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The adsorption and reaction of ethylene glycol and 1,2-propanediol on Pd(111): A TPD and HREELS study

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ABSTRACT

The reactions of ethylene glycol and 1,2-propanediol have been studied on Pd(111) using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). Both molecules initially decompose through O–H activation, forming ethylenedioxy ($-OCH_2CH_2O-$) and 1,2-propanedioxy ($-OCH_2CH(CH_3)O-$) surface intermediates. For ethylene glycol, increases in thermal energy lead to dehydrogenation and formation of carbonyl species at both oxygen atoms. The resulting glyoxal (O CHCH O) either desorbs molecularly or reacts through one of two competing pathways. The favored pathway proceeds via C–C bond scission, dehydrogenation, and decarbonylation to form carbon monoxide and hydrogen. In a minor pathway, small amounts of glyoxal undergo C–O bond scission and recombination with surface hydrogen to form ethylene and water. The same reaction mechanism occurs for 1,2-propanediol after methyl elimination and formation of glyoxal. However, this is accompanied by a minor pathway involving a methylglyoxal ($O{=}CHC(CH_3){=}O$) intermediate. The prevalence of the dehydrogenation/decarbonylation pathway in the current work is consistent with the high selectivity for C–C scission in the aqueous phase reforming of polyols on supported Pd catalysts.

1. Introduction

The growing complications associated with widespread petroleum usage have led to an increased interest in development of products from renewable sources. One of the largest and most diverse renewable feedstocks is plant biomass, which can be processed into fuels and chemicals in a biorefinery [1–4]. The ability to process diverse feedstocks increases the resilience of the refinery, but it also introduces technical challenges. The large number of functional groups in biomass-derived carbohydrates, such as polyols, results in a variety of potential reactions, not all of which are desirable. For this reason, a high level of selectivity for oxygenate conversion is extremely important [5]. Polyols such as ethylene glycol ($HOCH_2CH_2OH$) and 1,2-propanediol ($HOCH_2CH(CH_3)OH$) are biorefining intermediates in many important pathways and also serve as probe molecules for more complex oxygenates [6,7]. Studying ethylene glycol and 1,2-propanediol on Pd(111) can contribute to the fundamental understanding of how molecules with multiple hydroxyl groups react on transition metal surfaces and serve as an important step toward the design of highly selective catalysts.

The thermal chemistry of ethylene glycol has been studied on Pt(111) [8], Rh(100) [9], Rh(111) [10], Ni(100) [11], Cu(110) [12], Ag(110) [13], and Mo(110) [14]. On clean Ag(110) ethylene glycol adsorbs reversibly with its molecular structure intact. On each of the other surfaces ethylene glycol adsorbs through its oxygen atoms, followed by hydroxyl hydrogen activation, resulting in an ethylenedioxy ($-OCH_2CH_2O-$) surface intermediate. Monodentate ($-OCH_2CH_2OH$) species are also observed at higher surface coverages on Mo(110) and Rh(100) [9,14]. On most surfaces the dominant thermal reaction pathway involves either C–C or C–H bond scission. For example, on Cu(110) the ethylenedioxy species breaks down to form glyoxal ($(CHO)_2$) [12]. The same glyxoal species is seen on Ag(110) predosed with oxygen [13]. The dominant pathway for Rh(100), Rh(111), and Ni(100) involves C–C bond scission [9,11]. Only Mo(110) favors C–O bond scission, forming ethylene with 85% selectivity [14].

1,2-Propanediol is of particular interest due to the presence of both secondary and primary alcohol functionalities. Previous studies examining 1,2-propanediol on transition metal surfaces are limited, with only the Ag(110) surface having been examined [15]. On clean Ag(110) 1,2-propanediol desorbs without reaction. However, on oxygen-precovered Ag(110) it forms 1,2-propanedioxy ($-OCH_2CH(CH_3)O-$), which decomposes at higher temperatures through a mixture of O–H, C–H, and C–C bond scission and forms a variety of products. Formaldehyde, water, formate, and acetate form by 275 K; acetol evolves at 335 K; carbon dioxide, water, acetol, lactaldehyde, and 1,2-propanediol evolve at 360 K, and finally pyruvaldehyde, acetol, and lactaldehyde desorb at 415 K [15].

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One particular application of this work involves the aqueous phase reforming (APR) of polyols for the production of hydrogen gas and alkane products [16–21]. This process is carbon neutral and can occur at low temperature in a single reactor. Aqueous phase reforming occurs on a transition metal surface and requires a carbon–oxygen ratio of 1:1, which is satisfied by polyols such as ethylene glycol. The production of hydrogen gas proceeds through C–C bond scission to form carbon monoxide on the surface, followed by the water gas shift reaction to form hydrogen and carbon dioxide. Alternatively, light alkanes are formed through either hydrogenation of adsorbed CO and CO_2 or cleavage of C–O bonds. Given these competing reaction pathways, a high level of selectivity is necessary if a single product is desired, and the design of novel catalysts to achieve this selectivity is a necessary step in the development of the APR process. A good APR catalyst for the production of hydrogen must facilitate C–C bond cleavage and encourage removal of carbon monoxide species by the water–gas shift reaction. Palladium has shown very high selectivity for C–C bond cleavage, but has relatively low APR activity [20]. This is likely due to the strong bonding affinity for carbon monoxide. The production of CO is advantageous in applications where synthesis gas is the desired APR product. In the present study, a combination of high resolution electron energy loss spectroscopy and temperature programmed desorption is employed to give a detailed molecular understanding of how 1,2-propanediol and ethylene glycol react on a Pd(111) single crystal surface.

2. Experimental methods

Experiments were conducted in two ultrahigh vacuum (UHV) chambers described previously [22]. HREELS experiments were conducted in a stainless steel UHV chamber with an LK3000 high-resolution electron energy loss spectrometer (LK Technologies) and a model 981-2046 sputter gun for cleaning (Varian). The specular angle was 60° with respect to the surface normal and beam energy was 6.32 eV. The full-width half-maximum (fwhm) of the elastic peak in HREELS experiment was limited to 45 cm^{-1}. HREELS peak positions are reported to the nearest 5 cm^{-1}. To study thermal chemistry, the crystal was annealed to various temperatures and held constant for 2 min, after which it was cooled and scans were performed. All HREEL spectra are normalized to the elastic peak height.

TPD experiments were conducted in a separate chamber equipped with a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) and a model NGI3000-SE sputter gum for cleaning (LK Technologies). Fragmentation patterns for individual compounds were obtained by backfilling the TPD chamber to a pressure of $\sim 10^{-9}$ Torr. Reaction products were identified by comparing the fragmentation pattern obtained by backfilling the chamber with those obtained during TPD experiments. In both chambers the molecules were dosed to the sample using a direct dosing line facing the sample. While direct dosing methods reduce background adsorption and sample contamination, it makes direct comparison of exposures between chambers difficult. However, it is possible to quantify approximate dose size by comparing the area of the CO peak from a saturating dose (0.67 ML [23]) to the area of a CO peak from the experimental doses. Hydrogen yields were quantified in an analogous fashion by assuming that a saturating hydrogen dose produces 0.9 ML of desorbing H_2 [24]. TPD yields of other products were estimated using the technique developed by Ko et al. for calculation of mass spectrometer sensitivity factors. Coverage of each desorption product was determined by comparison with a saturating CO dose. Cooling below room temperature was accomplished using a liquid nitrogen reservoir located in contact with the sample. Both chambers had a base pressure of $\sim 10^{-10}$ Torr.

The polished Pd(111) crystals (Princeton Scientific) were cleaned primarily through cycles of cooling and heating in 5.0×10^{-8} Torr O_2 between 400 K and 900 K. Mild sputtering with Ar^+ ions (1–3 keV) and annealing were also utilized. The Pd(111) crystal was mounted onto a 1.5 mm tantalum disk and held onto a copper stage within each chamber using two metal clips. In the TPD chamber, temperature was measured using a thermocouple spot welded to the tantalum disk. In the HREELS chamber, temperature was measured using a thermocouple attached to the copper stage. Ethylene glycol, d_6-ethylene glycol, and 1,2-propanediol were obtained at reported >99% purity from Sigma-Aldrich and purified using repeated freeze–pump–thaw cycles. Doses of d_6-ethylene glycol, however, revealed significant contamination from ethylene glycol that was less than fully deuterated, as described in detail below. Ultrahigh purity H_2, O_2, CO, and Ar were obtained from Matheson Trigas.

3. Results

3.1. Temperature programmed desorption of ethylene glycol

TPD experiments were conducted for various exposures of ethylene glycol dosed at 173 K. Fig. 1 shows the results of a direct dose that resulted in the evolution of 0.15 ML of carbon monoxide. The major desorption traces are hydrogen and carbon monoxide with peaks at 315 K and 430 K respectively, consistent with previous studies examining ethylene glycol on Pt(111) and Ni/Pt(111) [8,25]. Molecular ethylene glycol desorbs in two peaks, with temperatures of 230 K (in multilayer desorption peak that does not saturate) and 260 K (monolayer desorption). These temperatures are similar to those seen for the multilayer and monolayer desorption of ethylene glycol on Ag(110) (225 K and 250 K) and Pt(111) (227 K and 266 K) [13,25]. Glyoxal (O CHCH O) is identified in a broad desorption feature which peaks at 415 K. Previous studies of ethylene glycol on Cu(110) and Ag(110) reported glyoxal desorption with peak temperatures of 390 K and 380 K respectively [12,13]. The increased glyoxal desorption temperature is in agreement with previous work showing that aldehydes interact more strongly with Pd(111) than Ag(110) or Cu (110) [26]. Ethylene is observed in a similarly broad peak centered at 415 K, which is significantly above the desorption temperature of ~320 K seen when pure ethylene is dosed onto Pd(111), indicating that it is a reaction limited product [27]. Previous studies of ethylene glycol on Mo(110) also report the reaction limited evolution of ethylene at 350 K and 390 K [14]. The water trace is convoluted with background desorption, but at high temperatures it decays in a similar manner as glyoxal and ethylene.

In every desorption product seen in Fig. 1, both hydroxyl groups have been dehydrogenated. This suggests that ethylene glycol

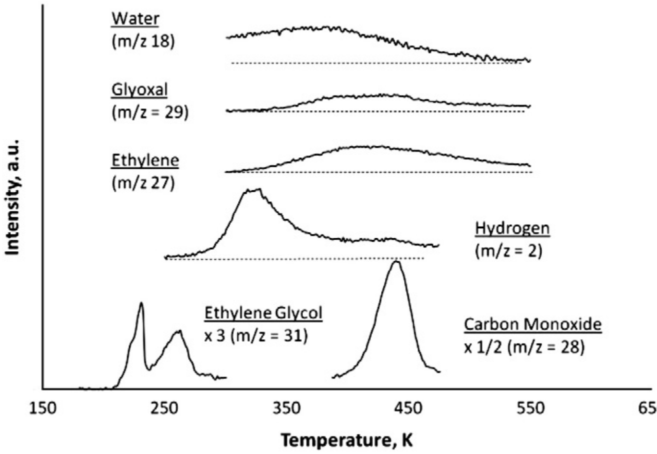

Fig. 1. Major TPD traces from ethylene glycol dosed onto Pd(111) at 173 K. Reported spectra are from a direct dose that led to desorption of 0.15 ML of CO. Dashed lines are included to guide the eye with respect to a baseline response. Peak subtractions have been carried out in order to deconvolute spectra with common fragments, so that each mass reports only the contributions from the product indicated.