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CH_2ClF adsorbed on TiO_2: study of the adsorbate-substrate interaction by IR spectroscopy and DFT calculations

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Abstract. Fourier-transform infrared spectroscopy has been used for the first time to study the adsorption of chlorofluoromethane (CH_2ClF) on TiO_2 at room temperature. The obtained spectra allow to deduce that the adsorbate-substrate interaction occurs through both the Cl and F atoms of the molecule and the surface Lewis acid site (Ti^{4+}) and by means H-bonds involving the CH_2 group and the surface Lewis basic sites (O^{2-} or OH^-). In order to better comprehend these interactions, a periodic quantum-mechanical study at DFT/B3LYP level has been carried out by considering the anatase (101) surface and focusing the attention on the determination of the energetically possible adsorbate-substrate structures. According to the comparison between the experimental and calculated vibrational frequencies, it can be concluded that the molecule can adsorb on the surface both through the Cl atom and an H-bond and by means the F atom and two H-bonds.

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Key words: chlorofluromethane, adsorbate-substrate interaction, TiO_2 surface, infrared spectra, quantum-mechanical simulations.

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1 Introduction

Chlorofluorocarbons, which are widely employed in the industrial field as refrigerants, give rise to serious problems at the atmospheric level because of their ozone depletion potential. For this reason, the presence of these compounds in the air should be limited.

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Among the possible techniques to remove a pollutant from the air, heterogeneous photocatalysis on TiO_2 represents a very interesting approach [1]. Since the adsorption of the compound on the surface corresponds to the starting point of its following decomposition, an investigation aimed to elucidate the interaction between the adsorbate and the substrate can provide useful information on the reaction mechanism and results in the development of successful applications. To this aim, the use of infrared spectroscopy allows to know details about the orientation geometry, e.g. the surface and molecular sites involved in the adsorption, by comparing the spectrum of the gas-phase molecule with that of the adsorbed one.

The adsorbate-substrate interaction between chlorofluoromethane (CH_2ClF) and TiO_2 at room temperature has been investigated through the analysis of the FTIR spectra above 1000 cm^{-1}, focusing mainly the attention on the bands referring to the C-H and C-F stretching modes. The assignments of the vibrations of the adsorbate have been done by considering those related to the isolated molecule.

Further information to better elucidate the adsorbate-substrate interaction have been obtained by performing periodic quantum-mechanical simulations at DFT/B3LYP level: the calculations have been carried out by focusing the attention on the anatase (101) which is reasonably present at the experimental level since it is one of the most stable surfaces of TiO_2 [2].

2 Experimental details

The sample of CH_2ClF has been obtained commercially (purity $\sim$ 99%) from SynQuest Labs and has been employed without further purification.

TiO_2 powder (P25 Degussa) has been pressed in the form of a self-supporting pellet ($\sim$ 20 $mg \cdot cm^{-2}$) which has been placed in a Pyrex cell equipped with CaF_2 windows. The TiO_2 has been preventively pre-treated at high temperature under vacuum before performing the adsorption experiments. The pre-treatment, which is necessary to remove the water and other possible adsorbed impurities, is described elsewhere [3]. The spectrum of the pre-treated TiO_2 shows some bands around 3000 cm^{-1} which are due to isolated OH^- groups [4]. These groups along with the surface under-coordinated oxygen ions (O^{2-}) correspond to the Lewis basic site of TiO_2.

The adsorption spectrum has been collected after the introduction of the gas into the cell at different values of pressure. The cut-off of TiO_2 allows the investigation of the spectral region from the lower limit of about 1000 cm^{-1}. All the spectra have been recorded with 20 scans at a resolution of 4 cm^{-1} employing the Bruker Vertex 70 FTIR spectrometer. The background is represented by the spectrum of TiO_2 obtained after the pre-treatment.