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Lignin-derived oxygenate reforming on a bimetallic surface: The reaction of benzaldehyde on Zn/Pt(111)

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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 benzaldehyde (C_6H_5CHO) on hydrogen-covered Pt(111) and Zn-modified Pt(111) surfaces. Benzaldehyde was found to interact with Pt(111) via both the phenyl ring and carbonyl of the aldehyde group. This bonding configuration facilitates unselective decomposition of the benzaldehyde to produce CO, H_2, and small hydrocarbon fragments at relatively low temperatures. On the other hand, benzaldehyde was found to bond to Zn-decorated Pt(111) surface exclusively via the carbonyl group in an η_2(C, O) configuration, with the phenyl ring tilted away from the surface. This configuration weakens C—O bond in the carbonyl facilitating its cleavage and helps prevent hydrogenation of the phenyl ring.

1. Introduction

There is an increasing interest in the development of technologies for converting lignocellulosic biomass into chemicals and fuels to reduce our dependence on non-sustainable traditional fossil fuels such as petroleum and natural gas [1–3]. Of the three components of biomass, cellulose, hemicellulose, and lignin, the conversion of the two former into more useful products has received the most attention from the research community [1,4–6]; however, lignin, which constitutes 15–30% by weight and up to 40% by energy content of biomass [7], is a valuable resource. Lignin is an amorphous polymer of oxygenated aromatic subunits (e.g. coniferyl and sinapyl alcohols) that gives plants their structural integrity. The aromatic nature of lignin makes it an attractive feedstock for the production of high value aromatic compounds [8,9].

Depolymerization of lignin via fast pyrolysis or other means produces a range of oxygenated aromatics with phenol, anisole, benzaldehyde, salicylaldehyde, and guaiacol being typical examples [8,10–13]. The high oxygen content in many of these molecules is problematic since it reduces their fuel value and suitability as feedstock for fine chemicals. Thus, upgrading by partial or complete oxygen removal is likely to be necessary for any commercial process using lignin as a starting material. This has motivated studies of the catalytic hydrodeoxygenation (HDO) of lignin-derived molecules [8,14]. Several studies of the use of supported group 10 metal catalysts (Ni, Pt and Pd) for this purpose have recently appeared in the literature [15–19]. These monometallic catalysts, however, are not highly selective for HDO and tend to also promote the undesired hydrogenation of the phenyl rings.

Bimetallic catalyst composed of a group 10 metal alloyed with a more oxyphilic metal, such as Fe, Sn, or Zn, has proven to be more selective for oxygen removal without ring hydrogenation [13–15,20–26]. Our previous studies of model PtZn catalysts have shown that at least for molecules containing aldehyde functional groups, the more oxyphilic Zn provides a binding site for the oxygen of the carbonyl group with the carbon being bound to Pt [27–29]. This bonding configuration results in a weakening of the C—O bond thereby facilitating its scission. The mechanism by which alloying with an oxyphilic metal decreases activity for hydrogenation of phenyl rings is less clear. It has been suggested, however, that it may decrease ring-surface interactions and alter the adsorption configuration [30–33]. The goal of the work reported here was to test this hypothesis and determine how alloying Pt with Zn affects the interaction of the phenyl rings in oxygenated aromatic compounds with the catalyst surface and the suitability of such catalysts for selective HDO of lignin-derived aromatic compounds. We have used a surface science approach in this work and studied the adsorption and reaction of benzaldehyde (C_6H_5CHO) on a Zn-decorated Pt(111) surface using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS).

2. Experimental

HREELS and TPD experiments were conducted in an ultrahigh vacuum (UHV) apparatus with a background pressure of 2×10^{-10} Torr. The system was equipped with a quadruple mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies). The Pt(111) single crystal substrate was 10 mm in diameter and oriented to within ±0.5°. The surface was cleaned by

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repeated cycles of 2 kV Ar^+ ion bombardment at 600 K for 40 min, annealing at 1200 K in 2×10^{-8} Torr O^2 for 15 min, and annealing at 1200 K in vacuum for 5 min. The Pt(111) crystal was spot-welded to two tantalum wires that were connected to UHV sample manipulator. The sample could be heated resistively and cooled to 110 K by conduction from a liquid N_2 reservoir.

Zn-decorated Pt(111) surfaces were prepared by exposing the Pt surface to a beam of Zn atoms produced using a thermal evaporative source that consisted of a small coil of Zn wire (Alfa Aesa, 99.99%) wrapped around a resistively heated tungsten filament. The Zn flux from the source was monitored using a quartz crystal microbalance (QCM) and the total amount of Zn deposited was further quantified by measuring the area of the high-temperature Zn desorption feature in the TPD spectra. We have previously characterized the structure of Zn-modified Pt(111) surfaces in detail [34]. For the Zn deposition conditions used here, the deposited Zn atoms remain on the surface and do not form an ordered overlayer.

The reactant, benzaldehyde (Sigma Aldrich, 99.5%) 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. Hydrogen was contained in a lecture bottle that was attached to the same dosing line. Since we were interested in HDO activity and the propensity of the model catalysts to hydrogenate the phenyl ring in benzaldehyde, experiments were conducted using surfaces saturated with H_2 which were obtained by exposing the surface to 10 L of H_2. A 0.6 L exposure of benzaldehyde was used in both the TPD and HREEL experiments. This exposure was chosen based on a series of TPD experiments on Pt(111) which showed that it was sufficient to saturate the surface with benzaldehyde at low temperatures.

HREEL spectra were collected using a 4 eV electron beam, oriented at 60° with respect to the surface normal. The intensity of the elastic peak varied between 10 k and 100 k cps and had a full width half-maximum of ~40 cm^{-1}. All TPD data were collected using a 3 K/s heating rate.

3. Results

3.1. Temperature programmed desorption (TPD)

TPD studies were performed for both Pt(111) and Zn-decorated Pt(111) surfaces that were pre-dosed with H_2 and then dosed with 0.6 L of benzaldehyde at a sample temperature of 115 K. As noted above, this benzaldehyde dosage was selected because it was sufficient to saturate each surface with the reactant as evidenced by a molecular benzaldehyde desorption peak at 200 K. Fig. 1 displays TPD data obtained from the Zn-free Pt(111) surface. In addition to the molecular benzaldehyde peak at 200 K, other desorption products including, H_2, CO, and CH_4, were observed at temperatures above 300 K. No other products were detected. CO was produced in a broad feature between 360 and 480 K which was composed of at least two overlapping peaks. This temperature range is consistent with desorption-limited CO from Pt(111) [35] and thus demonstrates that C—C bond scission in the adsorbed benzaldehyde commences at or below 360 K. Meanwhile, H_2 was produced in a large peak at 350 K which can be assigned to recombinative desorption of H atoms [35], and a series of smaller reaction-limited peaks between 440 and 700 K. A small amount of methane (m/e 16) was also observed at 420 K, again indicating that C—C bond cleavage in the benzaldehyde occurs below this temperature. These TPD results for benzaldehyde on Pt(111) are similar to those reported previously for other aldehydes, such as acetaldehyde and furfural [27,28,36], which also showed that the high activity of this surface for C—C bond scission results in decomposition of these molecules at relatively low temperatures.

Consistent with our previous studies [27,28], decoration of the Pt(111) surface with Zn atoms caused significant changes in reactivity toward benzaldehyde with the most notable being a shift of the major products, CO and H_2, to higher temperatures, and the emergence of toluene ($C_6H_5CH_3$) and H_2O as reaction products. These trends are apparent in Fig. 2 which displays TPD curves for H_2, CO, $C_6H_5CH_3$, and H_2O as a function of Zn coverage for H_2-saturated Pt(111) dosed with 0.6 L of benzaldehyde. Desorption of molecular benzaldehyde at 200 K was also observed, but is not included in the figure.

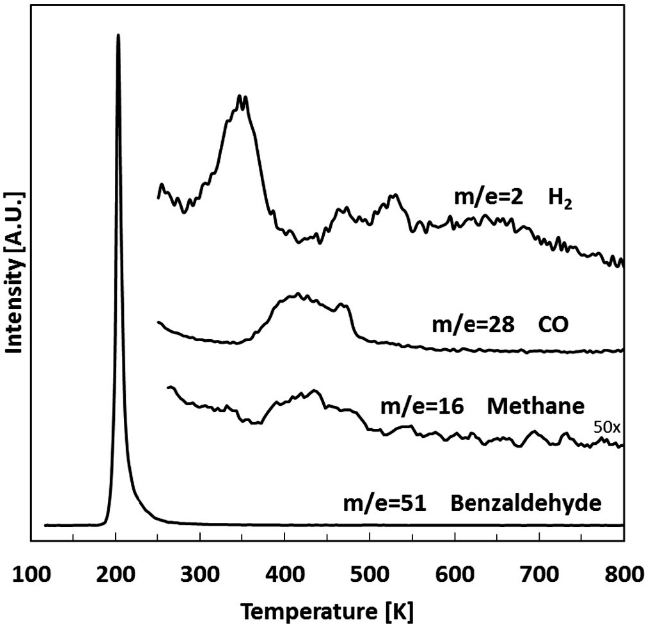

Fig. 1. TPD spectra obtained following exposure of the H_2-saturated Pt(111) surface to 0.6 L of benzaldehyde.

As shown in Fig. 2(b), the CO peaks shifted to higher temperatures with increasing Zn coverage. For 0.1 ML Zn the CO peaks are centered at 450 and 520 K, and merge into a single desorption-limited peak centered at 520 K upon increasing the Zn coverage to 0.4 ML. For this coverage range the total amount of CO produced also decreased somewhat with increasing Zn coverage. At higher Zn coverages the CO peak at 520 K continued to decrease in intensity and was not observed for Zn coverages ≥ 0.8 ML. These trends all point to the Zn-modified surfaces having a lower activity for C—C bond scission in the adsorbed benzaldehyde.

The H_2 desorption curves in Fig. 2(a) also show an increase in peak temperature with increasing Zn coverage. Upon addition of 0.1 ML of Zn, the primary H_2 desorption peak, which appears at 350 K on the Zn-free surface, shifted to 435 K. A very broad H_2 desorption feature between 560 and 830 K also emerged. Both of these features increased somewhat in temperature with increasing Zn coverage. The possible origins of the H_2 peaks will be discussed in detail below, but the shift to higher temperature suggests that they are reaction limited rather than desorption limited as was observed for Zn-free Pt(111).

As noted above, addition of Zn adatoms to the Pt(111) surface also resulted in the emergence of peaks for H_2O and toluene in the TPD spectra of the benzaldehyde-dosed surface. As shown in Fig. 2(c) a broad water peak centered at 490 K is apparent for the 0.1 Zn/Pt(111) surface and both increases in intensity and temperature with increasing Zn coverage. Note that water was not produced on the Zn-free surface and its production on the Zn-modified surfaces demonstrates that these surfaces are active for C—O bond scission in the adsorbed benzaldehyde. The production of toluene on the Zn-modified surfaces as shown in Fig. 2(d) is particularly interesting since this is the desired product for the HDO of the benzaldehyde reactant. (This product was identified using spectra for m/e 91, 77, and 51). For the 0.1 ML Zn/Pt(111) surface toluene is produced at 430 K. This peak grew in intensity when the Zn coverage was increased to 0.4 ML, but was absent for high Zn coverages as shown in the figure for 0.8 ML of Zn.

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