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TPD and HREELS study of the reaction of guaiacol on Zn-decorated Pt(111)

Daming Shi, John M. Vohs*

Department of Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104-6363, USA

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ABSTRACT

Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of guaiacol on Pt(111) and Zn-modified Pt(111) surfaces. It was found that the guaiacol molecule binds to the Pt(111) surface via the aromatic ring which facilitates unselective decomposition to produce CO, H_2 and small hydrocarbon fragments at relatively low temperatures. In contrast, on Zn-modified Pt(111) surfaces, guaiacol was found to bond to surface Zn sites via the oxygen atoms in the molecule producing a bonding configuration in which the aromatic ring is tilted away from the surface. Such a binding configuration facilitates the desired C—O bond cleavage while keeping the aromatic nature of the molecule intact.

1. Introduction

Lignocellulosic biomass is attracting more and more attention as a potentially sustainable, CO_2-neutral feedstock for fuels and chemicals [1–3]. The polyaromatic nature of the lignin fraction of biomass also makes it an attractive feedstock for aromatic compounds [2,4]. Currently, the most prevalent conversion technology for lignin relies on pyrolysis [2], which produces bio-oil, biochar, and synthesis gas as products. The bio-oil is a complex mixture of phenolic compounds and lignin-derived oligomers with high oxygen content [5]. It also contains 15–30% water. The bio-oil tends to have high viscosity, high acidity, low stability, as well as low heating value. Therefore, further upgrading of the bio-oil is needed in order to form useful products. Removal of some of the oxygen via hydrodeoxygenation (HDO) is an important step in the upgrading process, although this needs to be done while maintaining the aromatic nature of the constituent molecules in order to produce high-value products.

Selective hydrogenolysis of C—O bonds is the key step in the HDO upgrading of lignin-derived biomolecules. Recently there has been a number of studies reported in the literature on the use of group 10 metals, such as Pt [6–10], Pd [9–11], and Ni [11], as catalysts for this reaction. While all of these metals are active for C—O bond hydrogenolysis, they also promote the undesirable hydrogenation of aromatic rings and tend to deactivate due to coking. Alloying these group 10 metals with a more oxyphilic metal, such as Fe [9], Sn [12], or Zn [13] has been shown to be a promising strategy for designing more selective catalysts that maintain activity for C—O bond hydrogenolysis while simultaneously having low activity for ring hydrogenation. Insight into the mechanism by which alloying with a more oxyphilic metal affects activity and selectivity, however, is only starting to emerge.

In previous studies we have investigated the adsorption and reaction of aromatic oxygenates that contain aldehyde (benzaldehyde) [14] and alkoxide (anisole) [13] functionalities on model catalysts consisting of Pt(111) and Zn-decorated Pt(111) surfaces. These studies show that Zn addition to Pt alters the d-band of the metal in such a way that it decreases the binding of the aromatic group to the surface. These studies along with those for simpler oxygenates, such as methanol and acetaldehyde [15,16], also indicate that the Zn atoms provide bonding sites for the oxygen atoms in these molecules and that this may help facilitate selective cleavage of C—O bonds.

In the work described here we have expanded our previous investigations of the adsorption and reaction of lignin-derived model compounds on model catalysts consisting of Pt(111) and Zn-decorated Pt(111) surfaces [13,14] to include guaiacol which contains both alkoxide and hydroxyl functionalities. Temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to investigate reaction pathways and determine the bonding configurations of stable adsorbed intermediates formed from guaiacol. This study in conjunction with our previous work provide considerable new insight into how alloying a group 10 metal with a more oxyphilic metal, such as Zn, affects the reaction pathways, adsorbed intermediates, and active sites for C—O bond cleavage in aromatic oxygenates such as those found in pyrolysis oils produced from lignin.

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* Corresponding author.
E-mail address: vohs@seas.upenn.edu (J.M. Vohs).

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2. Experimental

Both TPD and HREELS experiments were conducted in a UHV apparatus described in detail in previous publications [16–18]. The system was equipped with a quadruple mass spectrometer (SRS RG-A200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies) and had a background pressure of 2×10^{-10} Torr. A Pt(111) single crystal substrate which was 10 mm in diameter and oriented to within ± 0.5° was spot-welded to two tantalum wires that were connected to the UHV sample manipulator. The Pt(111) surface was cleaned by repeated cycles of 2 kV Ar^+ ion bombardment at 600 K for 40 min, annealing at 1200 K under 2×10^{-8} Torr O_2 for 15 min, and annealing at 1200 K in vacuum for 5 min. The sample was heated resistively and cooled to 110 K by conduction from a liquid N_2 reservoir.

Zn deposition on Pt(111) was obtained by exposing the Pt surface to a beam of Zn atoms produced from a thermal evaporative source consisting of a coil of Zn wire (Alfa Aesa, 99.99%) around a resistively-heated tungsten filament. The Zn flux from this source was monitored using a quartz crystal microbalance (QCM) that was located midway between the source and the sample but positioned below the sample in order to not block the flux of atoms to the Pt crystal. One monolayer of Zn was assumed to have the same density of atoms as that on the Pt (111) surface, i.e., 1.51×10^{15} atoms/cm^2.

In a previous study [19] it was shown that Zn atoms vapor deposited on Pt(111) remain on the surface at temperatures below 600 K, while at higher temperatures they diffuse into the surface where they form a substitutional alloy in which the Zn primarily resides in the second layer [19]. Since the goal of the present study was to assess how addition of Zn to Pt influences reactivity, both through electronic effects and by providing specific sites for adsorption, we chose to use a Pt(111) surface decorated with Zn adatoms as a model PtZn alloy surface.

The guaiacol reactant (Sigma Aldrich, 99.8%) was contained in a glass vial attached to a stainless steel manifold that was connected to the main UHV apparatus via a variable leak valve that was equipped on the UHV side with a directional dosing tube. While dosing guaiacol the sample was positioned directly in front of the dosing tube allowing a lower base pressure to be maintained for vacuum chamber. Based on previous calibration studies the dosing tube enhanced the reactant gas pressure at the sample surface by a factor of 10-fold relative to that measured in the vacuum chamber.

TPD experiments as a function of the guaiacol dose were performed for the Pt(111) surface in order to determine the dosage that resulted in saturation of the low-temperature guaiacol peak from the Pt(111) surface which corresponds to the desorption of second layer guaiacol. Based on these experiments it was determined that saturation of the surface with guaiacol occurred for a 0.5 L (1 L = 10^{-6} Torr) dose and this dosage was used in all subsequent TPD and HREEL experiments. Note that this dose ensured that all the experiments in this study were done using surfaces that were completely saturated with chemisorbed guaiacol. A heating rate of 3 K/s was used in the TPD experiments and the HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The full width at half-maximum of the elastic peak obtained from the clean surface was typically 40 cm^{-1}. HREEL spectra were collected as a function of sample temperature. For temperatures greater than the dosing temperature the sample was heated at 3 K/s to the indicated temperature and then rapidly quenched to low temperature at which point the spectrum was collected.

3. Results and discussion

3.1. TPD of guaiacol on Pt(111) and Zn/Pt(111) surfaces

TPD results for Pt(111) dosed with 0.5 L of guaiacol are displayed in Fig. 1. In addition to a narrow guaiacol peak at 225 K, which based on previous studies of similar aromatic molecules on Pt(111) can be assigned to desorption of second layer physisorbed species [20], the only other desorbing species were H_2 at 340 and 435 K, and CO at 435 K. The fact that the CO and H_2 peaks at 435 K occur at the same temperature and have similar shapes suggests that they are reaction-limited products of the decomposition of a common adsorbed intermediate. Since CO was the only carbon-containing reaction product this decomposition reaction must also result in carbon deposition on the surface. Assuming that all of the oxygen in the guaiacol reactant is accounted for in the CO product along with the 7:2 carbon-to-oxygen ratio in the guaiacol reactant, the TPD data indicate that roughly 2.5 carbon atoms were deposited on the surface for every CO molecule produced. The lower-temperature H_2 peak at 340 K is consistent with a desorption-limited process [21] and thus demonstrates that dehydrogenation of at least a portion of the adsorbed guaiacol must occur below this temperature.

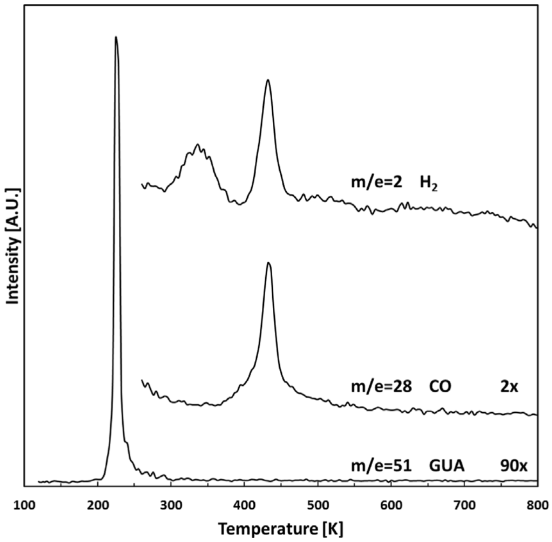

Fig. 1. TPD spectra obtained following exposure of the Pt(111) surface to 0.5 L of guaiacol (GUA).

For TPD studies of the reactivity of Zn modified Pt(111) surfaces a 0.4 ML Zn/Pt(111) surface was chosen as a representative model alloy surface. Consistent with our previous studies [14,22], addition of Zn adatoms to the Pt(111) surface caused a significant change in reactivity. Fig. 2 displays TPD data for a 0.4 ML Zn/Pt(111) surface dosed with

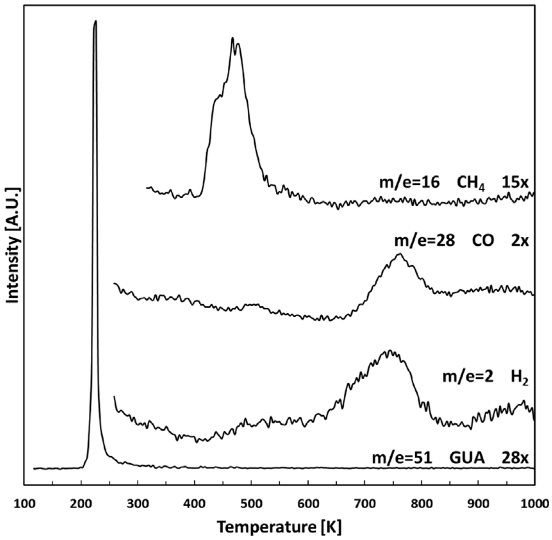

Fig. 2. TPD spectra obtained following exposure of the Zn/Pt(111) surface to 0.5 L of guaiacol (GUA) (These data are displayed on the same scale as those in Fig. 1.).