Formamide reactions on rutile TiO$_2$(0 1 1) surface

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ABSTRACT

The reaction of formamide over the (0 1 1) faceted TiO$_2$(0 0 1) surface has been studied by Temperature Programmed Desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS). Two main reactions were observed: dehydration to HCN and H$_2$O and decomposition to NH$_3$ and CO. The dehydration reaction was found to be three to four times larger than the decomposition at all coverages. Each of these reactions is found to occur in two temperature domains which are dependent upon surface coverage. The low temperature pathway (at about 400 K) is largely insensitive to surface coverage while the high temperature pathway (at about 500 K) shifts to lower temperatures with increasing surface coverage. These two temperature pathways may indicate two adsorption modes of formamide: molecular (via an η^1(O) mode of adsorption) and dissociative (via an η^2(O,N) mode of adsorption). C1s and N1s XPS scans indicated the presence of multiple species after formamide absorption at 300 K. These occurred at ca. 288.5 eV (–CONH–) and 285 eV (sp^3/sp^2 C) for the C1s and 400 eV–(NH$_2$), 398 eV (–NH=) and 396 eV (N≡) for the N1s and result from further reaction of formamide with the surface.

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1. Introduction

TiO$_2$ surfaces are among the most studied metal oxides surfaces because of their involvement in numerous processes extending, from photocatalysis [1] to biomaterials [2], and their properties and characteristics are probably the most understood [3,4]. Numerous important reactions have been seen on their surfaces, including dehydration of alcohols and carboxylic acids, oxidation/reduction and carbon–carbon bond forming reactions with simple organic molecules through condensation and carbonyl coupling reactions [5]. TiO$_2$ has also been linked to chemical processes relevant to the beginning of life [6,7], where, under photon irradiation, nucleic acid bases were formed from formamide (NH$_2$CHO) as well as HCN. This important observation has one main advantage compared to previous hypotheses related to the overall energy of such prebiotic processes. As the energy required to excite TiO$_2$ (3.0–3.2 eV) is relatively small compared to that required to excite small organic molecules (typically >5 eV), the reaction products under these conditions may not be subject to decomposition and therefore have long geological life allowing for further reaction with the surroundings.

Among the molecules investigated as biotic precursors formamide has been the most successful, in part because it contains C, O and N atoms. Formamide is a plausible biotic precursor due to its presence in outer space. HCN, which hydrolyses to formamide,

has been seen in the Interstellar Medium (ISM) and it is suggested that UV irradiation of meteoric/cometary ice promotes the production of formamide from HCN [8–10].

On a powdered TiO$_2$ surface, formamide has been shown to react to create nucleic acid bases and simple base derivatives under sunlight (as a UV source) and with temperatures from 373 to 453 K [6]. This work has been extended to rutile TiO$_2$(0 0 1) single crystal surfaces which gave similar results [7].

Formamide adsorptions and reactions have previously been studied on single crystal surfaces. On a Ni(1 1 1) surface [11] formamide absorbs in η^1 (N) fashion at 80 K forming multilayers. Above 220 K formamide decomposes to produce HNCO alongside H$_2$ with a secondary dissociation channel leading to CO, NH$_3$ and H$_2$. On Si (100) (2 × 1) surfaces [12] formamide adsorbs in a η^1 (O) fashion with HN≡C and HNCO species being the primary products, similar to Ni (1 1 1). These surfaces mostly preserve the CN bond but other surfaces promote C–N bond scission. On Ru(0 0 1) surface [13], formamide adsorption at 80 K leads to CH bond breaking and a re-hybridised CO bond. A η^2 (C,O) NH$_2$CO results, alongside some η^1 (O) NH$_2$CHO at high coverage. On the same surface pre-dosed with H [14] or O [15] initial adsorption is instead through a Lewis Acid–Lewis Base type interaction leading to η^1 (O) NH$_2$CHO. Electronic differences between O and H cause adsorbed formamide to decompose differently on their respective surfaces. The high relative work function of the O pre-dosed surface causes formamide to convert to η^2 (N,O) NHCHO by 260 K. Importantly, all reactions off the Ru(0 0 1 surface lead to CO and NH$_x$ products with no HCN type products detected as the CN bond is cleaved in thermal

decomposition on these surfaces. Formamide on Pt(1 1 1) [16] and Rh (1 1 1) [17] shows similar CN bond scission with CO and NH_x products being produced. Wu et al. performed IR studies of formamide on TiO_2 Degussa P25 powder [18]. Formamide was found to have two modes of adsorption, dissociative and molecular. These modes of adsorption were similar to the Si(0 0 1) (2×1) [12] surfaces where molecular and dissociative adsorption were also found. In addition, on the Ge(1 0 0)−2×1 [19] surface both dissociated and molecular formamide was seen at room temperature. Increasing the temperature increased the proportion of dissociated form while increasing the coverage decreased the proportion of the dissociated form. This later effect was attributed to either the dissociated product remaining but losing its interdimer interaction with Ge dimers or further reaction of the dissociated form in high coverage conditions.

A theoretical study recently studied the ability of formamide molecules to associate on an Ag(1 1 1) surface [20]. This showed that formamide could either chemisorb as a monomer (through Ag–O) bonds or physisorb as a polymer lying parallel to the surface with a structure nearly identical to gas phase formamide dimers and stabilised by hydrogen bonds between the formamide molecules.

In this work we present a study of the dark reaction of formamide on the surface of the (0 1 1) faceted TiO_2(0 0 1) single crystal by Temperature Programmed Desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS).

The TiO_2(0 0 1) surface is a highly unstable surface and easily undergoes surface reconstruction. The low temperature 2×1 reconstructed {0 1 1} facet forms at ~750 K and the high temperature {1 1 4} facet at ~1000 K [21,22]. The exact atomic arrangement of the 2×1 (0 1 1) surface has been a subject of many studies with the most promising model being published recently [23,24]. The comparison between the bulk-like surface structure and the 2 × 1 reconstructed-surface is presented in Fig. 1.
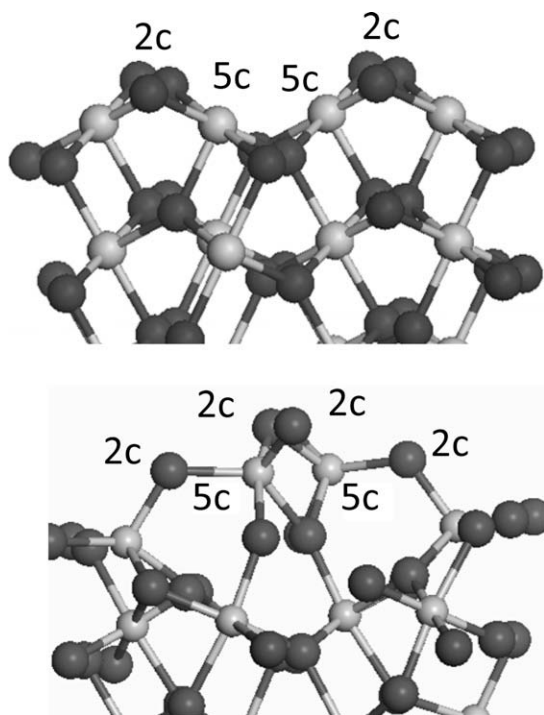

Fig. 1. The bulk-like surface (a) and the 2×1 reconstructed-surface of rutile TiO_2(0 1 1) single crystal according to the models of Refs. [23] and [24]. All Ti on the surface are 5fold coordinated whereas all O are 2fold compared to bulk values of 6 and 3, respectively; Oxygen: black balls and Titanium: grey balls.

2. Experimental

All experiments were conducted in two ultra-high vacuum (UHV) chambers of a design described in detail previously [25]. The gas phase of liquid formamide (BDH laboratories, 98% and 1% ammonium formate) was introduced into the chamber through a leak-valve after being frozen with liquid N_2 and thawed many times to remove dissolved gases. As the vapor pressure of formamide is very low at room temperature the glass bulb containing formamide was gently heated to 60–70 °C prior to dosing while the dosing line was kept continuously heated at about 60 °C.

The (0 0 1) TiO_2 single crystal surface was cleaned with sputter and anneal cycles. Typical conditions were Ar pressure: 5×10^{-5} torr, 25 mA emission current and 3 kV beam voltage for 15 min. This was followed by annealing up to 750 K with and without O_2 gas (up to 1×10^{-5} torr) for 15–20 min alongside several flashes up to 750 K before running an experiment. When annealing under O_2 pressure pumping off was conducted prior to cooling the surface to prevent further reaction of O_2 with interstitial Ti during the cooling process. This procedure was done until there was no detectable CO, CO_2 or H_2O peaks present in blank TPD runs or there was an absence of carbon in XPS scans.

XP spectra were gathered with the analyzer and X-ray source at 45° from the crystal face. Al K_α radiation was used and the analyzer settings were, 0.1 eV/step, 350 ms/step and pass energy of 25 eV (Ti and O) or 50 eV (C and N). XP spectra were imported into the XPSPEAK 4.1 program written by Kwok [26] which allowed the fitting of suitable peaks to the data. XPS spectra were run after 30 min pumping out of the chamber after introduction of formamide.

TPD traces were recorded with RGA for Windows with up to 12 peaks being continuously monitored and correlated with recorded temperatures from the thermocouple. Formamide was introduced to the chamber at various pressures then pumped out for 30 min before TPD spectra were run. During TPD the crystal was resistively heated at 1 K/s from 300 to 800 K with the MS shroud positioned directly above the crystal and within 1 mm from the crystal face. Quantitative analysis of TPD data was conducted via application of the trapezoid rule to obtain peak areas. Concentration of desorbing HCN, H_2O, NH_3, CO and NH_2CHO were corrected with respect to CO using the method outlined in Ko et al. [27]. Fragmentation of all non-formamide products was assigned from gas phase spectra obtained for the NIST chemistry web book [28]. Formamide fragmentation was obtained by analysis of gas phase formamide in our own chamber. The correction factors obtained as such were: HCN 1.2, H_2O 1.18, NH_3 1.76, and NH_2CHO 1.6.

3. Results and discussion

Fig. 2 presents the desorption profile of a TPD conducted following exposure of TiO_2(0 0 1) surface to 36 L of formamide at 300 K. Unreacted formamide desorbed in one broad peak (composed of two peaks depending on surface coverage, Fig. 3). Most of this desorption is attributed to HCN and H_2O. These peaks desorbed fully by 600 K. HCN desorbed in two temperature domains while water, although tracking HCN desorption, had a less pronounced desorption profile. Two other products were identified, CO and NH_3, both of which had largely desorbed by 450 K. We have previously investigated the adsorption and reaction of NH_3 [29] on this surface and found that ammonia desorbs by 340 K with a desorption activation energy equal to 92 kJ/mol. We have also computed for the adsorption of ammonia using PWDFT GGA and found the adsorption energy equal to 100 kJ/mol at a coverage $\theta = 0.5°$ [30]. The wide desorption of ammonia is most likely reaction limited as it is above ammonia's desorption temperature when dosed on