Evidence for Pyridinium Cation Formation during Coadsorption of Pyridine and Hydrogen on (2 × 1)Pt(110)

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In previous work, it was noted that cations can form during adsorption of gases on metal surfaces. In this paper, high-resolution electron energy loss spectroscopy is used to determine whether pyridinium cations ($C_5H_5NH^+$) can form on (2 × 1)Pt(110) under ultrahigh vacuum conditions. It is found that a new species forms when pyridine and hydrogen coadsorb on Pt(110) at 140 K. The new species has an HREEL spectrum that is consistent with the one expected for a pyridinium cation. There is also evidence that at low coverage, the molecular plane of pyridine is parallel to the surface at 100 K. At higher coverage, changes in the intensity of the in-plane versus out-of-plane vibrational modes show that adsorption phase transition occurs so that the molecular plane tilts with respect to the surface. These results are further confirmation of cation formation on metal surfaces.

Introduction

In recent papers,[1−8] there has been considerable interest in whether cations form during reactions on metal surfaces. So far, hydronium (H_3O^+)[1−4] and methoxonium (CH_3OH_2+)[5−8] have been observed experimentally. Methoxonium has also been found to be a key intermediate during methanol dehydration on Pt(110).

In this paper, an attempt will be made to see whether pyridinium cations ($C_5H_5NH^+$) form during adsorption of pyridine and hydrogen on Pt(110). We chose pyridinium for several reasons. First, thermodynamic calculations summarized in Appendix A indicate that the formation of pyridinium cations is thermodynamically favorable on (2 × 1)Pt(110) surfaces. Second, our ab initio calculations, described below, show that pyridinium cations have a distinct vibrational spectrum so that they can be easily detected. Third, Fujii and others[9−11] find that pyridinium cations desorb from a hot platinum filament when the filament is exposed to pyridine, so there is reason to suspect that pyridinium cations can form on platinum.

Our experiment is to coadsorb pyridine and hydrogen on a Pt(110) sample in UHV. Electron energy loss spectroscopy is then used to demonstrate that a new species forms during coadsorption of hydrogen and pyridine. The vibrational spectrum of the species is carefully measured and compared to ab initio calculations. The comparisons are then used to identify the species.

Experimental Section

The apparatus and sample preparation procedure have been described elsewhere.[4,5,12,13] The system consists of a standard stainless steel vacuum system with an LK 2000 EELS spectrometer, a physical electronics LEED/Auger spectrometer, and a Riber QX-100 mass spectrometer. The chamber is pumped with a Perkin-Elmer 120 L/s ion pump, a Ti sublimation pump,

and an Edwards E 600 L/s diffusion pump. Base pressures were routinely between 5×10^{-11} and 1×10^{-10} Torr. The sample was the same one used in previous studies.[4,5,12,13] It was cleaned by repeated cycles of oxidation, argon sputtering, and annealing to 1000 C, until no impurities could be seen in EELS.

During a typical experiment, the sample was cleaned and then cooled to 100 K. A desired amount of hydrogen or deuterium (99.98 atom % D, Aldrich Chemical) was dosed onto the surface at 100 K. Next, a desired amount of pyridine (99.9%, Fisher Scientific) or pyridine-d5 (C_5D_5N) (99.5% D, Cambridge Isotope) was dosed onto the sample. An EELS spectrum was then acquired. Subsequent spectra were taken by annealing the adsorbed layer to a desired temperature for 2 min, cooling it back to 100 K, and scanning an EELS spectrum with 6.65 eV incident electron beam. The resolution in the vibrational spectra using this electron impact energy was typically 7−10 meV. The quoted exposures in Langmuirs (L) are uncorrected for ion gauge sensitiviy factors.

Complete vibrational reference spectra of pyridine, pyridinium cations, 1,4-dihydro pyridine and pyridinyl radicals have been calculated using methods described elsewhere.[26,27] All calculations have been performed using the Gaussian 98 package.[14] Ground-state molecular geometry and harmonic vibrational frequencies were calculated at the B3LYP/6-311G(d,p) and MP2(full)/6-311G(d,p) levels. A detail in Gaussian calculations is that one needs to scale the calculated frequencies to account for the anharmonicity, as described by Scott and Radom.[26] We determined the scale factor λ for each level of calculation by minimizing the root-mean square (rms) error between the calculated spectrum of pyridine and the measured spectrum of Colson et al.[15] and King et al.[16] Then we use these scale factors to scale our calculated reference spectra. The scale factors were determined to be 0.9715 and 0.9609 for B3LYP/6-311G(d,p) and MP2(full)/6−311 g(d,p) calculations. The B3LYP/6-311G-(d,p) calculation gave an rms error of 12.8 cm^{-1}, while the MP2/6-311G(d,p) calculation gave an rms error of 38.4 cm^{-1}. Therefore, the B3LYP seems to be more accurate than the MP2.
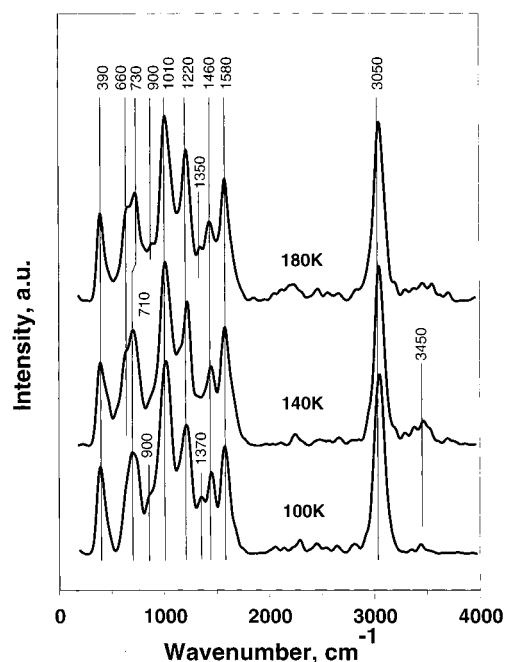
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Figure 1. Series of EELS spectra taken by exposing a clean 100 K (2 × 1)Pt(110) sample to 1.0 L of pyridine, scanning, and then sequentially annealing to successively higher temperatures.
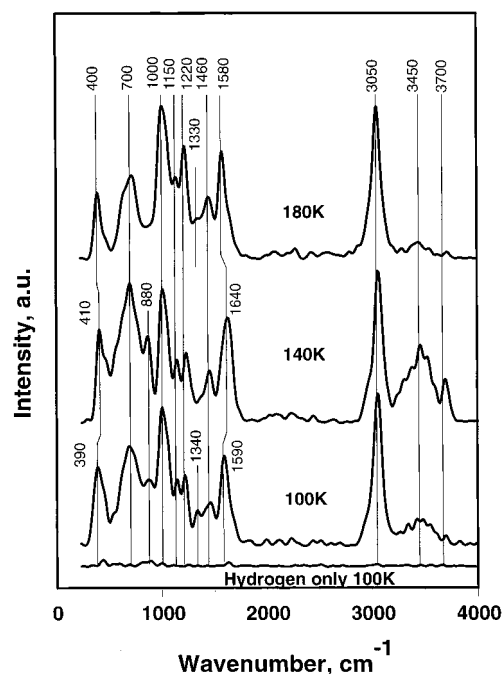

Figure 2. Series of high-resolution spectra taken by exposing a clean 100 K (2 × 1)Pt(110) sample to 3 L of H₂, then 1.0 L of pyridine, scanning, and then sequentially annealing to successively higher temperatures.

Experimental Results

Figure 1 shows a series of EELS spectra taken by exposing a clean 100 K (2 × 1)Pt(110) surface to 1.0 L of pyridine, annealing to an indicated temperature for 2 min and then scanning at 100 K. There are strong 390, 710, 1010, 1220, 1580, and 3050 cm⁻¹ peaks at 100 K. At 140 K, a small but distinct 3450 cm⁻¹ peak grows into the spectra. The 3450 cm⁻¹ disappears at 180 K.

Figure 2 shows a series of EELS spectra taken by exposing a clean 100 K (2 × 1)Pt(110) sample to 3 L of H₂, then 1.0 L

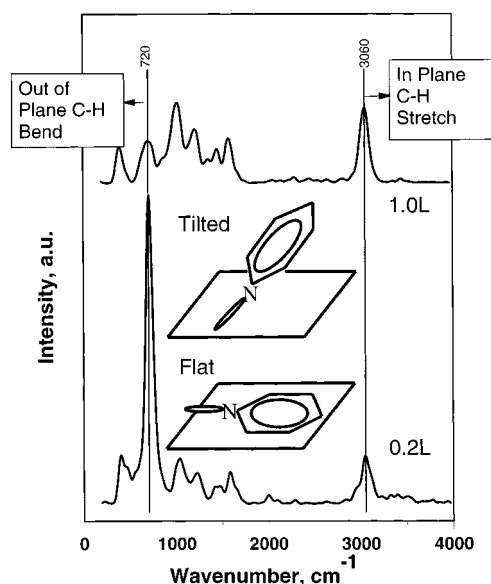**Figure 3.** Series of high-resolution spectra taken by exposing a clean 100 K (2 × 1)Pt(110) sample to desired amount of pyridine.
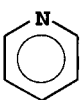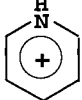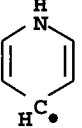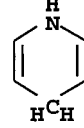
of pyridine, scanning, and then sequentially annealing to successively higher temperatures. The spectrum of hydrogen alone shows no discernible peaks. When pyridine is added at 100 K, strong peaks grow into the spectrum at 390, 700, 1000, 1150, 1220, 1340, 1600, and 3060 cm⁻¹. There is also a very weak peak at about 3450 cm⁻¹. The 3450 cm⁻¹ peak grows tremendously upon annealing to 140 K, and a new peak appears at 3700 cm⁻¹. A comparison of this spectrum to the pyridine spectrum (Figure 1) shows there is also a small increase in the 1140 cm⁻¹ peak and a shift in the 1590 cm⁻¹ peak to 1640 cm⁻¹. The 610 and 3450 cm⁻¹ peaks disappear upon annealing to 180 K. Simultaneously, the 1600 cm⁻¹ peak shifts to 1640 cm⁻¹.

Figure 3 shows how the 100 K EELS spectrum of pyridine on (2 × 1)Pt(110) vary with coverage. At a 0.2 L exposure, the 710 cm⁻¹ peak is 7 times larger than the 3050 cm⁻¹ peak, but at a 1 L coverage, the 710 cm⁻¹ peak is smaller than the 3050 cm⁻¹ peak.

Results: Ab Initio Calculations

Suitable reference spectra are needed in order to interpret the results above. There are no experimental reference spectra for some of the proposed species in the literature, and so we decided to calculate them. Table 1 summarizes our calculated reference spectra for pyridine, pyridinium, 1,4-dihydro pyridine, and nonplanar pyridinyl radical. All of the calculated spectra are similar. Pyridinium cations are predicted to have vibrational modes at 1620 and 3450 cm⁻¹. These modes are not seen in pyridine. Both pyridinyl radical and 1,4-dihydro pyridine have strong N−H modes at about 3540 cm⁻¹, but 1,4-dihydro pyridine also has strong C−H modes at about 2900 cm⁻¹. We have also considered other pyridyl species, but Inuzuka et al.,[17] and Nguyen et al.[18] suggest that the structure shown is the most stable. The results in Table 1 show that a peak at about 3450−3550 cm⁻¹ is expected whenever an N−H bond forms. Vibrational modes at about 2950 cm⁻¹ are expected if a species such as 1,4-dihydropyridene or 1-hydro-4-Pt-pyridine forms, since the hybridization of the pyridine ring changes during the radical formation process, producing an sp³ hybridized carbon. Pyridinium cations and pyridinyl radicals both have similar vibrational spectrum, but the ring mode at about 1300 cm⁻¹ is

TABLE 1: Vibrational Frequencies for a Number of Molecules Calculated at the B3LYP/6-311 g(d,p) and MP2/6-311 g(d,p) Levels

Assignment	Pyridine		Pyridinium		Pyridinyl radical		1,4-dihydro pyridine	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
					199, 262	105, 267	120	118
Ring deformation	373, 408	357,383	380, 392	363, 374	425	460, 477	382, 418	414,461
Ring deformation	599, 651	581,634	606, 628	589, 614	563, 591	557	503, 539	501, 546
CH bend	699, 743	664,702	661, 727	630, 694	609, 622, 671,693	612, 628, 750, 791	610	600
Ring def.	873	861	833, 859	834, 843	896, 901	871, 939,	699, 714	691, 698
CH bend	931, 975, 982, 988	894, 917, 924, 970	969, 984, 990	931, 945, 957	933, 959, 972	956, 974, 979	854, 918, 922, 938, 948	867, 880, 880, 938, 955, 958
CH bend + ring def.	1018, 1046 1062	1005, 1038, 1052	1019, 1024, 1048, 1052	988, 1003, 1044, 1044,	1010, 1043,	1020, 1063,	971, 1009, 1085	1020, 1085
CH -IP bend	1137	1127	1165, 1191	1152, 1186	1175, 1182	1180, 1197	1185, 1195	1172, 1176
CH bend	1207, 1246	1197,	1254	1260	1302(S), 1327	1258, 1322 (S)	1207	1208
Ring stretch	1344	1326, 1341	1321, 1375	1347, 1423	1418, 1423	1418, 1446	1317, 1351	1301, 1341
Ring deformation	1430, 1469	1416, 1450	1474, 1530	1463, 1512	1520	1583	1407, 1454, 1463	1390, 1449, 1457
Ring stretch	1573, 1580	1562, 1572	1602, 1619	1599, 1621	1618	1742	1646, 1698	1620, 1668
C-H stretch	3054, 3057, 3079, 3094, 3102	3076, 3077, 3095, 3111, 3118	3112, 3128, 3129, 3139, 3141	3120, 3137, 3138, 3148, 3150	3086, 3088, 3118, 3122, 3127	3115, 3116, 3148, 3148, 3161	2844, 2882, 3079, 3079, 3100, 3102	2897, 2971, 3099, 3100, 3120, 3121
N-H stretch			3451	3437	3546	3578	3537	3527

weak in pyridinium cations and strong in pyridinyl radicals since the pyridinyl radicals are nonplanar.

Discussion

The results here show that there is some interesting chemistry during pyridine and hydrogen coadsorption on Pt(110). Figure 1 shows that pyridine adsorbs molecularly onto clean Pt(110). The peak positions in the EELS spectra in Figure 1 agree with those of pyridine in the gas phase and on Pt(111) (Table 2). The spectra are also very similar to those reported previously[16] for pyridine adsorption on Pt(110), although our spectra have better resolution and signal-to-noise than those reported previously. These results demonstrate that pyridine adsorbs molecularly on clean Pt(110).

A new species seems to form when pyridine and hydrogen coadsorb on Pt(110). A comparison of Figures 1 and 2 shows that two new peaks, at 3450 and 3700 cm^{-1}, form when pyridine and hydrogen coadsorb. The 1140 cm^{-1} peak also grows, and the 1580 peak broadens and shifts to 1640 while the 1370 cm^{-1} peak disappears. These results imply that a new species forms when pyridine and hydrogen adsorb on Pt(110).

We have done several checks to see if these peaks are real. First, we looked for impurities. Chemisorbed water would show a peak at 3400 cm^{-1},[4] but if the 3450 cm^{-1} peak in Figure 2

were associated with a water impurity, one would expect the peak to grow as the sample is exposed to background gases. However, no significant growth of the peak at 3450 cm^{-1} was detected. The peak was absent in the hydrogen spectrum and the pyridine spectrum at 100 K. Further the background pressure was 1.5×10^{-10} Torr during these experiments, and the mass spectrometer showed virtually no water in the background. None of the species detected in the background have vibrations near 3500 cm^{-1}. Therefore, we conclude that a new species forms when pyridine and hydrogen coadsorb on (2 × 1)Pt(110).

Figure 2 shows that the species disappears when the surface is heated to 180 K to desorb the hydrogen. Further, in other data, we found that the species grows as the hydrogen coverage increases. Therefore, it appears that the species is some hydrogenated form of pyridine.

Species Identification using Quantum Mechanical Calculations. One can use the quantum mechanical calculations to identify the new species that forms when pyridine and hydrogen are coadsorbed onto a Pt(110) surface. Recall that several possible species could form when hydrogen reacts with pyridine: pyridinium cations, pyridinyl radicals (i.e neutral pyridinium), and 1,4-dihydro pyridine. The results in Table 2 show that whenever pyridine reacts with hydrogen to form a strong N−H bond, a new stretch near 3500 cm^{-1} should be observed.

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TABLE 2: Comparison of the Vibrational Frequencies Observed in Figures 1 and 2 to Those from the Previous Literature

| | | | Pt(110) [this work] | | | | | |
| | | | pyridine | | | pyridine + H$_2$ | | |
assignment	gas-phase pyridine[15]	pyridine on Pt(111)[19] at 120 K	100 K	140 K	180 K	100 K	140 K	180 K
ring deformation	403		390	390	400	390	410	400
ring deformation	601, 652	660		650	670			660 (sh.)
CH bend	700, 744	840	710	710	730	700	700	730
ring def.	856		890		900	890	870	
CH bend	936, 991							
CH bend + ring def.	1007, 1032, 1072, 1079	1050	1020	1010	1010	1000	1010	1010
CH −IP bend	1143 (w)					1140	1150	1140
CH bend	1218, 1227	1230	1220	1220	1210	1220	1230	1230
ring stretch	1362		1370		1350	1340		1350
ring deformation	1442, 1483	1470	1460	1460	1440	1470	1460	1460
ring stretch	1581, 1583	1610	1580	1580	1580	1590	1640	1580
C−H stretch	3030, 3042, 3072, 3087, 3094	3070	3060	3050	3050	3060	3070	3060
N−H stretch				3450 (w)		3450	3450 3700	3450

TABLE 3: Comparison of the Vibrational Frequencies Observed in during Hydrogen and Pyridine Coadsorption on Pt(110) to Those from the Ab Initio Calculations

assignment	calculated spectrum of C$_5$H$_5$NH$^+$	measured spectrum for H$_2$ and C$_5$H$_5$N coadsorption at 140 K	assignment	calculated spectrum of C$_5$D$_5$ND$^+$	measured spectrum for D$_2$ and C$_5$D$_5$N coadsorption at 140 K
ring deformation	380, 392	410	ring deformation	331, 338	350
ring deformation	606, 628		ring deformation	504, 578	550
CH bend	661, 727	700	CD bend	590, 600	
ring def.	833, 859	870	ring def.	650, 670	630
CH bend	969, 984, 990		CD bend	788, 804, 813	
CH bend + ring def.	1019, 1024, 1048, 1052	1010	CD bend + ring def.	821, 838, 850, 870	860
CH −IP bend	1165, 1191	1150	CD −IP bend	927, 946	
CH bend	1254	1230	CD bend	988	1000
ring stretch	1321, 1375		ring stretch	1073, 1294	1230
ring deformation	1474, 1530	1460	ring deformation	1324, 1365	1310
ring stretch	1602, 1619	1640	ring stretch	1540, 1569	1550
C−H stretch	3112, 3128, 3129, 3139, 3141	3070	C−D stretch	2301, 2312, 2317, 2329, 2333	2290
N−H stretch	3451	3450 3700	N−D stretch	2534	2530

If a dihydro species forms, the hybridization of the pyridine ring will change, producing an additional stretch at 2900 cm^{-1}. Pyridinium cations should not show any stretches in the region between 2900 and 3000 cm^{-1}, and the 1300 cm^{-1} mode should be attenuated. The spectrum of pyridinyl radicals should be very similar to that of pyridinium cations, except that the mode at 1350 cm^{-1} should be very strong and the N−H stretch should be centered above 3500 cm^{-1}

The spectra in Figure 2 show a clear peak at 3450 cm^{-1} and no strong vibrational modes near 2900 cm^{-1}. Further, the 1350 cm^{-1} peak is attenuated as the 3450 cm^{-1} peaks grow. The 1350 cm^{-1} peak should grow if pyridinyl radicals form. Therefore, it seems likely that the new species is a pyridinium cation or some closely related structure and not for example pyridinyl radicals or 1,4-dihydropyridine.

Table 3 compares the spectra more closely. Notice the good agreement between the experimental spectra and those calculated for pyridinium cation. In particular, there is a good correspondence between all of the peaks; the strong modes at 1620 and 3450 cm^{-1} expected for pyridinium are observed experimentally. This suggests that pyridinium cations probably form during pyridine and hydrogen coadsorption on Pt(110).

The calculations in Appendix A show that pyridinium cation formation is thermodynamically favorable on Pt(110). Moreover, pyridinium cations have been observed to desorb from platinum

by Fujii et al..[9−11] Therefore, it is reasonable to believe that pyridinium cations or some closely related species form during hydrogen and pyridine coadsorption on Pt(110).

There is one feature in the spectra that is not explained by the ab initio calculations. The 140 K spectrum in Figure 2 shows a strong feature at 3700 cm^{-1}. The 3700 cm^{-1} peak is not expected for isolated pyridinium, but it would be expected if the pyridinium formed a complex with pyridine or a hydrogen bonded ice structure on the surface. Such structures are likely under the conditions here. Therefore, we conclude that pyridinium is likely to form during hydrogen and pyridine coadsorption on Pt(110), but the species is likely to form an ice structure at 140 K.

Mechanism of Pyridinium Formation. We can speculate on the mechanism of pyridinium formation on Pt(110). Figure 3 shows that the vibrational spectrum of pyridine varies strongly with coverage during pyridine adsorption on Pt(110). The out-of-plane C−H bending motion at 740 cm^{-1} is much stronger at low coverage than at high coverage. In contrast, the in-plane motion of the C−H stretch at 3080 cm^{-1} is enhanced as the pyridine coverage increases. These data suggest that the bonding configuration of the pyridine changes with coverage.

Figure 3 illustrates two possible configurations of the pyridine. If the pyridine ring lies parallel to the metal surface, the in-plane modes (3050 cm^{-1}) should be suppressed due to screening

of the dynamic dipole by the surface. In contrast, the out-of-plane motion (710 cm^{-1}) should be enhanced. Conversely, if the pyridine is tilted, the in-plane should be strong and the out of plane modes should be suppressed. The data show a change with coverage. At low coverage, the out of plane modes dominate, while the in plane modes become more important as the coverage increases. Therefore, it seems that pyridine adsorbs in a flat configuration at low coverage and a tilted configuration at high coverage.

The data show that the high coverage form of pyridine reacts with preadsorbed hydrogen to form pyridinium cations, but the low coverage form does not. The pyridinium cation population falls when the surface is heated to 180 K. Previous results[16,19] show that there are two different forms of pyridine on Pt(111) and Pt(110). The low coverage form of pyridine corresponds to the flat species, while the high coverage form corresponds to pyridine in a tilted configuration. Grassian et al.[19] find that the tilted form of pyridine desorbs at 190 K from Pt(111), while the flat form desorbs at 260 K. In unpublished work, we measure 173 and 222 K on Pt(110). Notice that the pyridinium formation is suppressed just as the high coverage form of pyridine desorbs. The flat form of pyridine is still on the surface at 180 K, but no pyridinium is observed. Therefore, it seems that the flat form of pyridine is unreactive for pyridinium formation, and only the high-coverage, tilted form of pyridine reacts to form pyridinium.

Pyridine Adsorption on Clean Metal Surface. There is one other unusual feature in the data. There is a hint of a 3450 cm^{-1} peak at 140 K in the pyridine only spectrum in Figure 1. This peak is very similar to the spectra for pyridine onto H_2 preadsorbed Pt(110) surface, except the ratio of 3450 cm^{-1} to 3070 cm^{-1} at 140 K is a factor of 4 smaller in the pyridine on clean surface spectrum than that in the spectrum of coadsorbed hydrogen and pyridine.

We suppose that small quantities of pyridinium cations are forming even when we only dose the sample with pyridine. Indeed, it had been proposed that pyridine is decomposed to α-pyridyl species on surface at 300 K, while pyridine stay intact and lie flat on the surface at 120 K.[19] That means the pyridine transform from a flat structure to a tilted structure to form α-pyridyl species and release a surface H between 120 and 300 K. A similar scenario can be used to explain the data in Figure 1. Our data suggest that a small amount of the pyridine molecules are releasing surface H to form α-pyridyl species. Background hydrogen also contributes to the hydrogen pool on the surface. Once surface H adatoms form, they can combine with pyridine molecules to form a small amount of pyridinium cations. Our data show that the amounts of pyridinium cations are small unless we deliberately dose pyridine and hydrogen onto the surface. However, a small amount of pyridinium cation formation can be observed even in the absence of preadsorbed hydrogen. This is important because Fujii et al.[9-11] have found that pyridinium cations desorb from platinum and ruthenium surfaces, when only pyridine is dosed onto the sample. Evidently, a small fraction of the pyridine can decompose on platinum to yield the hydrogen necessary to form pyridinium cations.

Conclusions

In summary, in this paper we provide EELS evidence that pyridinium cations form when pyridine is adsorbed on a hydrogen pre-covered (2 × 1)Pt(110). Our data show that a new species forms during this reaction. The EELS spectra are consistent with those expected for pyridinium cations and are not consistent with pyridinyl radicals or other related species.
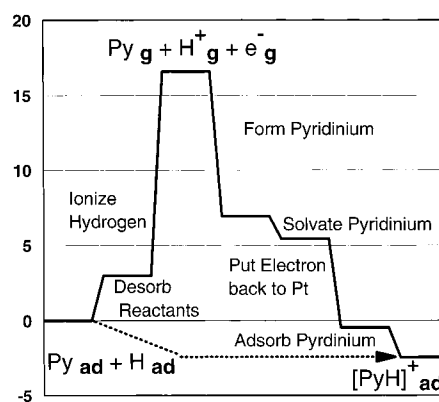

Figure 4. Thermodynamic pathway used to calculate the heat of adsorption of pyridinium cations on (2 × 1)Pt(110).

Moreover, pyridinium has determined to be thermodynamically stable on the Pt(110) surface, and pyridinium cations had been observed as a desorption species by Fujii.[9-11] Our results provide strong evidence that pyridinium cations can form when pyridine and hydrogen coadsorb on platinum showing once again[4,5] that ions can exist during reactions on solid surfaces.

Implications

The significance of this study is that it provides further evidence that cations can form on metal surfaces. Cationic intermediates on metals have been largely ignored in the catalysis literature, but the results here demonstrate that they can form. We suspect that the cationic intermediates will be particularly important in an acidic environment such as fuel processors or PEM fuel cells. The results here suggest that one should consider cationic intermediates in those systems.

In addition, aromatic compounds are one of the major components in logistic fuels such as jet fuels and diesel fuels. Pyridine is a model molecule for aromatic components in those fuels. This study implies that pyridinium ions can form in the reformer where platinum is a key component of sulfur-tolerant catalyst. This also implies that remaining pyridine in reformate can poison the water-gas shift catalyst and fuel cell catalysts which contain platinum.

Appendix

A. Estimation of the Thermodynamics of Pyridinium Cation Formation on *(2 × 1)*Pt(110). Earlier in the text, we noted that pyridinium formation should be thermodynamically favorable on platinum. The purpose of this section is to estimate the heat of formation of pyridinium on Pt(110).

Figure 4 shows the thermodynamic pathway used to do the calculations. We will desorb pyridine and hydrogen from the Pt(110) surface, ionize the hydrogen, recombine the molecule, and then readsorb the complex. The desorption energies of pyridine and hydrogen are about 0.45[19] and 2.52 eV[4,5] endothermic, respectively. Ionization of hydrogen is about 13.6 eV endothermic. The total energy of pyridinium formation and solvation is 11.15 eV exothermic.[20,21,22,23] Then it is 5.9 eV exothermic to put an electron back to the metal. Before the pyridinium ion is adsorbed onto the surface, it is already 0.46 eV exothermic. One needs to calculate the heat of adsorption of pyridinium to complete the calculation. According to the dipole model in Masel,[24] the adsorption of pyridinium onto the surface should be roughly 2 eV. The total free energy of adsorbed pyridinium cation formation would be about −2.46 eV (exothermic).

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