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Furan Decomposes on Pd(111) at 300 K To Form H and CO plus C_3H_3, Which Can Dimerize to Benzene at 350 K

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We report recent results on the products and mechanism of the reaction of furan with a clean Pd(111) surface. The desire to refine hitherto underutilized hydrocarbon sources requires the removal of significant quantities of sulfur-, nitrogen-, and oxygen-containing species.[1] The same catalysts are used for all three classes and typically consist of alumina-supported sulfides of Mo or W.[2] Oxygenated compounds are the most prevalent hetero compounds in liquids derived from coal and biomass, with furanic rings among the most important of these,[2,3] but removal of oxygen requires higher temperatures and significantly more hydrogen, on a molar basis, than removal of sulfur.[2,4] The addition of a late transition metal, such as Co or Ni, as a promoter has been reported to increase catalytic activity by an order of magnitude;[5] however, little is known about the surface chemistry of heterocycles on late transition metals. We report here initial results on the chemistry of furan on Pd(111) and relate the results to those for furan on Mo foils,[6] Cu(110),[7] Ag(110),[8] and O/Ag(110),[9] and for thiophene on Pd(111).[10]

The experiments are performed in an ultrahigh-vacuum chamber equipped for adsorption/desorption measurements utilizing both conventional and laser-induced heating methods. Details of the apparatus have been published elsewhere.[11] The Pd(111) crystal is cleaned by Ar^+ bombardment and by heating in oxygen. Furan (Aldrich Chemical Company 99+%) is purified by freeze−pump−thaw cycles. The Pd sample is cooled to 100 K and is then dosed with furan by backfilling the chamber. Exposures have been corrected for ion gauge sensitivities.

Temperature programed reaction (TPR) studies are performed using a 0.3 L (L = Langmuir = 10^{-6} Torr•s) exposure of furan and a heating rate of 3 K/s. These studies use Fourier transform mass spectrometry (FTMS); hence, a complete mass spectrum (*m/z* 10−650) of desorbing species is obtained every 2 s. The only species observed are furan, H_2, and CO (T_{max} = 265, 360, and 450 K, respectively). To estimate the relative yield of reversibly vs irreversibly adsorbed furan, the integrated areas under the thermal desorption traces are calculated for CO (*m/z* 28) and furan (sum of *m/z* 39 and 68 areas). The furan total is corrected using the ion gauge sensitivity (3.29)[12] as an estimate of the relative sensitivity by electron ionization in the mass spectrometer. The ratio of the *m/z* 28 area relative to the corrected total of *m/z* 28, 39, and 68 is approximately 0.4, indicating that 40% of the initial coverage of furan decomposes to yield CO. Direct formation of CO from furan has been observed on Mo(100) and Mo(110) surfaces, also.[13]

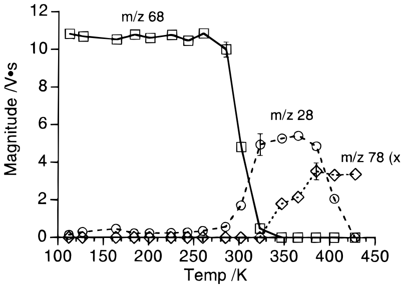

Figure 1. Profile of the magnitudes for selected masses observed in LITD/FT mass spectra, each obtained from a single laser shot at a different spot, after warming of a 0.3 L exposure of furan on Pd(111) to the temperatures indicated for 1 min. The plot shows a decay in furan (*m/z* 68) followed by growth of CO (*m/z* 28) and then benzene (*m/z* 78). The benzene signal has been increased by a factor of 10. Several spectra are obtained at each temperature, and error bars are displayed for the one data point with the largest scatter within each set.

For laser-induced thermal desorption (LITD), a Nd:YAG laser is focused onto the surface. Adsorbed molecules are vaporized from the surface as neutrals without substrate ablation. The neutrals are then postionized by an electron beam and detected by FTMS, yielding a complete mass spectrum of the postionized species for each laser pulse. The desorbed species have been shown to be representative of the surface composition in the majority of cases.[14,15] Unlike conventional thermal desorption, LITD rapidly achieves high surface temperatures and, under these conditions, entropically favored processes (such as direct desorption) can be favored.[16]

During the LITD experiments, the Pd sample is heated to a selected temperature and allowed to equilibrate for 1 min before the laser is fired. Figure 1 shows the signal intensities from the LITD/FT mass spectra for furan (*m/z* 68), CO (*m/z* 28), and benzene (*m/z* 78) as a function of sample temperature. Each spectrum is obtained from a single laser shot at a different spot on the surface. Several spectra are taken at each temperature, and the signal magnitudes are averaged for Figure 1. The LITD/FTMS signals are typically proportional to the surface concentrations for each species.[11] These data clearly illustrate the loss of furan accompanied by the growth of CO at 280−320 K followed by benzene above 350 K. The peak at *m/z* 78 is indicative of benzene and first appears at 350 K. No benzene is observed in TPR, since, as previous studies show, low coverages of benzene decompose on Pd(111) before desorbing[17] and our LITD signals for benzene are indicative of very low coverages. The benzene produced is only observed because the laser heating favors direct desorption. Above 380 K, the CO LITD signal decreases due to depletion by conventional desorption.

By 320 K, the furan signal has almost completely disappeared and CO formation is essentially complete. Presumably, by 320 K, C_3H_3 formation is also essentially complete; however, we see no evidence for this species in LITD. This species is probably too tightly bound or too labile to be desorbed intact, even with rapid laser heating.

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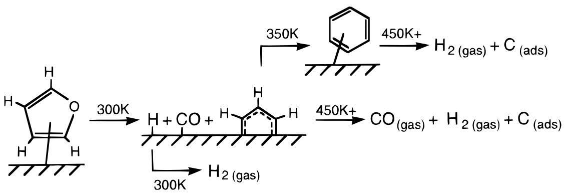
One might question whether laser heating drives some intermediate (such as a metallacycle with a C_6H_6 component) to benzene before or during desorption. Because of its rapidity, however, laser heating is likely to produce only subtle changes in the desorbing species.[18] Thus, changes in the LITD mass spectra as surface temperature is varied can still be correlated with changes in surface composition. Laser-driven recombination of C_3H_3 can be ruled out, since, if laser-driven recombination of two C_3H_3 species were an efficient process, benzene desorption would have been observed at 320 K when most of the C_3H_3 had formed. Clearly, something about the surface composition changes between 320 and 350 K. Our data indicate that C_3H_3 is stable for many minutes between 320 and 350 K on Pd(111). At 350 K, these species are able to dimerize to form a species similar, if not identical, to adsorbed benzene. It is somewhat surprising that C_3H_3 would be stable and mobile at these temperatures on group VIII metals, considering their dehydrogenating nature. Typically, alkyl fragments are only observed to recombine on coinage metals,[19] although methyl coupling to yield C_2 species has been observed on other late transition metal surfaces, including Pd, following the photodissociation of methyl halides.[20−22]

The data from LITD can be used to determine the relative yields of furan, CO, and benzene by making assumptions about the relative efficiency of laser-induced desorption for each species. Assuming that the efficiency is the same for each, we calculate that 60% of a 0.3 L exposure of furan decomposes to give CO (plus H and, presumably, C_3H_3) and 2% of the furan ends up as benzene. Thus, approximately 3% of the C_3H_3 species (assuming that CO and C_3H_3 are formed in equal quantities) form benzene; the remainder decompose on the surface. However, the benzene yields reported here are lower limits, since furan and CO are likely to have higher efficiencies for laser-induced thermal desorption than benzene. Both CO and furan desorb at lower temperatures (430 and 280 K, respectively, in TPR) than does benzene (520 K). In fact, as mentioned above, low coverages of benzene decompose completely in TPR. Therefore, the efficiency of thermal desorption in LITD is likely to be smallest for benzene.[16] Furthermore, the possibility of defect sites inducing the formation of benzene in such low yields may be argued; however, it is difficult to conceive how a defect would lead to benzene formation, since defects are usually associated with higher binding energies and enhanced decomposition.

H_2^+ is monitored in a separate experiment performed with a lower magnetic field strength. These experiments follow the same procedures outlined above; however, a slightly higher exposure (0.5 L) of furan is used (saturation requires ∼2 L[23]). TPR (3 K/s) shows H_2 evolution beginning at ∼300 K with the desorption peak centered around 360 K. (Hydrogen on clean Pd(111) desorbs with a peak centered at 310 K using a heating rate of 25 K/s.[24]) Using LITD, no significant signal for H_2 is observed after heating a furan-dosed Pd(111) surface. (Experiments on the dehydrogenation of cyclohexene on Pd(111), performed on the same day, did show a strong signal for H_2 from surface H using the same conditions described here.) The results from TPR and LITD indicate that H_2 evolution in TPR of furan on Pd(111) is rate limited by α-CH bond breaking.

Scheme 1



These experiments were carried out three times with identical results, as illustrated in Scheme 1. In contrast to these Pd results, other late transition metals, such as clean Cu(110)[7] and Ag(110),[8] yield no decomposition products during TPR. It has also been shown that Ni and Co are more effective than Zn in the promotion of Mo and W HDO catalysts.[25] It appears, then, that the Co and Ni group metals should be expected to be more effective promoters than the Cu and Zn group metals. However, furan coadsorbed with oxygen on Ag(110) has been shown to produce CO_2 and H_2O, both of which are evolved starting at about 300 K during TPR.[9] At higher temperatures (520 K), very small amounts of partial oxidation products, such as maleic acid, benzene, and bifuran, are evolved.[9] In these studies, benzene formation was also attributed to the cycloaddition of two C_3H_3 fragments, but only after oxidative activation of furan decomposition. The Pd surface used in our study does not require this highly oxidative environment.

FTMS monitors all masses from *m/z* 10 to 650 simultaneously, and all observed mass peaks can be attributed to furan, CO, hydrogen, and benzene. No C_4 species are observed. In contrast, studies of furan HDO over supported Mo/C catalysts show C_4 species as the major products.[5] HDS of thiophene on Mo or W catalysts results in only C_4 species,[6] and our recent results for thiophene decomposition on Pd(111) show exclusively C_4 products using LITD/FTMS and FT-TPR.[10] The formation of furan from adsorbed oxygen and acetylene on Pd(111) is also believed to occur via a C_4H_4 intermediate.[26] The exclusive production of CO, H, and the C_3H_3-derived benzene from furan is, therefore, an unexpected result. However, Gellman et al.[6] and Furimsky[2] both report that furan HDO on Mo-based catalysts does produce some C_3 product (primarily propene); however, Furimsky's data show that C_4 species are dominant by a factor of 3−5 over C_3 products. Furthermore, whereas HDO of furanic species over typical hydrotreating catalysts requires temperatures in excess of 670 K, Pd catalyzes rapid deoxygenation at 300 K. This may point to the fundamental action of late transition metal promoters in HDO catalysts. Our results also show, however, that significant amounts of carbonaceous material may be left behind on the Pd surface. These species may act to poison further catalytic reactivity unless removed, e.g., by hydrogen supplied to the feed.

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