Photocatalysis on oxides: Case studies on rutile and anatase TiO_2 single crystals surfaces

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Photo-induced chemical reactions at surfaces of wide bandgap semiconductors like TiO_2 are important because they are central to many promising applications related to energy conversion and other associated processes with environmental impact. In addition, because photo-catalytic reactions are largely non-activated processes depending only weakly on temperature the study of such reactions is relevant to understand fundamental processes occurring on dust particles in the earth's atmosphere as well as in space. Experimental data for photoinduced reactions on well-defined metal oxide single crystal surfaces, which would also provide the basis for a more thorough theoretical understanding, are scarce – in contrast to powder materials for which a rather large set of experimental data exists.
The main reason for this unfortunate lack of information for well-defined single crystals is the fact that spectroscopic techniques not involving electronic excitations have – due to technical difficulties – not been applied for studying photo-induced reactions on such model substrates. The technical difficulties result from the fact that the IR-intensity of adsorbate vibrational modes on oxide surfaces is about an order of magnitude weaker than for metal single crystals.
We have designed a new apparatus, which combines a state-of-the-art FT-IR spectrometer with a dedicated UHV-chamber [1] to monitor the adsorption and reaction of CO over TiO_2(110) single crystals using reflection–absorption infrared spectroscopy (RAIRS).
Here we will report on the first IR studies of CO-adsorption on TiO_2 single crystal surfaces and its photo-oxidation. The success of our experiment [2] may open a new era in vibrational spectroscopy on single crystal metal oxide surfaces. In addition to the experimental results on rutile TiO_2 we will discuss recent measurements for anatase TiO_2, where the photocross-section of CO photooxidation was found to be an order of magnitude larger than for rutile [3].

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