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Chemisorbed Benzoate-to-Benzene Conversion via Phenyl Radicals on Cu(110): Kinetic Observation of Conformational Effects

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Free radical intermediates are crucially important in heterogeneous catalysis.[1,2] Such species are short-lived and difficult to observe.[3] In this communication, we report the thermal generation of phenyl radicals on a surface as well as conformational effects in their abstraction of hydrogen atoms from neighbor molecules containing C−H bonds. It is known that the chemisorbed benzoate species, made from benzoic acid deprotonation on atomically clean Cu(110), adopts two structural conformations depending on the surface coverage. At a coverage of 0.25 ML (saturated benzoate layer), the species exists entirely in an upright conformation.[4−6] As the coverage is reduced, upright benzoate species tilt over as the aromatic ring experiences additional attractive forces with the surface in a less dense layer. We have examined the kinetics of thermal decomposition of benzoate, finding that the scission of the C−C bond to form phenyl radicals and CO_2 is energetically favored in the tilted species. The phenyl radical generated forms benzene by abstraction of H atoms from C−H bonds on neighbor benzoate species, and tilting causes the relative yield of benzene, compared to CO_2, to increase. Two separate chambers have been used for temperature-programmed reaction (TPR) and scanning tunneling microscopy (STM) experiments. All TPR experiments here were done in a UHV chamber with the base pressure of 4×10^{-11} Torr, and all the spectra were obtained with the crystal bias of −75 V to ensure there is no electron beam damage from the QMS filament. A commercial LT-STM (Omicron) was used to investigate the surface morphology with a tungsten tip. Figure 1a shows STM evidence for an ordered benzoate layer consisting entirely of upright species at 0.25 ML saturation coverage, and the assignment to upright species is consistent with the literature.[4] Figure 1b shows that a mixture of upright and tilted benzoate species exists at a lower benzoate coverage after annealing to 610 K, with the upright species filling in spaces between the tilted species (β phase). After a second annealing step at 610 K, almost all species are desorbed except the tilted benzoate cluster species, as shown in Figure 1c.

Figure 2 shows a series of temperature-programmed reaction (TPR) spectra plotting the evolution of benzene and CO_2 from benzoate layers at different initial coverages. Decomposition of benzoate begins near 500 K. The inset in Figure 2 shows that, as the initial benzoate coverage is decreased, the relative yield of benzene increases by a factor of ~2. Since benzene and CO_2 are observed in a monotonically varying ratio over the entire coverage range, we assume that we are observing a common decomposition step, with a branching ratio influenced by surface conformational effects. As the decomposition occurs, benzoate species tilt over (as seen by STM, Figure 1), and decomposition is accelerated.

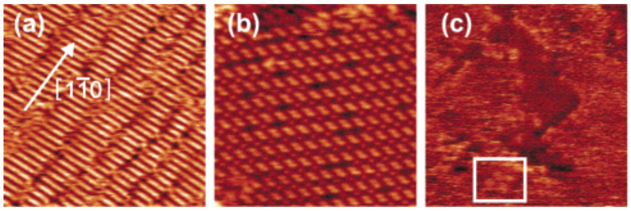

Figure 1. Sequence of STM images before and after annealing. (a) Starting c(8 × 2) surface (300 Å × 300 Å, −1.89 V, 0.32 nA). (b) Image of a β phase domain after the first annealing step at 610 K (247 Å × 247 Å, −1.89 V, 0.29 nA). The features in the image correspond to alternating rows of paired and single upright benzoates. (c) Image showing a remnant of the lowest coverage ordered phase after a second annealing step at 610 K (153 Å × 153 Å, −2 V, 0.55 nA). The four protrusions in the box are the only stable molecular features present in the image and correspond to tilted benzoate species.

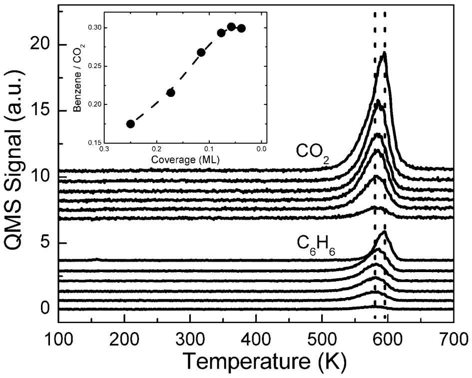

Figure 2. Coverage-dependent TPR spectra of CO_2 and benzene from benzoate chemisorbed on Cu(110). The temperature range between the two vertical dotted lines indicates the increase in the peak temperature for both CO_2 and benzene between the lowest and the highest initial coverage. The inset shows the yield ratio for decreasing initial coverage. The dashed line is a guide to the eye. The heating rate is 2 K/s.

To test additional conformational effects in the H atom abstraction process, we performed studies of the isotopomer benzene yields from a pure saturated layer of benzoate-4-d_1 species, as shown in Figure 3. Our line-of-sight mass spectrometry shows that phenyl radicals do not desorb at a detection sensitivity of ~1% of a monolayer. Biphenyl (156 amu) is a very minor product observed at about 580 K. Only 1.6 mol % of benzene-d_2 (80 amu) species is produced after correcting for the natural abundance of ^{13}C in the benzoate, whereas equivalent hydrogen atom abstraction probabilities by phenyl radicals from all positions on the benzoate species would have yielded 20 mol % benzene-d_2. Thus the phenyl radical is more effective in abstracting H atoms from the 2-,3- and 5-,6-positions than from the 4-position, and this is probably due to the close proximity of the phenyl radical to the surface at the instant of hydrogen atom abstraction. The 4-position of an upright or a tilted benzoate species presents a C−D bond which is farthest from the surface and, therefore, less subject to abstraction by phenyl. The inset in Figure 3 shows Arrhenius plots of the kinetics of evolution of benzene and CO_2 for two initial benzoate coverages. These data were obtained by analysis of the leading-edge of the appropriate TPR curves,[7] such as those in Figure 2. At all initial benzoate coverages, the activation energy for CO_2 evolution is ~29 kcal/mol. At low benzoate coverage, where tilted benzoate species

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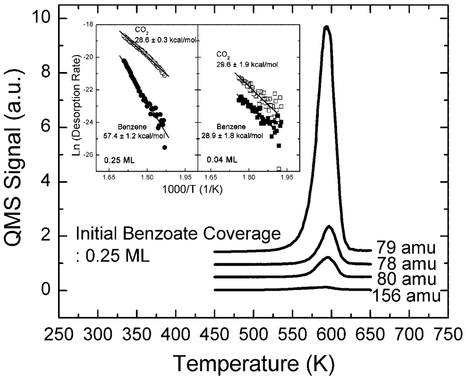

Figure 3. TPR spectra from benzoate-4-d_1 on the Cu(110) surface. A saturation coverage (0.25 ML) was used, and the heating rate was 2 K/s. The 79 amu is, in this case, the benzene-d_1 (C_6H_5D) molecule and 80 amu is benzene-d_2 ($C_6H_4D_2$). Inset shows the plot of Ln of the desorption rate versus 1/*T* at two different initial benzoate coverages (open symbols are CO_2; filled symbols are benzene).

predominate, the same activation energy is observed for benzene evolution. However, for experiments beginning with the fully covered surface at 0.25 ML benzoate coverage, where upright species predominate, the activation energy for benzene evolution is ∼57 kcal/mol. Thus retardation of the relative yield of benzene and a factor of 2 increase in the activation energy for benzene formation is found under conditions where the coverage is high and the benzoate species is predominantly present in the upright conformation.

A schematic representation of the sequence of events leading to benzene and CO_2 formation is shown in Figure 4. Here, an upright benzoate species converts to a tilted conformation, and C−C bond scission occurs as a result of the enhanced interaction of the molecule with the surface. The product CO_2 is desorbed immediately, leaving a phenyl radical on the surface. The major product, benzene, is formed from mobile phenyl species by H atom abstraction from undecomposed benzoate species. Such a kinetically favorable process is often seen for phenyl radical species on surfaces.[8,9]

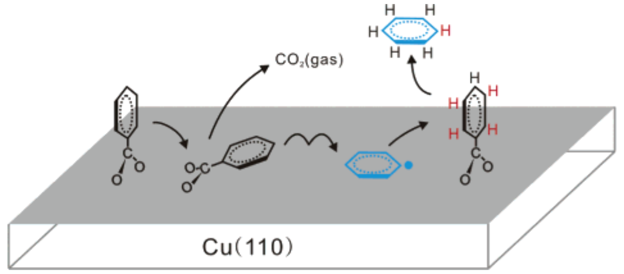

Figure 4. Schematic of the decomposition reaction of the benzoate species adsorbed on the Cu(110) surface. The upright benzoate species at higher coverage changes its geometry to the tilted species. The phenyl radical species generated from C−C bond scission preferentially attacks C−H bonds at the 2-,3- and 5-,6-positions of neighboring benzoate species, as colored red. CO_2 and benzene are the major decomposition products. From Auger spectroscopy studies, we know that species containing C and O remain on the surface after benzene desorbs, indicating that we are observing only one branch of the surface reaction by mass spectroscopy.

This study illustrates the profound role of the molecular conformation of the chemisorbed benzoate species on two sequential surface reaction processes: (1) the formation of the active surface-bound phenyl radical from tilted benzoate species; and (2) the benzoate interaction with the mobile surface-bound phenyl radical to produce benzene by hydrogen abstraction preferentially from C−H bonds nearest the surface.

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References

(1) Bent, B. E. *Chem. Rev.* **1996**, *96*, 1361−1390.
(2) Zaera, F. *J. Mol. Catal.* **1994**, *86*, 221−242.
(3) Radziszewski, J. G.; Nimlos, M. R.; Winter, P. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 7400−7401.
(4) Frederick, B. G.; Leibsle, F. M.; Haq, S.; Richardson, N. V. *Surf. Rev. Lett.* **1996**, *3*, 1523−1546.
(5) Pascal, M.; Lamont, C. L. A.; Kittel, M.; Hoeft, J. T.; Terborg, R.; Polcik, M.; Kang, J. H.; Toomes, R.; Woodruff, D. P. *Surf. Sci.* **2001**, *492*, 285−293.
(6) Lee, J.; Kuzmych, O.; Yates, J. T., Jr. *Surf. Sci.* **2005**, *582*, 117−124.
(7) Habenschaden, E.; Küppers, J. *Surf. Sci.* **1984**, *138*, L147.
(8) Xi, M.; Bent, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 7426−7423.
(9) Xi, M.; Bent, B. E. *Langmuir* **1994**, *10*, 505−509.

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