

Adsorption of organic molecules on calcite {10.4}: The big picture

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Organic molecule interaction with calcite surfaces is of broad interest, because calcite is common in nature: as a biomineral, as the main constituent of limestone and chalk, where significant quantities of oil and drinking water reserves are found, and it is widely used in industrial products and found in everyday life, for example, as scale in pipes and tea kettles. A vast literature on organic molecule adsorption on calcite exists but unfortunately, each study reports on only a few molecules so the picture is fragmented and the data are of limited applicability. Our aim was to present the big picture, with a comprehensive study, covering a range of organic molecules, to answer two fundamental questions: How do the common functional groups of organic molecules interact with calcite? And what effect have the side groups?

We derived adsorption energies and geometries for 38 molecules on calcite {10.4}, using density functional theory (DFT). Our results show that carboxylic acids (R-COOH) have the strongest interactions, followed by primary amines (R-NH₂) and alcohols (R-OH). Thiols (R-SH), nitriles (R-CN) and aldehydes (R-CHO) have the weakest interactions (Figure 1). We also investigated the effects of replacing the H atom with methyl (-CH₃), ethyl (-C₂H₅) and phenyl (-C₆H₅) side groups. From the adsorption energies, we derived desorption temperatures and these agree well with measurements from temperature programmed X-ray photoelectron spectroscopy (XPS).

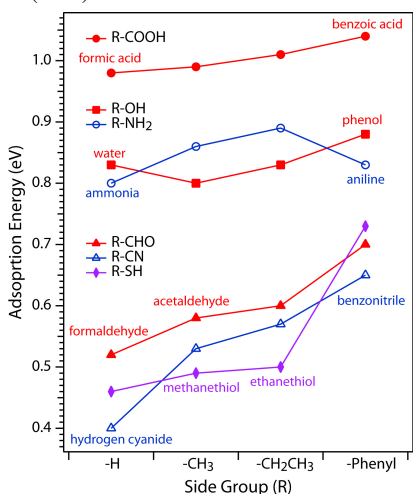


Figure 1: Adsorption energies of organic molecules with various functional groups, where an H atom is replaced by side groups, i.e. methyl, ethyl and phenyl.