Development of a high temperature CO2 sorbent based on hydrotalcite for a H2-rich syngas production from biomass.

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Research Article

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Abstract

In order to adapt hydrotalcite based sorbents (LDO) to high temperature CO_2 sorption and suitable temperature for tar steam reforming, the addition of CaO was investigated, maintaining their structure to keep porosity and accessibility but mostly assure the CO_2 sorption stability during sorption/desorption cycles. In co-precipitation synthesis, various interlayer anions with different sizes and valences (carbonate, oxalate, and stearate) and various pH values were studied for different Mg/Ca ratios. The characterization of these sorbents (LDO) by TGA, XRD, N_2 adsorption, SEM, sorption capacity, and sorption/desorption stability (cyclic TGA) permitted to understand the effect of the various synthesis conditions and to highlight the interest of oxalate use as interlayer anion. Typical LDH *sand roses* were formed with carbonate and oxalate anions after calcination until Mg/Ca/Al ratio = 1/2/1. For carbonate, this optimal ratio reached the highest sorption capacity and CaO sites accessibility at 600°C, better than pure CaO. However, the best stability during cycles was obtained with the sorbent from oxalate and Mg/Ca/Al ratio = 1.5/1.5/1 at pH 10 for which sorption results were almost the best values observed. For these two samples, the observed macroporosity were associated to the highest specific surface area and pore volume.

Statement of Novelty

In hydrotalcite structure, a width interlayer space permits to integrate various anions (CO_3^{2-}, SO_4^{-2}, or NO_3^{-}) in order to modify CO_2 sorption kinetics and capacity. The spheroidal “sand rose” morphology observed with CO_3^{2-} anions explained the large BET surface area and the better CO_2 sorption capacity. Stearate (and longer molecules) exchange was extensively studied as long-carbon-chain organic anion and allowed a better CO_2 capture performance.

This work focuses on another interlayer anion (oxalate) with the same valence of carbonate (2), a shape and valence different to stearate (1), and not yet reported in the literature. The novelty is to demonstrate that oxalate can replace carbonate as interlayer anion and moreover stearate by a less toxic one.

Full Text

Figures

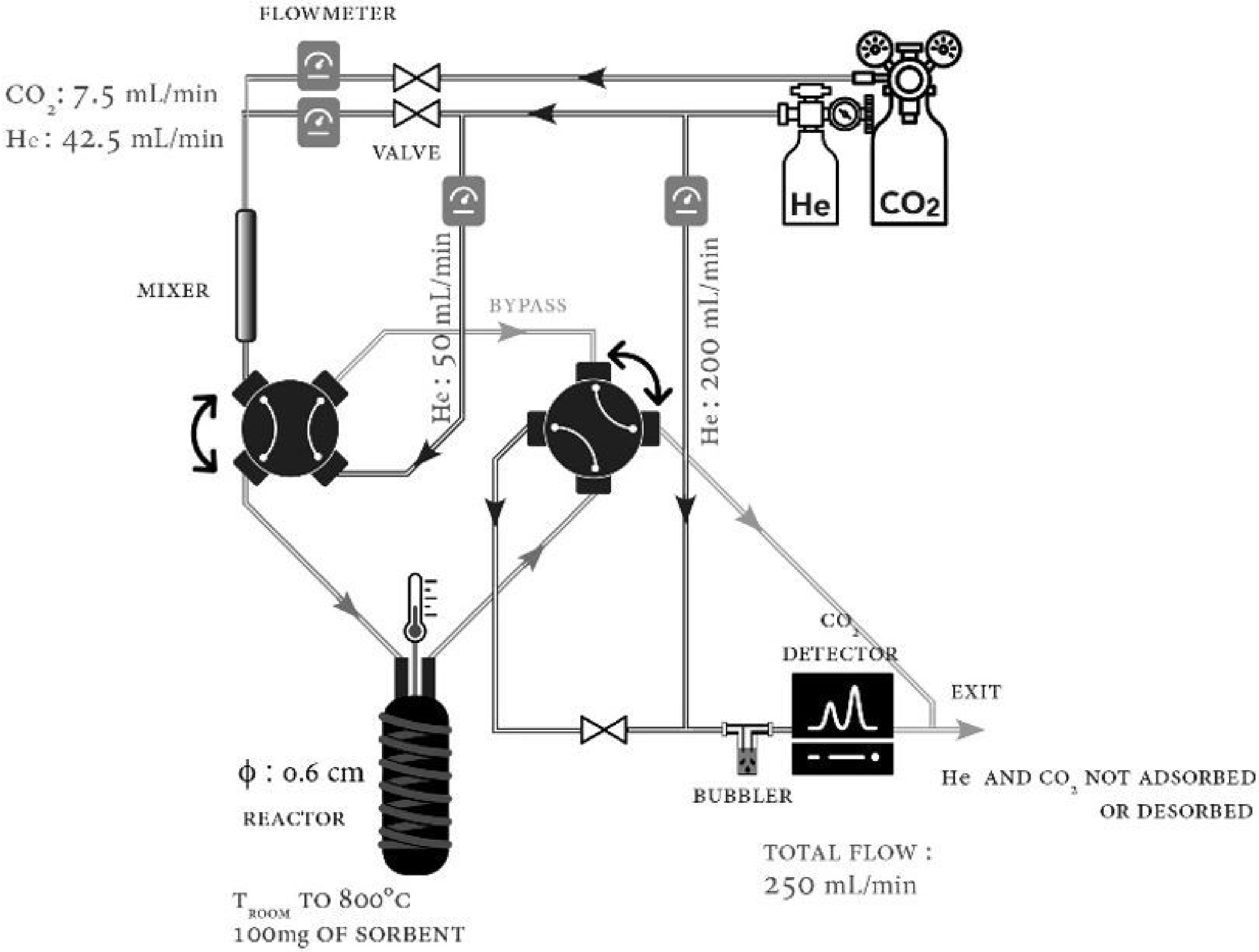

Figure 1

Setup for sorption capacity measurement

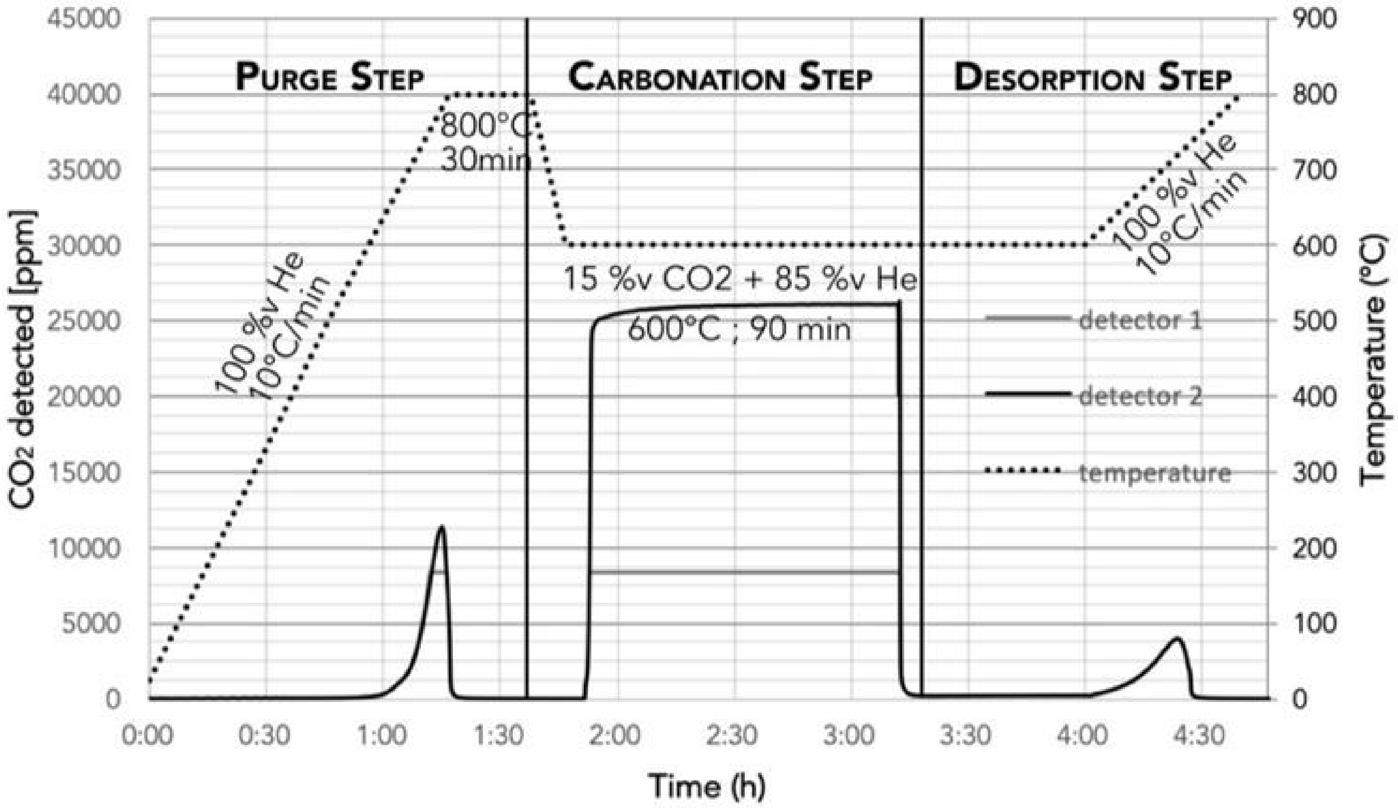

Figure 2

Raw curve of CO2 sorption capacity for 0/3/1CO3·pH10 sample taken as an example

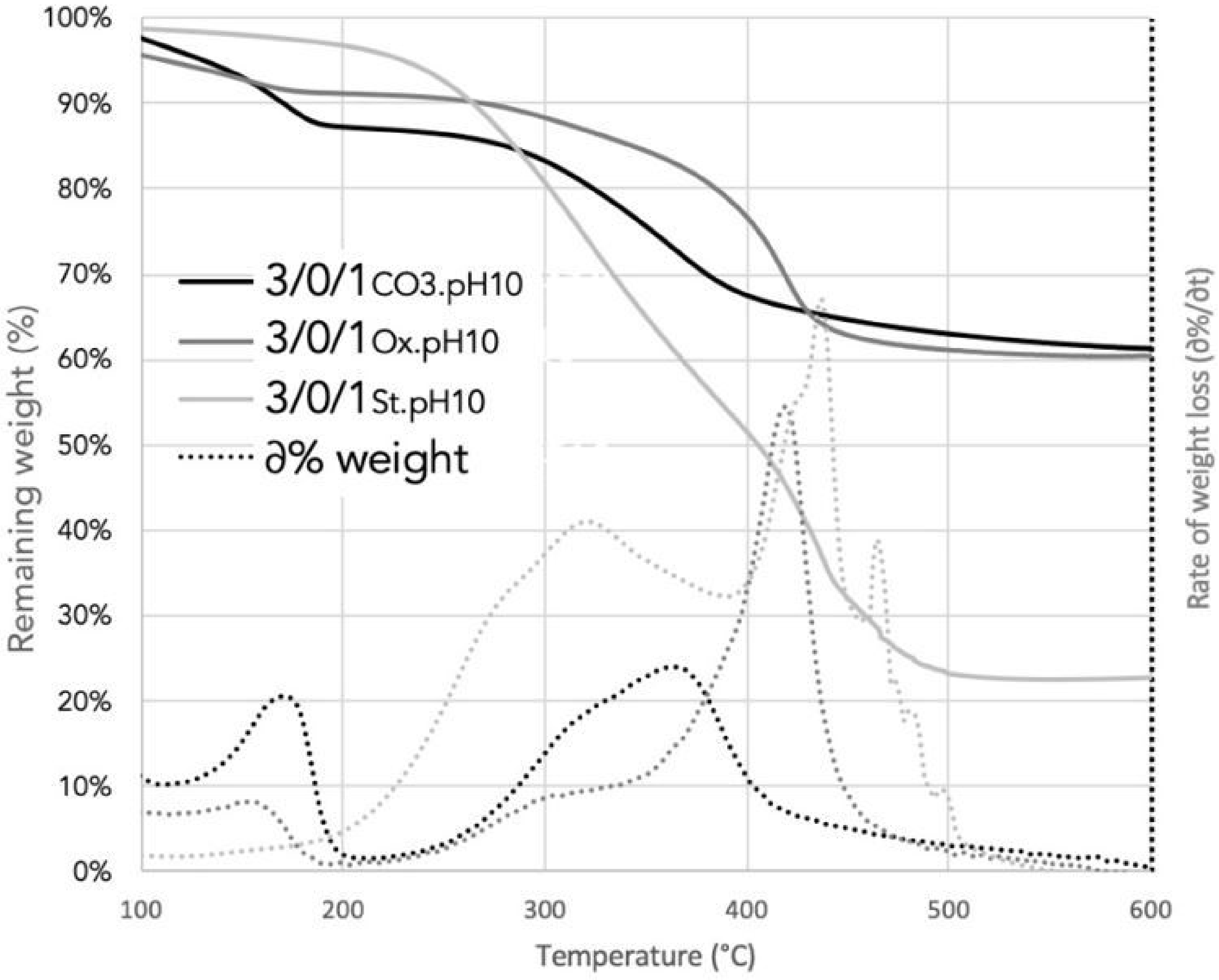

Figure 3

TGA oxidation of 3/0/1 .pH10 samples with various anions

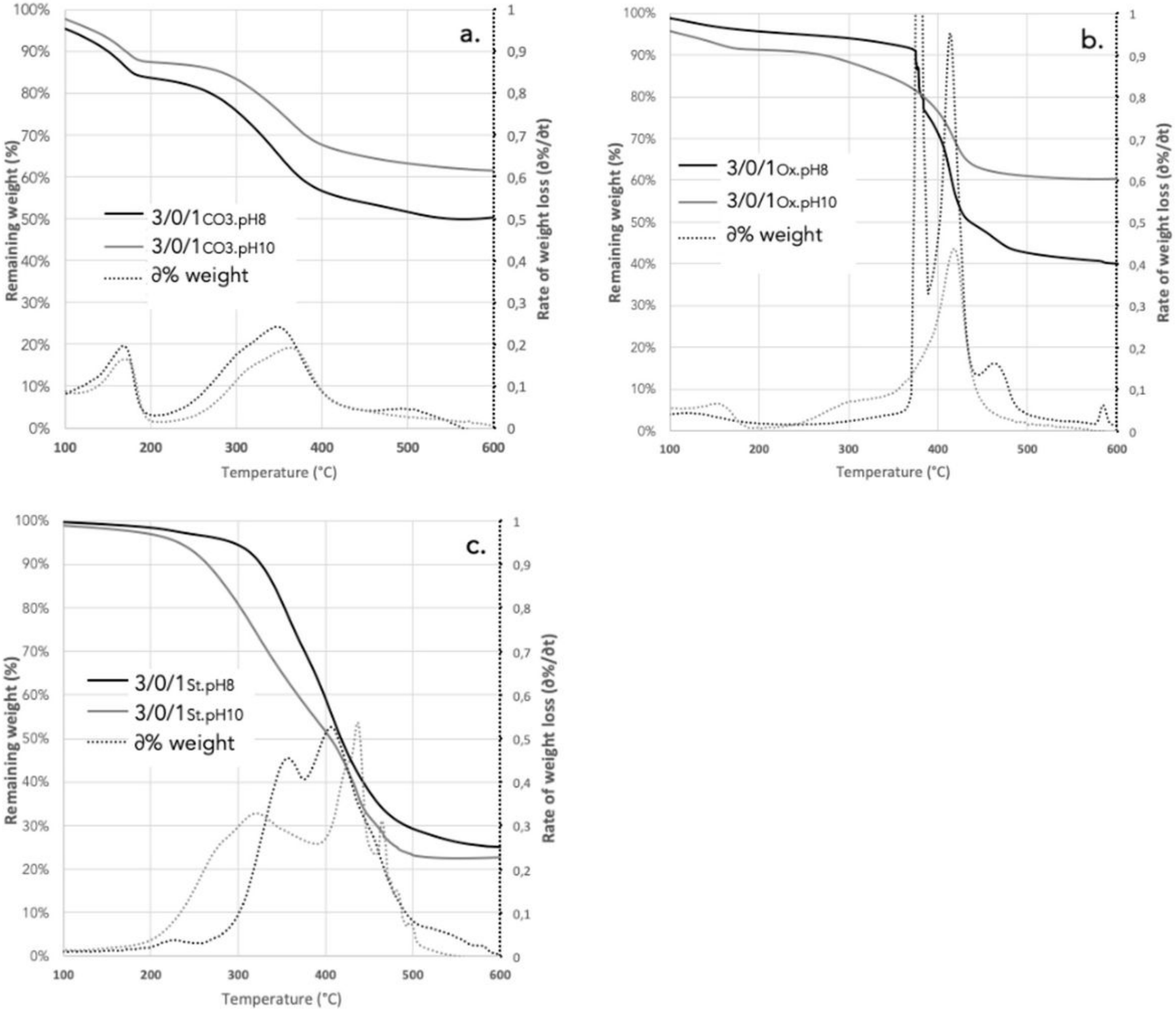

Figure 4

TGA oxidation of 3/0/1 LDH versus pH for a) carbonate, b) oxalate, and c) stearate interlayer anion

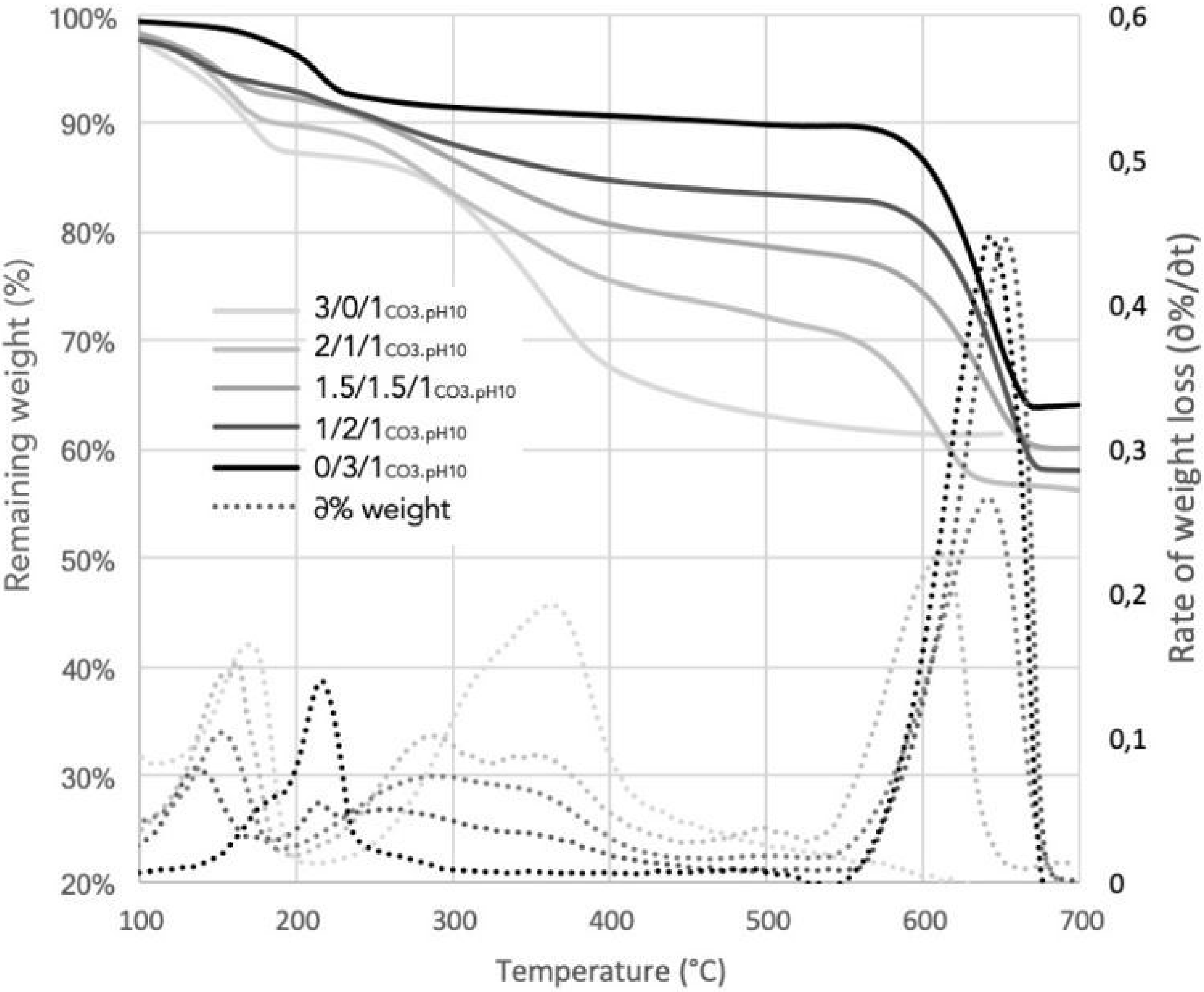

Figure 5

TGA oxidation of Mg/Ca/AlCO3·pH10 samples with various Mg/Ca ratios

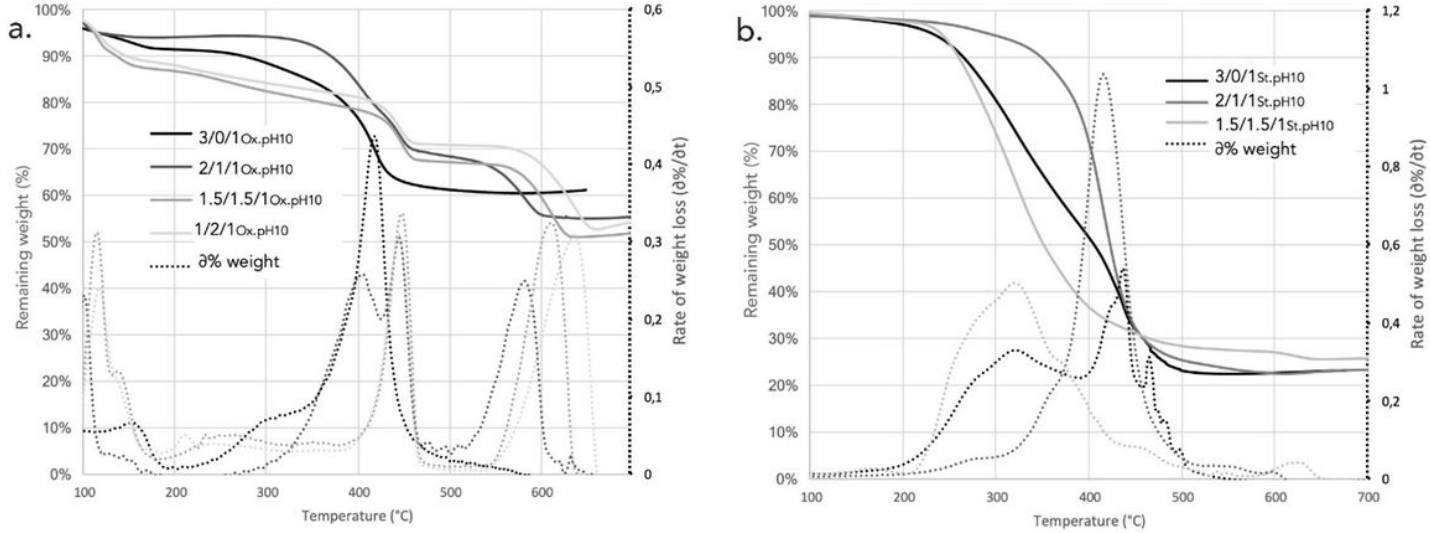

Figure 6

TGA oxidation of a) Mg/Ca/AlOx·pH10 and b) Mg/Ca/AlSt·pH10 samples with various Mg/Ca ratios

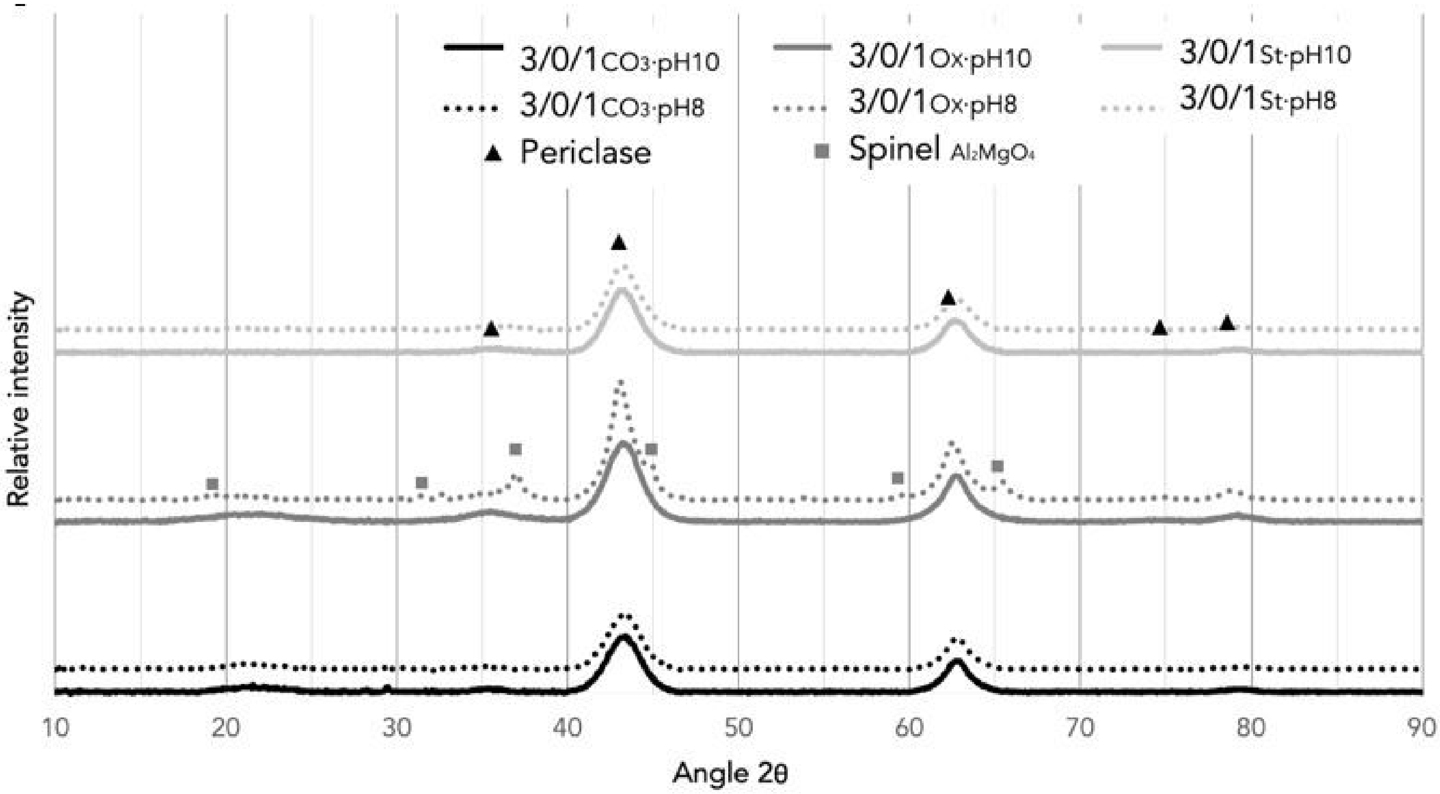

Figure 7

X-Ray diffractograms of LDO samples calcined at 500°C prepared from LDH 3/0/1 ratio, according to interlayer anions and to pH values

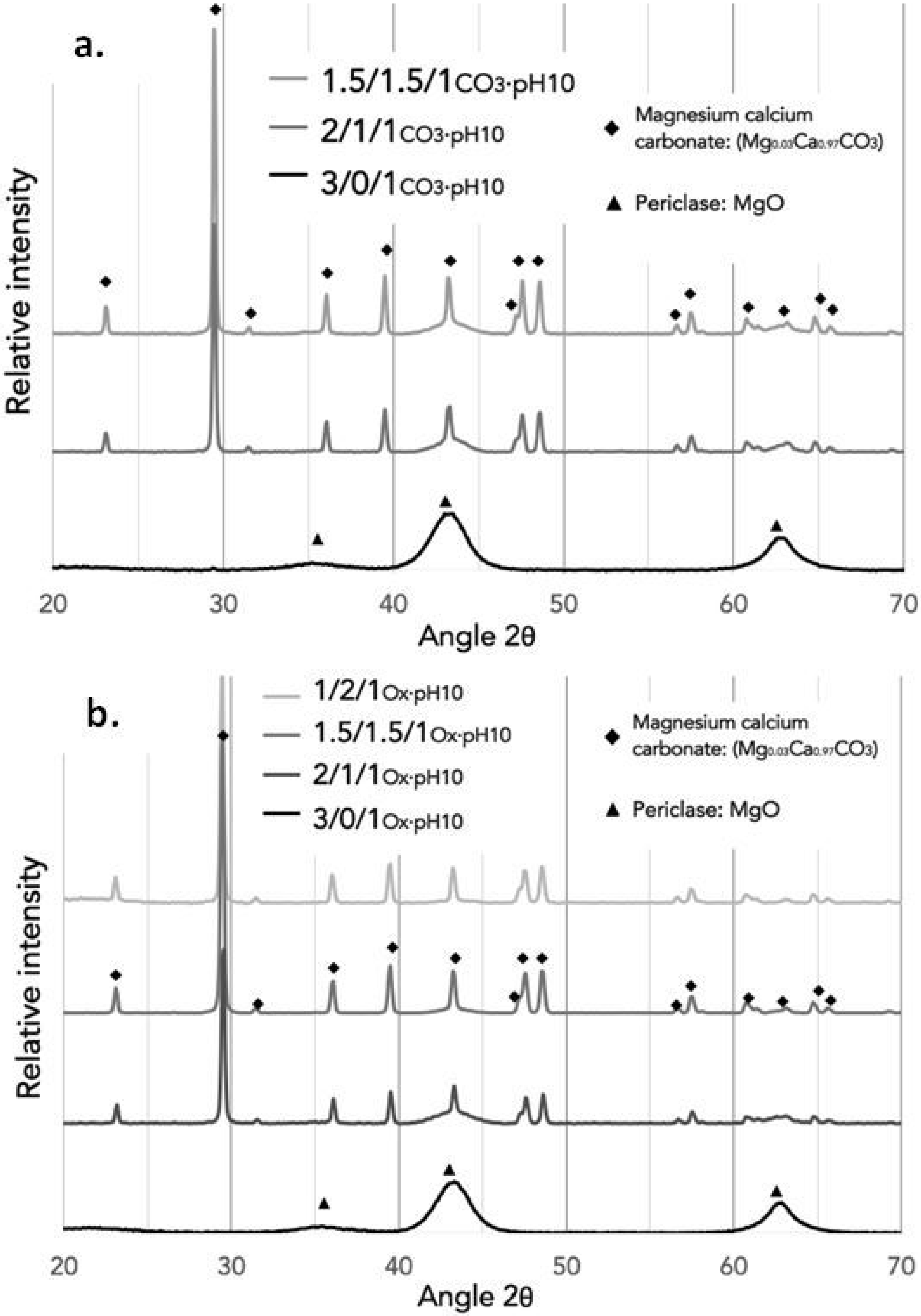

Figure 8

X-Ray diffractograms of LDO samples prepared from LDH a) carbonate and b) oxalate interlayer anion and pH 10, calcined at 500°C, according to Mg/Ca ratios

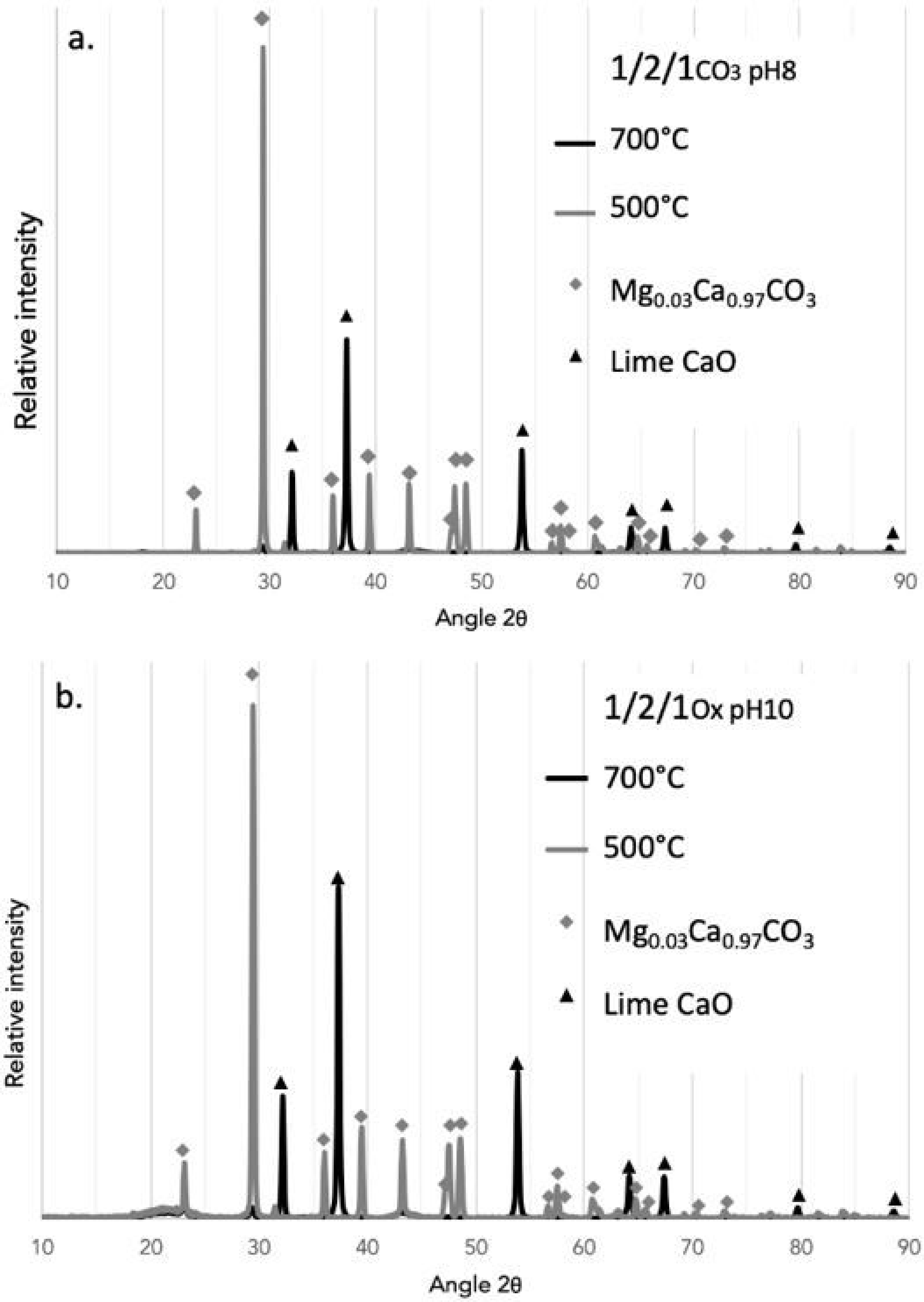

Figure 9

X-Ray diffractograms of LDO samples prepared from a) 1/2/1CO3.pH8, and b) 1/2/1Ox.pH10 LDH according to calcination temperature

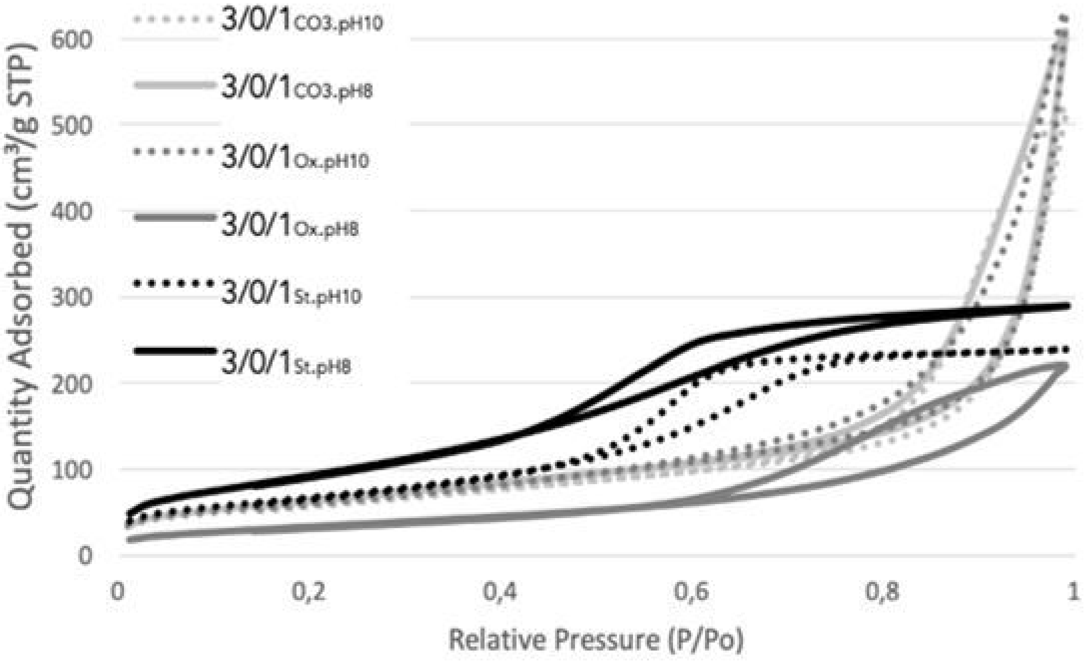

Figure 10

BET adsorption/desorption isotherms of LDO samples calcined at 500°C from 3/0/1 LDH versus pH and interlayer anion

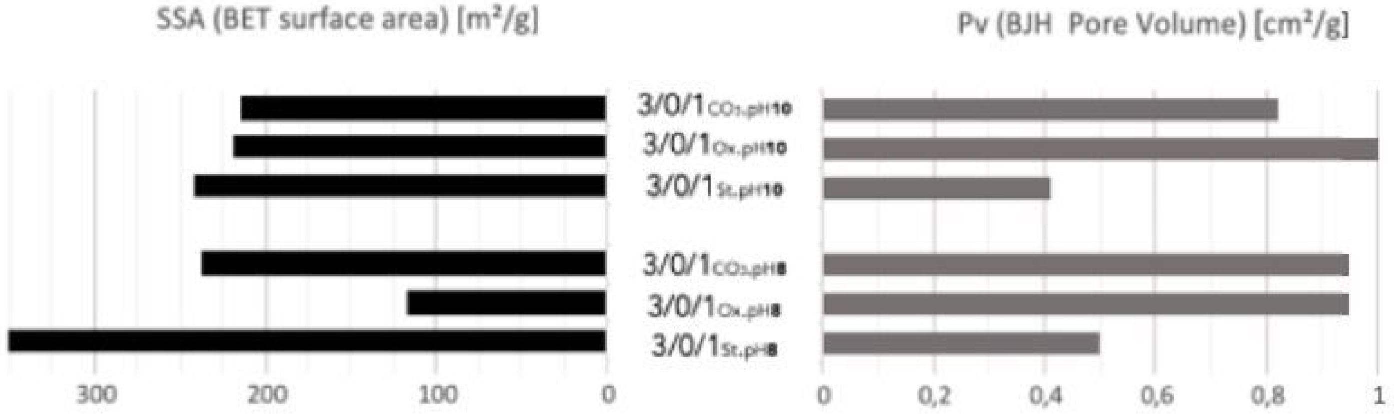

Figure 11

BET surface area (SSA) and BJH pore volume (Pv) for LDO samples calcined at 500°C from 3/0/1 LDH versus pH and interlayer anion

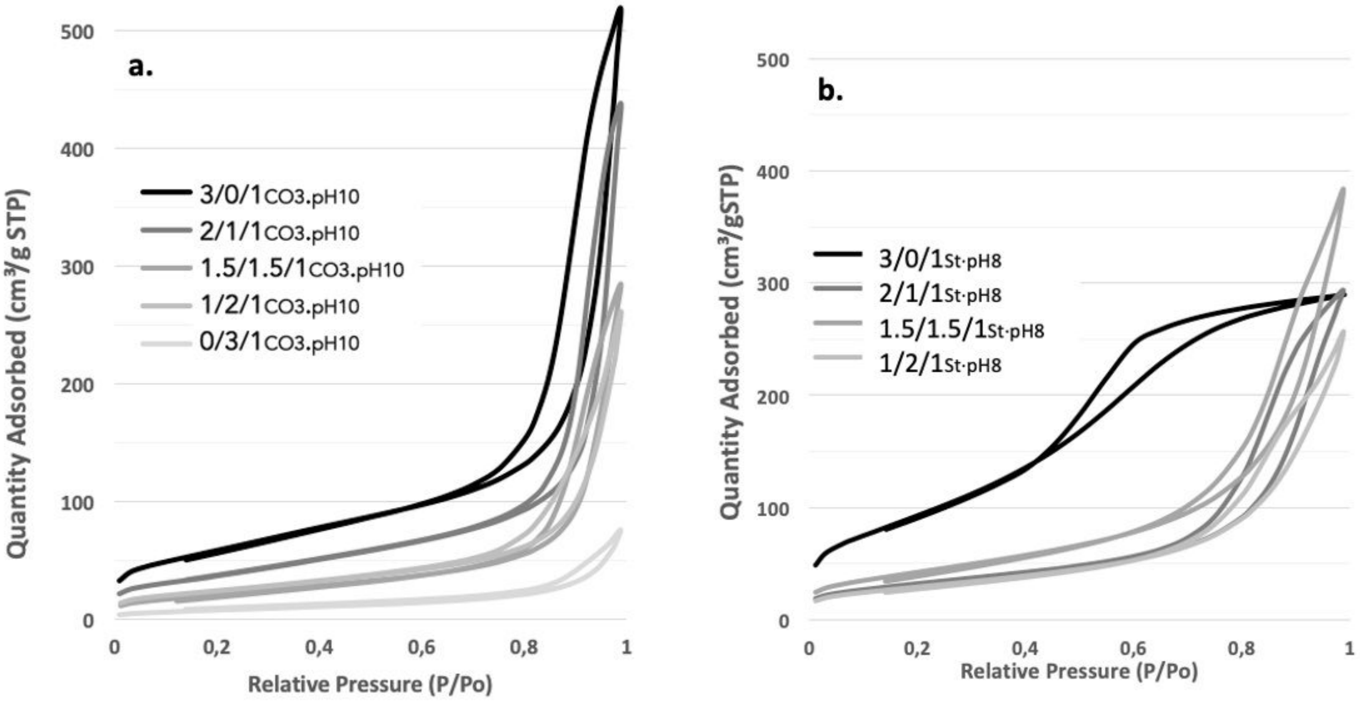

Figure 12

BET adsorption/desorption isotherms of LDO samples calcined at 500°C a) from carbonate LDH, and b) from stearate LDH with various Mg/Ca ratios

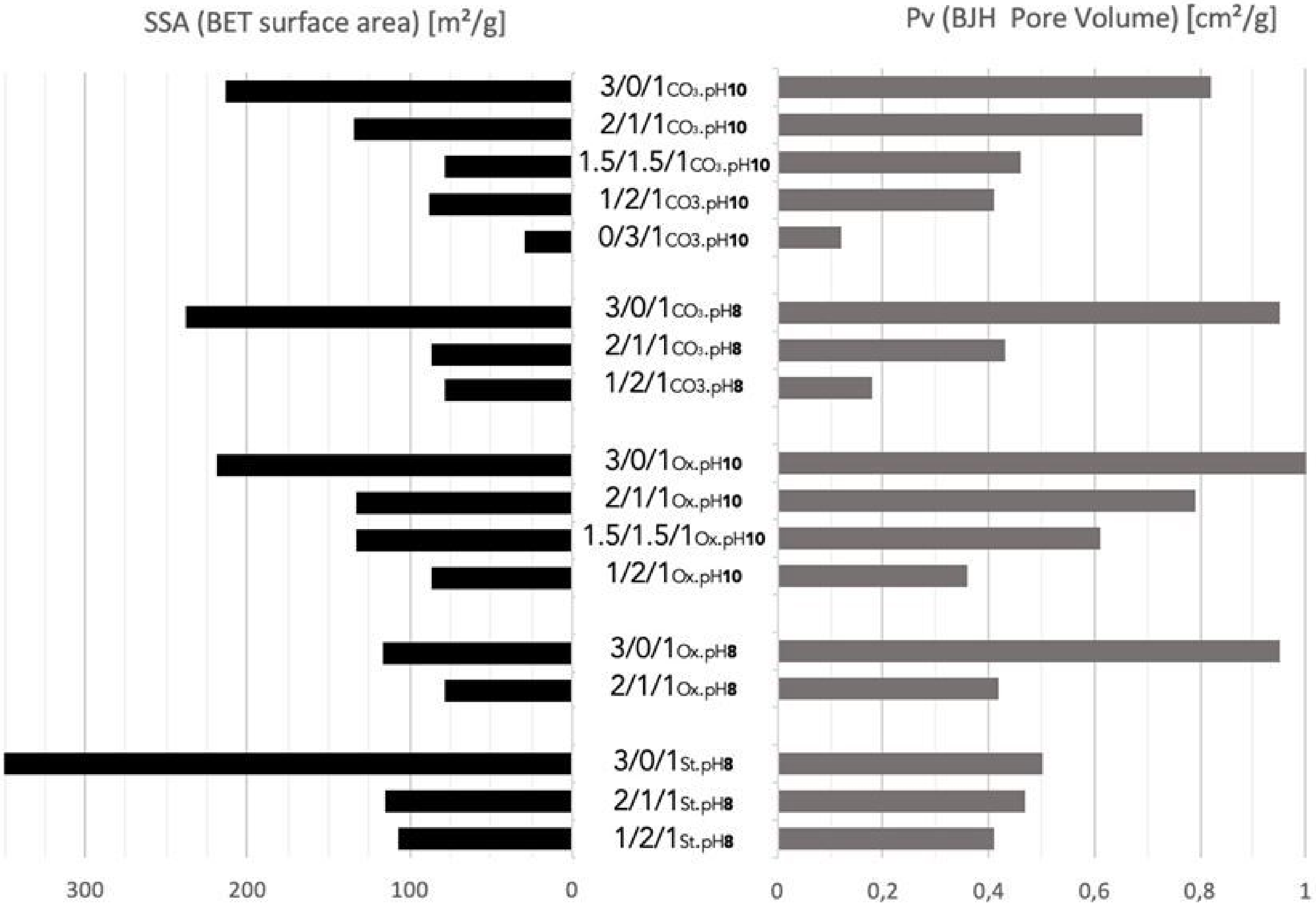

Figure 13

BET surface area (SSA) and BJH pore volume (Pv) for LDO samples calcined at 500°C from 3/0/1 LDH versus pH and interlayer anion

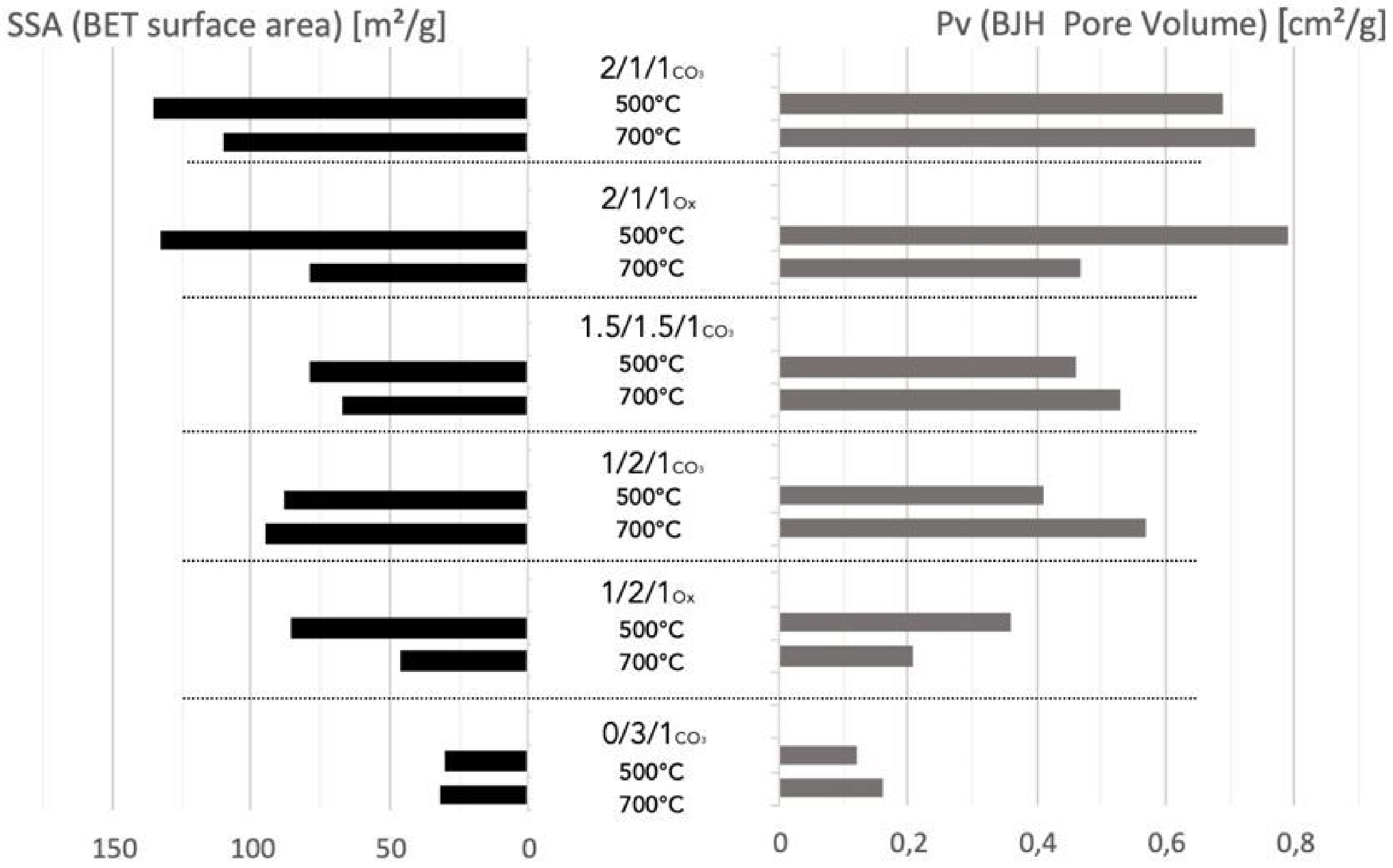

Figure 14

BET surface area (SSA) and BJH pore volume (Pv) for LDO samples from Mg/Ca/AlCO3.pH10 and Mg/Ca/AlOx.pH10 versus composition and calcination temperature

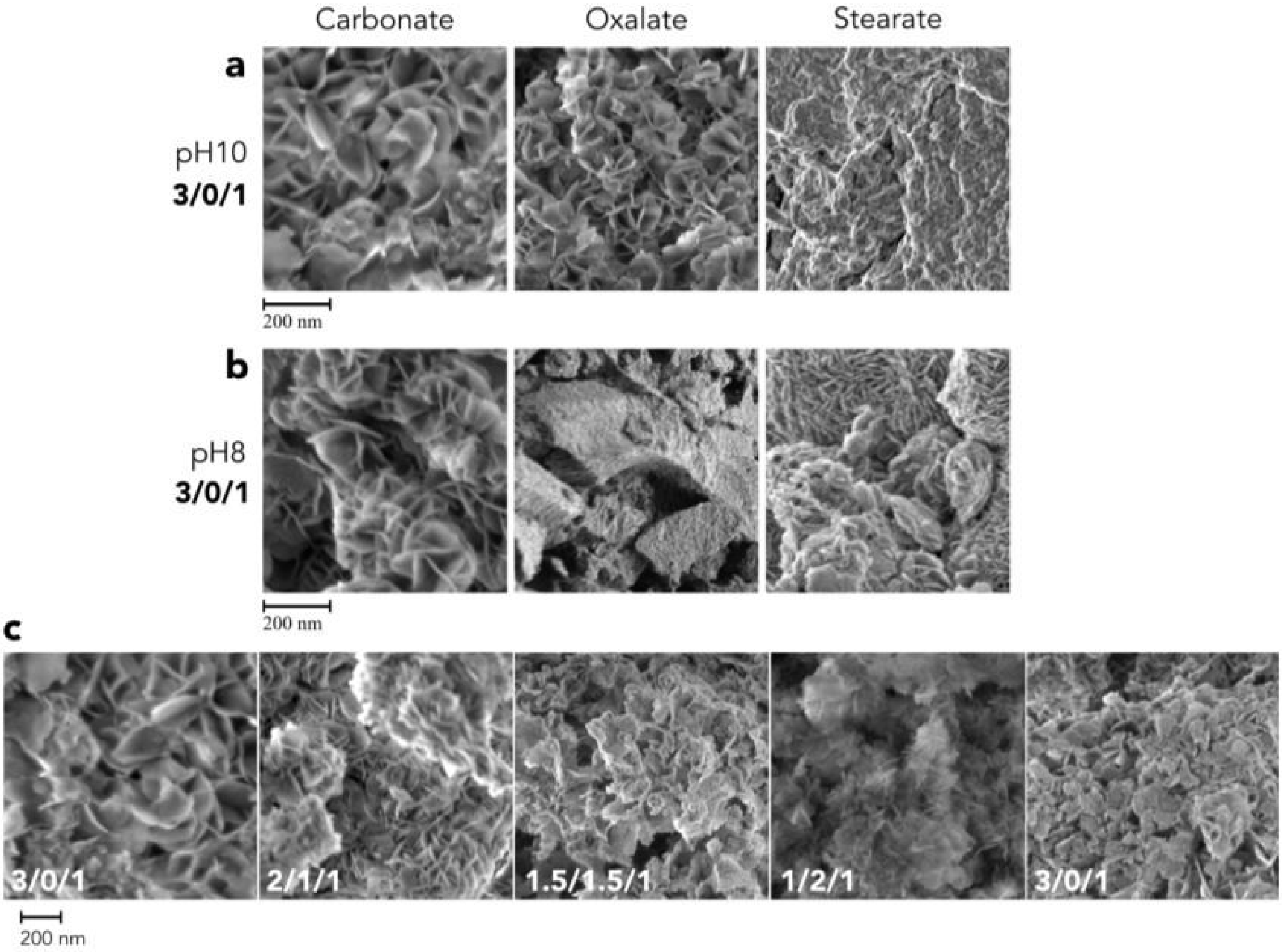

Figure 15

SEM pictures of a) Mg/Ca/Al·pH10 samples versus interlayer anion, b) Mg/Ca/Al·pH8 samples versus interlayer anion, and c) Mg/Ca/AlCO3·pH10 samples versus Mg/Ca ratio calcined at 500°C

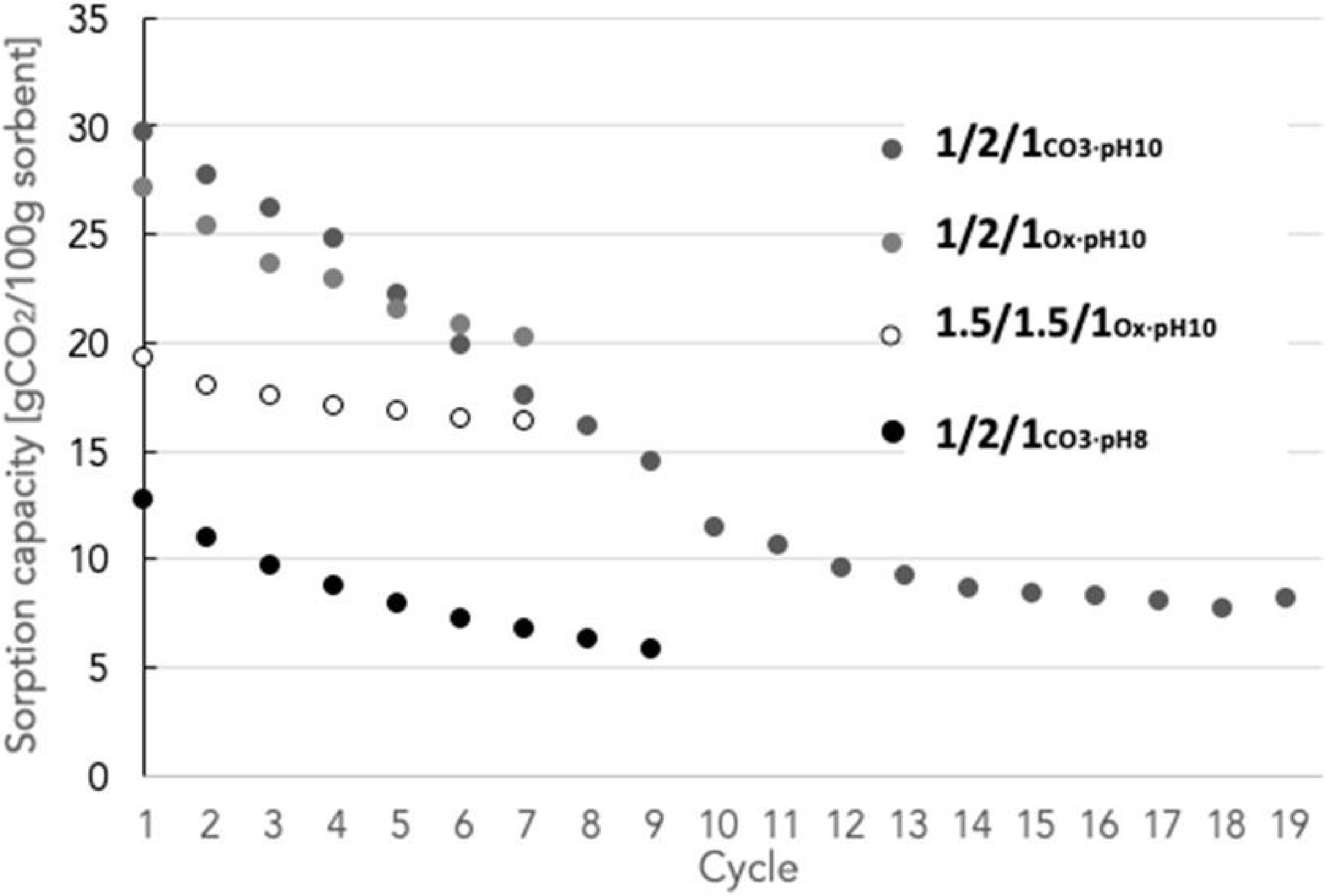

Figure 16

Sorption capacity versus absorption/desorption cycles number for various sorbents at 500°C