Supplementary information

Tunable acidity in mesoporous carbons for hydrolysis reactions

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Paragraph S.1 Pulse liquid phase adsorption experiments for acidity and basicity determination

To determine surface acidity of the three carbon samples (and also basicity for CMC), a modified HPLC line (Fig. S1) has been used. Solid-liquid acid-base titration with pulse injections of probe molecule (PEA for acidity and BA for basicity) solutions at constant temperature has been performed. The setup allowed determining the surface sample acidity/basicity in different liquids where the probes were dissolved. Titrations performed in non-polar and aprotic liquids (like cyclohexane) allow determining *intrinsic* acidity/basicity, because in this case there are not any interactions between the surface functionalities and the liquid. On the other hand, working in polar and/or protic liquids (like water), surface acid/base centers of the sample can interact with the liquid with, for example, hydrogen bond, or coordinating bond, among other types of interactions. Choosing to determine the acidity/basicity of the sample in the same liquid in which it work (in the present case, reaction of sucrose hydrolysis occurred in water), this allows to measure the *effective* acidity/basicity, which directly correlates with the functional performance (in the present case, catalytic activity).

The mobile phase, in which the probe is dissolved and in which basic/acid probe adsorption is being performed on the sample surface, is withdrawn from a reservoir and, by means of a pump (model L-6200A Merck Hitachi,) it is sent to the sample holder (maintained at constant temperature, typically 30°C±1°C), where the sample to be analyzed was packed. Successively, the mobile phase flows into an UV-Vis detector (model L-4250 Merck Hitachi) that quantifies the probe still present in solution (amount of probe not adsorbed on the sample) to be then, finally, discharged in a collection flask.

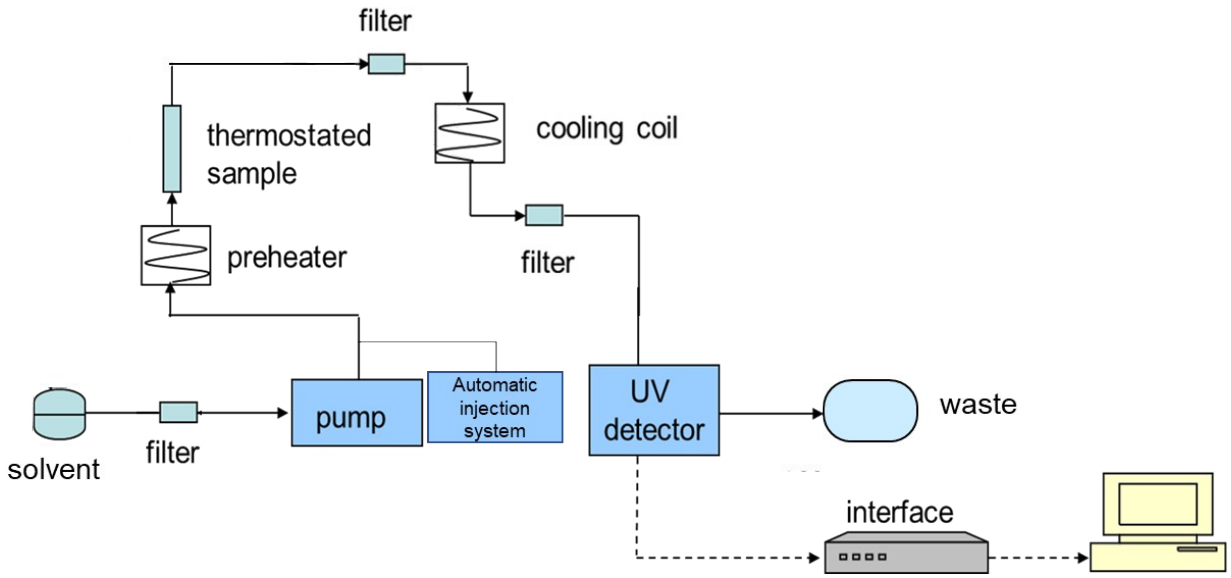

Fig. S.1.1 Scheme of the modified HPLC adsorption line for the collection of pulse liquid-solid titrations of carbon samples in liquid.

Through an automatic sampler (model AS-2000A Merck Hitachi), a small and precise volume (typically from 10 to 50 μL) of the solution of the chosen probe (PEA or BA) in the chosen liquid at known concentration (typically 0.1 M), is injected into the line and flows through the sample. The operation is repeated until saturation of the acid/base sites of the sample surface is attained.

The non-adsorbed probe is revealed by the UV-vis detector as a peak whose area is directly proportional to the quantity of probe, by suitable calibration experiments. The peak area tends to increase with the number of injections, as the quantity of probe adsorbed by the sample tends to diminish. Once saturation is attained, the peak areas have constant value.

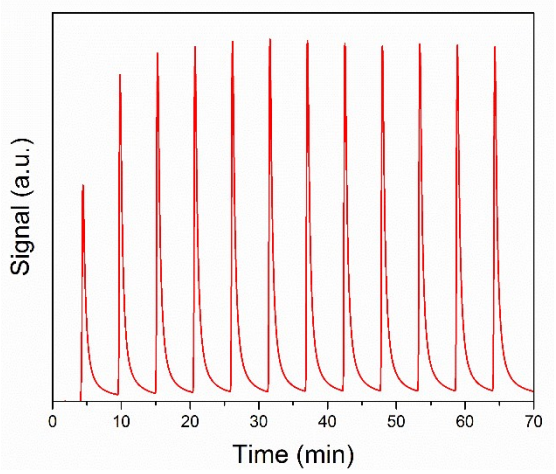

Fig. S.1.2 Example of the obtained chromatogram from pulse liquid phase adsorption experiments.

It is possible to quantify the number of surface acid/base sites by computing the amount of probe adsorbed and assuming a given stoichiometry between the probe and the surface acid/base site:

$$probe\ adsorbed_i = \frac{[probe]\cdot V_{Inj}}{m_{cat}} \cdot \frac{A_{sat} - A_i}{A_{sat}}$$

where:
probe adsorbed (mmol g^{-1}) = quantity of probe molecule adsorbed on the sample during the *i*-injection;
[probe] (mol L^{-1}) = concentration of the injected probe (PEA or BA) solution;
V_{Inj} (mL) = volume of the single *i*-injection;
m_{cat} (g) = mass of sample put in the sample holder;
A_{sat} = average chromatographic area of the peaks at saturation (when constant area value is attained);
A_i = chromatographic area of the *i*-peak.

When a 1:1 stoichiometry between the probe and the site is assumed, the number of acidic/basic sites of the analyzed sample corresponds to the total amount of probe molecule adsorbed:

$$total\ acid/base\ sites = \sum_{0}^{i} probe\ adsorbed_{"i"}$$

It is then possible to express the total number of surface acid/base sites of the sample as mequiv. g^{-1} or μequiv. m^{-2}.

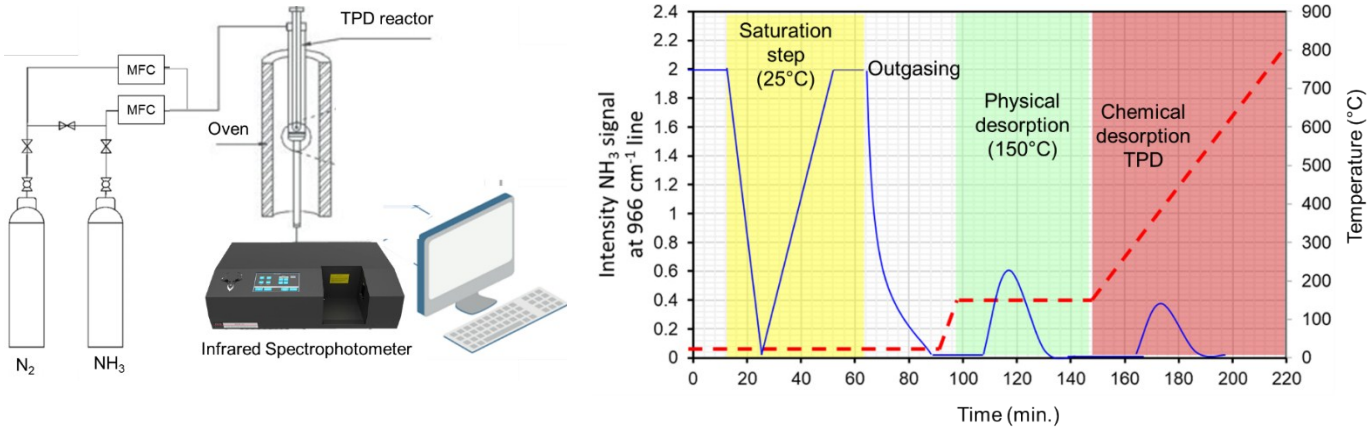

Fig. S.1.3 Scheme of the NH_3-TPD experimental set-up (top) and typical output (bottom).

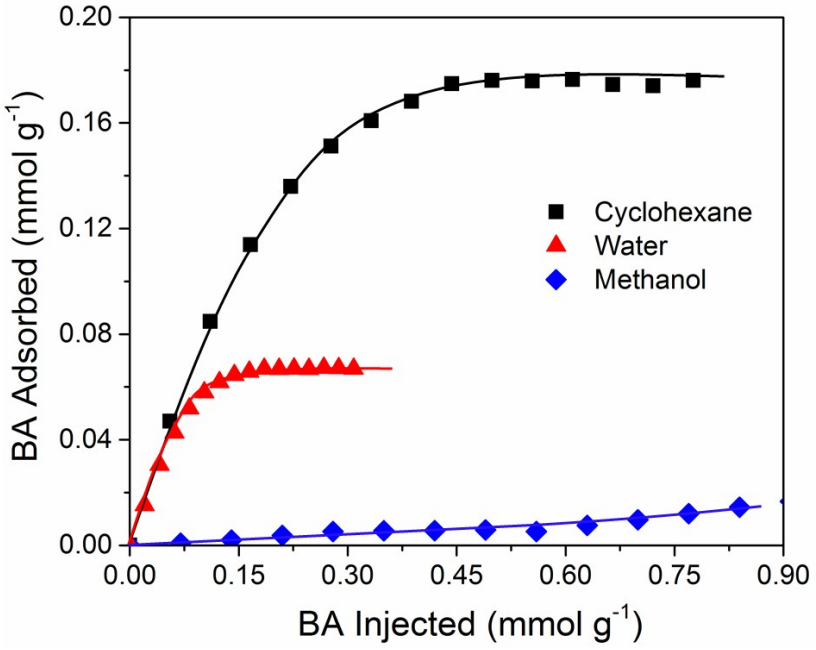

Fig. S.1.4 Results of the CMC basicity obtained from the pulse liquid phase adsorption experiments with BA in three different solvents: cyclohexane, water; and methanol (BA was monitored at λ = 254 nm) Titrations have been performed under the same conditions described for the surface acidity measurements in the experimental section.

Table S.1.1 Results of acidity and basicity titrations determined with PEA and BA probes, respectively by pulse liquid phase adsorption experiments in different solvents (T = 25 ± 2°C).

Sample	**Acidity**					
	cyclohexane		water		methanol	
	mequiv. g^{-1}	μequiv m^{-2}	mequiv. g^{-1}	μequiv. m^{-2}	mequiv. g^{-1}	μequiv. m^{-2}
CMC	0.499	0.341	0.484	0.330	0.173	0.118
HCMC10	0.843	0.633	0.839	0.630	0.263	0.198
HCMC40	1.182	1.399	1.118	1.323	0.248	0.294
Amberlite IR-120(H)[a]	-	-	2.270	-	-	-

Sample	**Basicity**					
	cyclohexane		water		methanol	
	mequiv. g^{-1}	μequiv. m^{-2}	mequiv. g^{-1}	μequiv. m^{-2}	mequiv. g^{-1}	μequiv. m^{-2}
CMC	0.175	0.120	0.0669	0.0457	0.0501	0.0342

[a] Data from reference [45]

As shown in Fig. S3 and reported in Tab S1, CMC exhibits a limited number of surface basic sites. The trend of the basic site accessibility *vs.* nature of solvent is the same of that has been found for acidity.

Basicity of the HCMC10 and HCMC40 samples has not been determined as the acidic functionalization performed on CMC for the sample preparation has suppressed any basicity.

Paragraph S.2 NMR characterization of the carbon samples

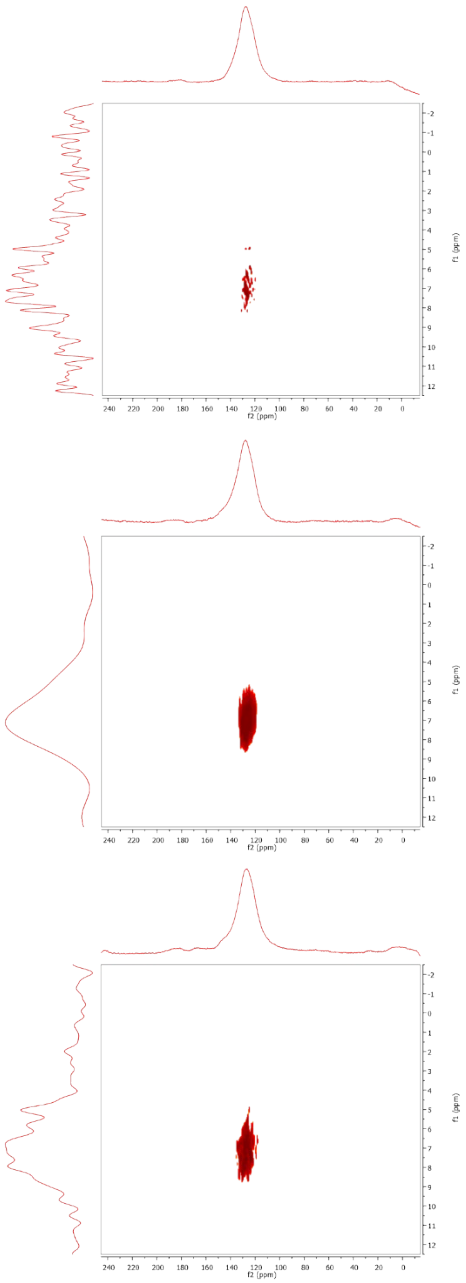

Fig. S.2.1 ^{1}H-^{13}C 2D dipolar coupling NMR spectra of a) CMC; b) HCMC10; c) HCMC40.

Paragraph S.3 Surface composition from XPS analysis

Table S.3.1 Percent surface composition of CMC, HCMC10, and HCMC40

	Surface composition (at.%)		
	C	O	Other (N, Si, Cl)
CMC	92.1	7.4	0.5
HCMC10	88.6	10.6	0.8
HCMC40	84.3	13.8	1.9

Paragraph S.4 Kinetic results of catalytic hydrolysis of sucrose

Tables S.4.1-S.4.4 report all the data and results collected during the catalytic tests of sucrose hydrolysis performed on the Amberlite IR-120(H), CMC, HCMC10, and HCMC40 samples. As reported in the experimental section, sucrose hydrolysis reaction has been performed in aqueous solution ($V_{solution}$ = 150 mL, [Sucrose] ≈ 100 mM) at 80°C, and under vigorous stirring (400 RPM). Catalyst to solution volume ratio has been kept constant at *ca.* 0.0067 g mL^{-1}.

Table S.4.1 Results of catalytic hydrolysis of sucrose on Amberlite

Reaction time	Concentration				Conversion	Selectivity		Yield	
	Sucrose	Glucose	Fructose	Total	Sucrose	Glucose	Fructose	Glucose	Fructose
(h)	(meq. monosaccharides L^{-1})				(%)	(%)		(%)	
0	94.89	0	0	94.89	0	0	0	0	0
1	54.27	21.56	20.08	95.91	42.81	53.08	49.43	22.72	21.16
2	36.12	28.97	31.17	96.26	61.93	49.29	53.04	30.53	32.85
3	22.1	35.26	37.66	95.02	76.71	48.44	51.74	37.16	39.69
4	7.28	38.30	48.77	94.35	92.33	43.71	55.67	40.36	51.40

Table S.4.2 Results of catalytic conversion of sucrose on CMC

Reaction time	Concentration				Conversion	Selectivity		Yield	
	Sucrose	Glucose	Fructose	Total	Sucrose	Glucose	Fructose	Glucose	Fructose
(h)	(meq. monosaccharides L^{-1})				(%)				
0	91.71	0	0	91.71	0	0	0	0	0
1	71.23	10.55	10.06	91.84	22.33	51.51	49.12	11.50	10.97
2	57.34	17.36	17.18	91.88	37.48	50.51	49.99	18.93	18.73
3	49.24	21.1	20.88	91.22	46.31	49.68	49.16	23.01	22.77
4	42.65	24.66	24.4	91.71	53.49	50.26	49.74	26.89	26.61
ca. 23	2.24	45.01	44.65	91.90	97.56	50.31	49.90	49.08	48.69

Table S.4.3 Results of catalytic conversion of sucrose on HCMC10

Reaction time	Concentration				Conversion	Selectivity		Yield	
	Sucrose	Glucose	Fructose	Total	Sucrose	Glucose	Fructose	Glucose	Fructose
(h)	(meq. monosaccharides L^{-1})				(%)				
0	87.44	0	0	87.44	0	0	0	0	0
1	72.12	7.75	7.3	87.17	17.52	50.59	47.65	8.86	8.35
2	61.04	13.49	13.09	87.62	30.19	51.10	49.58	15.43	14.97
3	51.6	18.25	17.59	87.44	40.99	50.92	49.08	20.87	20.12
4	44.96	21.5	21.55	88.01	48.58	50.61	50.73	24.59	24.65
ca. 23	1.37	43.05	42.87	87.29	98.43	50.02	49.81	49.23	49.03

Table S.4.4 Results of catalytic conversion of sucrose on HCMC40

Reaction time	Concentration				Conversion	Selectivity		Yield	
	Sucrose	Glucose	Fructose	Total	Sucrose	Glucose	Fructose	Glucose	Fructose
(h)	(meq. monosaccharides L^{-1})					(%)			
0	90.82	0	0	90.82	0	0	0	0	0
1	60.5	15.63	14.65	90.78	33.38	51.55	48.32	17.21	16.13
2	35.75	27.74	26.8	90.29	60.64	50.37	48.67	30.54	29.51
4	18.48	35.39	37.04	90.91	79.65	48.92	51.20	38.97	40.78
ca. 23	0.71	45.19	44.48	90.38	99.22	50.15	49.36	49.76	48.98