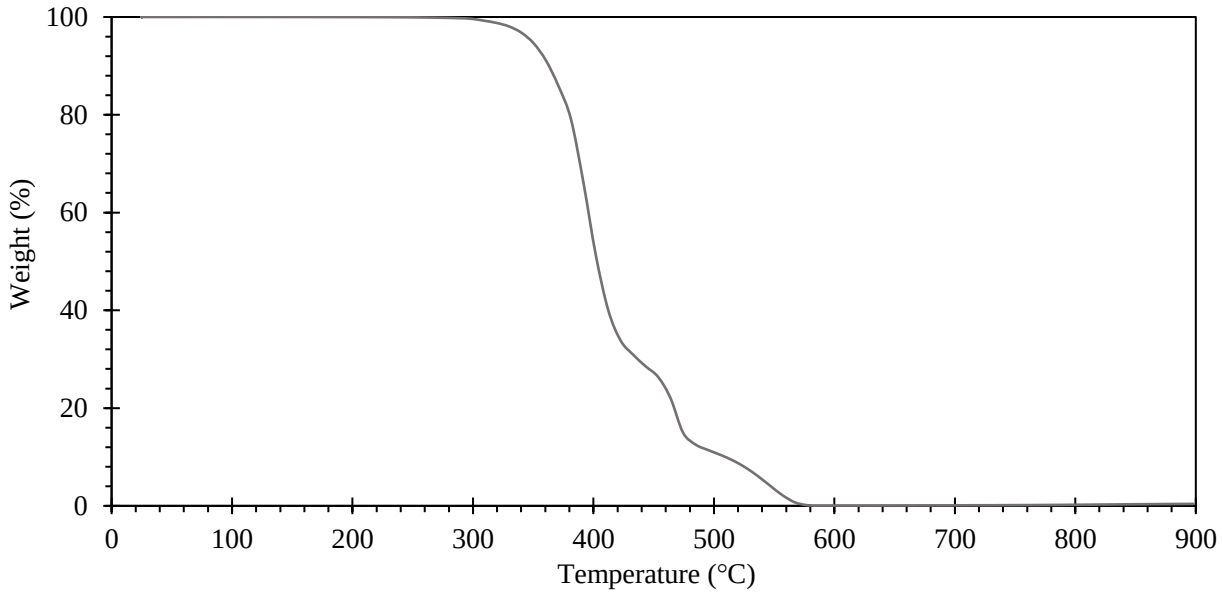


Fig. S4. A10. TGA analysis (under air) of copper (II) acetate.

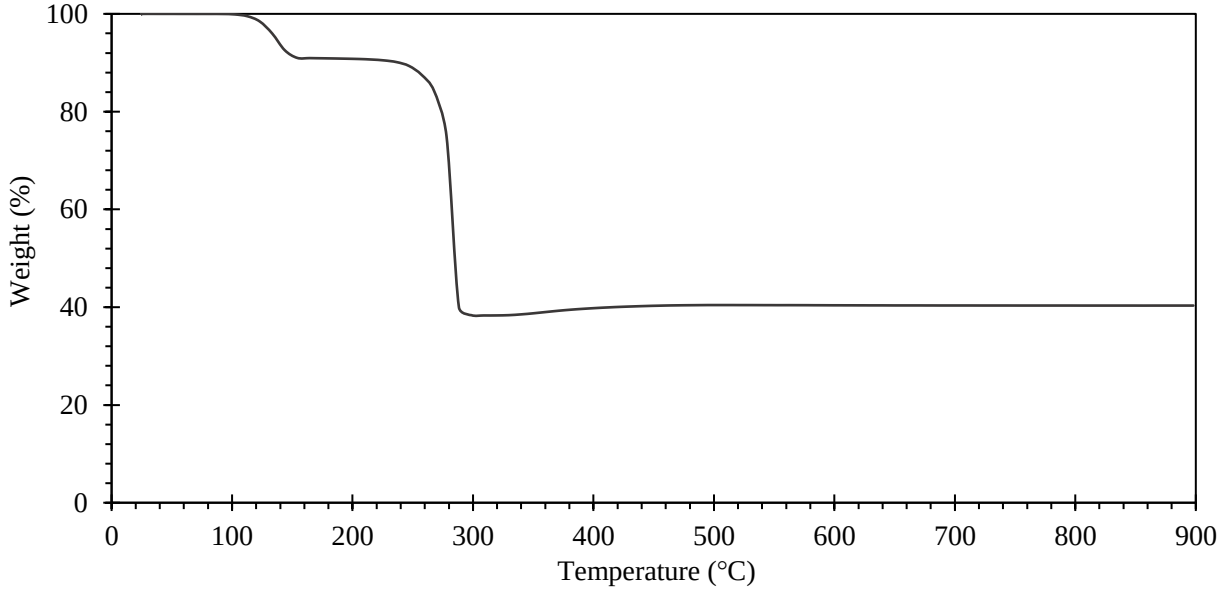


Fig. S4. B. Weight losses during decomposition of the HKUST-1 materials and calculated value for a perfect Cu_3BTC_2 structure. Error bars of 1% are shown, corresponding to the typical error for TGA measurements.

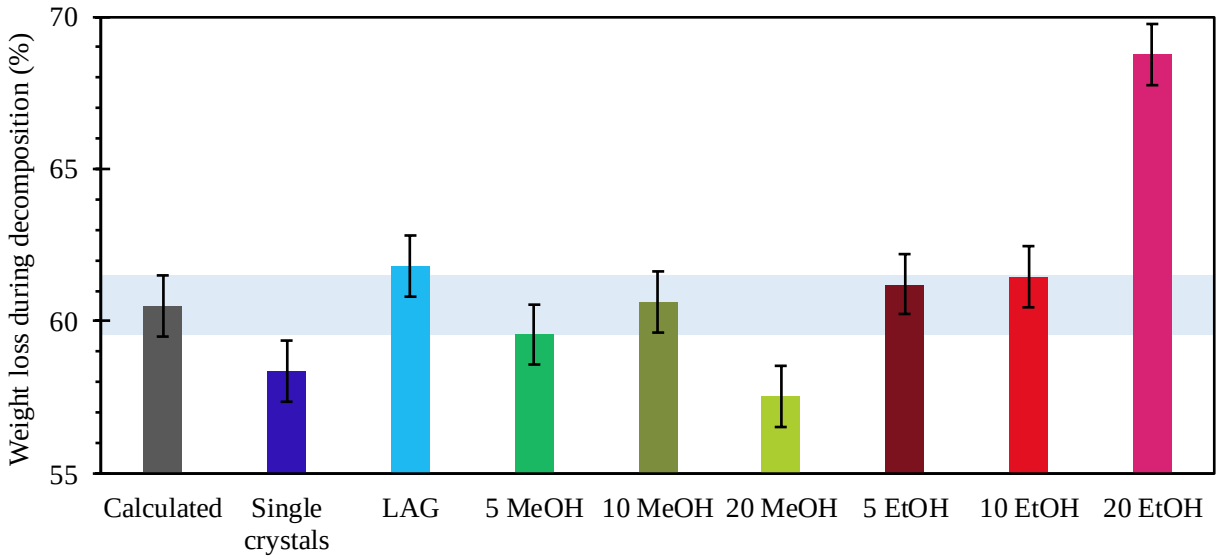


Fig. S4. C. Decomposition temperatures of the HKUST-1 materials determined by TGA under air.

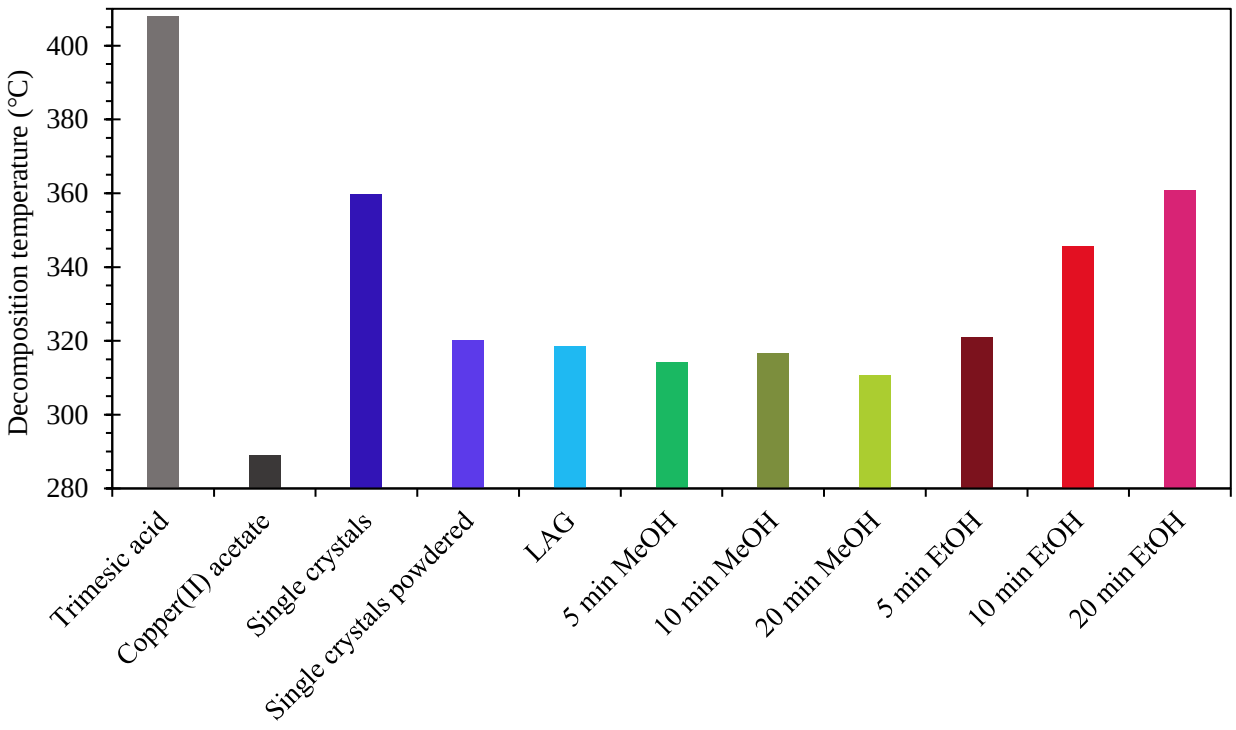


Fig. S5. A. Cu^{I}/Cu^{II} surface ratios determined by XPS for the HKUST-1 materials *(the single crystal samples were ground before analysis, the resulting data is thus not representative of the external surface composition whereas it is for all the other samples that were analyzed as such).*

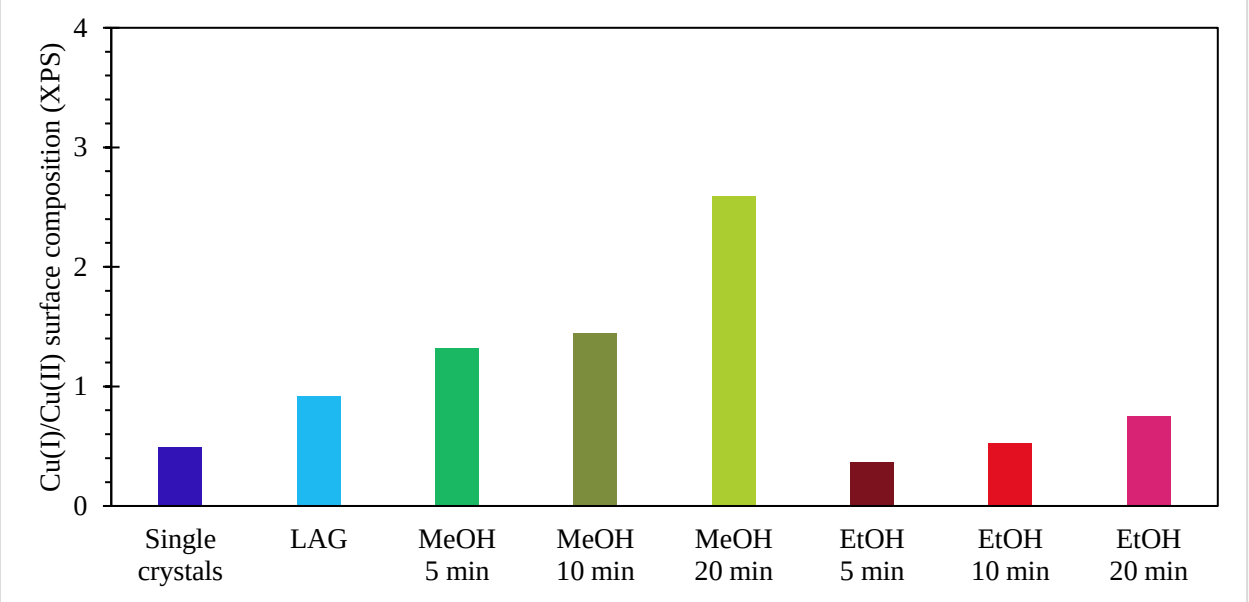


Fig. S5. B. Cu/O and Cu/C atomic ratios determined by XPS for the HKUST-1 materials.

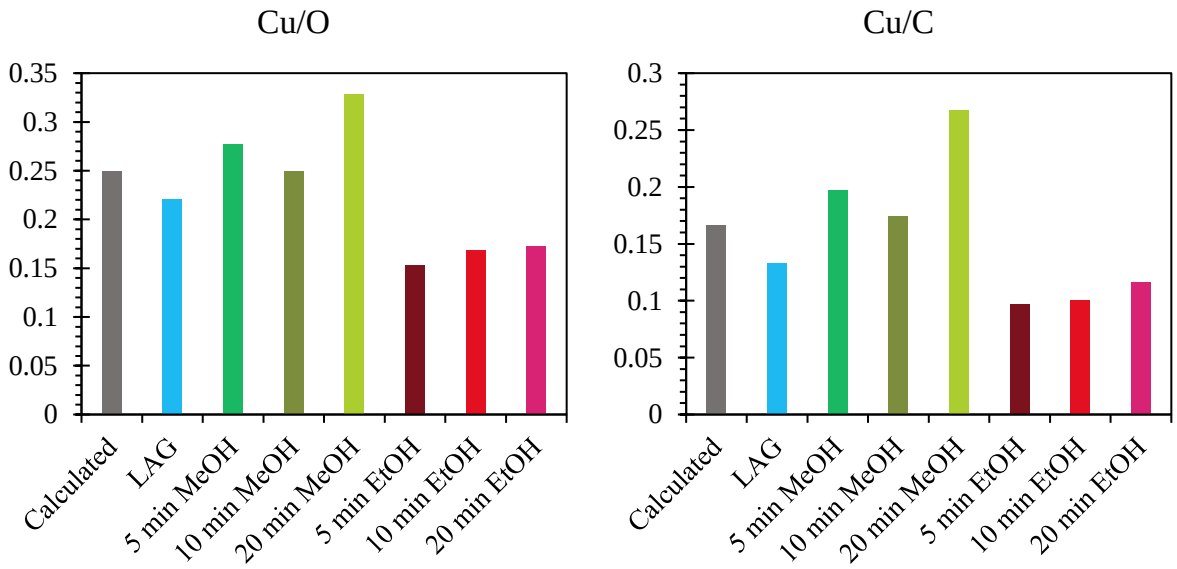


Fig. S5. C. Cu2p region of the XPS spectra of the HKUST-1 materials.

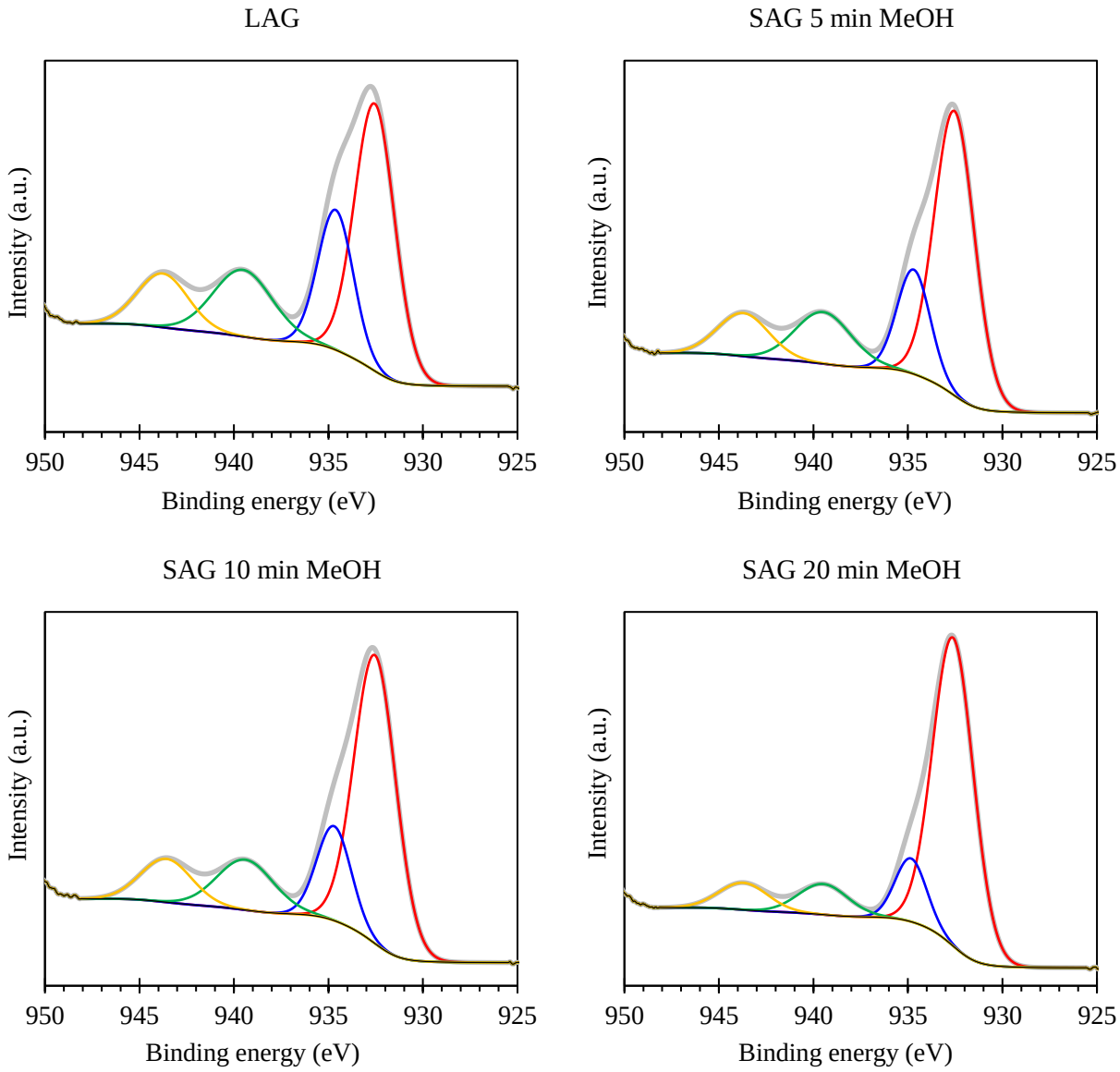
Attribution of deconvolution peaks:

Red: Cu(I) $2p_{3/2}$

Blue: Cu(II) $2p_{3/2}$

Green: Cu(II) $2p_{sat.}$

Yellow: Cu(II) $2p_{sat.}$



Attribution of deconvolution peaks:

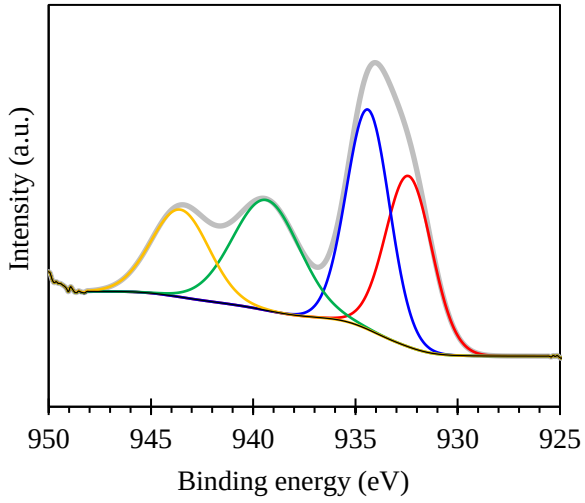
Red: Cu(I) $2p_{3/2}$

Blue: Cu(II) $2p_{3/2}$

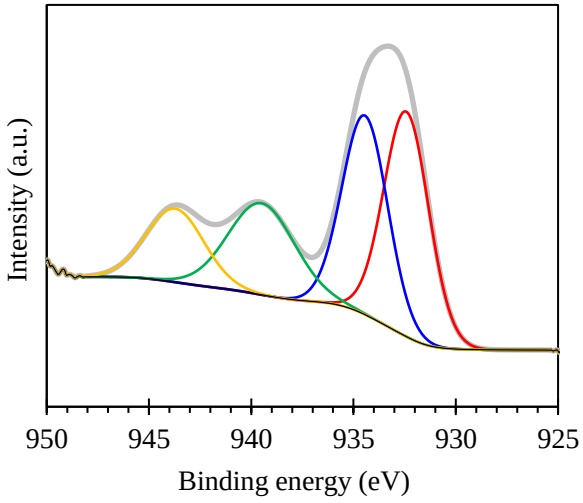
Green: Cu(II) $2p_{sat.}$

Yellow: Cu(II) $2p_{sat.}$

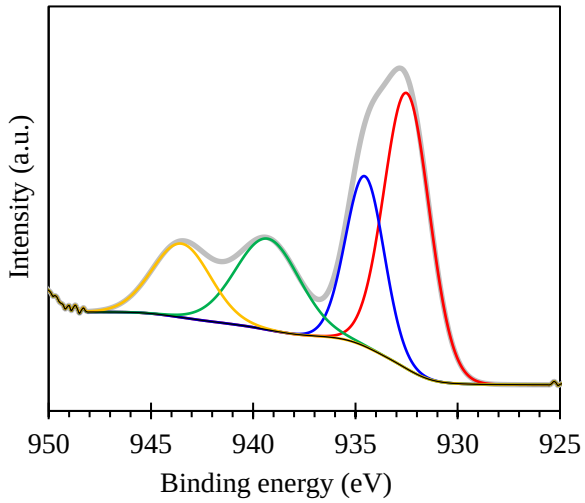
SAG 5 min EtOH



SAG 10 min EtOH



SAG 20 min EtOH



- Fig. S5 -

Table S1. CO_2 uptakes for illustrative porous materials.

Type of material	Material	Uptake (mmol/g)	Uptake (weight %)	T (K)	P	Reference
MOF	HKUST-1 SAG EtOH washed samples	0.5†	2.0	300	1 bar	*This study*
	HKUST-1 single crystals	3.9†	17.0	300	1 bar	*This study*
	HKUST-1	1.8†	8.1	300	1 bar	1
	MIL-96	3.7	16.3†	303	3.5 bar*	2
	ZIF-100	1.0	4.2†	298	850 torr	2
	MIL-102	3.4	15.0†	304	3 MPa*	2
	MIL-53	7.5	33.0†	304	20 bar*	2
	MIL-53	10.0	44.0†	304	30 bar*	2
	Mg-MOF-74	6.8†	30.1	298	1 bar	2
	Ni-MOF-74	4.4†	19.4	298	1 bar	2
	MIL-100(Cr)	2.2†	9.5	298	1 bar	2
	HKUST-1	2.9†	12.8	313	1 bar	2
MOF and corresponding post-synthetic modified derivatives	MIL-101	0.3	1.5†	298	0.15 bar	2
	MIL-101-PEI (polyethyleneimine)	4.2	18.5†	298	0.15 bar	2
	Mg-MOF-74	5.3†	23.4	298	760 torr	2
	Mg-MOF-74-TEPA (tetraethylenepentamine)	6.1†	26.9	298	760 torr	2
MOF composite materials	HKUST-1	6.9	30.1†	273‡	1 bar	2
	GO@HKUST-1	9.0	39.7†	273‡	1 bar	2
	ZIF-8	2.2	9.6†	273‡	1 bar	2
	ZIF-8/CNT	2.2	9.7†	273‡	1 bar	2
Activated carbon	from African palm shell	4.4	19.4†	298	n.a.	3
	from almond shell	2.1	9.2†	298	n.a.	3
	from rice husk	1.3	5.7†	298	n.a.	3
	from cotton stalk treated with NH_3 at 900°C	1.8	7.9†	298	n.a.	3
	Filtrasorb 400	11.1	48.9†	318	16 MPa*	4
	Filtrasorb 400	8.0	35.2†	318	5 MPa*	4
	Fibers (ACF A10)	4.4†	19.5†	273‡	100 kPa	5

† Converted values. * Pressures well above 1 bar and should thus not be directly compared to the results of this study. ‡ Temperatures well below 300 K and should thus not be directly compared to the results of our study. n.a. = non available.

1 Y. Chen, X. Mu, E. Lester and T. Wu, *Prog. Nat. Sci. Mater. Int.*, 2018, **28**, 584–589.

2 T. Ghanbari, F. Abnisa and W. M. A. Wan Daud, *Sci. Total Environ.*, 2020, **707**, 135090.

3 A. Mukherjee, J. A. Okolie, A. Abdelrasoul, C. Niu and A. K. Dalai, *J. Environ. Sci. (China)*, 2019, **83**, 46–63.

4 Y. Gensterblum, P. van Hemert, P. Billemont, A. Busch, D. Charriére, D. Li, B. M. Krooss, G. de Weireld, D. Prinz and K. H. A. A. Wolf, *Carbon N. Y.*, 2009, **47**, 2958–2969.

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Fig. S6. GC kinetic follow-up of the concentration of styrene, *cis* and *trans* cyclopropane and diethyl maleate and fumarate during the catalytic cyclopropanation of styrene with EDA using the LAG synthesized HKUST-1 material as catalyst.

The plot was obtained by using the following equation:

$$N_C = \frac{I_X}{I_{Styrene} + I_{trans-cyclopropane} + I_{cis-cyclopropane}}$$

In which N_C is the normalized concentration of the species X, I_X is the measured intensity of the GC signal of compound X, and $I_{Styrene}$, $I_{trans-cyclopropane}$ and $I_{cis-cyclopropane}$ are the intensities of the peaks observed for styrene, trans-cyclopropane and cis-cyclopropane respectively.

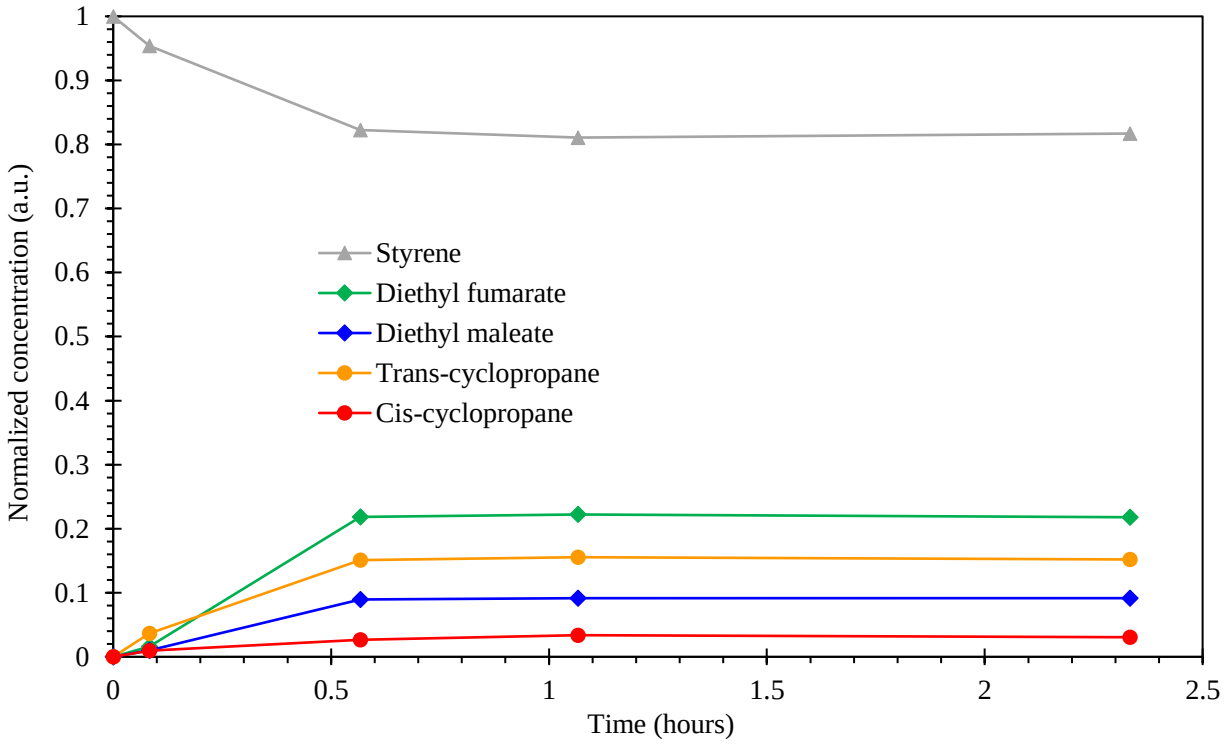


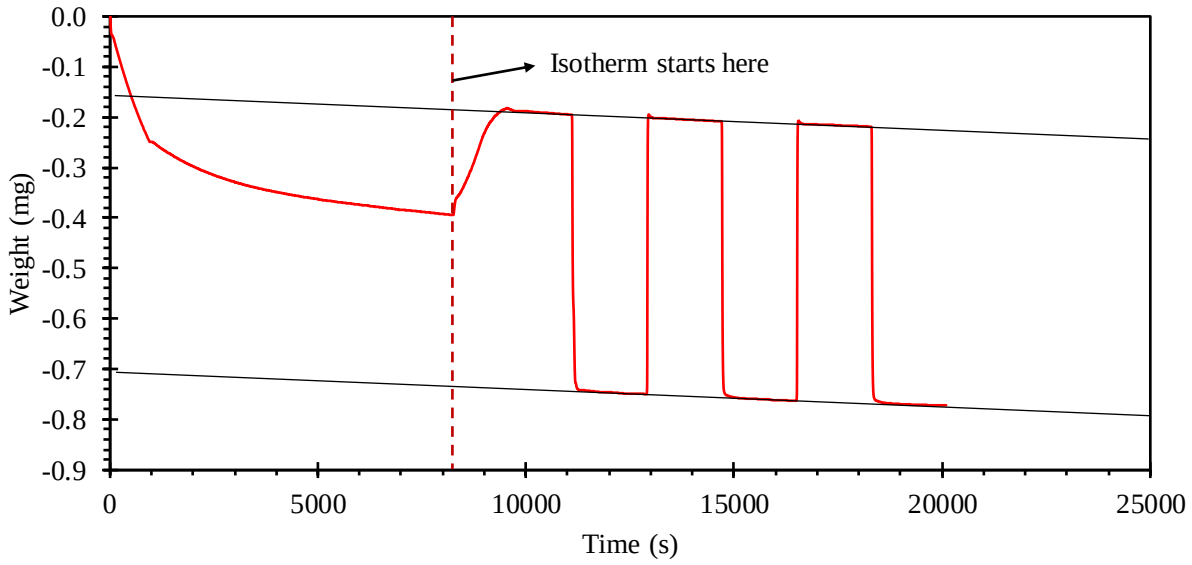
Table S2. Conversions and selectivity of the reaction of styrene with EDA obtained with the different tested catalysts.

Material	Conversion (%)	Selectivity (%)			
	EDA	Diethylfumarate	Diethylmaleate	*Cis*-cyclopropane	*Trans*-cyclopropane
None	0	-	-	-	-
Single crystals	92.6	36.1	19.8	13.0	31.1
LAG	100	26.0	10.8	20.4	42.9
5 min MeOH	7.2	49.0	30.2	6.3	14.6
10 min MeOH	15.2	38.7	28.6	13.4	19.3
20 min MeOH	100	25.7	12.9	20.6	40.8
5 min EtOH	1.9	*	*	*	*
10 min EtOH	0	-	-	-	-
20 min EtOH	0	-	-	-	-

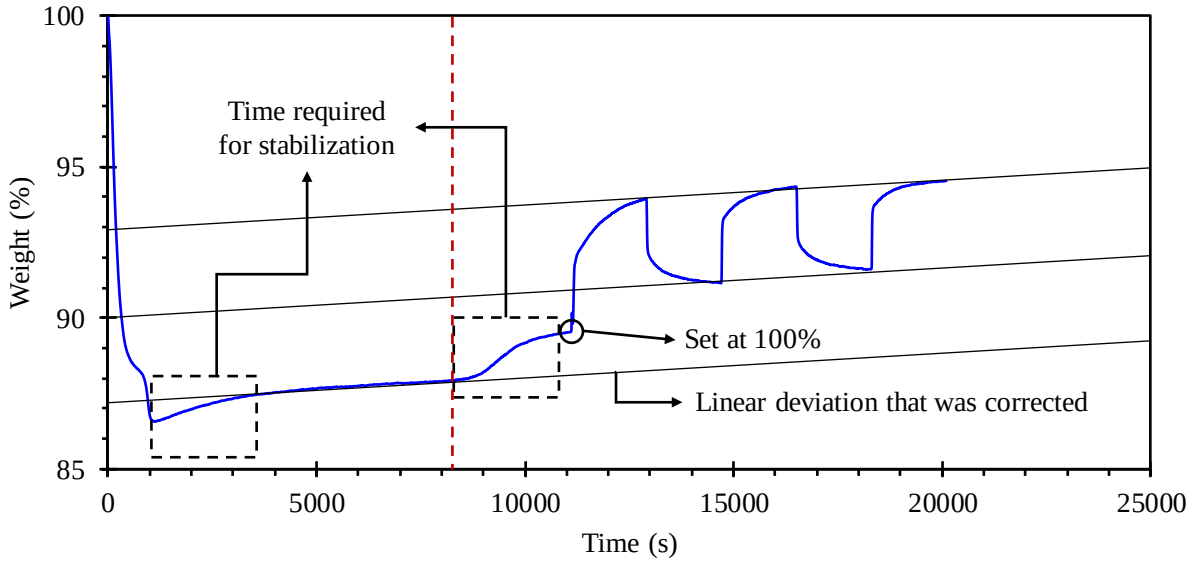
* The conversion obtained for the 5 min EtOH sample is too low to calculate the selectivity with acceptable accuracy.

B. Corrections applied on the raw data of the gravimetric CO_2 sorption and reproducibility test.

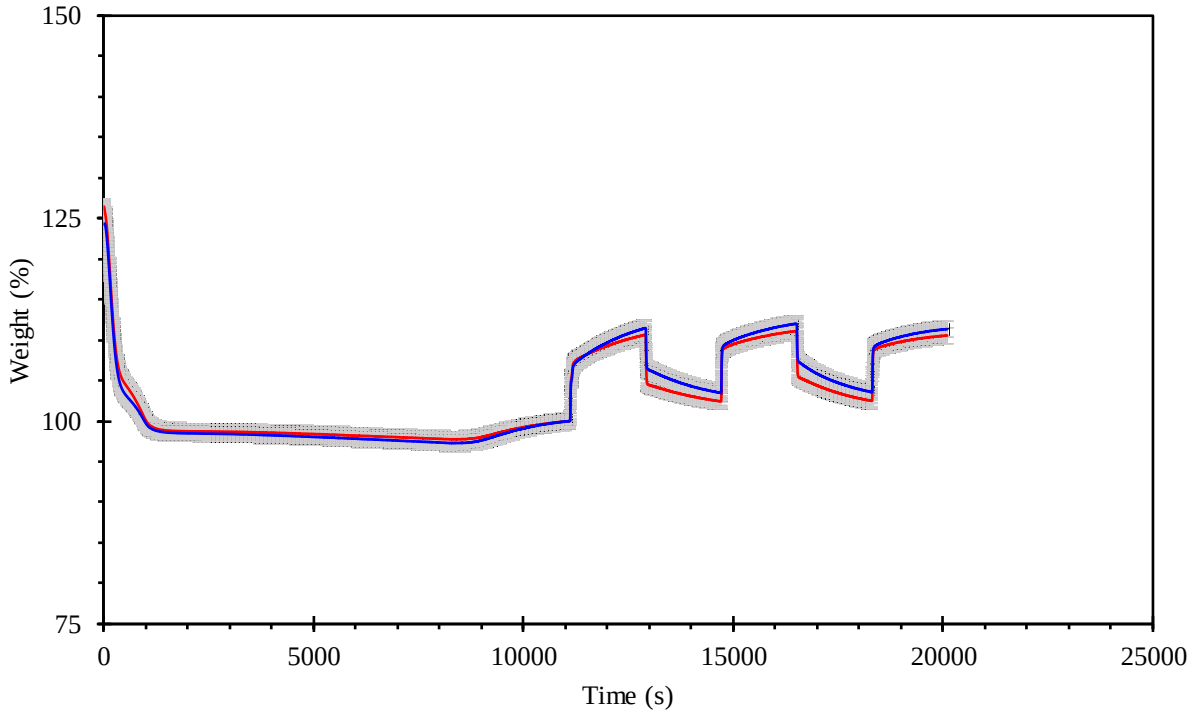
Blank measurement (automatically corrected by TGA software)



Raw data with automatic blank correction from TGA software for the 5 min EtOH sample and indication of the applied corrections



Reproducibility test, showing two measurements of HKUST-1 LAG sample (red and blue curves) with the applied corrections, the grey zone around the curves are error bars set at 1%, which is the typical value for error in TGA measurement.



C. Measurement and calculation of T_1 for styrene *(measured on a Bruker AVANCE 500MHz spectrometer)*.