Supporting Information for:

Cation Dependant Carbonate Speciation and the Effect of Water

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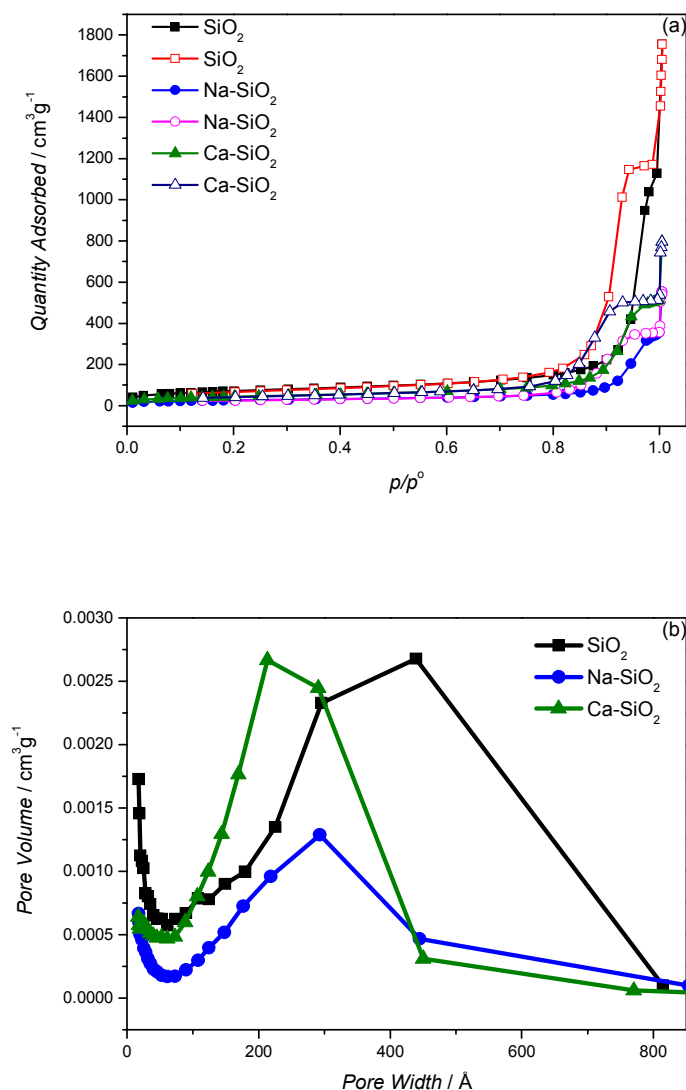[3] Consorzio INSTM, UdR Torino, via G. Giusti, 9 - 50121 Firenze (Italy).

Figure S1 - (a) N$_2$ adsorption-desorption isotherms and (b) pore size distribution plots of SiO$_2$, Na-SiO$_2$ and Ca-SiO$_2$ as prepared. Isotherms are of Type IV classification and exhibit H1 hysteresis loops, indicating that the parent material is mesoporous, a feature preserved following doping. A shift to smaller pore width values is evidenced upon doping, with a decrease in total pore volume more evident for Na-SiO$_2$.
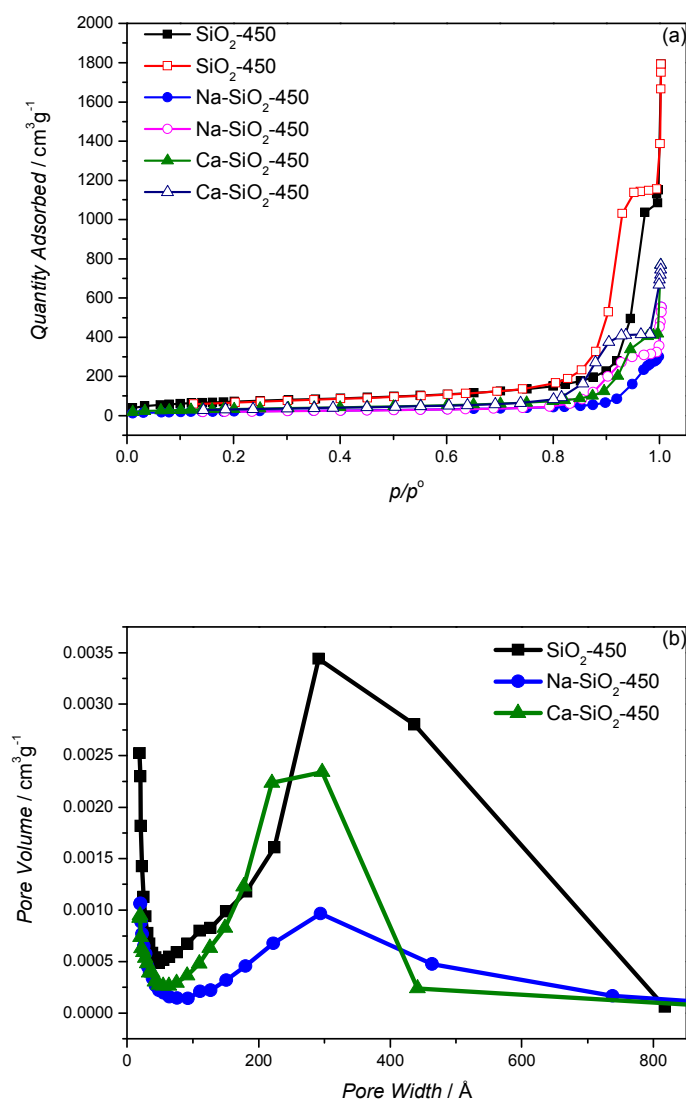
Figure S2 - (a) N$_2$ adsorption-desorption isotherms and (b) pore size distribution plots of SiO$_2$, Na-SiO$_2$ and Ca-SiO$_2$ after calcination. Isotherms are of Type IV classification and exhibit H1 hysteresis loops, indicating that upon calcination the material is mesoporous. A general loss in pore volume is evidenced across a wide range of pore values as compared to Figure S1.
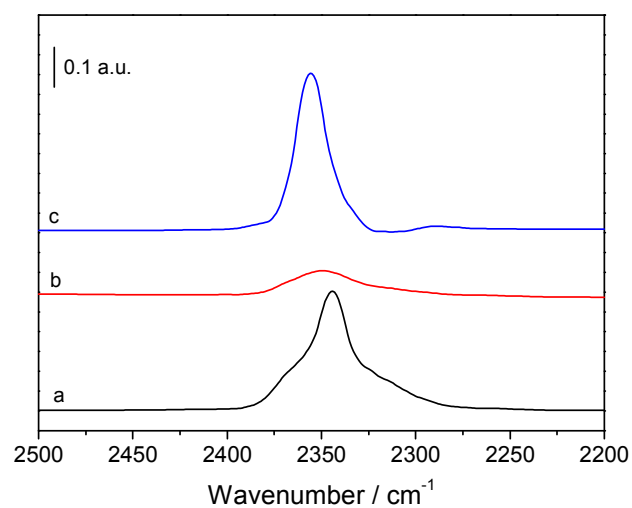
Figure S3 – FTIR spectra in the 2500-2200 region relative to ν_3 mode of molecular (physi)sorbed CO_2. Curves a-b-c refers to plain SiO_2, Na-SiO_2 and Ca-SiO_2, respectively, after thermal treatment at 400 °C *in vacuo.*

Calculation of surface coverage after cation-exchange

Concentration of surface hydroxyl groups taken – 4.6 and 4.9 OH nm^{-2} for least-squares and arithmetical mean respectively.

Water treated silica surface area = 252 m^2 g^{-1}

Considering the surface area and the concentration of OH groups on the surface, there will be 1.16×10^{21} and 1.23×10^{21} surface hydroxyl groups per gram of SiO_2.

Considering the EDX results for Na-SiO_2 determining a value of 4.85 wt% Na$^+$, this equates to 1.27×10^{21} atoms (2.11 mmol) of Na per gram of Na-SiO_2.

Considering the EDX results for Ca-SiO_2 determining a value of 4.16 wt% Ca^{2+}, this equates to 6.25×10^{20} atoms (1.04 mmol) of Ca per gram of Ca-SiO_2.

Given the concentration of OH groups, the amount of available Na$^+$ ions and an assumption of direct exchange of one H$^+$ for each Na$^+$ it can be determined that the surface coverage is 109.6 and 102.9 % for least-squares and arithmetical mean OH concentration respectively.

Given the concentration of OH groups, the amount of available Ca^{2+} ions and an assumption of direct exchange of two H$^+$ for each Ca^{2+} it can be determined that the surface coverage is 107.9 and 101.2 % for least-squares and arithmetical mean OH concentration respectively.

Coverage (θ) is defined as the amount of adsorption sites (OH) occupied by adsorbate ions (Na/Ca), expressed as a percentage of available surface sites based on the assumed concentrations for amorphous silica above.