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Biomass-derived oxygenate reforming on Pt(111): A demonstration of surface science using D-glucose and its model surrogate glycolaldehyde

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ABSTRACT

Molecules derived from cellulosic biomass, such as glucose, represent an important renewable feedstock for the production of hydrogen and hydrocarbon-based fuels and chemicals. Development of efficient catalysts for their reformation into useful products is needed; however, this requires a detailed understanding of their adsorption and reaction on catalytically active transition metal surfaces. In this paper we demonstrate that the standard surface science techniques routinely used to characterize the reaction of small molecules on metals are also amenable for use in studying the adsorption and reaction of complex biomass-derivatives on single crystal metal surfaces. In particular, Temperature Programmed Desorption (TPD) and High Resolution Electron Energy Loss Spectroscopy (HREELS) combined with Density Functional Theory (DFT) calculations were used to elucidate the adsorption configuration of D-glucose and glycolaldehye on Pt(111). Both molecules were found to adsorb in an η_1 aldehyde configuration partially validating the use of simple, functionally-equivalent model compounds for surface studies of cellulosic oxygenates.

While the utilization of H_2 in “clean” fuel cells is often touted as a green energy conversion technology, reforming of carbonaceous fossil fuels, such as CH_4, is responsible for 96% of global H_2 production [1]. Although this approach may have efficiency advantages over burning these fuels directly, it results in net CO_2 emissions and has a considerable carbon footprint. The goal of a clean energy conversion technology based on H_2 is thus contingent on the development of a carbon neutral means of H_2 production [2]. Catalytic aqueous phase reforming of biomass-derived sugars (e.g. glucose) using noble metal catalysts is one route for achieving this goal [3,4]. A detailed understanding of the catalytic pathways involved in this process is needed, however, for this technology to be fully developed. Unfortunately, it is generally thought that the complexity of C_6 cellulosic oxygenates along with their low vapor pressures precludes the use of ultra-high vacuum (UHV) surface analysis methods that have been so successful in mapping out the energetics and pathways of surface-catalyzed reactions of simpler molecules [5,6]. Herein we show that this is not the case and demonstrate the successful use of UHV techniques, temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS), coupled with density functional theory (DFT) to determine the bonding configuration of D-glucose on the Pt(111) surface and products of its decomposition. Furthermore, similarities in the surface bonding of glycolaldehyde ($HOCH_2-CH{=}O$), the smallest model compound containing the primary functional groups in glucose, demonstrates the validity of using this molecule as a surrogate in studies of the reaction pathways of sugars on catalytic surfaces.

The low vapor pressure of solid D-glucose prevents its introduction into the UHV environment using conventional leak valve methodology; therefore, in this study D-glucose was introduced into the system using an effusion source consisting of a resistively heated quartz tube filled with solid D-glucose (Sigma Aldrich, 99.5% pure). The low stability and high vapor pressure of glucose at the chamber bakeout temperature required that the quartz tube be housed in a high-vacuum ($\sim 5\times 10^{-9}$ torr) side chamber that was isolated by a gate valve from the main UHV system (maintained at 2×10^{-10} torr base pressure). This experimental setup is shown schematically in Fig. 1. Controlled molecular deposition of D-glucose onto the atomically clean Pt(111) surface was performed by heating the effusion cell to a temperature (typically 400 K) sufficient to obtain a reproducible flux of glucose molecules while remaining below the temperature marking the onset of thermal decomposition of glucose, 438 K [7,8]. This was followed by opening of the gate valve to allow this flux to impinge on the Pt(111) surface for a controlled time. Glucose exposures were measured in torr-seconds based on ion gauge pressure measurements from the background of the chamber, though it should be noted that they may not be respective of the local pressure in the molecular beam.

The flux from the effusion source was verified by mass spectrometry (UTI quadrupole) to be D-glucose rather than smaller molecular fragments. This is demonstrated by the TPD data for M/e = 73, a characteristic mass fragment for D-glucose [9], displayed in Fig. 2a. This

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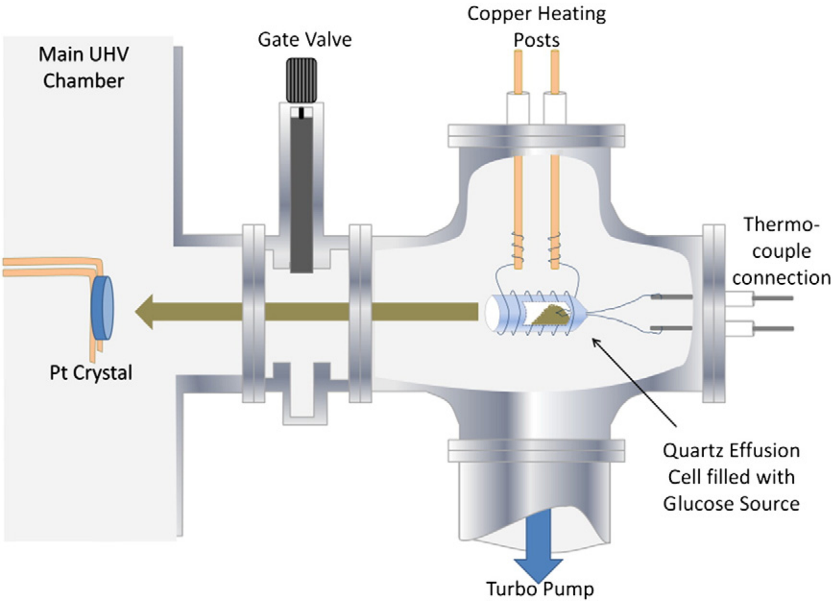

Fig. 1. Schematic of the experimental apparatus that was used for dosing glucose into the UHV analysis system.

spectrum was obtained following a 5×10^{-6} Torr-seconds D-glucose exposure producing a multilayer coverage on the Pt(111) crystal held at 120 K. The spectrum contains a narrow peak at 357 K, whose shape is indicative of zero-order desorption kinetics, which is typical for physisorbed multilayers on metal surfaces [10]. The assignment of this peak to D-glucose was further confirmed by the appearance of identical peaks at M/e values for the other primary glucose cracking fragments (M/e = 31, 43, 57, 60, 61, 71) with the expected relative intensities as reported in the NIST mass spectrometry database [9].

CO and H_2 were the only reaction products detected during TPD from the glucose-dosed Pt(111) surface, resulting from reaction of chemisorbed glucose in the first monolayer. The CO and H_2 desorption spectrum from the multilayer glucose coverage is displayed in Fig. 2b. Both H_2 and CO were found to desorb in broad peaks centered at 404 K. It is noteworthy that the molecular surrogate glycolaldehyde reacted similarly on Pt(111) to form exclusively CO and H_2, as shown in Fig. 3, although there was some variance in the peak shapes and positions relative to those for glucose.

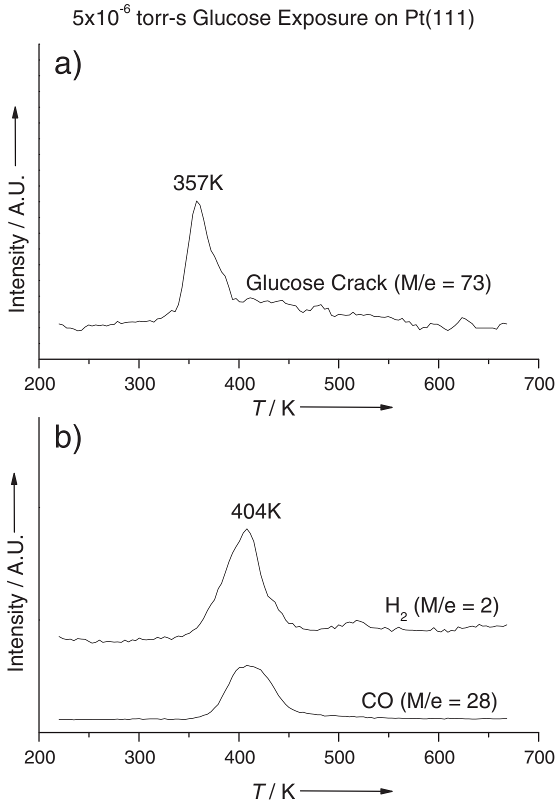

Fig. 2. TPD spectra following a 5×10^{-6} torr-second D-glucose exposure on Pt(111) for (a) main glucose crack (M/e = 73) and (b) H_2 (M/e = 2) and CO (M/e = 28).

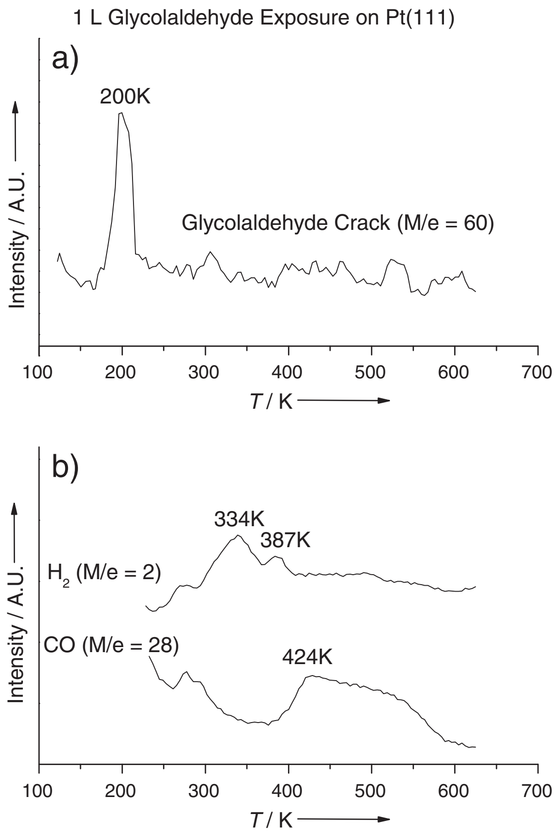

Fig. 3. TPD spectra following a 1 L glycolaldehyde exposure on Pt(111) for (a) main glycolaldehyde crack (M/e = 60) and (b) H_2 (M/e = 2) and CO (M/e = 28).