# Electronic Supplementary Information

## Characterization of the starting $CaCO_3$

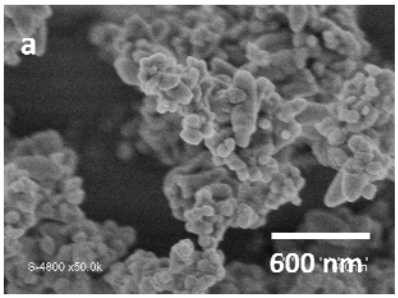


**Fig. S1**: SEM image of the starting $CaCO_3$

## Characterization of calcium phosphonate model compounds

The layered calcium phosphonate salts $Ca(PhPO_3H)_2$ and $Ca(C_{12}H_{25}PO_3H)_2$ were characterized by XRD, $^{31}P$ MAS NMR and FTIR. The powder XRD patterns of these layered compounds (Fig. S2) were dominated by a very intense reflection at 5.8° and 2.8°, respectively, corresponding to interlayer distances of 1.55 and 3.40 nm.

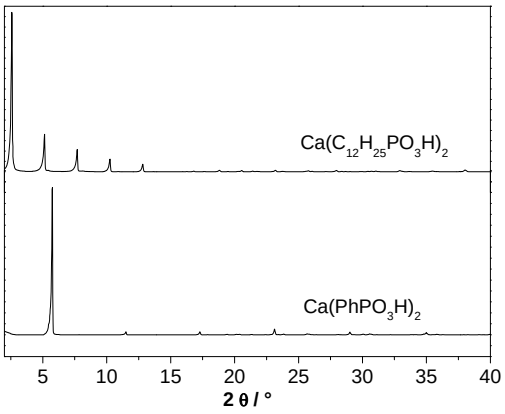


**Fig. S2.** Powder XRD patterns of the model calcium phosphonate compounds.

The $^{31}P$ MAS NMR spectra of the model compounds (Fig. S3) showed sharp resonances at 9.9 ppm ($Ca(PhPO_3H)_2$) or 25.4 and 30.1 ppm ($Ca(C_{12}H_{25}PO_3H)_2$).

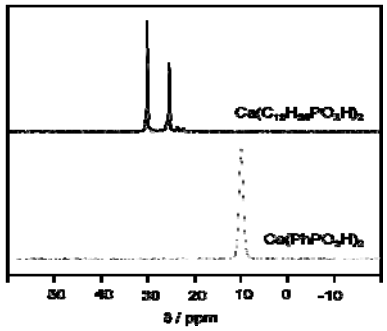


**Fig. S3.** $^{31}P$ MAS NMR spectra of the model calcium phosphonate compounds.

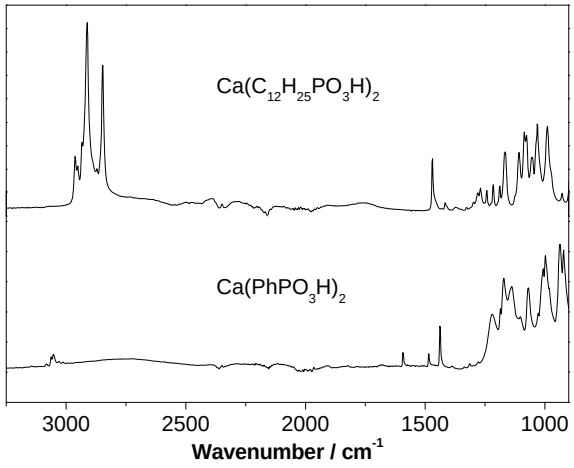


**Fig. S4.** FTIR spectra of the model calcium phosphonate compounds.

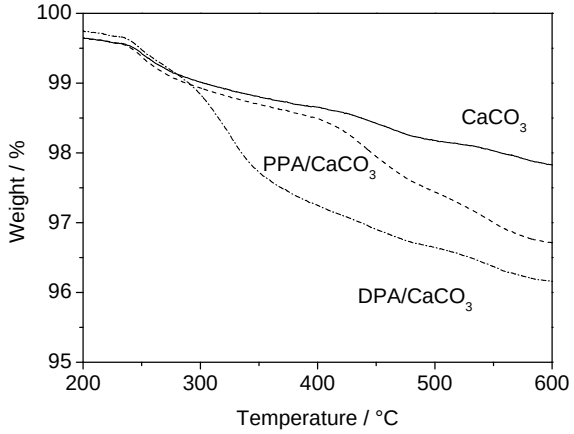


**Fig. S5** : TGA curves for the starting $CaCO_3$ and $CaCO_3$ reacted with PPA and DPA (10 molecules of phosphonic acid/$nm^2$) in THF a 22°C for 63 h.

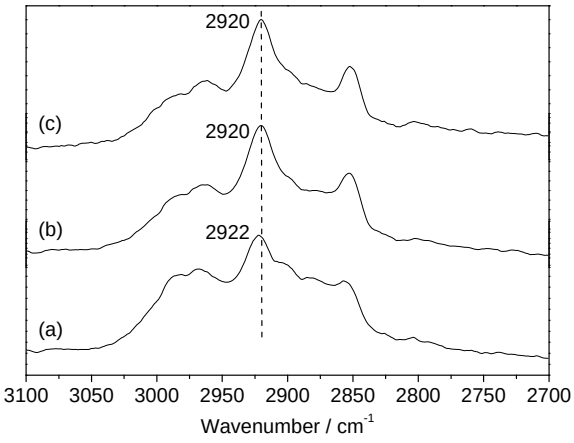


**Fig.S6** FTIR spectra of $CaCO_3$ reacted at 22 °C in THF with (a) 5 DPA/$nm^2$ for 2 h; (b) 5 DPA/$nm^2$ for 63 h; (b) 10 DPA/$nm^2$ for 63 h.