

Supporting Information for:

Selective carbon deposition on γ -alumina acid sites: towards the design of catalyst supports with improved hydrothermal stability in aqueous media.

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1. Experimental

1.1. Determination of the boehmite content by XRD

A calibration curve was first made using mechanical mixtures of alumina and boehmite for the determination of the percentage of AlOOH in the solid from XRD. The amount of boehmite was calculated by measuring the area $A_{(020)}$ of the (020) reflection of boehmite at $2\theta = 14.5^\circ$. This curve was then used to estimate the boehmite content in samples after hydrothermal treatments.

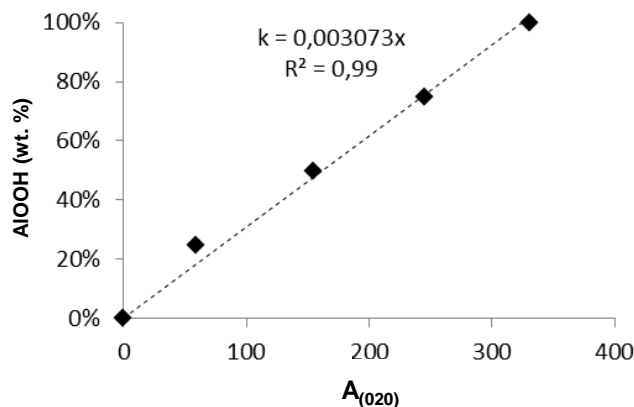


Figure S1 Percentage of boehmite (wt. %) in solids as a function of the area of the diffraction peak at $2\theta = 14.5^\circ$ in XRD patterns

Abi Aad et al. showed that no significant amount of amorphous aluminum hydroxide was precipitated during an hydrothermal treatment of alumina by comparing this method of quantification with another based on TGA analysis.^{1,2} Furthermore, we did not detect any aluminum species in liquid phases recovered after HT treatments, indicating that all the aluminum dissolved during the treatment has precipitated. This method is therefore appropriate to give a good estimation of the total amount of alumina that has dissolved during the treatment.

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- 1 Abi Aad, J.; Casale, S.; Michau, M.; Courty, P.; Diehl, F.; Marceau, E.; Carrier, X., *ChemCatChem* 2017, 9, 2186–2194.
 - 2 Abi Aad, J.; Courty, P.; Decottignies, D.; Michau, M.; Diehl, F.; Carrier, X.; Marceau, E., *ChemCatChem* 2017, 9, 2106–2117.

1.2. Determination of the carbon content in C/alumina composites

The carbon content was determined by thermogravimetric analysis. Composites were heated under air flux (25 mL/min) from room temperature to 1000°C with a heating ramp of 10°C min. In order to account for the weight loss due to dehydration of the support in this temperature range, a TGA curve was first recorded for pure alumina (Figure S2).

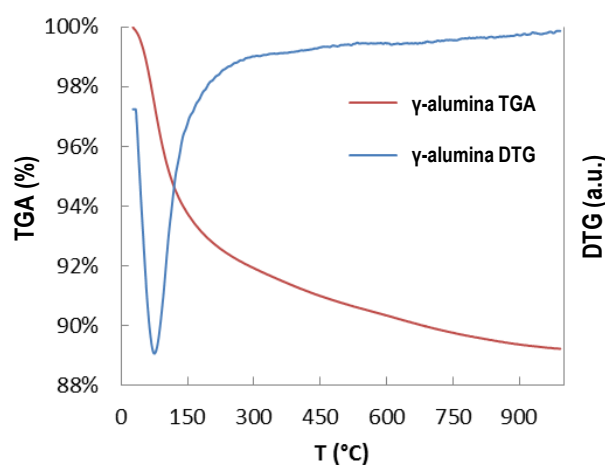


Figure S2 Evolution of the mass (TGA) and corresponding derivative (DTG) of γ -alumina with temperature in air

The contribution of γ -alumina was then deduced from the weight loss of the composite, typically in the 200-750°C range (Figure S3).

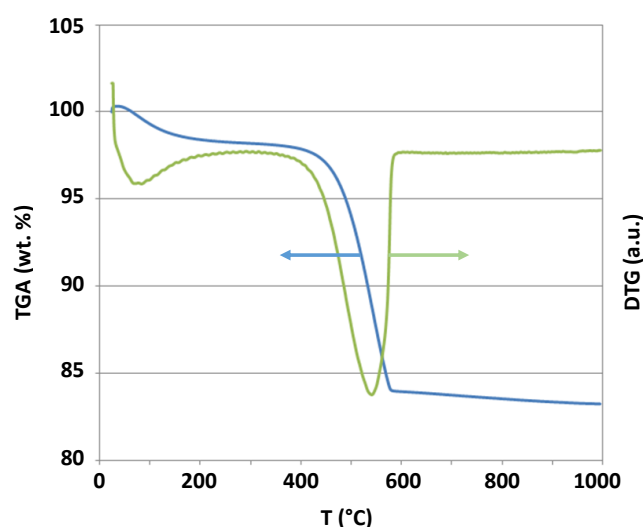


Figure S3 Evolution with temperature of the mass (TGA) and corresponding derivative (DTG) of CA-CVD-12, a C/ γ -alumina composite prepared by CVD of ethanol containing 12 wt. % carbon heated in air

1.3. Determination of the free alumina surface by ethanol adsorption followed by ATG

Experimentally, the sample is first pretreated at 200°C for 2 h under He flow (60 mL/min) to remove physisorbed water from the surface. After cooling at 30°C, the sample is saturated with ethanol by flowing He passing through an EtOH saturator kept at 25°C. The weakly adsorbed EtOH is then removed at 30°C under a dry He flow (60 mL/min) for 1 h (purge). The proportion of free alumina surface is therefore estimated using the following equation:

$$\%Al_2O_3 \text{ accessible surface} = \frac{\text{EtOH adsorbed after purge (}/nm^2)}{\text{EtOH adsorbed after purge on pure alumina (}/nm^2)} * 100$$

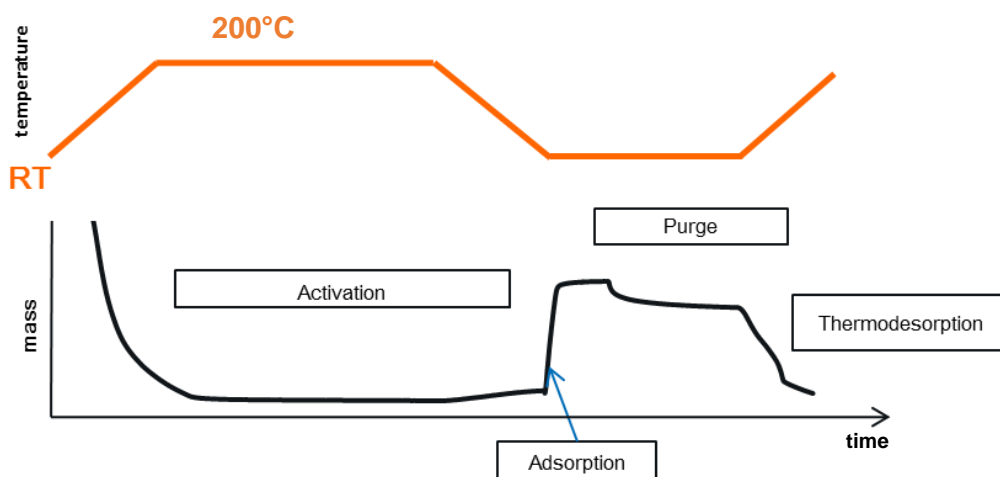
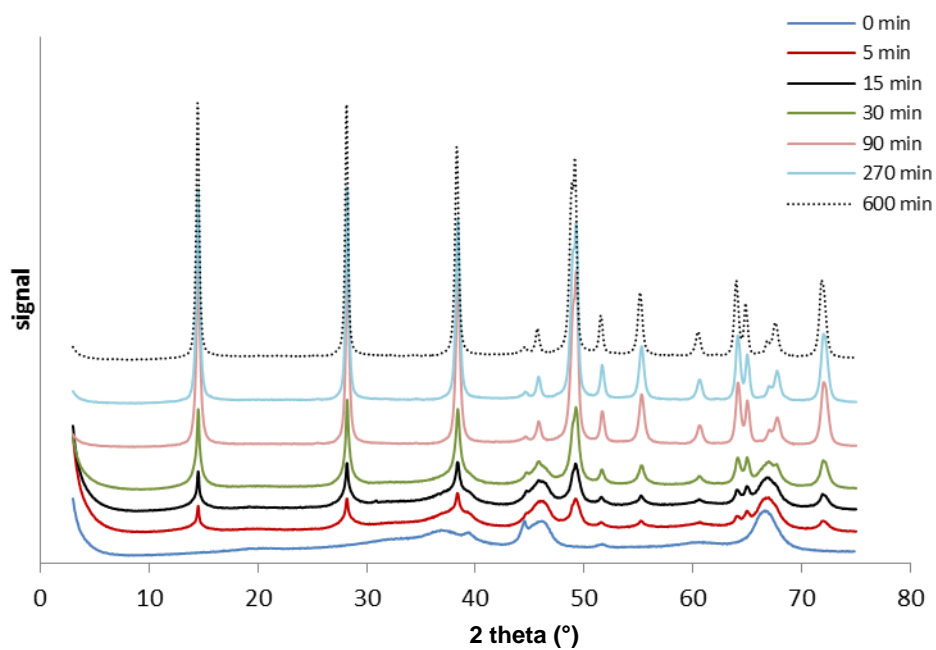


Figure S4 *Process of ethanol adsorption for the determination of the accessible surface of alumina. The black curve corresponds to the original γ -alumina*

2. Results and discussion

2.1. Stability of pure γ -alumina in water



Treatment duration time (min)	AlOOH ^a (wt. %)	S _{BET} ^b (m ² /g)	V _p ^b (mL/g)
0	0	212	0.55
5	12%	236	0.47
15	18%	272	0.47
30	43%	211	0.45
90	96%	53	0.37
270	97%	48	0.35
600	100%	45	0.32

^aestimated from XRD patterns using the correlation curve in Fig. S2

^bdetermined with N₂ sorption isotherms analysis

Figure S5 XRD patterns (top) and corresponding structural and textural characteristics (Table, bottom) of solids recovered after treating γ -alumina for different periods under HT conditions (H₂O, 200°C)

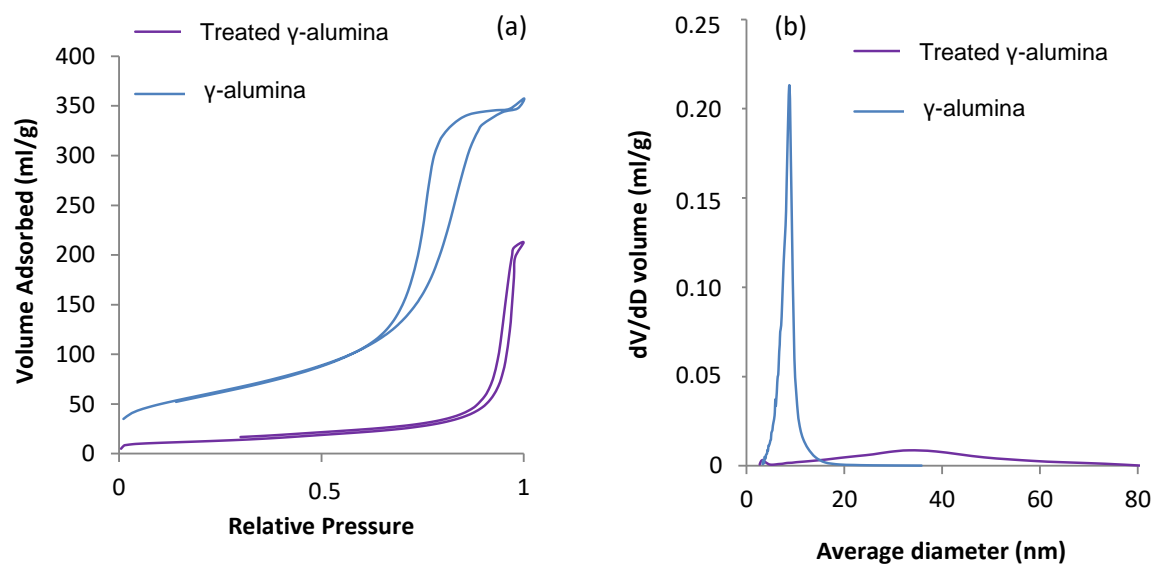


Figure S6 N_2 adsorption/desorption isotherms (a) and pore size distribution curves calculated using the BJH method on the desorption branch (b) of γ -alumina before (blue) and after (purple) HT test (H_2O , $200^\circ C$, 10 h)

2.2. Stability of γ -alumina in the presence of sorbitol

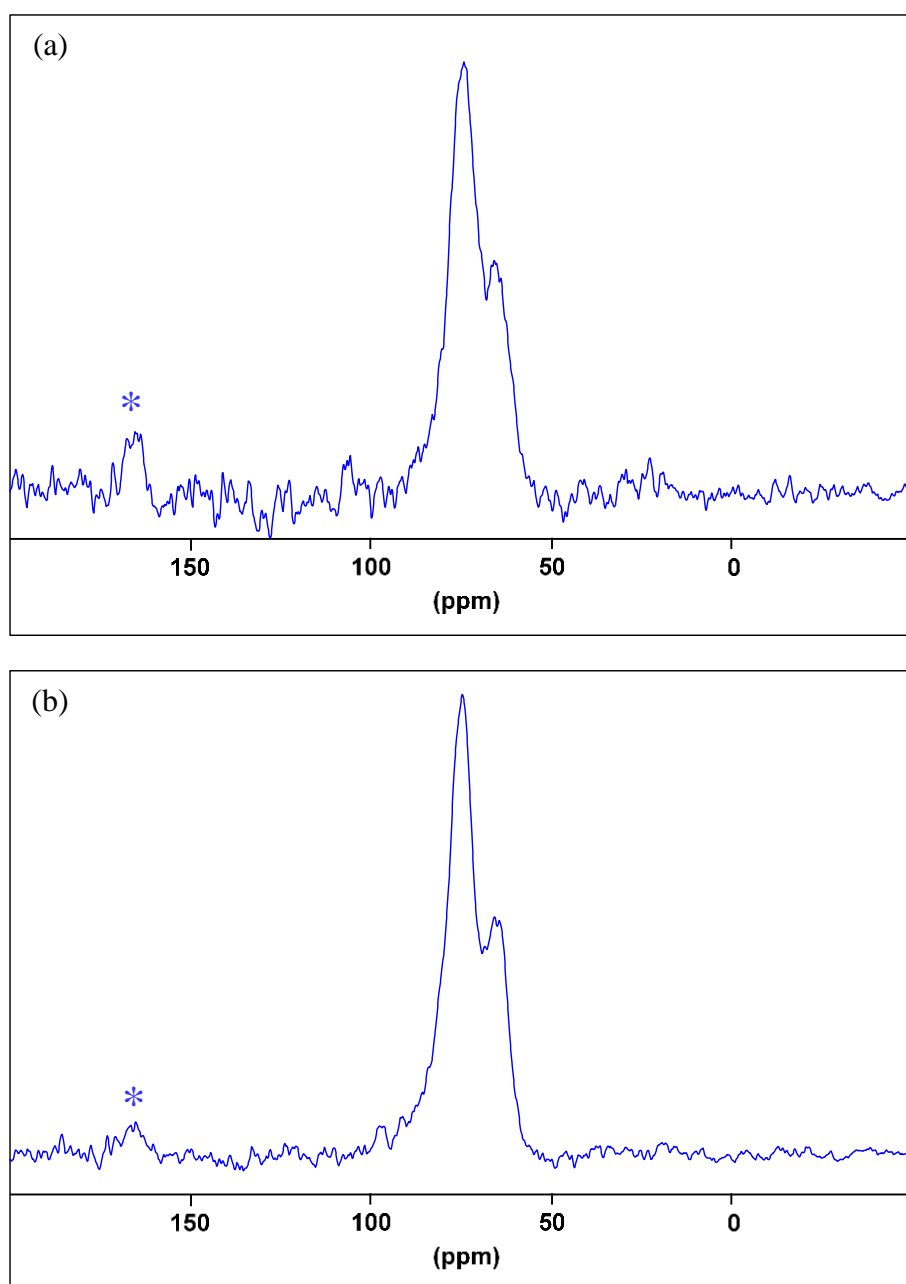
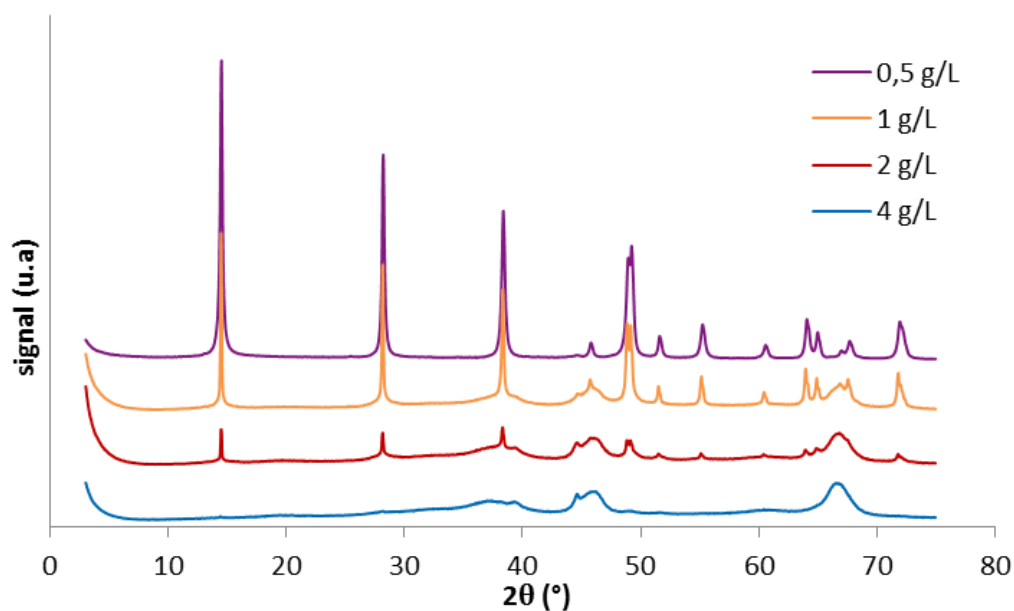


Figure S7 ^{13}C NMR spectra of sorbitol/alumina compounds obtained after treating γ -alumina at 25°C (a) or 200°C (b) in a 2.5 wt. % aqueous solution of sorbitol for 10h. Asterisks denote spinning side bands



Sorbitol concentration (g/L)	%AlOOH (wt. %) ^a	Sorbitol content after adsorption (wt. %) ^b
0.27	95%	0.45%
0.52	59%	0.84%
1.00	35%	1.73%
2.26	4%	1.94%
4.04	0%	2.15%
8.36	0%	2.67%
15.02	0%	2.91%

^aestimated from XRD patterns using the correlation curve in Fig. S2

^bestimated by HPLC analysis of the liquid phase

Figure S8 XRD patterns of γ -alumina treated for 10 h at 200°C in aqueous solutions of sorbitol with different concentrations. The table lists the corresponding boehmite and sorbitol contents after hydrothermal tests

2.3. New design of C/alumina materials

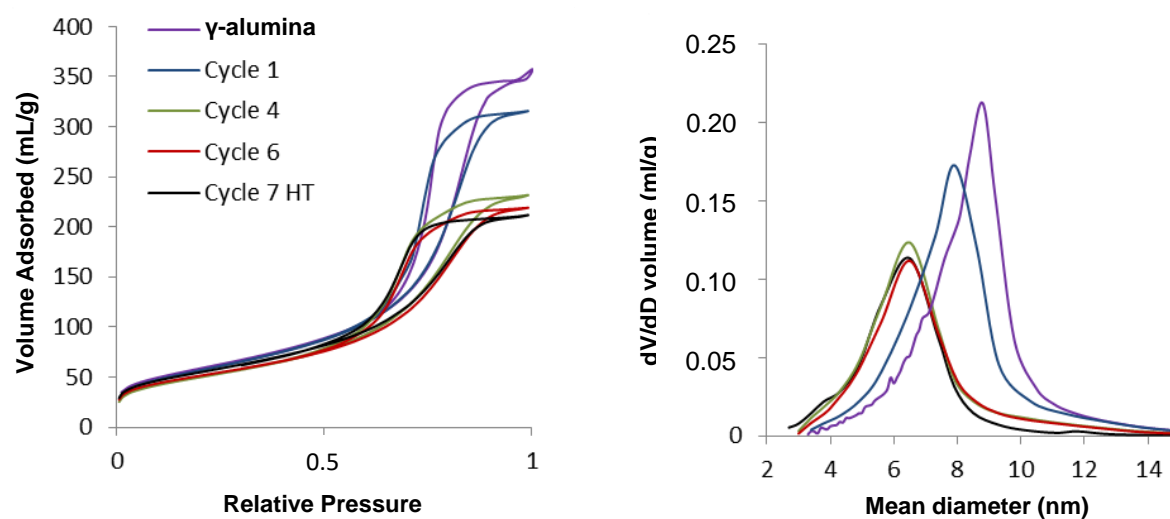


Figure S9 N_2 adsorption/desorption isotherms (left) and corresponding BJH pore size distributions (right) of samples prepared by sorbitol adsorption/pyrolysis cycles

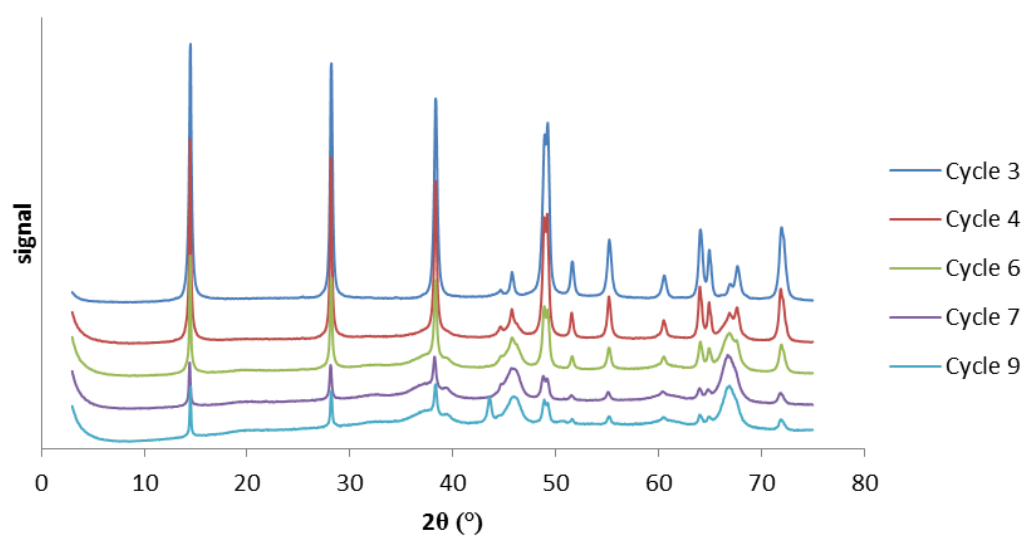


Figure S10 XRD patterns of C/ γ -alumina composites obtained by sorbitol adsorption/pyrolysis cycles after a hydrothermal treatment of 10 h at 200°C

2.4 Comparison with C/alumina composites obtained following conventional methods

2.4.1. Impregnation/pyrolysis of sucrose

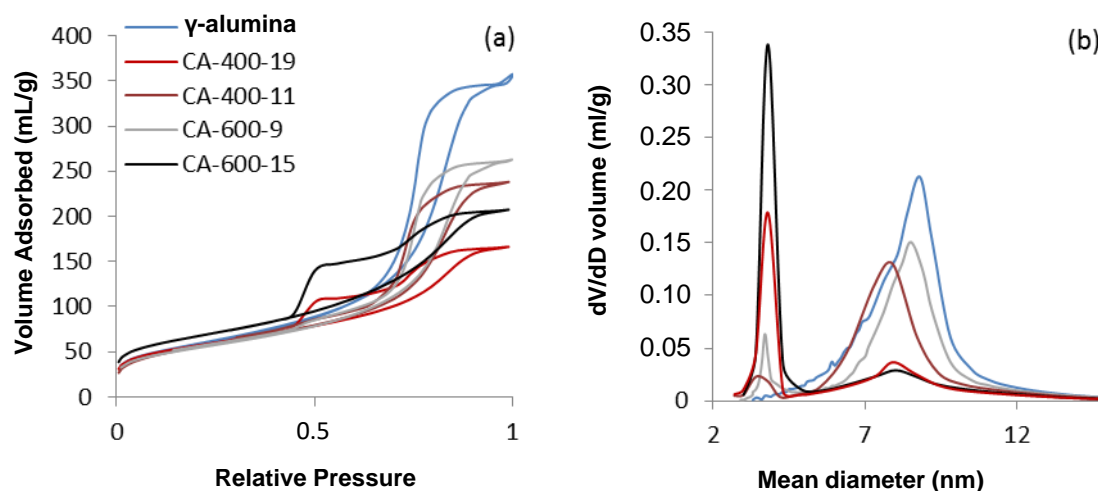


Figure S11 N_2 adsorption/desorption isotherms (a) and pore size distribution calculated according to the BJH method applied to the desorption branch (b) of composites obtained by impregnation of sucrose followed by pyrolysis. Solids are denoted CA-X-Y with X = pyrolysis temperature ($^{\circ}\text{C}$) and Y = carbon content

^{13}C solid-state NMR confirms that carbon formed at 400°C still contains oxygenated species such as aromatics at $\delta = 150$ ppm, carboxylic acids and derivatives at $\delta = 180$ ppm, aldehydes and / or ketones around $\delta = 200$ ppm as well as alkyl chains between 0 and 50 ppm (a). By contrast, the spectrum of the sample prepared at 600°C shows a single signal at ca. 120 ppm characteristic of graphitic carbon (b).

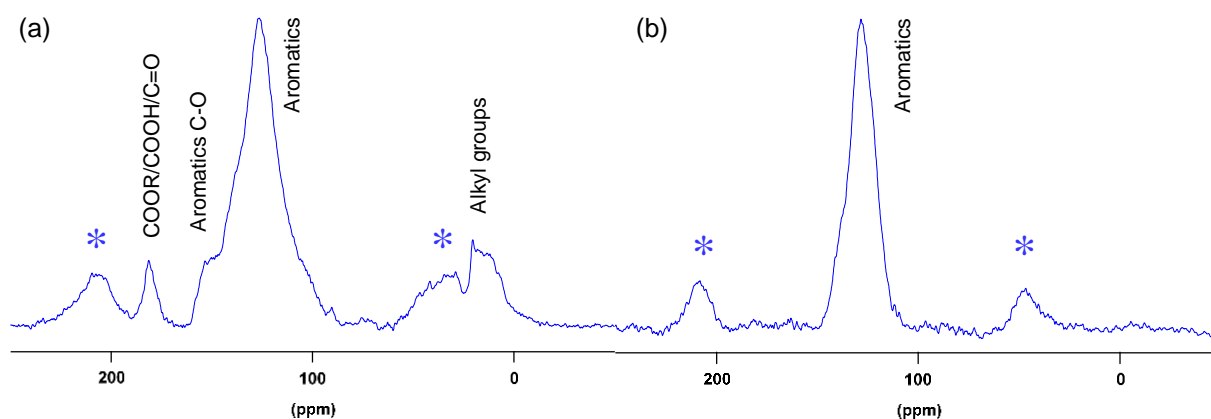


Figure S12 ^{13}C NMR spectra of CA-400-11 (a) and CA-600-9 (b.) Asterisks denote spinning side bands

Raman spectroscopy leads to the same conclusion. At 400 °C, the fluorescence background is more intense than the carbon characteristic bands and only the G band can be detected at 1600 cm^{-1} . For the sample pyrolyzed at 600 °C, the two characteristic D and G bands at 1346 cm^{-1} and 1600 cm^{-1} can be distinguished (Figure S14). The intensity ratio $I(\text{D})/I(\text{G})$ is equal to 0.75, which is representative of a semi-graphitic type carbon. Both NMR and Raman spectroscopic techniques show that pyrolysis at 400°C leads to a carbonaceous and poly-oxygenated phase resulting from an incomplete degradation of sucrose.

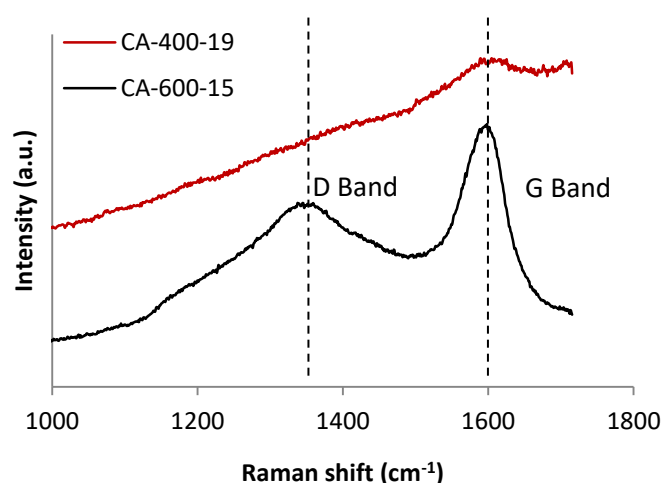


Figure S13 Raman spectra in the region of carbon D and G bands for samples CA-400-19 and CA-600-15

2.4.2. CVD of ethanol

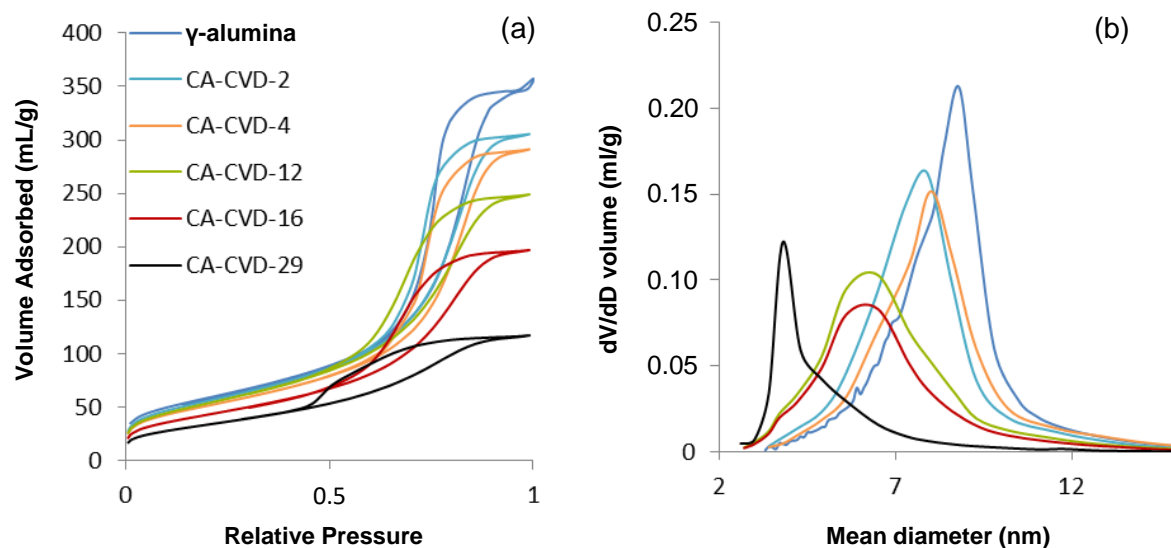


Figure S14 N_2 adsorption/desorption isotherms (a) and pore size distribution calculated according to the BJH method applied to the desorption branch (b) of composites obtained by CVD of ethanol. Solids are denoted CA-CVD-X with X = carbon content

The chemical nature of the carbon phase is quite similar to that obtained after pyrolysis of sucrose at 600 °C. The Raman spectrum of CA-CVD-29 (Figure S16) is characteristic of a semi-graphitic carbon with a I(D)/I(G) ratio of 0.65, close to the value of 0.75 obtained for CA-600-15.

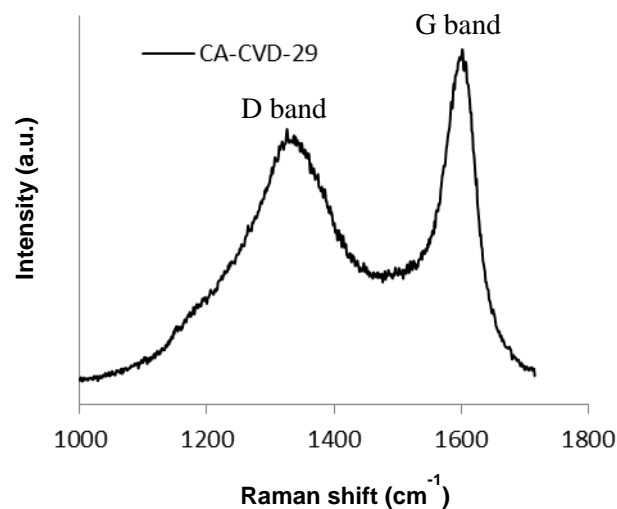


Figure S15 Raman Spectrum of Sample CA-CVD-29

2.5. Stability of C/alumina composites

2.5.1. Stability of γ -alumina impregnated with sucrose

γ -alumina was impregnated with sucrose (0.41 g sucrose/g of alumina; final carbon content = 14 wt. %), dried and directly subjected to a series of hydrothermal treatments (water, 200°C, 10h) without pyrolysis. Table S1 lists the main properties of the solid after 1, 2 and 3 successive treatments in water.

Table S1 *Chemical and structural properties of sucrose/ γ -alumina after several treatments for 10 h at 200 ° C in liquid water*

Sample name	Number of HT treatments	C (wt. %)	SBET ^a (m ² /g)	Dp ^a (nm)	Vp ^a (mL/g)	% AlOOH ^b
SA-HT-1	1	14	232	5.4	0.36	12
SA-HT-2	2	13	278	5.0	0.39	15
SA-HT-3	3	13	268	5.4	0.40	19

^aestimated from N₂ adsorption/desorption isotherms

^bpercentage of boehmite estimated from XRD patterns using the correlation curve in Fig. XX

Sample SA-HT-1, which possesses a carbon content of 14 wt. %, has a very low boehmite content of 12% after the first HT treatment (Table S1 and Figure S17). This sample is more stable under hydrothermal conditions than sample CA-400-11 (45% AlOOH formed). In the literature, it is known that sucrose reacts in situ under HT conditions to form a highly oxygenated carbon phase of the humic type.³ The formation of decomposition compounds of sucrose thus participates in the stabilization of alumina.

SA-HT-1 was then dried and subjected again to HT conditions to give the sample SA-HT-2; then SA-HT-2 was dried and treated again to give SA-HT-3. The increase in the content of boehmite formed is low, typically from 12 wt. % AlOOH after one HT treatment to 19 wt. % AlOOH after three treatments. The protection against hydration is also demonstrated by TEM (Fig. S17): the picture of SA-HT-3 recovered after 3 successive hydrothermal treatments shows small entangled platelets, similar to the starting pristine γ -alumina.

3 Sevilla, M.; Fuertes, A.B., Chem. Eur. J. 2009, 15, 4195 – 4203.

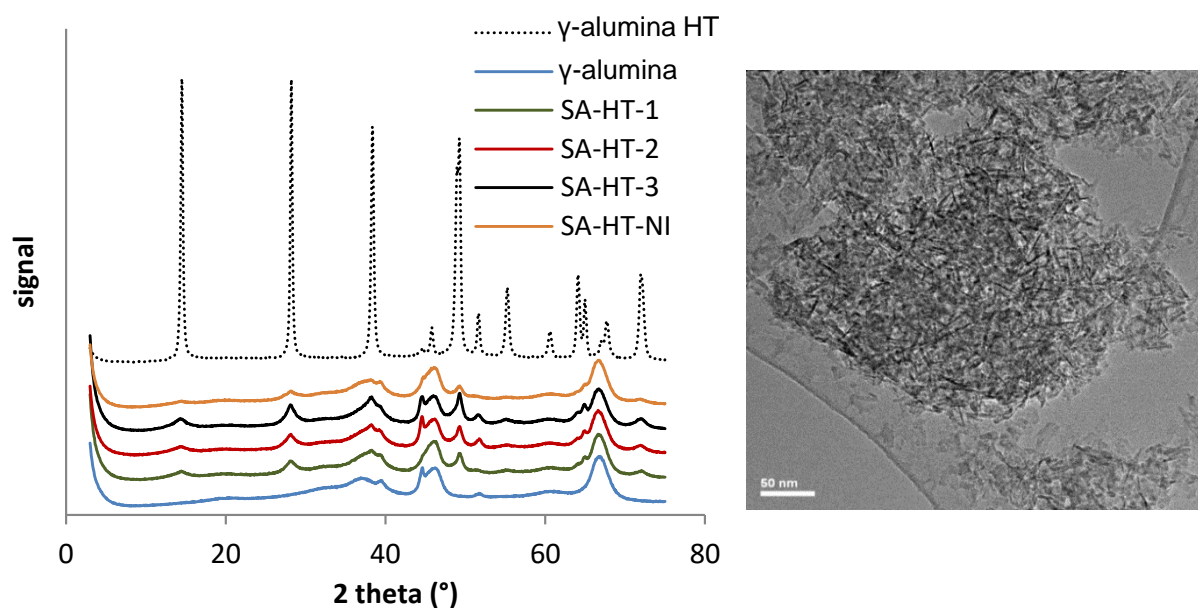


Figure S16 XRD patterns of sucrose/ γ -alumina samples after 1, 2 and 3 successive HT treatments. Patterns of pure γ -alumina before and after HT treatment are also presented for comparison. The solid denoted SA-HT-NI corresponds to the treatment of 5 g of pure γ -alumina in 100 mL of an aqueous solution of sucrose (21 g/L), which corresponds approximately to the amount of carbon necessary to cover the surface of alumina with a graphite monolayer (14 wt.%). The TEM image on the right shows SA-HT-3 recovered after 3 successive hydrothermal treatments

The carbon phase content is close to 13 wt. % in all samples and varies very little between each HT treatment, indicating that the proportion of carbon phase leached under aqueous conditions is negligible. The carbon phase formed contains a very low proportion of aromatics with a majority of aliphatic oxygenated and protonated carbon species (Figure S17).

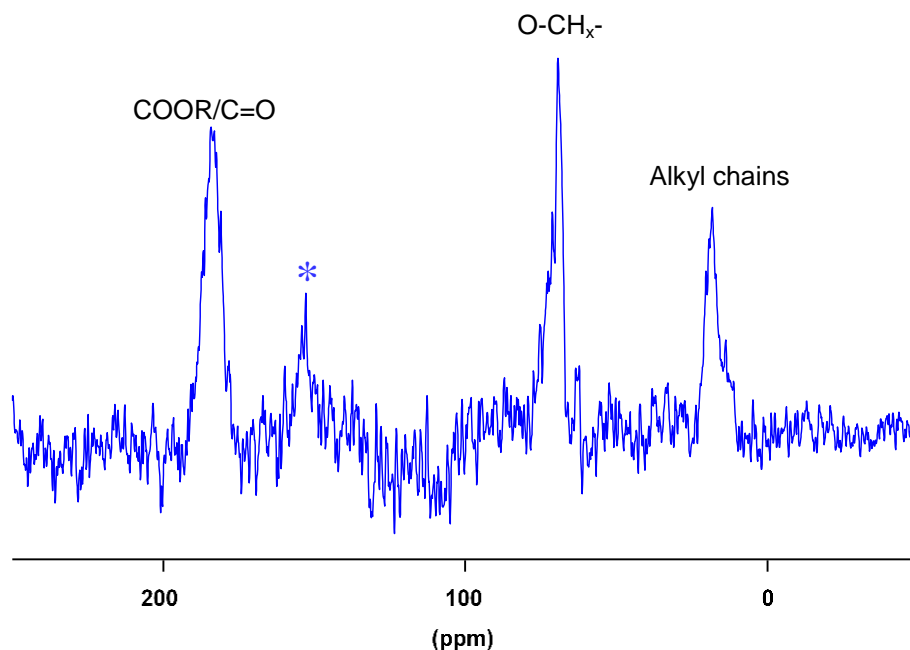


Figure S17 ^{13}C NMR spectrum of sample SA-HT-1

After all tests, the recovered liquid phase is acidic, with a pH value close to 3.5, and it possesses a yellow-brown color (Fig. S18). The color is much more pronounced than for a sample pyrolyzed at 400 °C. The solution likely contains a complex mixture of oxygenated organic products resulting from the decomposition/polymerization of sucrose under HT conditions (5-HMF, levulinic acid, humins, acetic acid, etc.). The complexity of the mixture makes difficult the identification of processes responsible for the protection of alumina. Two main hypotheses can be considered:

- Oxygenated organic compounds present in solution adsorb on γ -alumina accessible surface and polymerize, forming a protective carbonaceous layer well distributed over the entire surface.
- Oxygenated molecules just adsorb on the surface (without subsequent polymerization), which prevents alumina dissolution by modification of the surface chemistry.⁴

4 Copeland, J.R.; Shi, X.R.; Sholl, D.S.; Sievers, C., *Langmuir* 2013, 29, 581–593



Figure S18 *Supernatant liquid phase after one hydrothermal treatment (corresponding solid SA-HT-1).*

For comparison, 5 g of pure γ -alumina were treated hydrothermally in 100 mL of an aqueous solution of sucrose with a concentration of 21 g/L, (0.42 g sucrose/g alumina), which corresponds approx. to the carbon content in impregnated compounds (14 wt. %C). The stability is very good (only 8 % boehmite detected by XRD), suggesting that the adsorption of products resulting from the in-situ decomposition of sucrose under HT conditions is enough to protect γ -alumina from dissolution.

2.5.2. Stability of C/ γ -alumina composites obtained by impregnation/pyrolysis of sucrose

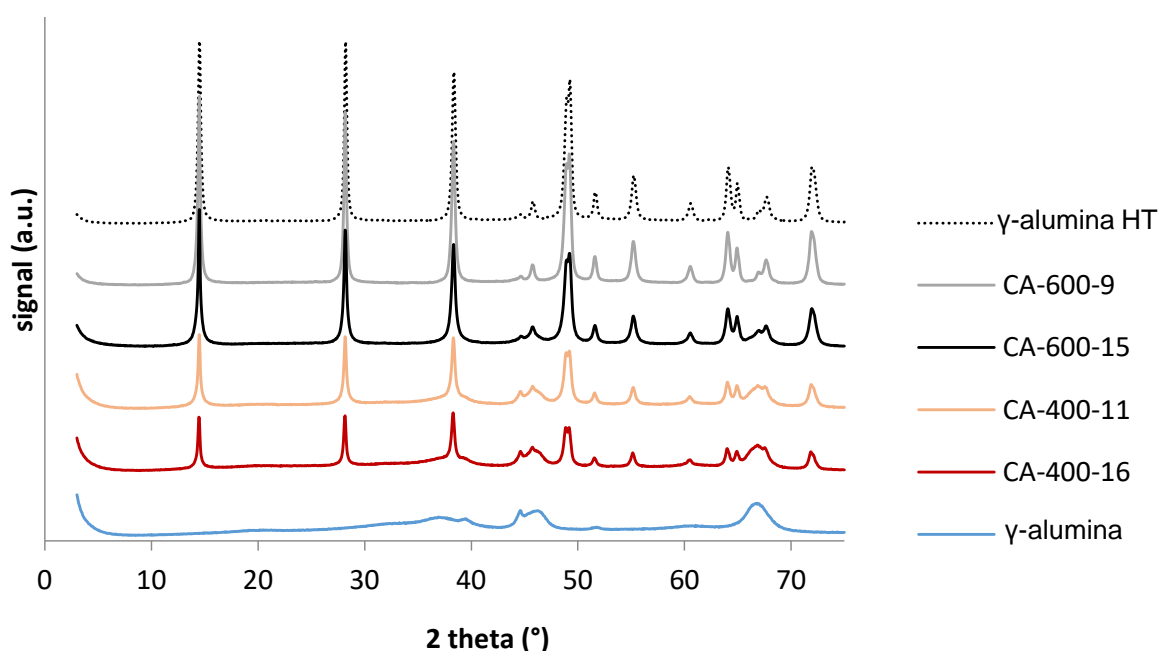


Figure S19 *XRD patterns of C/ γ -alumina composites treated in water at 200°C for 10 h. Composites were prepared by impregnation of different amounts of sucrose and pyrolyzed at 400 or 600°C. Patterns of γ -alumina before and after the same hydrothermal treatment are also plotted for comparison*

2.5.3. Stability of C/ γ -alumina composites obtained by CVD of ethanol

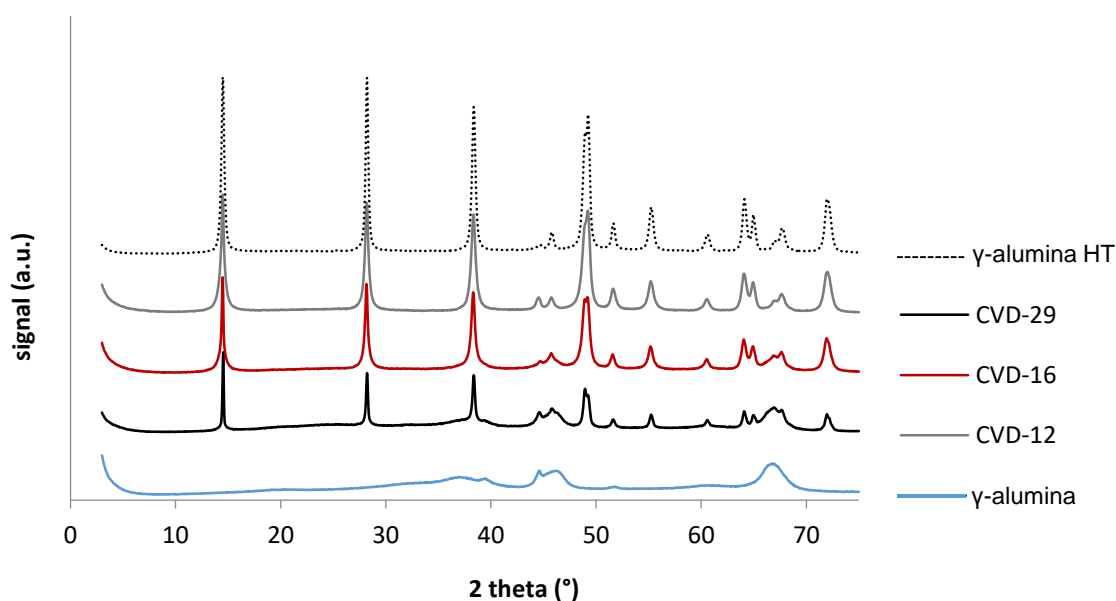


Figure S20 XRD patterns of C/ γ -alumina composites treated in water at 200°C for 10 h. Composites with various carbon contents were prepared by CVD of ethanol. Patterns of γ -alumina before and after the same hydrothermal treatment are also plotted for comparison

2.5.4. Stability of C/ γ -alumina composites obtained by sorbitol adsorption/pyrolysis cycles

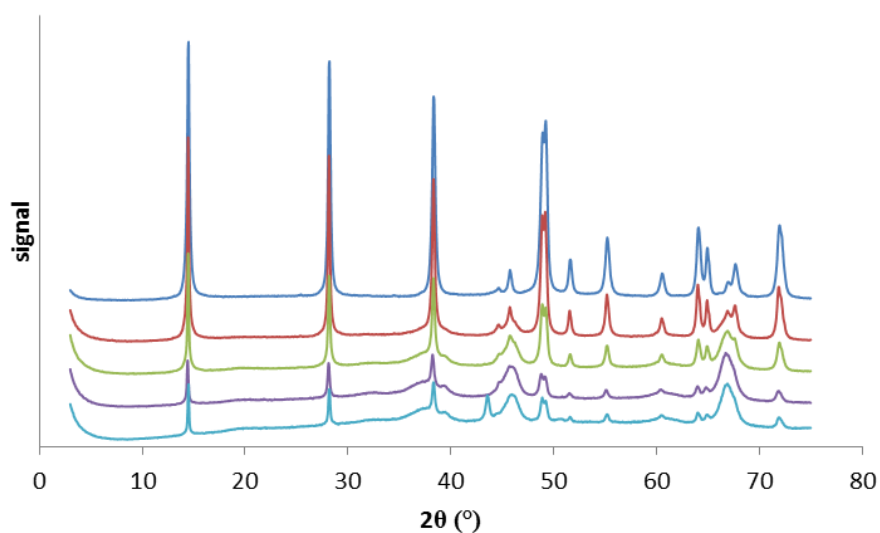


Figure S21 XRD patterns of C/ γ -alumina composites treated in water at 200°C for 10 h. Composites were prepared using successive adsorption/pyrolysis cycles of sorbitol