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CO_2 adsorption on Cr(1 1 0) and Cr_2O_3(0 0 0 1)/Cr(1 1 0)

S. Funk, T. Nurkic, B. Hokkanen, U. Burghaus *

Department of Chemistry, Biochemistry, and Molecular Biology, North Dakota State University (NDSU), Fargo, USA

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Abstract

We attempt to correlate qualitatively the surface structure with the chemical activity for a metal surface, Cr(1 1 0), and one of its surface oxides, Cr_2O_3(0 0 0 1)/Cr(1 1 0). The kinetics and dynamics of CO_2 adsorption have been studied by low energy electron diffraction (LEED), Aug er electron spectroscopy (AES), and thermal desorption spectroscopy (TDS), as well as adsorption probability measurements conducted for impact energies of $E_i = 0.1–1.1$ eV and adsorption temperatures of $T_s = 92–135$ K. The Cr(1 1 0) surface is characterized by a square shaped LEED pattern, contamination free Cr AES, and a single dominant TDS peak (binding energy $E_d = 33.3$ kJ/mol, first order pre-exponential $1 \times 10^{13}\ s^{-1}$). The oxide exhibits a hexagonal shaped LEED pattern, Cr AES with an additional O-line, and two TDS peaks ($E_d = 39.5$ and 30.5 kJ/mol). The initial adsorption probability, S_0, is independent of T_s for both systems and decreases exponentially from 0.69 to 0.22 for Cr(1 1 0) with increasing E_i, with S_0 smaller by ~0.15 for the surface oxide. The coverage dependence of the adsorption probability, $S(\Theta)$, at low E_i is approx. independent of coverage (Kisliuk-shape) and increases initially at large E_i with coverage (adsorbate-assisted adsorption). CO_2 physisorbs on both systems and the adsorption is non-activated and precursor mediated. Monte Carlo simulations (MCS) have been used to parameterize the beam scattering data. The coverage dependence of E_d has been obtained by means of a Redhead analysis of the TDS curves.

Keywords: CO_2; Cr(1 1 0); Cr_20_3(0 0 0 1); Kinetics; Adsorption dynamics

1. Introduction

The applications of Cr and its oxides are numerous and diverse. Cr/Cr_2O_3 is a catalyst or a part of multi-component catalysts for the polymerization of olefins [1], the hydrogenation of alkenes [2], the reduction of NO [3], the decomposition of N_2O_4 [3], the H–D exchange reaction in e.g. ethylene [4], and is a catalyst in the reforming of hydrocarbons [5]. In material science, Cr_2O_3 is interesting because of its uncommon magnetic properties [6]. Chromium is used as binder layers in the production of magnetic recording media [7], as a coating, for alloying [8], and as an additive in corrosion-resistant steel [9]. A very recent application is the use as a hardener in high temperature lubricants for high-speed rotating equipment bearings operating without oil developed at NASA Glenn [10]. The acidic probe molecule chosen for this study, CO_2, has frequently been used to characterize the basicity of oxide surfaces [11]. Furthermore, CO_2 is the carbon feedstock for surface reactions such as methanol synthesis.

Beginning with early work up to recent studies, much attention has been paid to water [12] and oxygen adsorption [8,12–15] (leading to the oxidation of Cr-surfaces) to gain a deeper understanding of corrosion. Literally all surface science techniques have been applied to characterize the system CO/Cr(1 1 0) [16]. However, little is know about CO_2 adsorption dynamics/kinetics on Cr metal single crystal surfaces.

Cr_2O_3 forms stable bulk oxides of the corundum structure. However, large single crystals are not readily available. Therefore, the procedure of choice [14] is to oxidize Cr(1 1 0) single crystals at ultra-high vacuum conditions. By doing so, a polar Cr_2O_3(0 0 0 1) surface oxide is formed. This procedure's success can be controlled by detecting a hexagonal low energy electron diffraction (LEED) pattern which differs from the Cr support's square shaped LEED pattern [17]. Scanning tunneling microscopy (STM) data confirm the formation of an oxide film with hexagonal unit cell [18]. Chromium [14] and oxygen terminated [11,19] surfaces have been reported.

A thorough infra-red study revealed the formation of a mixed physisorbed/chemisorbed CO_2 adlayer at 90 K [20]; the

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* Corresponding author. Tel.: +1 701 231 9742; fax: +1 701 231 8831.
E-mail address: uwe.burghaus@ndsu.edu (U. Burghaus).
URL: http://www.chem.ndsu.nodak.edu

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formation of carbonates or a dissociation could be ruled out. In thermal desorption spectroscopy (TDS) measurements, two low temperature structures (at 180 and 120 K) and a broad feature at ~350 K have been observed. The low temperature desorption peaks are assigned to physisorbed CO_2 (linear upright and linear tilted) and the room temperature structure to carboxylate (bent $CO_2^{\gamma-}$) species. The latter are only present for the Cr-terminated surface. For the oxygen terminated Cr_2O_3(1 0 1 2) surface a single broad TDS peak was observed [11] and assigned to physisorbed linear CO_2 adsorbed on chromyl oxygen sites.

We are aware of molecular beam scattering studies with CO_2 on ZnO(0 0 0 1) [21], Pd(1 1 1) [22], Cu(1 1 0) [23], Ni(1 0 0) [24], Cu-on-ZnO [21], and Zn-on-Cu(1 1 0) [25]. Besides nickel, for all of these systems non-dissociative and non-activated molecular adsorption was observed. The adsorption dynamics is dominated by an extrinsic (trapping above occupied sites) precursor state which frequently leads at large impact energies, E_i, and low adsorption temperatures, T_s, to an initial increase in the adsorption probability, $S(\Theta)$, with coverage, Θ (adsorbate-assisted adsorption). Adsorption dynamics data obtained by molecular beam scattering on Cr metal surfaces or Cr oxides are, to the best of our knowledge, not available. However, initial adsorption probabilities, S_0, estimated by TDS and Auger electron spectroscopy (AES) measurements showed a decrease in S_0 of CO on the oxide as compared with the Cr(1 1 0) surface [26]. Molecular beam scattering with CO on Cr/Ru surface alloys revealed precursor mediated adsorption [27].

In this study, we attempt to correlate qualitatively the surface structure with the chemical activity for a metal surface, Cr(1 1 0), and one of its surface oxides, Cr_2O_3(0 0 0 1)/Cr(1 1 0), by means of CO_2 as a probe molecule. Although the adsorption kinetics shows distinct differences, the adsorption dynamics for both systems are qualitatively similar, except for a slightly smaller reactivity on the oxide which appears to scale qualitatively with the surface to CO_2 mass match.

2. Experimental procedures

The measurements have been conducted by a triple-differentially pumped supersonic molecular beam system [28]. The scattering chamber contains a mass spectrometer, combined low energy electron diffraction (LEED)/AES system, and a sputter gun. According to the reproducibility and the signal-to-noise ratio of the adsorption transients, the error in S_0 is (without averaging independent measurements) below ±0.03. The $S(\Theta)$ curves have been smoothed—conserving, however, the shape of the adsorption isotherm. The impact energy, E_i, of the CO_2 molecules could be varied within 0.12–1.09 eV by using a pure CO_2 beam and by seeding 3% CO_2 in He, combined with a variation of the nozzle temperature within 300–650 K. The impact energy has been calculated as detailed in Ref. [28]. TDS measurements can be experimentally critical in regard to contributions not originating from the sample. Therefore, a number of precautions have been taken. The mass filter is equipped with an 8 mm (O.D.) aperture which is smaller than the crystal (10 mm × 10 mm) and the sample to detector distance is less than 2 mm. The sample holder consists of a Mo four-pin ceramics feed through with the air side connected to a stainless steel rod which acts as the reservoir for $1N_2$. Thus, no bulky parts have been used in designing the sample holder and the metal pins on which the sample is mounted stick directly in the $1N_2$ reservoir [29,30]. Finally, CO_2 has been dosed on the sample with the molecular beam system, keeping the background pressure while dosing the gas below 5×10^{-8} mbar. The coverage is given in ML assuming saturation at ~92 K. The crystal (MaTeck) has been cleaned by high temperature sputter/annealing cycles, as detailed below. The cleanliness and crystallographic order have been checked by AES and LEED. The crystal could be cooled down from 800 K to a temperature of $T_s \sim 92$ K (within ~10 min) by fluxing He gas through a dewar containing $1N_2$ [31]. The reading of the thermocouple has been calibrated in situ by multilayer TDS measurements of *n*-butane, *n*-hexane, and *n*-nonane, assuming a pre-exponential factor of 1×10^{28} l/(s cm^2) [32], and respective binding energies of 22.4, 31.5, and 43.1 kJ/mol [33].

3. Qualitative discussion and data presentation

3.1. Sample cleaning and characterization with LEED and AES

Obtaining atomically clean Cr surfaces is extremely difficult, as discussed extensively in the literature. We followed the recipe of Ref. [16]: high temperature Argon sputter cycles (700 K, 500 eV, 4 μA, 30 min) followed by high temperature (800 K, 2 min) annealing in vacuum. AES from the as received sample (Fig. 1a) showed a C-line (277 eV) with an intensity 2.8-times larger than the most intense Cr-line (495 eV) as well as an oxygen AES peak (515 eV). Removing the carbon containing impurities appeared to be relatively simple (~40 cleaning cycles). However, a total of ~300 cycles (8 weeks cleaning) were required to reduce the AES O-line below the detection limit (Fig. 1b). The so cleaned surface revealed a rather sharp square shaped (1 × 1) LEED pattern (Fig. 1e)

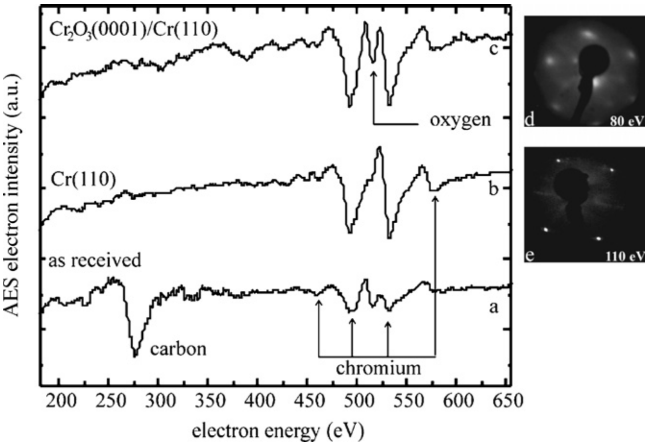

Fig. 1. AES spectra of the (a) as received, (b) the cleaned, and (c) oxidized surface as well as the LEED patterns for the (d) surface oxide and (e) the clean Cr(1 1 0) surface are shown.