The use of bimetallics to control the selectivity for the upgrading of lignin-derived oxygenates: Reaction of anisole on Pt and PtZn catalysts

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ABSTRACT

The adsorption and reaction of anisole on Pt and PtZn catalysts were investigated using both model single crystal and high surface area supported metal catalysts. Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) studies of the interaction of anisole with Pt (1 1 1) demonstrated that there is a strong interaction between the phenyl ring of anisole and the surface, resulting in C—O and C—H bond scission at relatively low temperatures. In contrast, anisole was observed to bond to a Zn-modified Pt(1 1 1) surface primarily via the oxygen at Zn sites or possibly adjacent Pt sites, with the phenyl ring tilted away from the surface. Such bonding configuration facilitated selective C—O bond cleavage producing phenyl groups and methoxide groups with the latter being bonded to the Zn sites. These results suggested that PtZn may be an effective catalyst for hydrodeoxygenation (HDO) of lignin-derived aromatic oxygenates with low activity for ring hydrogenation. This hypothesis was then tested and verified by investigating the reaction of anisole and H_2 over high surface area carbon-supported Pt and PtZn catalysts.

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1. Introduction

Lignocellulosic biomass is emerging as an attractive, sustainable carbon feedstock for the production of fuels and chemicals [1–3]. While in recent years much effort has been focused on catalytic processing of the cellulosic fraction of biomass for this purpose [4–6], the lignin fraction is also a useful resource and provides a feedstock for the production of high-value aromatic compounds [2,7]. The refractory nature of lignin, however, makes its conversion to useful products more challenging than that of cellulose. Depolymerization of lignin is generally achieved via fast pyrolysis which produces a complex liquid mixture containing a range of substituted aromatics [8]. This bio-oil is highly oxygenated and subsequent hydrodeoxygenation (HDO) is usually required.

Conventional metal-sulfide based hydrotreating catalysts (e.g. sulfided CoMo) have been suggested for use in the upgrading and deoxygenation of lignin-derived aromatic oxygenates; unfortunately, they tend to produce less desirable ring saturation products and also rapidly deactivate due to coking [9–12]. Some success has been obtained using group 10 metal catalysts (i.e. Ni, Pd, Pt), but they also promote hydrogenation of the aromatic rings [13,14]. Alloying a group 10 metal with a second more oxyphilic metal

(e.g. Fe, Sn, Zn) [15–18], however, has emerged as a promising strategy for producing HDO catalysts that exhibit high selectivity for the production of aromatic hydrocarbons from lignin-derived oxygenates. Multiple studies have shown that alloying Pt or Pd with Sn or Fe weakens the interaction of the aromatic ring with the metal surface, and it has been proposed that this may affect the ring hydrogenation activity by altering the bonding configuration of aromatic oxygenates from one where the ring is lying flat on the surface to one where adsorption occurs primarily via the oxygen functionality [19–21].

Recently our group has undertaken a series of mechanistic studies of the adsorption and reaction of benzaldehyde and other small aldehydes on Pt—Zn model catalysts consisting of a Pt(1 1 1) surface decorated with Zn adatoms [22–24]. Our studies of benzaldehyde on these catalysts provide direct evidence that alloying does indeed alter the bonding configuration of the phenyl ring with the ring tilting away from the surface upon Zn addition. Furthermore, these previous studies show that aldehydes bond to the Zn/Pt (1 1 1) surface via the carbonyl in an η_2-configuration in which the oxygen in the carbonyl is bonded to a Zn site and the carbon is bonded to an adjacent Pt site. This bonding configuration results in a weakening of the C=O bond which helps facilitate its cleavage.

In the work described here we have extended our previous studies of the reactivity of Zn-modified Pt surfaces to include the adsorption and reaction of anisole ($CH_3OC_6H_5$). This molecule

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was chosen as a model aromatic compound that contains a C—O—C linkage which is commonly found in lignin-derived oxygenates [25–27]. Temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to characterize the pathways and intermediates involved in the reaction of anisole on both Pt(1 1 1) and Zn/Pt(1 1 1) surfaces. Based on the results for the model catalysts we have predicted trends in selectivity for the reaction of anisole on high surface area supported Pt and PtZn catalysts. These predictions were then tested by measuring product selectivity for the reaction of anisole over Pt/C and PtZn/C catalysts under typical HDO reaction conditions. The results from the model and high surface area catalysts together provide useful insight into the active sites in bimetallic HDO catalysts as well as how alloying can be used to limit activity for ring hydrogenation.

2. Experimental

The model catalyst studies in this work were conducted in an ultra-high vacuum (UHV) apparatus described in detail in previous publications [22,28,29]. The system had a background pressure operated at 2×10^{-10} torr and was equipped with a quadruple mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies). A Pt(1 1 1) single crystal substrate that 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(1 1 1) 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 O₂ 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 N₂ reservoir.

Zn deposition on Pt(1 1 1) was obtained by exposing the Pt surface to a beam of Zn atoms produced from an effusive source consisting of a coil of Zn wire (Alfa Aesar, 99.99%) around a resistively heated tungsten filament. A quartz crystal microbalance (QCM) was used to monitor the Zn flux from the source 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 [22,30]. Detailed characterization of the structure of Zn-modified Pt(1 1 1) surfaces has been reported previously [30]. In that study it was shown that for initial submonolayer amounts of Zn deposited with Pt(1 1 1) sample held at or below room temperature, the Zn diffuses into the surface upon annealing between 600 and 700 K with the equilibrium structure being one where the Zn atoms reside in the second and third layer below the surface. For this structure there are no Zn sites present on the Pt(1 1 1) surface. Since for this study we wanted to investigate how Zn affects reactivity via electronic interactions and its potential role as an active site for HDO, we chose to investigate Pt(1 1 1) surfaces that were decorated with Zn adatoms that were formed by Zn deposition with the Pt(1 1 1) sample below room temperature. Our previous studies have shown that Zn adatoms influence the electronic property of nearby surface Pt atoms in a manner similar to that in the bulk alloy [22].

For the UHV studies the anisole reactant (Sigma-Aldrich, 99.7%) 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. A saturation exposure of anisole (0.6 L) was used in both the TPD and HREEL experiments. 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.

Micro flow reactor studies were also carried out to determine the reactivity of carbon supported Pt and PtZn catalysts for the HDO of anisole and to provide comparison data to the model catalyst studies. Pt/C catalysts with 10 wt% Pt were prepared by impregnation of carbon black (Vulcan XC-72R) with a water/ethanol (4:1) solution of tetraammineplatinum (II) nitrate (Pt(NH₃)₄(NO₃)₂, 99.99%, Alfa Aesar). The 10 wt% PtZn/C samples were prepared by co-impregnation with water/ethanol (4:1) solution of Pt(NH₃)₄(NO₃)₂ and Zn(NO₃)₂·6H₂O. Prior to reaction studies the catalysts were reduced in flowing 5% H₂/He to 673 K with a heating ramp of 2 K/min, and then to 773 K with heating ramp of 1 K/min at which point it was held for 2 h. PtZn catalysts were prepared with Pt:Zn molar ratios of 1:1 (PtZn/C) and 1:3 (PtZn₃/C). Both the PtZn/C and PtZn₃/C catalysts had a total metals loading of 10 wt%.

A high-pressure flow reactor that was similar to that described by Luo et al. [31] was used in the reactor studies. The reactor consisted of a 20 cm long, stainless-steel tube (4.6-mm ID) that was heated in a tube furnace. A 1 wt% liquid solution of anisole (Sigma-Aldrich, 99.7%) dissolved in *n*-heptane (Sigma-Aldrich, 99%) was introduced into the reactor by an HPLC pump (Series III, Lab Alliance). The pump was also used to monitor the total pressure which was controlled by a back pressure regulator (KPB series, Swagelok) that was located downstream from the reactor. The pressure was fixed at 27.5 bar for all the experiments performed in this study. Hydrogen (Airgas, UHP grade) contained in a regulated, high-pressure cylinder was delivered to the reactor through 2.44 m of capillary tubing (50.8 µm ID, Valco Instrument, Inc.). The H₂ flow rate was a function of the cylinder outlet pressure and the pressure drop across the capillary tube. For a typical experiment, the liquid flow rate was set as 0.1 ml/min, while the H₂ flow rate was kept constant at 5 ml/min (STP).

For each catalyst test, 0.05 g of the catalyst was packed into the middle portion of the reactor and held in place by glass wool. Prior to rate measurements, each catalyst was pretreated by heating in 27.5 bar of flowing H₂ at 573 K for 30 min. Fresh samples were used for each experiment at a specified reaction condition. The liquid phase reaction products were collected at room temperature and a GC–MS (QP-5000, Shimadzu) was used for identification and quantification of the produces. Product selectivity was quantified using solutions with known concentrations as standards. The reactivity data presented here were obtained 60 min after starting the reaction in order to allow steady state to be obtained.

3. Results and discussion

3.1. Reaction of anisole on Pt(1 1 1)

The initial studies of the adsorption and reaction of anisole were performed for the Zn-free Pt(1 1 1) surface. TPD data collected as a function of coverage were used to determine the dosage required to saturate the surface with anisole, as determined by the appearance of a molecular anisole peak at 185 K corresponding to desorption of adsorbed multilayers. Based on these results, a 0.6 L anisole dose, which gives a coverage slightly more than one monolayer, was chosen for the more detailed TPD studies.

Fig. 1 displays a complete set of TPD data obtained from the Zn-free Pt(1 1 1) surface for the 0.6 L anisole dose. The two low-temperature anisole desorption peaks at 185 and 215 K correspond to physisorbed multilayers and chemisorbed anisole, respectively. The only reaction products detected for this surface were H₂ and