Unveiling CO_2-derived species adsorbed on TiO_2 through the synergistic combination of Density Functional Theory (DFT) and Vibrational Spectroscopy

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Titanium dioxide (TiO_2) is widely recognized as a next-generation metal oxide catalyst due to its photocatalytic activity, economic viability, and environmental friendliness. Anatase represents the most common TiO_2 crystal phase investigated and employed for remediation purposes, although its capability to adsorb target molecules strongly depends on the exposed crystal facet. (001) anatase is one of the most reactive surfaces, and its ability to chemisorb CO_2 has been demonstrated by several studies. Its presence in commercial TiO_2 as exposed facet is limited in favour of others, mainly the more stable (101). Identifying the specific adsorption geometry remains a challenge as the configuration and the orientation of the adsorbate compounds with respect to the surface are difficult to address. This study proposes a novel approach to solve this issue, combining Density Functional Theory (DFT) simulations with Fourier Transform InfraRed (FTIR) and Raman spectroscopies to enable the investigation of adsorbates on (001) anatase. Simulations revealed a typical and almost exclusive behaviour of this crystal plane driven by its interaction with water molecules, which play a fundamental role in the CO_2 adsorption. Measurements conducted on samples synthesized and treated accordingly with the computational results confirmed the theoretical predictions, as new spectral features were observed and associated with carbonates and bicarbonates, presumably formed upon CO_2 adsorption.
On the other hand, (001) anatase poses problems in terms of industrial scalability, due to the synthesis recipes reported in the literature, which employ toxic and potentially dangerous compounds and procedures, such as hydrofluoric acid and isopropanol at hydrothermal conditions. Consequently, new structures were considered starting from commercial TiO_2 and treated by solutions of metal hydroxides. Simulations revealed the possibility to obtain almost the same kind of (bi)carbonate structures observed on (001) anatase but on a (101) anatase enriched by Ca^{2+}. Thus, a new synthesis including Degussa P25 (commercial TiO_2) impregnated in a $Ca(OH)_2$ solution at low concentration was proposed, with a synthesis process potentially scalable. The combination of DFT and Raman spectroscopy confirmed the presence of bicarbonates on this surface, at frequencies slightly shifted with respect to the one observed for the stoichiometric (001) anatase.
Although the work is still ongoing, these investigations provide valuable insights into the behaviour of the materials, confirming the synergistic ability of DFT and vibrational spectroscopy to address adsorbates, also representing a novel approach to achieve detailed surface descriptions.

References

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