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σ-Bond Metathesis on a Surface: Dehydrogenation of Cyclohexane on Hydrogen-Saturated Pt(111)

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We describe here the effect of coadsorbed hydrogen on the initial step in the dehydrogenation of cyclohexane on Pt(111). Many industrial catalytic processes take place in the presence of large background pressures of hydrogen.[1] Methods for studying these reactions and surface intermediates at high pressures are somewhat limited.[1] Several researchers have explored the effect of coadsorbed hydrogen on various hydrocarbon adsorption and dehydrogenation reactions in an ultrahigh vacuum (UHV) environment, but most of these studies did not involve saturation amounts of surface hydrogen.[2−9] Cyclohexane adsorption on Pt(111) has been well characterized using many of the available modern surface analytical techniques.[10] The C_6H_{12} molecule is known to adsorb intact in the chair conformation at low temperatures with the three cyclohexane axial hydrogens sitting over the 3-fold hollow sites of the Pt(111) surface.[11] This direct cyclohexane axial hydrogen/Pt interaction gives rise to a soft C−H stretch mode observed in vibrational spectra for submonolayers of cyclohexane on Pt(111) at temperatures below 170 K.[12] Dehydrogenation of cyclohexane on Pt(111) begins at a surface temperature of approximately 200 K with the initial formation of a C_6H_{11} species.[13,22]

UHV surface techniques used in this work to characterize the $H/C_6H_{12}/Pt(111)$ system include Auger electron spectroscopy (AES) to obtain elemental composition, high-resolution electron energy loss spectroscopy (HREELS) for vibrational studies, thermal desorption spectroscopy (TDS) to monitor desorption products, work function measurements (retarding field method[14]), and laser induced thermal desorption-Fourier transform mass spectrometry (LITD-FTMS) to determine the molecular composition of the adsorbed species. Three separate ion-pumped vacuum chambers with base pressures of 1×10^{-10} Torr were used to obtain the spectra.[15−17]

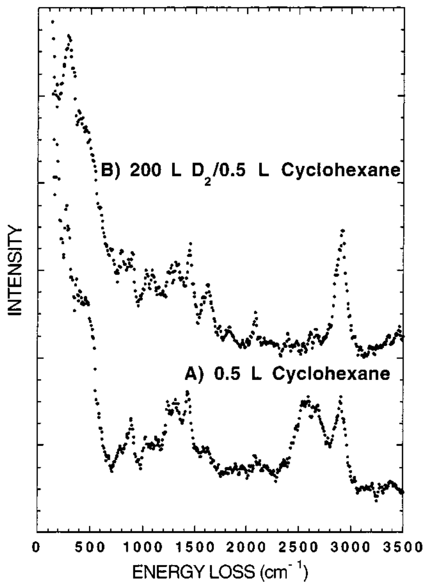

Figure 1. HREELS vibrational spectra following 0.5 L exposure of cyclohexane to a Pt(111) surface at a surface temperature of 135 K. (A) Cyclohexane on clean Pt(111). (B) Cyclohexane adsorbed on Pt(111) previously exposed to 200 L D_2. The baselines of the spectra have been adjusted to offset the spectra for easy viewing. The peaks in spectrum B at ~2100 and ~1600 cm^{-1} are due to CO and water respectively that adsorbed from the chamber background during the course of the experiment.

Figure 1 shows the vibrational (HREELS) spectra of cyclohexane adsorption on Pt(111) at 135 K for a 0.5 L (1 L = 1×10^{-6} Torr·s) exposure of cyclohexane (Figure 1a) and a 200 L D_2 exposure followed by a 0.5 L exposure of cyclohexane (Figure 1b). These spectra were obtained using an LK 2000 HREELS spectrometer.[15] For a 0.5 L cyclohexane exposure to clean Pt (Figure 1a) a number of vibrational modes are observed in the vibrational “fingerprint” region below 1500 cm^{-1}. What is most interesting in this spectrum is the appearance of the broad soft C−H stretch mode centered at about 2600 cm^{-1} which accompanies the other expected hydrocarbon C−H stretch modes at 2920 cm^{-1}. In Figure 1b the major consequence of a 200 L D_2 exposure coadsorbed with a 0.5 L exposure of cyclohexane is the complete disappearance of the soft C−H stretch mode of cyclohexane in the spectrum. It is important in evaluating this spectrum to know that AES results show that preadsorbed deuterium has no effect on the sticking coefficient of cyclohexane.

In other experiments, TDS data on Pt(111) following cyclohexane adsorption at temperatures of 110 K show that a 200 L D_2 exposure lowers the maximum desorption temperature of a submonolayer coverage of cyclohexane from approximately 230 K on a clean Pt surface to approximately 180 K on the deuterated Pt surface.[18] Our TDS experiments and LITD-FTMS[21] together with bismuth postdosing thermal desorption spectroscopy (BPTDS) work by Campbell et al.[19] show that a C_6H_{11} species results from the initial step for the dehydrogenation of cyclohexane in the presence of surface deuterium on Pt. Our data also indicate that the order of adsorption is irrelevant in these particular coadsorption experiments; the deuterium can be adsorbed before or after the cyclohexane and similar results are obtained in the HREELS and TDS work.

Work function experiments indicate that a saturation monolayer of cyclohexane adsorbed on clean Pt(111) at 110 K leads to a maximum work function change of −0.65 eV. When 200 L H_2

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(1) Somrojai, G. A. *Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.

(2) Berlowitz, P.; Megiris, C.; Butt, J. B.; Butt, H. H. *Langmuir* **1985**, *1*, 206.

(3) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.

(4) Zaera, F. *J. Am. Chem. Soc.* **1988**, *111*, 4240.

(5) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 5090.

(6) Janssens, S.; Hemminger, Zaera *J. Catal.* **1997**, *177*, 284.

(7) Lutterloh, C.; Biener, J.; Pöhlmann, K.; Schenk, A.; Küppers, J. *Surf. Sci.* **1996**, *352−54*, 133.

(8) Lutterloh, C.; Biener, J.; Schenk, A.; Küppers, J. *J. Chem. Phys.* **1996**, *104* (6), 2392.

(9) Johnson, A. D.; Maynard, K. J.; Daley, S. P.; Yang, Q. Y.; Ceyer, S. T. *Phys. Rev. Lett.* **1991**, *67*, 927.

(10) Koel, B.; Blank, D. A.; Carter, E. *J. Mol. Catal. A* **1998**, *131*, 39.

(11) Madey, T. A.; Yates, J. T. *Surf. Sci.* **1978**, *76*, 397.

(12) Demuth, J. E.; Ibach, H.; Lehwald, S. *Phys. Rev. Lett.* **1978**, *40*, 1044.

(13) Xu, C.; Koel, B. E. *Surf. Sci.* **1993**, *292*, L803.

(14) Anderson, P. A. *Phys. Rev.* **1935**, *47*, 958.

(15) Flores, C. Ph.D. Dissertation, Department of Chemistry, University of California, Irvine, 1986.

(16) Land, D. P. Ph.D. Dissertation, Department of Chemistry, University of California, Irvine,1989.

(17) Pansoy-Hjelvik, L. Ph.D. Dissertation, Department of Chemistry, University of California, Irvine,1994.

(18) Perry, D. A. Ph.D. Dissertation, Department of Chemistry, University of California, Irvine, 2000.

(19) Campbell, C. T.; Campbell, J. M.; Dalton, P. J.; Henn, F. C.; Rodriguez, J. A.; Seimanides, S. G. *J. Phys. Chem.* **1989**, *93*, 806.

(20) Hemminger, J. C. In *Laser Spectroscopy and Photo-Chemistry of Metal Surfaces Part I*; Dai, H.-L., Ho, W., Eds.; World Scientific: Singapore, 1995.

(21) Land, D. P.; Pettiette-Hall, C. L.; Hemminger, J. C.; McIver, R. T., Jr. *Acc. Chem. Res.* **1991**, *24*, 42.

(22) Pansoy-Hjelvik, M. E.; Schnabel, P.; Hemminger, J. C. *J. Phys. Chem.* In press.

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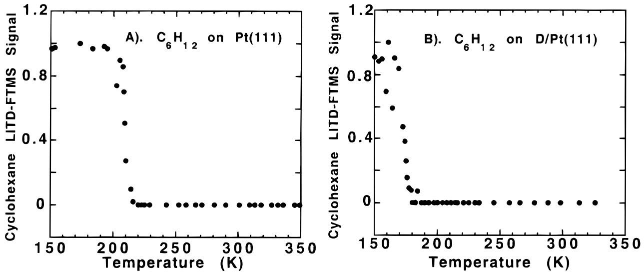

Figure 2. LITD-FTMS survey results for cyclohexane adsorbed on (A) clean Pt(111). (B) Pt(111) that had been pre-dosed with 200 L D_2.

is exposed to Pt(111) a work function change of −0.3 eV is observed. After H_2 exposure cyclohexane adsorption on the hydrogenated Pt surface causes no change in work function.[18] This is clear evidence that the electronic structure of the cyclohexane adsorption is significantly altered by the presence of preadsorbed hydrogen. The combination of the TDS and work function measurements together point to the fact that cyclohexane is more weakly bonded to the hydrogenated (or deuterated) Pt(111) surface, and that the electronic structure of the cyclohexane−Pt interaction is substantially modified by the surface hydrogen. Dehydrogenation and molecular desorption are competing pathways for cyclohexane adsorbed on Pt(111).[10,22] A combination of Auger electron spectroscopy and integration of thermal desorption spectra show that, in the absence of coadsorbed H or D, 25% of the cyclohexane desorbs when 0.25 monolayer of cyclohexane is adsorbed on Pt(111) followed by heating of the sample. 75% of the cyclohexane is dehydrogenated, eventually forming benzene.[22] In the hydrogen coadsorption experiments presented here, more of the weakly bonded cyclohexane desorbs without reaction; however, Auger spectroscopy and integration of thermal desorption spectra indicate that 50% of the adsorbed cyclohexane remains on the surface and is dehydrogenated.[22] HREELS vibrational spectra indicate that the eventual dehydrogenation product is still benzene in these coadsorption experiments.[18]

We have used LITD-FTMS to follow cyclohexane dehydrogenation with and without coadsorbed deuterium as a function of increasing temperature. In a typical LITD-FTMS survey experiment the molecular composition of the surface is probed by irradiating a small spot on the sample with a pulsed laser (KrF excimer laser, 248 nm, 20 ns pulse width) which results in a rapid temperature jump at the surface sufficient to cause molecular desorption. The laser-induced temperature jump is sufficiently rapid that intact molecular desorption is favored over thermally activated surface reactions.[20] Desorbed neutrals are then ionized by electron ionization (70 eV) and detected by Fourier transform mass spectrometry.[21] Next the sample is heated to a higher temperature and cooled to the starting temperature, the laser is moved to another spot on the sample, and the next data point is obtained. Figure 2a displays a LITD-FTMS survey experiment for a submonolayer coverage of cyclohexane adsorbed on clean Pt(111) at 150 K.[22] Notice that the cyclohexane signal is constant up to approximately 200 K where the amount of cyclohexane on the surface then is observed to decrease. Figure 2b shows the same type of LITD-FTMS survey experiment as in Figure 2a except that a 200 L D_2 exposure is also coadsorbed with a submonolayer coverage of cyclohexane. One can see that in the presence of surface deuterium the cyclohexane signal begins to decrease at a temperature of approximately 160 K. Part of the decrease in cyclohexane signal can be attributed to molecular desorption. However, as pointed out previously, even in the presence of coadsorbed D, 50% of the cyclohexane is dehydrogenated to initially form C_6H_{11}, and eventually form benzene.[18,22] The LITD-FTMS data of Figure 2 are a clear indication that a 200 L D_2 exposure lowers the onset of cyclohexane dehydrogenation by approximately 40 K. This corresponds to an approximate 20% decrease in activation energy for cyclohexane dehydrogenation due to the presence of a large concentration of surface deuterium.[22]

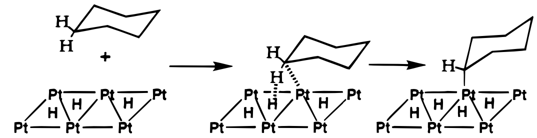

Figure 3. Schematic of how a σ-bond metathesis mechanism might proceed for the initial stage in the dehydrogenation of cyclohexane on a hydrogen-saturated Pt(111) surface.

We now have HREELS spectra that show that coadsorbed deuterium inhibits the soft C−H mode of adsorbed cyclohexane, TDS data pointing to a more weakly bonded cyclohexane molecule on a hydrogenated Pt surface, work function measurements that provide evidence for different electronic structure of the bonding of cyclohexane on the hydrogenated Pt(111) surface, and LITD-FTMS experiments revealing that a saturation exposure of surface hydrogen lowers the onset of cyclohexane dehydrogenation from 200 K to approximately 160 K.

All of our results are consistent with a different mechanism being operative for the initial step in the dehydrogenation of cyclohexane on a hydrogenated Pt(111) surface as compared to cyclohexane adsorbed on a clean Pt surface. Oxidative addition of hydrogen to the electron-rich Pt surface, which is what occurs when cyclohexane decomposes on the clean Pt surface, does not seem likely on the hydrogenated Pt surface since the surface hydrogen presumably binds to the surface orbitals that would be necessary for such a mechanism to be viable. A reasonable alternative would involve the direct involvement of the surface hydrogen in the transition state of the dehydrogenation mechanism. Along these lines, we propose that on a hydrogenated or deuterated Pt surface our results are consistent with a σ-bond metathesis mechanism for the initial step in the dehydrogenation of cyclohexane. σ-bond metathesis is well characterized in the organometallic literature,[23] but to the best of our knowledge it has never been proposed to occur on an extended single-crystal surface before. Figure 3 shows a schematic of the proposed σ-bond metathesis mechanism. Within this mechanism hydrogen of the cyclohexane will be within close proximity of a surface hydrogen. In the square transition state a surface hydrogen directly interacts with the hydrogen of the hydrocarbon as the corresponding carbon interacts with the Pt surface. Once the reaction has gone through the transition state there is an H_2 molecule and a C_6H_{11} that forms a direct C−Pt bond on the surface. The immediate fate of the hydrogen is unclear. Direct formation of H_2 could occur. However, it is also possible that as the reaction proceeds past the transition state the two hydrogens end up separately bonded to the Pt surface. Within the model proposed here the major role of the surface hydrogen is to help activate the C−H bond of the cyclohexane.

Our experiments show that the initial step in the dehydrogenation of cyclohexane is dramatically altered by the presence of saturation amounts of surface hydrogen or deuterium. The hydrocarbon−surface interaction is substantially weakened, yet the activation energy for initial dehydrogenation is lowered by approximately 20%. While other possible explanations may exist, our results are consistent with a σ-bond metathesis mechanism for the initial step in the dehydrogenation of cyclohexane on a hydrogenated Pt surface.

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(23) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.