

## AN IN SITU SPECTROSCOPIC STUDY OF NANOSTRUCTURED AMINOSILANE-GRAFTED SILICA ADSORBENTS FOR CO<sub>2</sub> CAPTURE.

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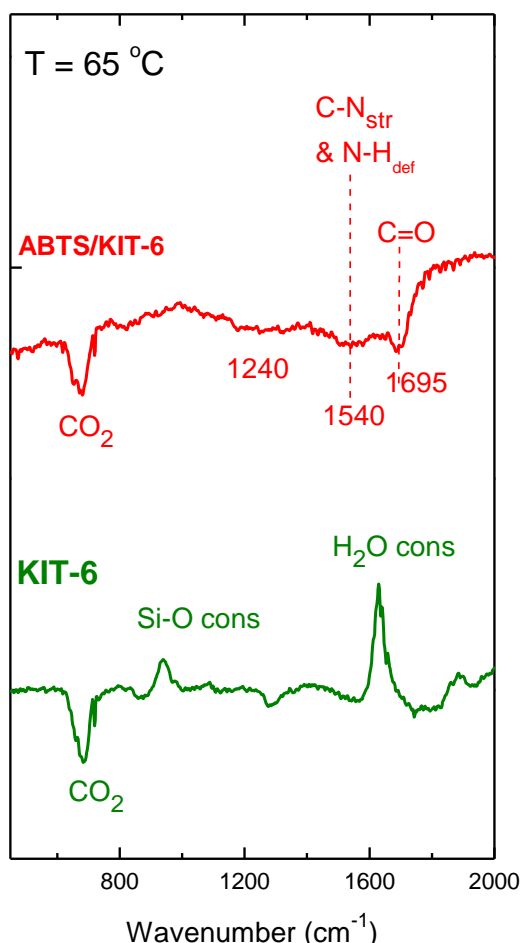
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### ABSTRACT

The present study is a part of an ongoing collaborative project targeting the design and synthesis of hybrid functionalised nanostructured materials for capturing CO<sub>2</sub>. To this end, CO<sub>2</sub>-phylic amine entities are organised on robust porous materials and hybrids. Grafting is chosen as the means of functionalization instead of physical impregnation, which is the common method reported in the literature. Primary, secondary, tertiary and poly aminosilanes are tested on the same adsorbent either individually or by combining more than one type of aminosilane. *In situ* molecular spectroscopy (Raman and FTIR) in the temperature range of interest (*i.e.*, 25 – 65 °C) is applied under flowing inert (He) or CO<sub>2</sub>-containing gas mixtures in order to shed light on mechanisms and interactions of gases with the adsorbent supports and the amine surface functionalities.



The FTIR spectra of the as synthesised materials show that grafting results in consumption of free surface silanols and a perturbation of Si-O-Si functionalities (broadening and red shift of pertinent bands), caused by the grafting of aminosilanes into the adsorbent. Moreover, presence of amine and methyl /methylene groups is evidenced by bands due to (N-H)<sub>def</sub> and (CH<sub>2</sub>/CH<sub>3</sub>)<sub>def</sub> modes.

A comparison of *in situ* FTIR spectra obtained at 65°C under flowing inert (He) and CO<sub>2</sub> gas for the bare KIT-6 adsorbent and an aminosilane-grafted material shows (Fig. 1) a thoroughly different mechanism of CO<sub>2</sub> capture by the two materials. In the case of bare KIT-6 silica, capture proceeds via consumption of water molecules (retained by the surface by H-bonds) and of free surface silanols. The CO<sub>2</sub> capture by the aminosilane-grafted material results presumably in H-bonded silylalkyl-carbamate formation evidenced by emergence of bands at ca. 1690 (primarily C=O), 1540 (N-H<sub>def</sub> and C-N<sub>str</sub>) and 1240 cm<sup>-1</sup>.

**KEYWORDS:** CO<sub>2</sub> capture; nanostructured silica; aminosilanes; *in situ* FTIR; silylalkylcarbamate

**Figure 1.** Difference *in situ* FTIR spectra obtained for bare KIT-6 silica adsorbent and aminosilanised ABTS/KIT-6 at 65°C under flowing inert (He) and CO<sub>2</sub> gas. The spectrum obtained under He is subtracted in each case from the spectrum obtained under CO<sub>2</sub>