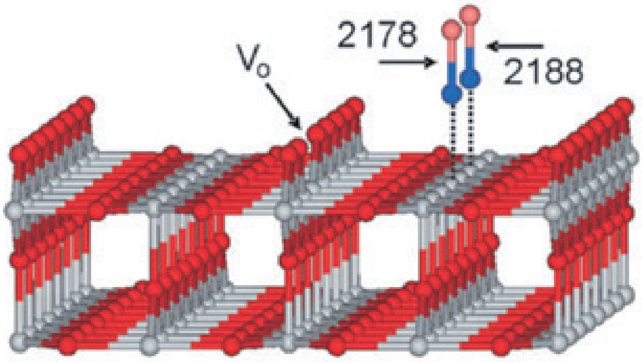

Application Note AN M107

FT-IR Spectroscopy in Ultrahigh Vacuum: Surface Science Approach for Understanding Reactions on Catalytic Oxide Powders

Introduction

The fundamental advantage of using FT-IR spectroscopy in vacuum is to avoid the absorption of atmospheric moisture and other gas species (CO_2). Vacuum spectrometers provide a better stability and reproducibility in comparison to the dry air/nitrogen purged spectrometers. Furthermore, the UHV adaption allows IR characterization of samples that have to be prepared and stored under UHV conditions without sample-transfer in air, and therefore enables the closely combination of FT-IR technique with other UHV experimental methods.

The amount of defects on an oxide surface is crucial for its catalytic activity. To understand the role of the defects in particular is the precondition for investigating numerous catalytic reactions in details. Recently, the oxygen defects on titanium dioxide (TiO_2) have been considered using scanning tunneling microscopy (STM) combined with density functional theory (DFT) calculations. Unfortunately, many standard experimental techniques in this research field can only be applied to single crystalline oxides in a straightforward fashion, but not to powders or nanoparticles, which is the technologically most important form of oxide materials. In contrast, FT-IR spectroscopy is not limited to the single crystalline phase only, but can also be applied to powders, nanoparticles etc. with high sensitivity.

Therefore ultrahigh vacuum FT-IR spectroscopy (UHV-FTIRS) was applied to both the well-understood single crystal reference system and the powder particles, in order to determine the density of O vacancies and to demonstrate the role of O vacancies for the surface chemistry of formaldehyde on TiO_2. For this purpose CO was used as a probe molecule to identify the defect sites on rutile TiO_2 (r-TiO_2) surface [1].

Experimental

An UHV-FTIRS apparatus dedicated to the spectroscopic characterization of oxides, single crystals as well as powders was developed. The schematic build-up of this innovatively designed system is shown in Fig. 1. It combines a Bruker VERTEX 80v vacuum FTIR spectrometer with a PREVAC UHV system consisting of load-lock, preparation, distribution, measurement, magazine, and analysis chambers. The UHV system enables additional characterizations using combined measurement techniques, such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS). The FTIRS experiments on the r-TiO_2 single crystal and powder samples were performed in the UHV chamber dedicated for IR measurements (UHV-IR chamber, see Fig. 2), which is internally adapted in the sample compartment of the VERTEX 80v spectrometer. The adaption is realized by vacuum-compliant window flanges which are mounted directly to the window fitting of the UHV chamber. The spectrometer can be demounted from and attached to the UHV-IR chamber by simply sliding backwards and forwards along its supporting frame. The unique feature of this dedicated design is the entire evacuated optical path to avoid absorption of atmospheric moisture and other background signals from gas phase (CO_2), thus providing the possibility to record IR data with highest sensitivity and stability. This is an essential prerequisite for monitoring molecular species adsorbed on oxide surfaces, since the optical properties of oxides result in a decreased signal-to-noise ratio (SNR) by one to two orders of magnitude relative to metals. A spectrometer internal motorized off-axis paraboloidal mirror in front of the spectrometer sample compartment together with another motorized 90° off-axis ellipsoidal mirror adjusted to the detector can be driven in two positions respectively for transmission (powders) and IR reflection absorption spectroscopy (IRRAS) measurements at grazing incidence with an incident angle of 80° to surface normal (for flat substrates such as single crystals) [2].

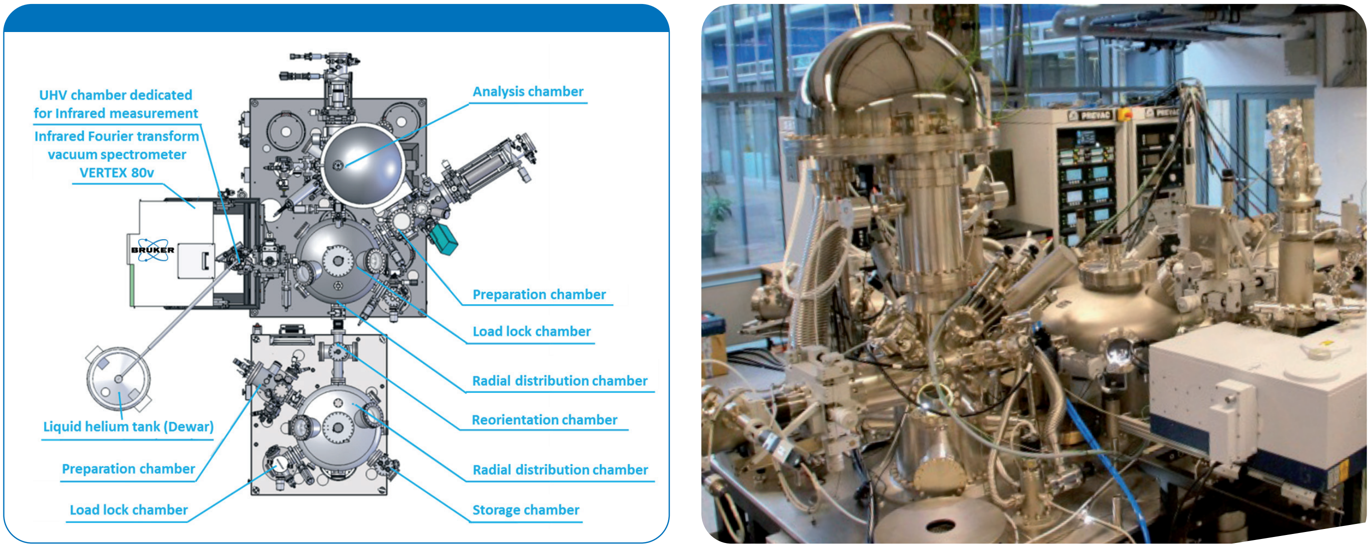

Fig. 1: a) Schematic drawing of the UHV system (PREVAC, www.prevac.eu) combined with the Bruker vacuum FT-IR spectrometer VERTEX 80v. b) A photo of the UHV system at Institute of Functional Interfaces (IFG) in Karlsruhe Institute of Technology (KIT).

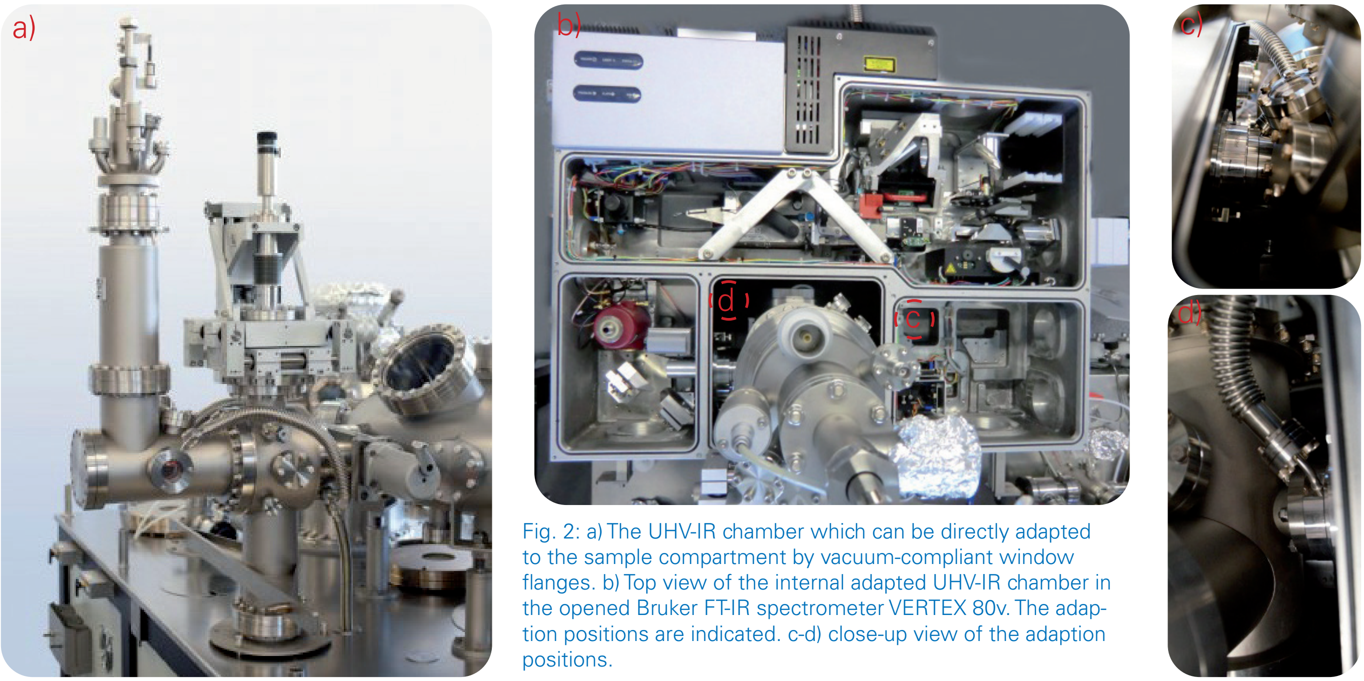

Fig. 2: a) The UHV-IR chamber which can be directly adapted to the sample compartment by vacuum-compliant window flanges. b) Top view of the internal adapted UHV-IR chamber in the opened Bruker FT-IR spectrometer VERTEX 80v. The adaption positions are indicated. c-d) close-up view of the adaption positions.

In order to identify the defects, CO was adsorbed onto perfect and reduced r-TiO_2 surface. The reduction was carried out by controlled sputtering or over-annealing at elevated temperature (900 K) to produce O vacancies. The r-TiO_2 single-crystal measurements were performed using IRRAS and the data for powder samples were recorded in transmission geometry. The low-vacancy (perfect) surface of the powder sample was achieved by deposing the powder to a small amount of oxygen in UHV at 110 K.

Results

Fig. 3 presents the surface structure model of r-TiO_2. As supported by calculations and previous works, the exposed CO molecules will populate only the adsorption sites labeled 1 and 2 in Fig. 3 (and sites located further away from the O vacancy), but not bind to the Ti atoms exposed within or next to the O vacancy (labeled 0).

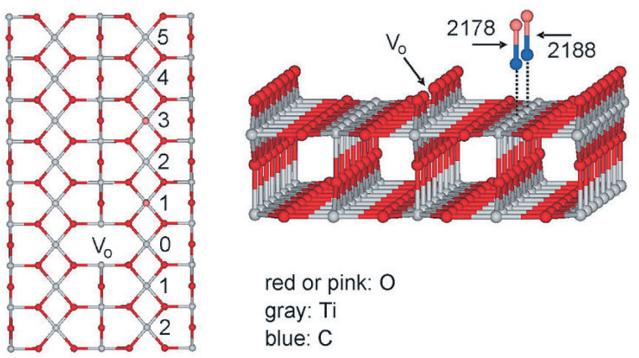

Fig. 3: Ball-and-stick model of the r-TiO_2 surface. The CO molecules adsorbed at different Ti sites (labeled 0-5) are sketched [1].

The IRRAS data shown in Fig. 4 (left) demonstrate that on a fully oxidized (perfect) r-TiO_2 surface with low density of defects only one absorption band at 2188 cm^{-1} is visible in the CO-stretching regime related to CO adsorbed on perfect parts of the surface (labeled 2-5 in Fig. 3), whereas on reduced r-TiO_2 a second band at 2178 cm^{-1} appears which is assigned to CO bound to Ti cations located on sites labeled 1 in Fig. 3. On the basis of the intensity ratio of the two bands and considering the maximum coverage of CO on r-TiO_2 at 110 K, the concentration of O vacancies can be estimated to an amount of around 10%.

The same procedure was applied to the r-TiO_2 powder particles. The FTIR spectra are shown in Fig. 4 (right). On oxidized powder particles (A in Fig. 4 right) only one absorption band at 2184 cm^{-1} related to CO bound to Ti cations distant to O vacancies or other defects was detected. On reduced powder particles (B in Fig. 4 right) a new band appears at 2174 cm^{-1} related to CO adsorbed on site 1 which is in accordance with the IRRAS data for r-TiO_2 single crystal surface. Furthermore, the defect density on the powder particles can be calculated from a comparison of the relative band intensities and amounts to about 8%.

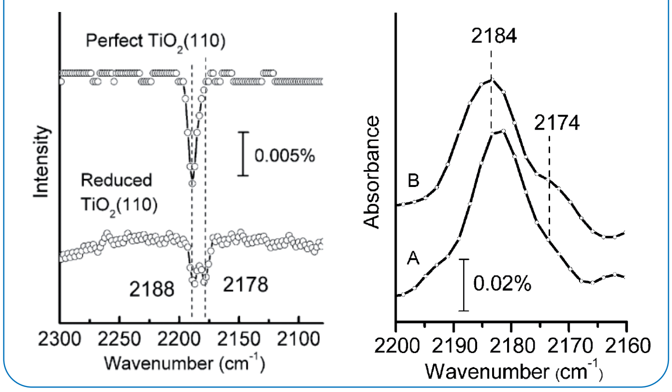

Fig. 4: Left: IRRAS data for CO adsorbed on perfect and reduced r-TiO_2 single-crystal surface at 110 K. The absorbance amounts to 10^{-5} au. Right: UHV-FTIRS data for CO adsorbed on oxidized (A) and reduced (B) r-TiO_2 powder particles at 110 K recorded in transmission mode [1].

To demonstrate the potential of this established method for determining defects densities in a semi-quantitative fashion, the reductive coupling of formaldehyde to ethylene catalyzed by TiO_2, an important C-C coupling reaction was investigated. Formaldehyde was exposed to both oxidized and reduced r-TiO_2 powder particles and IR spectra were recorded (data not shown here). Only on the reduced powder the intermediate of the catalyzed surface reaction was identified and the yield of ethylene correlates well with the above estimated density of defects on the r-TiO_2 powder particles.

Further approaches of UHV-FTIR adaption

An additional possibility to adapt FTIR spectroscopy to an existing UHV system, which has been used more frequently by customers, is to use the vacuum chambers W109/UHV (Bruker) matched to VERTEX 70v/80v consisting of two chambers (see Fig. 5). One is adapted to the spectrometer and contains a kinematic base plate with transfer optics. The other free-standing chamber includes further transfer optics and detector mount. Both chambers are prepared for a vacuum tight adaption to the UHV system. In this case, the UHV system will be arranged outside the spectrometer sample compartment (external adaption) providing more flexibility and space for voluminous UHV chambers with combined techniques. Also for this approach transmittance as well as IRRAS configuration is available (see Fig. 6). More details are described elsewhere [3].

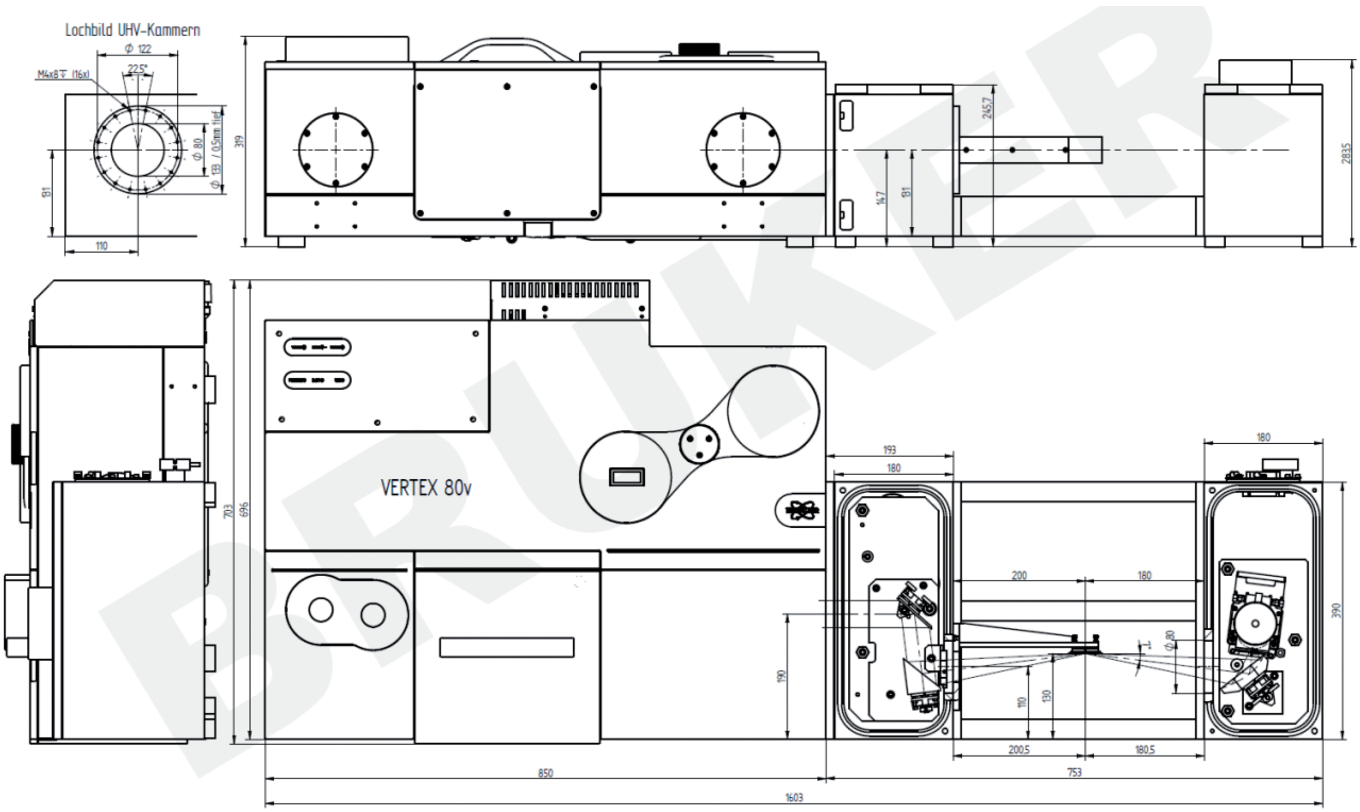

Fig. 5: Technical drawing of the Bruker VERTEX 80v FT-IR vacuum spectrometer with the external UHV adaption (W109/UHV).

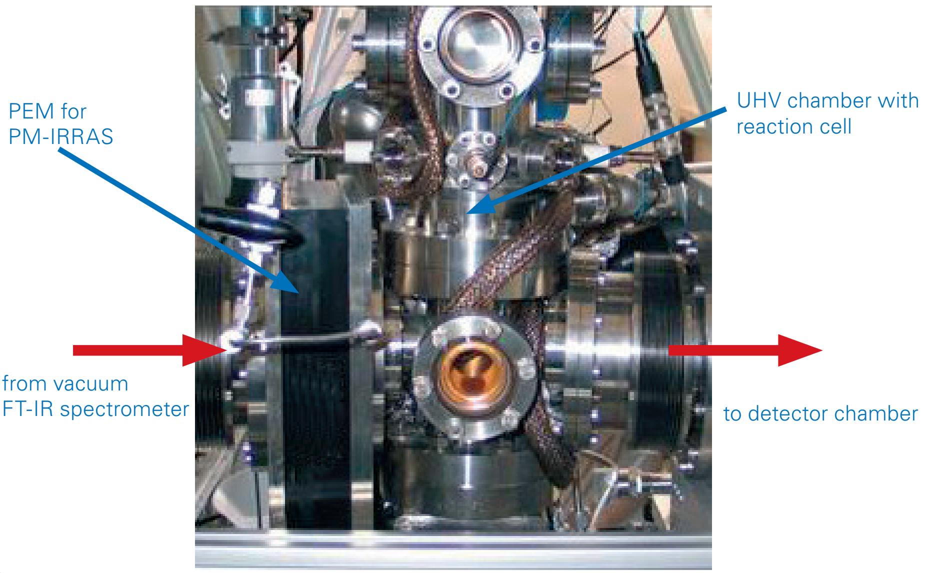

Fig. 6: Experimental setup combining a UHV surface analysis chamber with a UHV-high-pressure reaction cell optimized for PM-IRRAS [4].

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Bruker Scientific LLC
Billerica, MA · USA
Phone +1 (978) 439-9899
info.bopt.us@bruker.com

Bruker Optics GmbH & Co. KG
Ettlingen · Germany
Phone +49 (7243) 504-2000
info.bopt.de@bruker.com

Bruker Shanghai Ltd.
Shanghai · China
Tel.: +86 21 51720-890
info.bopt.cn@bruker.com

www.bruker.com/optics