SUPPLEMENTARY INFORMATION

Assessing the functional groups in activated carbons through a multi-technique approach

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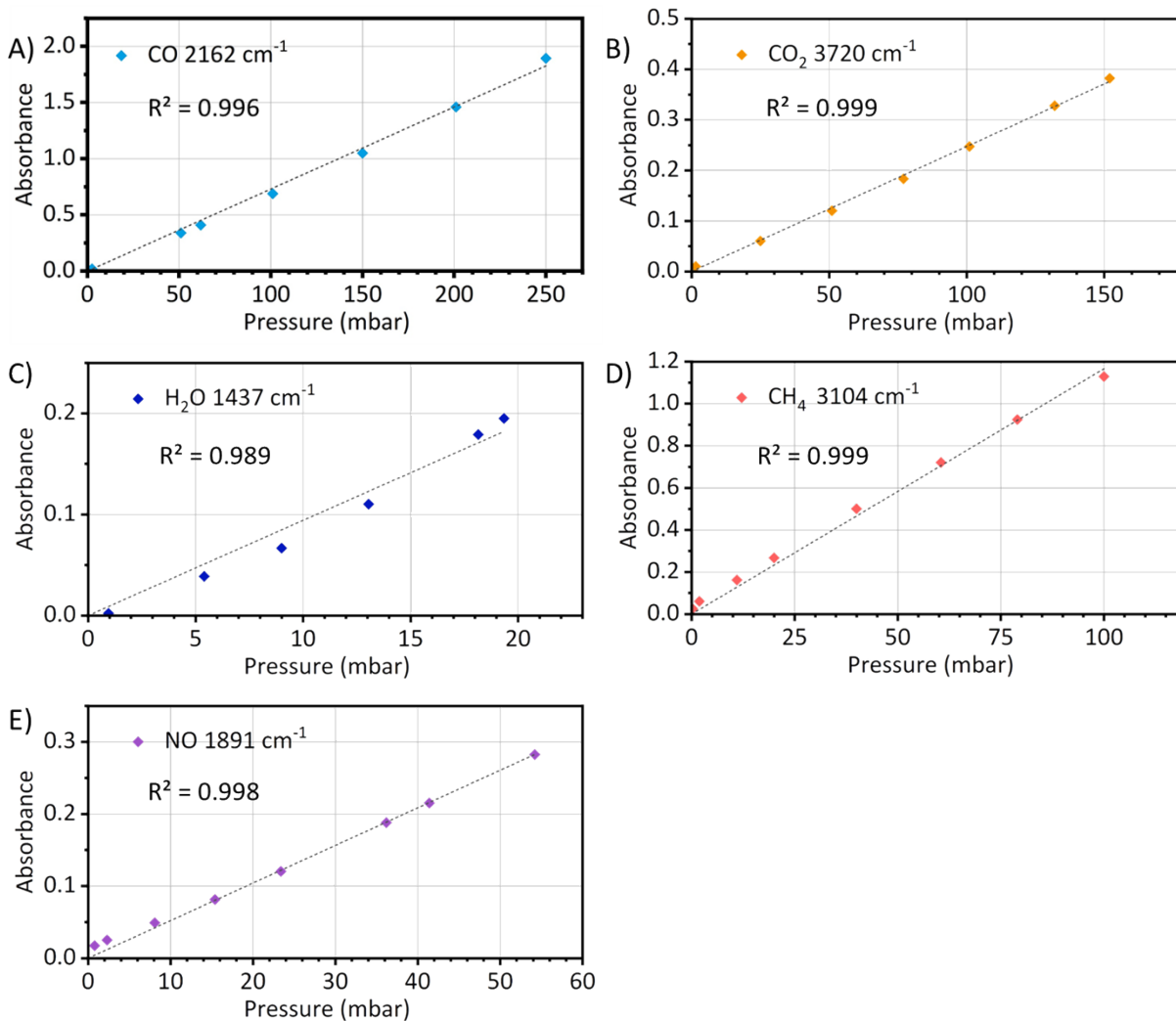
S1: Gases calibration lines

Figure S1: calibration lines pressure vs absorbance for the quantification of the released gasses from the infrared spectra for CO (A), CO_2(B), H_2O (C), CH_4 (D) and NO (E). The frequency of the roto-vibrational peak used for the calibration is indicated in the legends.

S2: Correction for uneven temperature distribution

During some test measurements performed by filling the system with a known amount of a reference gas (CO or CO_2), a progressive increase in the measured IR absorbance was observed as the temperature ramp proceeded. The effect is caused by the uneven temperature distribution in the apparatus during the TPD-IR runs, which results in gas concentration gradients with the highest concentrations being detected in the cold sections (such as the IR gas cell) and the lowest ones in the hot ones (the heated quartz tube). The entity of the resulting absorbance

increase approaches 10% of the initial value when reaching 700°C, and thus could not be ignored. This effects appears to be strongly setup-dependent and cannot be accounted for analytically. Thus, we calculated an empirical relation describing the increase in the absorbance as a function of the temperature by using the data collected during the measurements of test runs performed in the presence of a known amount of gases. Four different test runs were used, which were performed using 28 and 167 mbar of CO and 78 and 132 mbar of CO_2. The results of these runs showed a good level of repeatability, regardless of the reference gas employed or of the initial gas pressure. Figure S2 reports the ratio between the absorbance measured at a given temperature T (Abs), and the absorbance measured at room temperature (Abs0) as a function of the temperature of the ramp measured during the four test runs. The observed trend was fitted with a third degree polynomial, from which a correction factor Abs/Abs0 was calculated for each temperature. Then, the absorbance of the measured IR spectra were divided by the Abs/Abs0 correction factor correspondent to the temperature at which they were collected, obtaining the expected absorbance value at room temperature.
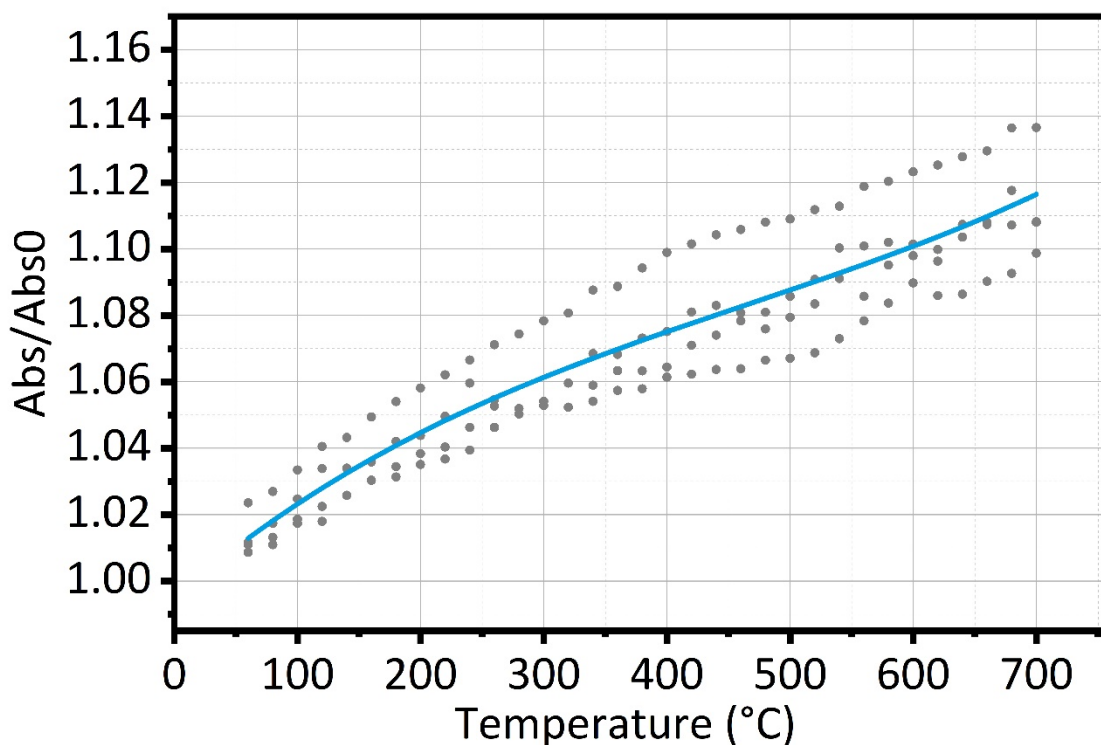

Figure S2: Regression curve describing the ratio between the IR absorbance observed at a given temperature (Abs) and the absorbance at room temperature (Abs0) as a function of the temperature.

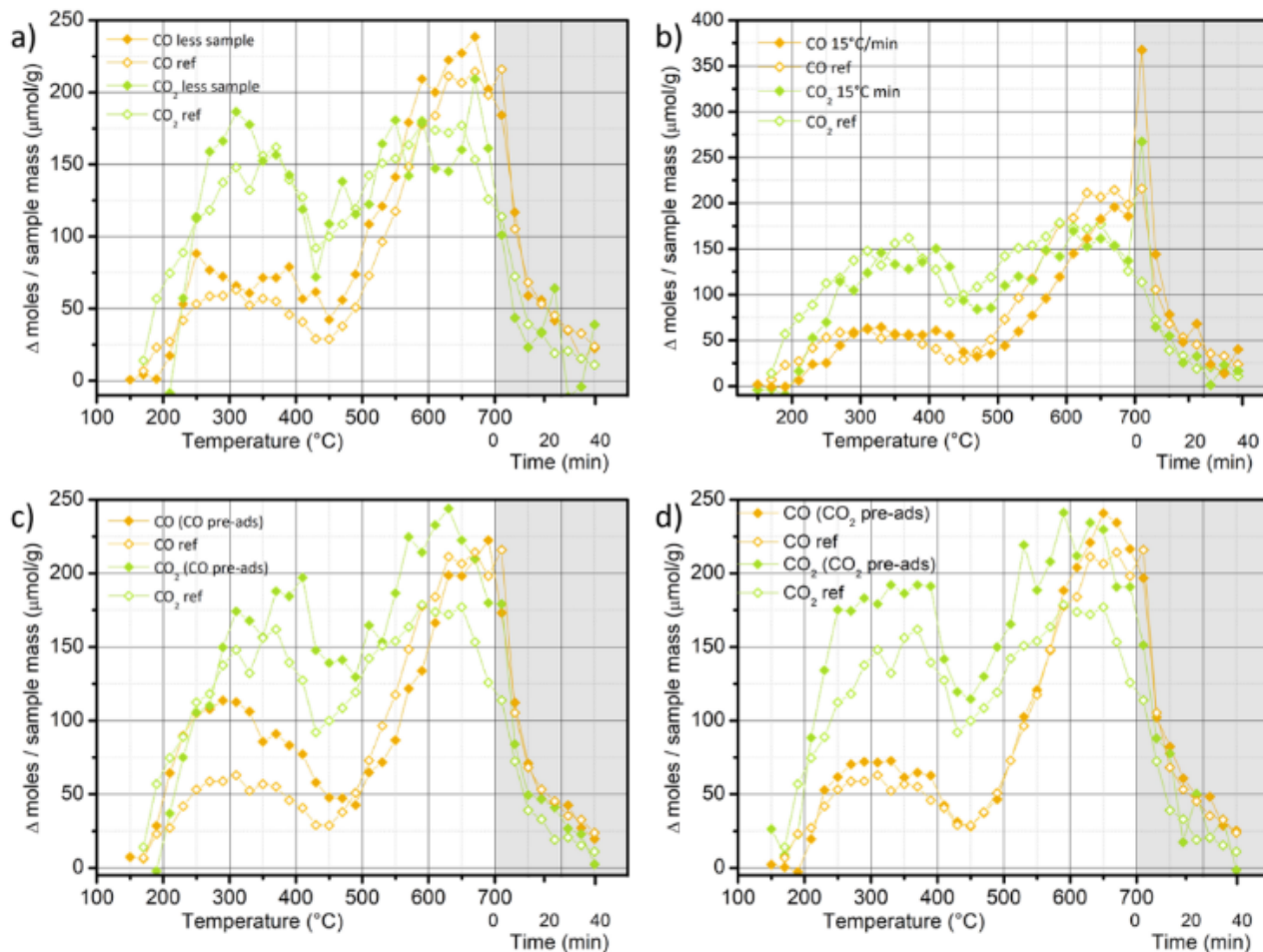## S3: Evaluation of the relevance of secondary reactions on the TPD results

Figure S3: Differential TPD plots of CO and CO_2 for Cchemi-Ox in different conditions (filled symbols), compared to the reference measurements (empty symbols). a) Ten times less sample; b) heating ramp of 15 °C/min; c) with CO pre-adsorption; d) with CO_2 pre-adsorption. Each point reports the number of moles of gas evolved by the carbon between the collection of two consecutive IR spectra (i.e. in a temperature interval of 20 °C for the ramp and every 5 min for the isotherm). The data collected during the temperature ramp segment are reported on a white background, while those collected during the isotherm segment are shown on a grey background.
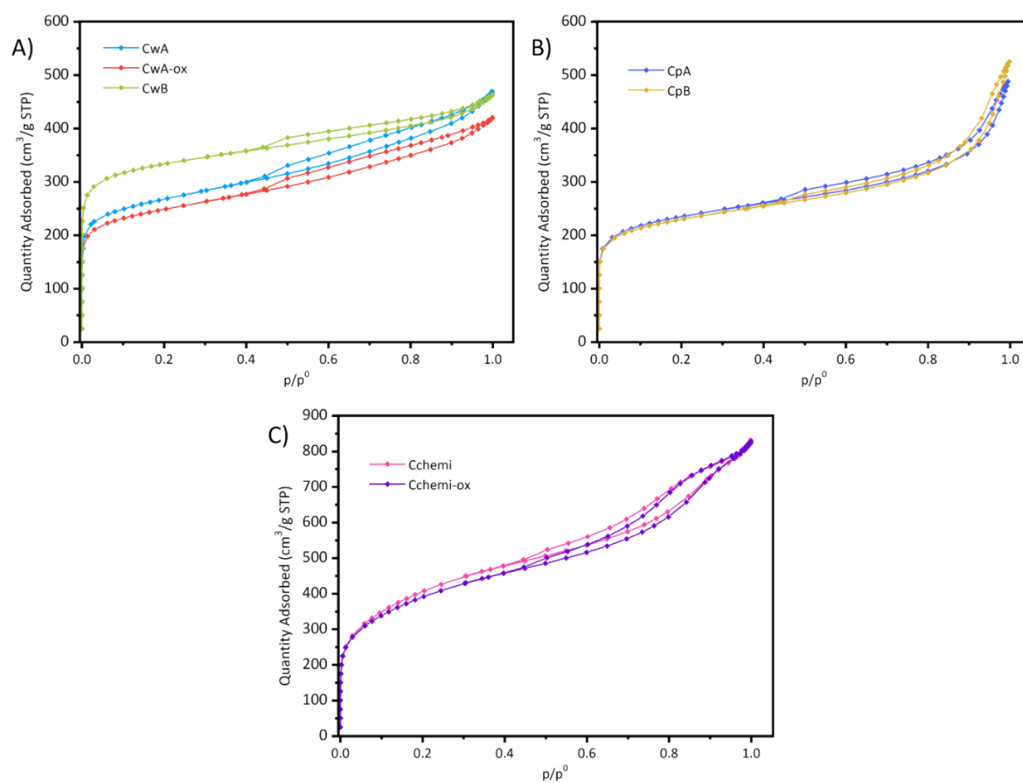
S4: Adsorption isotherms

Figure S4: adsorption isotherms of CwA, CwA-ox and CwB (A), CpA and CpB (B), and Chemi and Cchemi-ox (C), as determined by N_2 physisorption.

S5: Hydrophilicity vs textural proprties
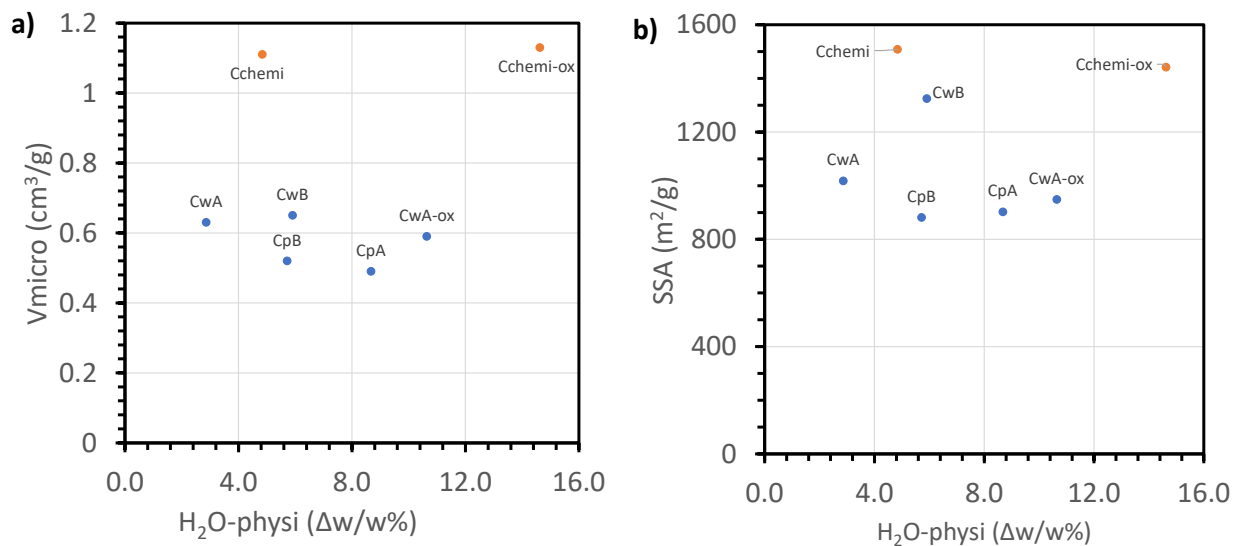
a)

b)

Figure S5: part a) weight percentage of physisorbed water vs micropores volume for all the seven activated carbon samples considered. The micropores volume differs between chemically activated samples (orange dots) and steam activated ones (blue dots), but no clear trend with the amount of physisorbed water can be observed. Part b) weight percentage of physisorbed water vs specific surface area. Again, no clear trend between the variables can be observed.

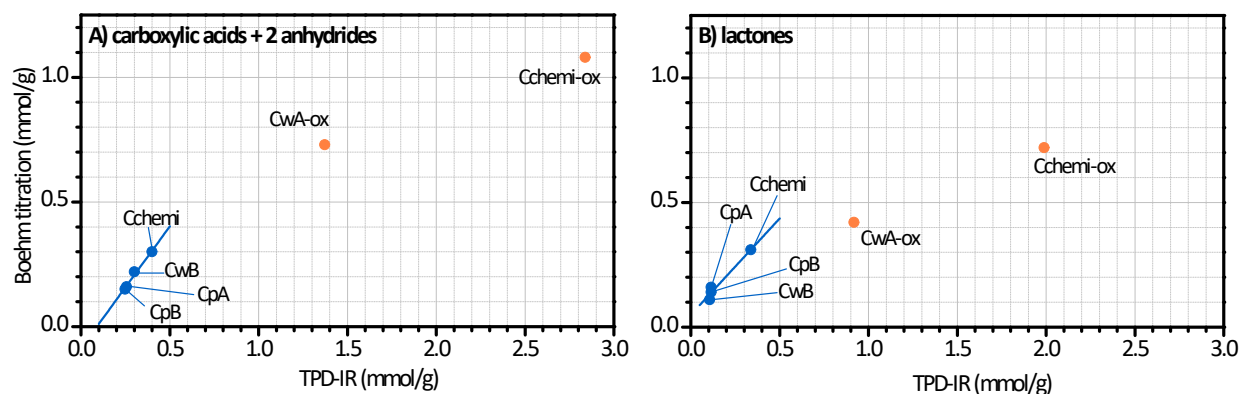## S6: Attempts to combine TPD-IR with Boehm titration

Figure S6: Concentration of carboxylic acids + 2 anhydrides (part A) and lactones (part B) as determined by TPD-IR plotted against the same values obtained by Boehm titration, excluding CwA from the series of data. Two different trends can be observed, one for the physically activated carbons and Cchemi (blue), and one for the two oxidized carbons (orange). The linear fit for the pristine carbons is reported as a blue line (R^2 = 0.98 and 0.96 for parts A and B, respectively).