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Supporting Information

ABSTRACT: Furfural is a key bioderived platform chemical whose reactivity under hydrogen atmospheres affords diverse chemical intermediates. Here, temperature-programmed reaction spectrometry and complementary scanning tunneling microscopy (STM) are employed to investigate furfural adsorption and reactivity over a Pt(111) model catalyst. Furfural decarbonylation to furan is highly sensitive to reaction conditions, in particular, surface crowding and associated changes in the adsorption geometry: furfural adopts a planar geometry on clean Pt(111) at low coverage, tilting at higher coverage to form a densely packed furfural adlayer. This switch in adsorption geometry strongly influences product selectivity. STM reveals the formation of hydrogen-bonded networks for planar furfural, which favor decarbonylation on clean Pt(111) and hydrogenolysis in the presence of coadsorbed hydrogen. Preadsorbed hydrogen promotes furfural hydrogenation to furfuryl alcohol and its subsequent hydrogenolysis to methyl furan, while suppressing residual surface carbon. Furfural chemistry over Pt is markedly different from that over Pd, with weaker adsorption over the former affording a simpler product distribution than the latter; Pd catalyzes a wider range of chemistry, including ring-opening to form propene. Insight into the role of molecular orientation in controlling product selectivity will guide the design and operation of more selective and stable Pt catalysts for furfural hydrogenation.

INTRODUCTION

The development and sustainability of a bioresource-based chemical industry is strongly dependent on new heterogeneously catalyzed processes capable of selectively transforming bioderived organic molecules into valuable chemical intermediates, platform chemicals, and commercial products. In this respect, fundamental understanding of the underlying mechanistic aspects governing these heterogeneous processes is crucial. Lignocellulosic and oleochemical biomass-derived molecules are most attractive because of their abundance and the plethora of products that can be derived from them. Furfural is one of the most promising renewable platform compounds,1−4 itself obtainable via the acid-catalyzed hydrolysis of C5 sugars such as xylans and xylose.3,5

Furfural can be upgraded for a range of applications, finding use as a process agent for generating lubricating oils and in the flavorings and perfume industry where subtle structural alterations unlock diverse flavorings.3 However, the majority of furfural (>62%) is hydrogenated to furfuryl alcohol for use as an adhesive, resin, or corrosion-resistant coating.2,6 Furfuryl alcohol is also a chemical building block to many other useful compounds in the fine chemical and pharmaceutical industries, as shown in Scheme 1,7 offering a route to 2-methyl furan, a potential biofuel, or tetrahydrofurfuryl alcohol (B) which can in turn undergo ring-opening hydrogenation to the polymer precursor 1,5-pentanediol (D).8 While 2-methyl furan production is reported for Pd hydrogenolysis catalysts in the liquid phase,9,10 it is observed only at high temperature over Pt.11−15

Large-scale furfural upgrading already occurs in China, South Africa, and the Dominican Republic, utilizing ~280 000 tons of furfural per annum.1 However, current processes rely on a copper chromite catalyst which damages both ecologies and human health.16,17 This copper chromite catalyst operates at high pressure (up to 30 bar) and high temperature (up to 473
K), affording acceptable selectivity and reasonable activity, but in light of its associated hazards, a replacement catalyst is urgently sought (especially if the transition from a petrochemical to biobased economy proceeds apace).2,18

Furfural hydrogenation has been studied in both the vapor and liquid phase31,19−23 and is highly sensitive to reaction conditions over Pt catalysts. In general, liquid-phase hydrogenation is conducted at lower temperature than vapor-phase studies, hindering direct comparison because of the widely differing product distributions.

Higher temperature favors ring-opening or total hydrogenation of furfural, while mild conditions favor furfuryl alcohol and furan.11,20,24 Liquid-phase hydrogenation is complicated by poor hydrogen solubility in the reaction medium and competitive solvent coupling reactions to form 1° and 2° alcohols (prolific in furfural chemistry);11,12,14 hence, high hydrogen pressures are common. Vapor-phase studies require temperature only >435 K to vaporize furfural at atmospheric pressure.25 However, the key factors determining product selectivity and activity are not well-established. Many transition-metal catalysts are reported for the hydrogenation of furfural to furfuryl alcohol, including Ni, Pd, Co, Cu, Rh, Ir, and Ru.15,22,23,26−29 Platinum has been particularly explored under mild reaction conditions,11 for vapor-phase hydrogenation, with high reaction temperatures yielding a spectrum of small molecules including methyl furan.20,26 In contrast, over Pd, an array of products forms during liquid-phase furfural hydrogenation,30 such as acetal, ketals, and polymeric species, in addition to ring-opening products.31

Adsoption of unsaturated oxygenates over Cu, Ni, Pd, and Pt(111) single-crystal surfaces and Zn adatom modified Pt(111)32−45 has been the focus of both experimental and theoretical investigations. For furfural, reactively formed furan (a decarbonylation product from furfural and furfuryl alcohol) behaves differently from molecular furan over Pd(111), the former being more prone to thermal decomposition to propylene.39,46 Density functional theory (DFT) calculations have highlighted multiple reaction pathways for furfuryl alcohol hydroglenolysis over Pd(111) accompanied by the formation of adsorbed water; calculations suggest that the latter byproduct hinders furfural hydrogenation over Cu(111).32 Furfural adsorption and decomposition over Pt(111) and Zn-modified Pt(111) have been extensively investigated using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy by Shi and Vohs.38 They report that furfural adsorbs at low temperatures through the aromatic ring on Pt(111) driving unselective decomposition to CO and H2 upon heating. Surface modification with Zn adatoms favors furfural adsorption through the carbonyl carbon and associated ring tilting away from the Pt(111) surface.38 This molecular reorientation suppresses thermal decomposition and ring hydrogenation in favor of hydrodeoxygenation (HDO) of the C=O bond.

Here we utilize temperature-programmed reaction spectrometry (TPRS) and scanning tunneling microscopy (STM) to elucidate salient features of furfural’s adsorption and hydrogenation over Pt(111) and correlate coverage-dependent orientation and self-assembly with selectivity toward hydrogenation versus decomposition pathways. Furfural adsors in a hydrogen-bonded planar network at low coverage, adopting a tilted geometry for a densely packed furfural adlayer. Adsorption geometry and hydrogen coadsorption influence selectivity toward both evolved products and surface carbon. Preadsorbed hydrogen promotes hydrogenation to furfuryl alcohol over decarbonylation to furan and passivates Pt(111) toward molecular decomposition. These results specifically allow us to discuss the fundamental surface behavior of furfural that leads to the selectivity of platinum versus other precious metal catalysts, such as palladium, in this important hydrogenation reaction. They also identify the critical importance of surface hydrogen concentration in both selectivity and deactivation as a result of surface coking by carbon. In consequence, the present findings help pave the way toward replacement catalysts for the undesirable copper chromite catalyst packages currently employed.

![Scheme 1. Furfural and Its Derivatives: (A) Tetrahydrofuran, (B) Tetrahydrofurfuryl Alcohol, (C) 1,2-Pentanediol, and (D) 1,5-Pentanediol](image)

### EXPERIMENTAL SECTION

TPRS was conducted in an ultrahigh vacuum (UHV) chamber operated at a base pressure of 3 × 10−10 Torr, equipped with an Omicron 4 grid retarding field analyzer for low-energy electron diffraction (LEED) or Auger electron spectroscopy (AES) and a VG 300 quadrupole mass spectrometer whose ionizer was positioned 6 mm from the front face of the sample. The Pt(111) single crystal could be cooled to 140 K and resistively heated to above 1000 K, monitored by a K-type thermocouple attached to the sample. Furfural (Sigma-Aldrich, 99%), furan (Sigma-Aldrich, ≥ 99%), 2-methyl furan (Sigma-Aldrich, 99%), and furfuryl alcohol (Sigma-Aldrich, 98%) were purified by several freeze−pump−thaw cycles. All organic molecules, H2 (Energas, 99.99%), and O2 (Energas, 99.999%) were delivered to the sample by backfilling the chamber to the required pressure. TPD and TPRS measurements were performed with a linear heating ramp of 9.9 K s−1. Selectivity calculations (see the Supporting Information) from the mass spectrometry data include corrections for mass spectrometer sensitivity and molecular ionization cross section achieved by admitting a known pressure of each molecule into the vacuum system, measuring the intensity of the mass fragments, and correcting the pressure gauge reading based on the theoretical ionization cross section. Mass fragments for molecular identification were as follows; furfural (m/z 96 and 39), furan (m/z 68 and 39), furfuryl alcohol (m/z 98, 81, and 39), and methyl furan (m/z 82, 53, and 39). Additional ions were also monitored to identify potential products tetrahydrofuran (m/z 72), tetrahydrofurfuryl alcohol (m/z 102), 2-methyltetrahydrofuran (m/z 82), and propene (m/z 42); however, none of these latter molecules were detected from furfural with and without coadsorbed H2. Exposures are quoted in Langmuirs (L), where 1 L is 1 × 10−6 Torr s−1 and have been corrected for ion gauge sensitivity. STM measurements were carried out in a separate custom built UHV
The single-crystal Pt(111) surfaces were cleaned by repeated cycles of Ar+ (99.999% Messer) sputtering (1 keV, 5 μA) for 40 min and annealing at 1000 K. This process was followed by exposure to 5.5 × 10⁻⁷ Torr O₂ (Energas, 99.95%) for 25 min at 815 K. The sample was finally annealed to 1000 K. Surface cleanliness was confirmed by LEED, AES, or STM.

### RESULTS AND DISCUSSION

#### Adsorption and Reactivity of Furfural on Pt(111).

Figure 1a shows TPRS acquired after clean Pt(111) was exposed to 0.15 L furfural at 140 K. The evolved products were unreacted furfural (m/z 96) and reactively formed furan (m/z 68), CO (m/z 28), H₂ (m/z 2), and H₂O (m/z 18). A total of 72% of the adsorbed furfural desorbed intact (main peak at 227 K with a smaller more strongly bound feature at 280 K), whereas ~22% reacted to furan which desorbed at 291 K. The remainder formed surface carbon (see below), CO, and H₂.

The small feature at 280 K in the desorption spectrum of furfural is associated with desorption from step edges of the crystal, and it does not increase significantly in intensity, as shown in Figure S1a. Note that furfural multilayer peaks on Pt(111) appear at 190 K (Figure S1a,b). Note that the 227 K peak in the furan desorption corresponds to furfural, which shares a m/z 68 fragment with furan. This m/z 68 fragment is sufficiently weak that we can be confident it is not the main contributor to the furan desorption at 291 K, and indeed the 280 K furfural peak is clearly offset in temperature from the former, confirming their different chemical origins. Carbon monoxide desorption due to furfural decarbonylation occurred at 384 K, coincident with the temperature for chemisorbed CO desorption over Pt(111), indicating the former’s appearance was desorption-rate limited; hence, decarbonylation occurs below 384 K. H₂ desorption from furfural decomposition occurred at 415, 488, and 604 K. All three H₂ desorption peak temperatures are higher than that of chemisorbed H₂ over clean Pt(111); hence, their appearance was reaction-rate limited (see Figures 1a and S2a,b).

Liberation of surface atomic hydrogen from furfural decomposition (Figure 1a) does not lead to any self-hydrogenation products, presumably because the temperature for surface hydrogen formation is higher than the desorption temperature of furfuryl alcohol and methyl furan (Figure S3a,b). The hydrogen desorption peak area can be used to estimate the amount of residual carbon on Pt(111) following the temperature ramp as described in the Supporting Information. We estimate ~6% of the total adsorbed furfural adlayer remains as carbonaceous deposits. Figure 1b presents furfural total conversion and product selectivity as a function of exposure, revealing lower reactivity over crowded surfaces (conversion decreasing from 28% to 9%) while furan selectivity (and the amount of residual carbon) were coverage-independent. This fall in furfural conversion and subsequent plateau occurs around 0.45 L, coinciding with saturation of the furfural monolayer (Figure S1a). This saturation exposure is similar to that of 0.6 L reported by Shi and Vohs, with higher exposure rapidly populating multilayers.

A microscopic view of furfural on Pt(111) at two different coverages was obtained by STM (Figures 2a–c and 3a–c).
Desorption Enthalpies for Furfural and Furan on Pt(111). Enthalpies of furfural and furan desorption from Pt(111) were determined from a Redhead analysis,\textsuperscript{49} assuming a common pre-exponential factor of 10\textsuperscript{13} s\textsuperscript{-1} as widely adopted for organic adsorbates including phenol,\textsuperscript{50} benzene,\textsuperscript{51} and naphthalene.\textsuperscript{52} The desorption enthalpy of chemisorbed furfural in the main desorption peak at 227 K was \(~56\) kJ mol\textsuperscript{-1} (Figure 1a). This value appears to be close to the value calculated for the desorption of phenol (57 kJ mol\textsuperscript{-1}) and cyclopentane (58 kJ mol\textsuperscript{-1}) on similar Pt(111) surfaces.\textsuperscript{50,53} Furfural desorption from Pd(111) occurs at a far higher temperature 365 K\textsuperscript{36} and hence must be associated with a far greater activation barrier. Redhead analysis for reactively formed furan from flat-laying furan (Figure S4) reveals a desorption enthalpy of \(~73\) kJ mol\textsuperscript{-1}, close to that of unsubstituted aromatics such as benzene with 68 kJ mol\textsuperscript{-1} over Pt(111).\textsuperscript{51} DFT calculations for furfural on precious metals\textsuperscript{39,54,55} have produced different values depending on the metal used and are sensitive to the inclusion of dispersive interactions.\textsuperscript{54} A comparative study suggested that furfural adopts both C=C ring and C=O bonding motifs over Pd, whereas on Pt, adsorption occurs only through the C=C ring. The latter adsorption geometry is consistent with the ability of furfural to form the hydrogen-bonded networks described above. The stronger adsorption of furfural over Pd(111) versus Pt(111) undoubtedly underpins their different reactivity: furfural evolves furan (365 K), CO (460 K), and H\textsubscript{2} (330 and 410 K) over Pd(111) but also undergoes extensive ring decomposition leading to propylene (385 K).\textsuperscript{37,38} In contrast, propylene was not observed over Pt(111) in this work.

Investigation and Quantification of Surface Carbon Product during Furfural Desorption from Pt(111). As discussed above, furfural adsorption over Pt results in carbon deposition, presenting a major technological drawback to utilizing Pt for large-scale furfural hydrogenation. Figure 5a,b shows consecutive TPRS profiles following a 0.25 L furfural exposure over Pt(111), without cleaning the surface each cycle. Figure 5a shows a 47% drop in furfural desorption intensity between the first and second cycle, with the amount of reactively formed hydrogen (Figure 5b) reduced by a similar amount (40%). However, between the second and third exposure, the furfural and hydrogen desorption intensities decrease by only a further 5% and 3%, respectively. These

Figure 3. (a) STM image (T = 125 K, V\textsubscript{r} = –1.58 V, I\textsubscript{t} = 0.16 nA) with high furfural coverage dosed to a Pt(111) surface at 95 K. At coverages without any bare Pt, the line profile (b) across the line (highlighted by a square) indicated in panel a in the same color shows that the molecular features (example outlined in purple) are separated by \(~0.36\) nm. The statistical separation of molecular features across the same direction is displayed in panel c. The scale bar (black line) in the STM image is 2 nm.

Figure 4. Temperature-dependent STM images of the molecular layer on Pt(111) after dosing \(~0.1\) L furfural at 157 K. (a) After the the sample is heated to 245 K, molecular species consistent with furan, such as the ones in dotted circles, can be found (V\textsubscript{r} = 1.06 V, I\textsubscript{t} = 0.10 nA). (b) After further heating to 265 K, some furan molecules have desorbed, reducing the surface coverage (V\textsubscript{r} = –0.45 V, I\textsubscript{t} = 0.07 nA). The scale bar (black line) in the STM images is 2 nm.
observations demonstrate the number of available adsorption sites has decreased significantly, indicating the accumulation of significant (carbonaceous) residues. Furthermore, the initial decrease in furfural desorption of ∼47% between cycles one and two is significantly greater than the proportion of adsorbed furfural calculated to decompose to carbon (∼20% from Figure 1b). This suggests that any carbon deposits are likely uniformly distributed across the Pt(111) surface and hence block a large number of furfural adsorption sites. The formation of carbonaceous deposits from furfural is reportedly favored at 377−385 K over Pt catalysts during gas-phase hydrogenation,20,56 comparable to the desorption temperature for reactively formed hydrogen (indicative of hydrocarbon decomposition) from furfural over Pt(111) shown in Figure 1a. High furan yields during liquid-phase hydrogenation of furfural over Pt nanoparticles is also reported around 343 K,11 in agreement with that for the desorption of reactively formed furan from Pt(111) in this work at 323 K. CO formed through furfural decarbonylation to furan may also be responsible for site-blocking and poisoning of Pt catalysts at temperatures below that necessary for desorption of the former.11 Poisoning by carbon laydown typically requires catalyst reactivation (e.g., through calcination) and concomitant loss in metal surface area or changes in particle morphology and hence is often considered irreversible. In contrast, reversible CO poisoning may be mitigated by higher-temperature operation.

**Furfural Hydrogenation on Pt(111).** Hydrogen adsorption over clean Pt(111) was first studied by TPRS (Figure S2b) as a function of exposure. The desorption temperature of molecular hydrogen decreased with increasing H2 exposure in accordance with the expected second-order kinetics reported by Gebhardt and Koel.57 Hydrogen coverages were calculated according to the work of Ertl and co-workers wherein θHsat was 0.8 ML.58 Furfural and hydrogen were codosed, employing a H2 exposure of 100 L (corresponding to ∼0.4 ML) to ensure vacant Pt sites were available for furfural adsorption. Figure 6a shows data from TPRS of a 100 L H2 exposure and subsequent 0.35 L furfural exposure at 140 K over Pt(111). Furfural exhibits a multilayer desorption peak at ∼222 K, indicating site blocking by carbon deposits. (b) Corresponding decrease in H2 signal during adsorption–desorption cycles showing a decrease in reactive furfural due to carbonaceous deposits.

![Figure 5](image1.png)

**Figure 5.** (a) Repeated exposure of furfural (0.25 L), followed by desorption, without surface cleaning in between cycles, showing diminished overall monolayer adsorption feature intensity at 222 K, indicating site blocking by carbon deposits. (b) Corresponding decrease in H2 signal during adsorption–desorption cycles showing a decrease in reactive furfural due to carbonaceous deposits.

![Figure 6](image2.png)

**Figure 6.** (a) TPRS for Pt(111) exposed to 100 L H2 followed by 0.35 L furfural. (b) Reactively formed furan production from furfural over Pt(111) surfaces. (c) Furfural reactivity over Pt(111) pre-exposed to 100 L H2 as a function of furfural exposure. Molecular adsorption was performed at 140 K in all cases.
recombinative desorption of molecularly adsorbed hydrogen (Figure S2b). Additional hydrogen desorption must arise from the coadsorbed furfural and indeed are identical to those observed following furfural adsorption over clean Pt(111) at 415, 488, and 604 K (Figure 1a). As noted in an earlier section, furfural autohydrogenation over Pt(111) does not occur (Figure 1a); however, the observation of furfuryl alcohol in the presence of coadsorbed hydrogen indicates that furfural hydrogenation is possible over Pt(111) under UHV, provided that a high concentration of hydrogen adatoms is available at a relatively low surface temperature.

Reversing the dosing sequence, such that Pt(111) was first exposed to 0.25 L furfural followed by 100 L H2, suppressed hydrogenation pathways to both furfuryl alcohol and methyl furan, affording a conversion and selectivity similar to that seen over clean Pt(111). The main product observed is furan desorbing at 291 K (Figure 6b). Figure 6c shows furfural conversion and selectivity as a function of furfural exposure over Pt(111) precovered with 100 L H2. The results are in excellent agreement with the reaction pathways proposed in Scheme 1. At low furfural exposures (corresponding to a high ratio of surface H(a):furfural), the stepwise hydrogenation of furfural to furfuryl alcohol, and its subsequent HDO to methyl furan, is favored. At high furfural exposures (a low surface H(a):furfural ratio), insufficient surface hydrogen is available to further hydrogenate reactively formed furfuryl alcohol, which hence becomes the dominant product; however, in the latter scenario, more furfural desorbs molecularly.

The preceding insight enables us to predict the selectivity to furfuryl alcohol during furfural hydrogenation (Figure 7); higher surface hydrogen concentrations encountered in gas-phase furfural hydrogenation are expected to favor methyl furan relative to furfuryl alcohol, whereas the latter should be favored in the liquid phase. This is precisely as reported in the literature.11,12,20,59

![Figure 7. Gas-phase selectivities to molecular products for furfural with and without H2 and for different orders of exposure to the two reactants.](image)

CONCLUSIONS

The hydrogenation of furfural on Pt(111) was found to be highly sensitive to the conditions, in particular, surface crowding and associated changes in the adsorption geometry, used to carry out the catalytic reaction. On clean Pt(111), furfural adopts a planar motif at low coverages and a more tilted geometry as the coverage is increased. The extent of decarbonylation to furan was found to depend strongly on the coverage (and therefore adsorption geometry): at low coverage, the planar motif results in a much greater conversion to furan than occurs in the higher-coverage tilted molecules. The formation of surface carbon and possible consequences for practical catalyst deactivation processes have also been investigated and discussed.

Control of the furfural coverage on the surface is critical to the reaction selectivity, with hydrogenation and hydrogenolysis being possible at higher coverages. A strong correlation between the reactivity of the Pt(111) surface with that of Pt dispersed systems was observed, which enables the prediction of the activity and selectivity of Pt-based catalysts under practical conditions in the liquid and the gas phase. The order in which the surface encounters hydrogen and furfural is critically important. When furfural encounters a bare surface, it hinders the subsequent dissociative chemisorption of hydrogen and resulting hydrogenation activity. In contrast, when furfural encounters preadsorbed atomic hydrogen, furfuryl alcohol and methyl furan are produced; the former is a product of direct furfural hydrogenation, and the latter is a secondary product arising from the HDO of furfuryl alcohol (requiring a high ratio of surface H(a):furfural). At a low surface H(a):furfural ratio, insufficient surface hydrogen is available to further hydrogenate reactively formed furfuryl alcohol, which hence becomes the dominant product. Our results indicate that control over the furfural adsorption geometry, and surface hydrogen concentration, are key considerations for the design and operation of practical Pt catalysts for this important bioeconomy transformation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b01744.

Additional TPR spectra as well as the protocols used for calculating reagent conversion and product selectivities (PDF)

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**Notes**

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REFERENCES


