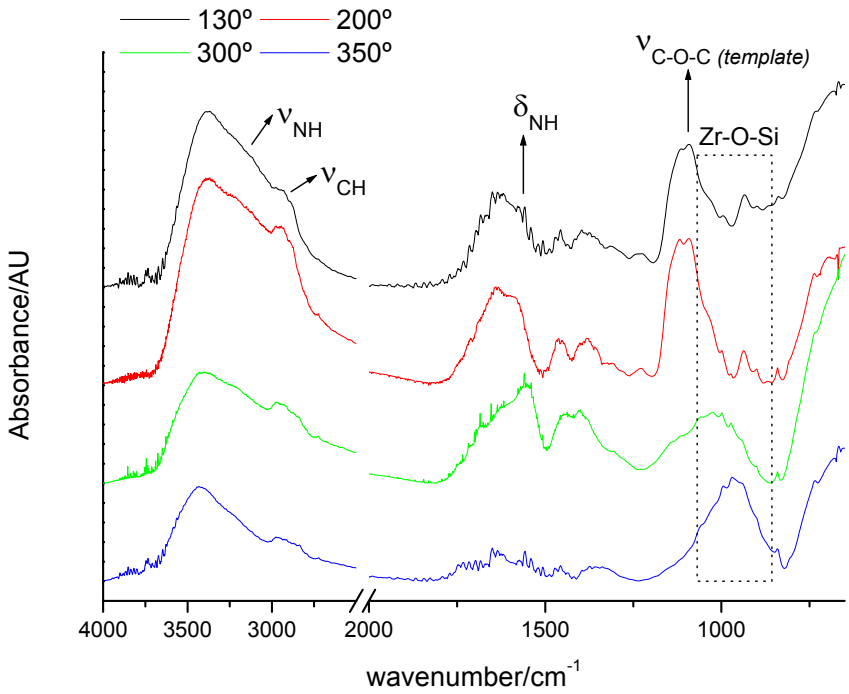
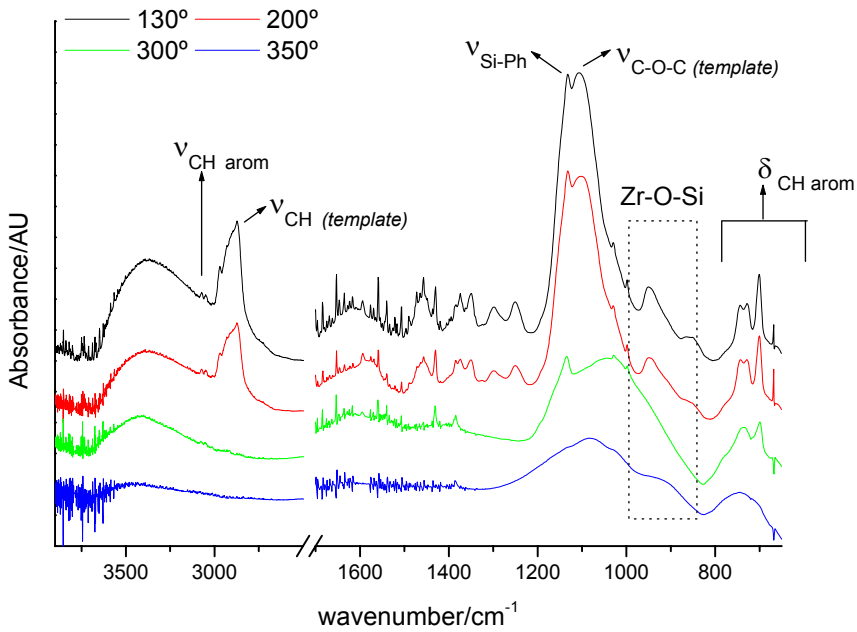
- *Detailed FTIR spectra of ZSA91 (dip coated on KBr pellets) with different thermal treatments*



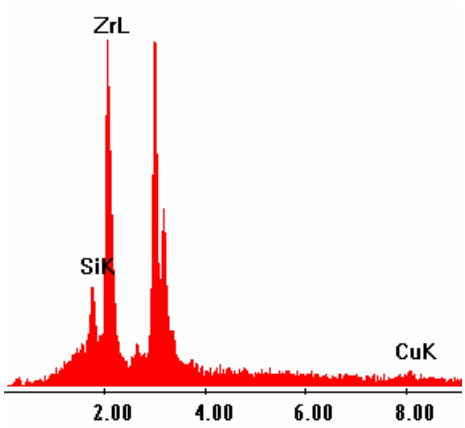
Bands corresponding to the template (ν_{CH} at 2850-2920; $\nu_{C\text{-}O\text{-}C}$ at 1038 and 1118 cm^{-1}) are lost upon thermal treatment until 300ºC, while NH (ν_{NH} at 3200 cm^{-1}, δ_{NH} at 1570cm^{-1}; broad primary amine band at 650-895 cm^{-1}) and a fraction of the CH species (remaining CH bands at 2850-2920 cm^{-1}) are conserved until 350ºC indicating that the propylamino dangling groups are conserved. Si-O-Zr bands are observed at 960-1000 cm^{-1} and no Si-O-Si bands (1000-1200 cm^{-1}) are observed, ruling out phase segregation.



- *Detailed FTIR spectra of ZSP82(dip coated on KBr pellets) with different thermal treatments*

Bands corresponding to phenyl vibrations (weak ν_{CH} at 3056 and 3079 cm^{-1}; ν_{Si-Ph} at 1133 cm^{-1}, C-H oop deformation at 704 and 740 cm^{-1}) suffer no significant degradation until 200°C and they are clearly observed until 300°C, when the template is totally eliminated (no more bands at 2850-2920 -ν_{CH}- and 1038 and 1118 cm^{-1} -ν_{C-O-C}- are observed). Treatment at 350ºC causes function lost as evidenced by the phenyl bands disappearance.

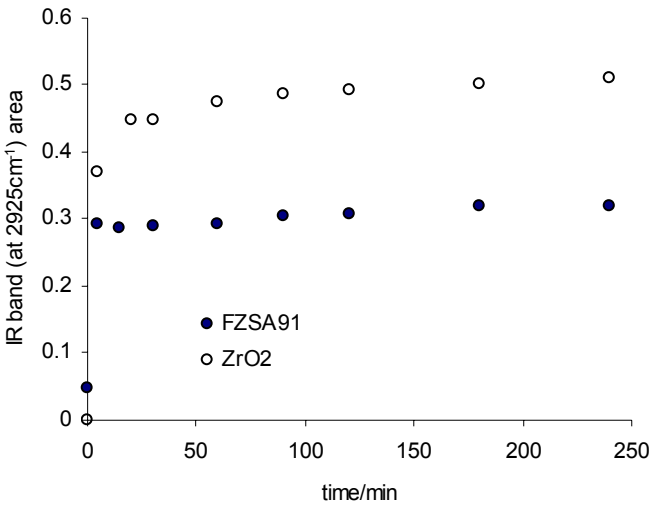
- *Cu(II) adsorption in ZSA82 as assessed by EDS*

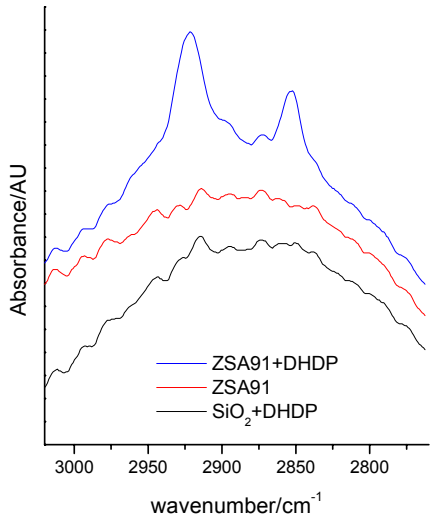


Si/(Zr+Si)	0.24
Cu/Si	0.24

After 200min immersed in a Cu(II) solution (150ppm), ZSA82 film presents a Cu/Si relation of 0.24, indicating the pores and the functions attached to them are accesibles to cations. SiO_2 or ZrO_2 films doesn't adsorb copper in the same conditions, showing the amino function is esential to cations adsorption .

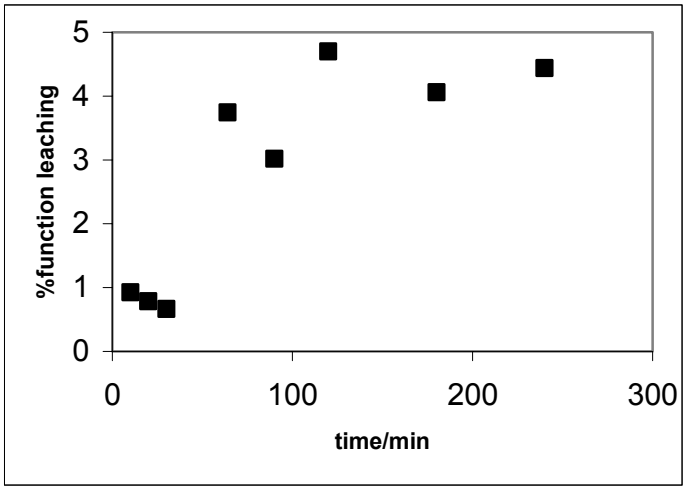
- *DHDP (sl 0.01M in THF) adsorption into ZrO_2 and FZSA films as a function of time*





The CH bands at 2800-2900 cm^{-1} are followed by FTIR in transmission mode by placing the film directly in the measurement chamber. In this way of measurement, only

the additional CH band (different from the original function, i.e. propylamino groups) are observed, as is show at the right figure.
Adsorption kinetics of DHDP show a fast incorporation (80% of the total amount within 5 minutes, left figure), in a lower quantity than in cubic ZrO_2 films with comparable thickness (450-470 nm as assessed by ellipsometry, data treatment by Maxwell-Garnett approximation) and porosity (30%), thus accessibility. This suggests that a fraction of the surface sites is not available for complexation, and it should be thus occupied by the R functions. Additionally, SiO_2 films with comparable thickness and accessibility do not adsorb DHDP, showing the specific phosphate-Zr interaction.



- *Leaching of DHDP-functionalised ($ZrSi(CH_2)_3)O_2$ (Si/Zr+Si=0,1) in THF as a function of time*

Leaching is performed by dipping a bifunctionalised film in THF, in which DHDP is soluble. The % leaching is estimated by analysing the relative decrease of the ν_{CH} FTIR band. *Ca*. 5% leaching is observed in the first five hours; less than 10% is lost within 2 days leaching. Analogous results are obtained with monododecyl phosphate; slightly higher leachings (*ca*. 15-20%) are obtained with Ti-based hybrids (work in progress).