Catalysis Letters Vol. 83, No. 1–2, October 2002 (©2002)

Measurement of the metal surface acidity/electronegativity of Pt(110)

I.C. Lee and R.I. Masel *

University of Illinois, Department of Chemical Engineering, Urbana, IL 61801, USA

Received 11 January 2002; accepted 29 May 2002

In previous work, it has been found that a hydrogen-covered Pt(110) surface is acidic, but quantification of the acidity has not yet been done. In this paper a spectroscopic method is developed to measure the acidity of a metal surface for the first time. The technique involves measuring the intensity of the N–H stretch from the $C_5H_4XNH^+$ that forms when hydrogen coadsorbs with pyridine, 2-fluoropyridine and 3-fluoropyridine. The Bethe approximation is then used to estimate the metal surface acidity/electronegativity (MSAEL). The proton affinity/MSAEL of Pt(110) has been determined to be 907 ± 4 kJ/mol at high coverage. This is the first time the MSAEL has been measured on a metal surface. Implications for fuel cell catalysis are discussed.

KEY WORDS: metal surface acidity/electronegativity; Pt(110); pyridine; pyridinium.

1. Introduction

Many recent papers [1–15] have shown that hydrogen-covered metal surfaces can be acidic. Hydronium cations ($H_3O^+(H_2O)_x$) [2–5], methoxonium cations ($CH_3OH_2^+$) [6–9] and pyridinium cations ($C_5H_4XNH^+$) [10,11] have been identified spectroscopically when multilayers of bases such as water, methanol, pyridine or substituted pyridines adsorb onto hydrogen-covered platinum surfaces. Pyridinium cations have also been observed to desorb from the surfaces [12–14]. The ions are stable on metal surfaces, as further discussed in Appendix A.

In this paper, we wish to use the observation of ion formation to measure the acidity of the metal surfaces. At this point, no one has quantified the acidity of metal surfaces, but the acidity determines the rate of many of the processes seen in fuel cells [39] and other systems [40]. In previous work [5–8,10] we have shown that the stability of metal cations is determined by a combination of the metal surface acidity and the electronegativity. The acidity determines whether protons can be added to a neutral species to form an ion or radical. The electronegativity determines whether the resultant species will be ionic [1]. At this point, no one has determined these two quantities on metal surfaces, so quantification of the ideas is not possible at present.

The purpose of this paper is to develop techniques to measure the metal surface acidity/electronegativity (MSAEL) of single-crystal surfaces. Our approach will be to use the stability of a series of pyridinium cations ($C_5H_4XNH^+$) to infer the MSAEL. To put this in perspective, years ago Parry [16] showed that pyridine adsorption could be used to probe the strength of the Brønsted and Lewis acid sites on commercial zeolite catalysts. Gorte and co-workers [17–19] proposed proton affinity as an intrinsic measure of zeolite acidity. Dines *et al.* [20] and Satsuma *et al.* [21] used diazines as pK_a indicators to measure the surface acidity of various oxide surfaces. At this point, no one has used a similar technique to quantify the acidity of a single-crystal surface, but there is no reason that the measurements cannot be done.

This study will use the stability of a series of pyridinium cations to quantify the MSAEL of a Pt(110) surface. In previous work we found that pyridinium ions form when pyridine, 2-fluoropyridine and 3-fluoropyridine [10,11] adsorb onto a hydrogen-covered Pt(110) surface, while Fujii [12–14] has observed desorption of the pyridinium cations from hot filaments. Pyridinium is one of the most stable ions in the NIST tables [31–33]. It has a lower electron affinity than platinum, so it would be expected to be stable on Pt(110). The thermodynamics of pyridinium formation are favorable on Pt(111), as outlined in Appendix A of ref. [10]. The cationic species also have easily identifiable EELS spectra. Importantly, calculations [11,22] show that the molar adsorption coefficient (*i.e.*, IR intensity) for the N–H stretch is virtually identical in all three molecules. Consequently, the intensity of the N–H mode can be used to quantify coverages.

In this study, we will measure the EELS spectra of the cations that form when pyridine, 2-fluoropyridine and 3-fluoropyridine adsorb onto a hydrogen-saturated Pt(110) surface. *Ab initio* calculations will be used to infer the concentrations of the various species from the measurements. A simple model will then be used to infer the MSAEL.

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* To whom correspondence should be addressed.

2. Experimental

The apparatus and sample preparation procedure have been described elsewhere [4,6,23–26]. 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 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 work [4–6,23–26]. 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 was dosed onto the surface at 100 K. Next, a desired amount of pyridine or fluoropyridine (99.9%, Lancaster) 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 a 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 gauge factors.

One detail of estimating the concentration of pyridinium $C_5H_4NH^+$ relative to that of pyridinium $C_5H_5NH^+$ is calibration. In the work below, we will use the intensity of the N–H stretching mode at about 3450 cm^{-1} to quantify coverages, so we need to know how the intensity of the 3450 cm^{-1} varies in the various cations. *Ab initio* calculations were used to do so. The complete spectra of pyridine and 2-fluoropyridine and 3-fluoropyridine were calculated at the B3LYP/6-311G(d,p) level. All calculations have been performed using the Gaussian 98 package [27]. Ground-state molecular geometry and harmonic vibrational frequencies were calculated at the B3LYP/6-311G(d,p) level. 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 [28]. We have determined the scale factor of this level of calculation to be 0.9659 by minimizing the root-mean square (r.m.s.) error between the calculated and experimental spectra of several azabenenzes [22].

3. Results

Figure 1 illustrates the electron energy loss spectra when we adsorbed pyridine, 3-fluoropyridine or 2-fluoropyridine onto a hydrogen-precovered Pt(110) at 100 K, annealed to 140 K and then scanned at 100 K. A spectrum of pyridine on clean Pt(110) is included for comparison. The pyridine spectrum is similar to those reported previously [29,30], except that our instrument has better resolution and signal to noise ratio.

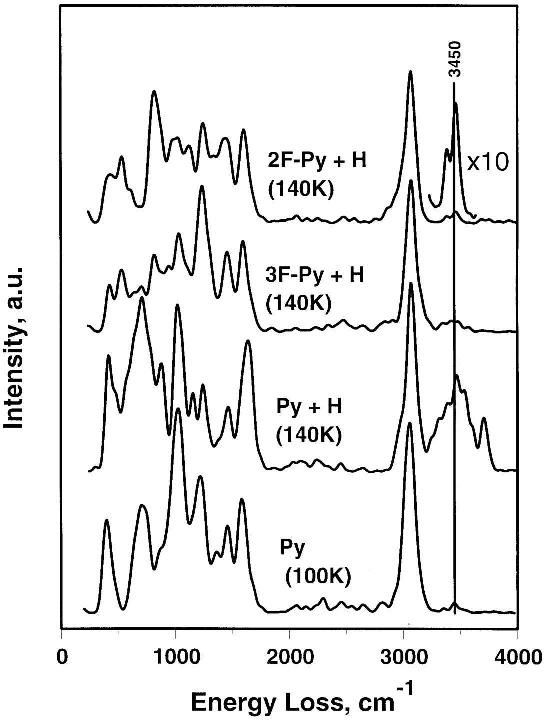
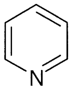
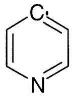
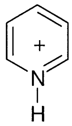
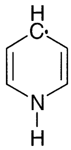
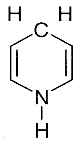


Figure 1. A series of high-resolution spectra taken by exposing a clean 100 K (2 × 1)Pt(110) sample to (a) 1.0 L of pyridine and scanning at 10 K, (b) 3 L of H_2, then 1.0 L of pyridine, annealing to 140 K, and finally scanning at 100 K, (c) similar to (b) except dosing 3-fluoropyridine, and (d) similar to (b) except dosing 2-fluoropyridine.

Note that there are some significant differences between the spectrum of pyridine on a clean surface and a hydrogen-covered one. There are extra peaks at 1150, 3450 and 3700 cm^{-1}. The peak at 1350 cm^{-1} disappears, and the 1580 cm^{-1} peak shifts to 1640 cm^{-1}. Clearly, a new species forms when pyridine and hydrogen coadsorb onto Pt(110).

In a previous paper [10], we have identified the new species as a pyridinium cation (*i.e.*, $C_5H_5NH^+$). Recall that Fujii [12–14] has found that pyridinium cations desorb from metal surfaces when surfaces are exposed to pyridine and hydrogen. The fact that ions desorb implies that ions must form on metal surfaces. Table 1 compares the spectrum of coadsorption of pyridine and hydrogen in figure 1(b) with calculated spectra of pyridine, 4-pyridyl radical, pyridinium cation, pyridinyl radical and 1,4-dihydro pyridine calculated as described elsewhere [10,11,22]. Briefly, there are three distinct features that lead us to assign the species seen in EELS as a pyridinium cation ($C_5H_4NH^+$) and not one of the other species in table 1: (i) the presence of a strong N–H stretching peak at 3450 cm^{-1}; (ii) the absence of a strong peak between 1300 and 1400 cm^{-1}; and (iii) the absence of a strong sp^3 C–H stretching peak around 2900 cm^{-1}. A few small peaks seen in the spectrum of pyridinium cations in zeolites are not seen in

Table 1
A comparison of coadsorption of pyridine and hydrogen in the spectra calculated at the B3LYP/6311G(d,p) level.

Assignment	Py + H_2 onto Pt(110) at 140 K [this work]	 Pyridine	 4-Pyridyl radical	 Pyridinium	 Pyridinyl radical	 1,4-dihydro pyridine
					197, 260	119
Ring deformation	410	371, 406	366, 429	377, 389	422	380, 416
Ring deformation		596, 648	598, 623	602, 625	560, 588	501, 535
CH bend	700	695, 738	688, 743,	657, 723	605, 619, 667, 689	607
Ring def.	870	868	801	828, 854	891, 896	695, 710
CH bend		926, 970, 976, 982	929, 947, 950	963, 978, 985	927, 953, 967	849, 913, 917, 933, 942
CH bend + ring def.	1010	1012, 1040, 1056	1003, 1037, 1041	1013, 1018, 1043, 1046	1004, 1037	966, 1003, 1080
CH –IP bend	1150	1130	1187	1158, 1184	1169, 1175	1178, 1189
CH bend	1230	1199, 1239	1221, 1271	1247	1294(s), 1319	1200
Ring stretch		1337	1358	1314(w), 1367(w)	1410(w), 1415(s)	1309, 1343
Ring deformation	1460	1421, 1460	1420, 1486	1466, 1522	1511	1399, 1446, 1454
Ring stretch	1640	1564, 1570	1561	1593, 1610	1609	1636, 1689
C–H stretch	3060	3036, 3039, 3061, 3076, 3085	3032, 3034, 3073, 3075	3094, 3110, 3111, 3121, 3122	3068, 3070, 3100, 3103, 3109	2828(s), 2865(s), 3061, 3062, 3982, 3084
N–H stretch	3450 3700			3431	3525	3517

our spectrum. However, these peaks are missing from the solution phase spectrum of pyridinium [37,38]. Lee and Masel [10] provide additional justification for this assignment: one should refer to that paper for details. Similarly, Lee and Masel [11] provide evidence that fluorinated pyridinium cations form when 2- or 3-fluoropyridine adsorb onto a hydrogen-covered Pt(110) surface, as shown by the presence of the 3450 cm^{-1} peak and other features in the spectrum.

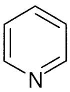
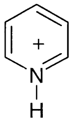
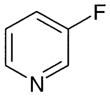
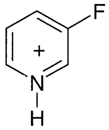
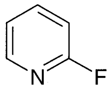
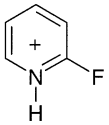
Note that the intensity of the 3450 cm^{-1} peak in figure 1 is large when pyridine adsorbs onto a hydrogen-covered Pt(110) surface, but the intensity is reduced when 3-fluoropyridine or 2-fluoropyridine are used. According to our previous calculations [11,22] the molar absorption coefficient (*i.e.*, the IR intensity per mole) for the N–H stretch is virtually identical in pyridine and 2- and 3-fluoropyridine. Consequently, the fact that the N–H stretch is stronger in pyridine than in 2- or 3-fluoropyridine implies that the concentration of pyridinium cations is higher with pyridine than with 2- or 3-fluoropyridine.

One can quantify the concentrations more carefully by measuring the areas under the 3450 cm^{-1} peak in figure 1, adjusting for the slight intensity variations using the *ab initio* calculations [11,2] and using the intensity of the 3050 cm^{-1} peak as an internal standard. Table 2 summarizes how the relative concentration of the cation varies for three azabenzene indicators. The proton affinity of the various indicators is included for reference [31–33]. Note that there is a general correlation between the concentration of the cations and the proton affinity of the base. Stronger bases produce more ions.

We propose that the results in table 2 can be used to quantify the MSAEL of the surface. Recall that if the cations were not interacting on the surface, then the equilibrium concentration of the cations should follow a Langmuir-like expression:

$$\theta_{\text{cation}} = \frac{K\theta_{\text{total}}}{1+K}. \tag{1}$$

Table 2
A comparison of the intensity of the relative concentrations of the cationic species estimated from the data in figure 1 to the proton affinities of substituted pyridine [31–33].

Azabenzene	Cations	Relative concentration	Proton affinity (kJ/mol) [31–33]
		1.00	930.0
		0.26	902.0
		0.04	884.6

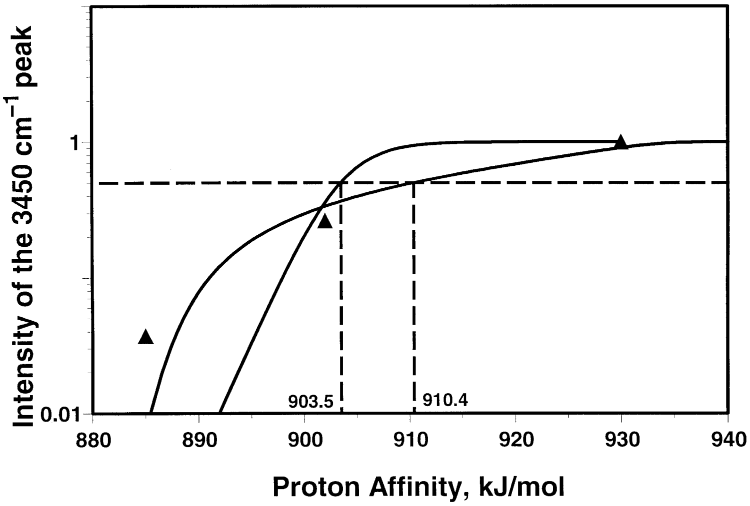


Figure 2. The relative pyridinium cation coverage inferred from the data in figure 1 and as a function of the proton affinity of the base. Lines calculated for the Langmuir model with $\mathrm{PA}_{\mathrm{surface}}$ of 903.5 kJ/mole, and the Bethe approximation with $\mathrm{PA}_{\mathrm{surface}}$ of 910.4 kJ/mole, $h = 4$ kJ/mole and $n = 6$ ($nn = 6^2 - 1 = 35$) are also included in the figure.

In equation (1), θ_{cation} is the cation concentration, θ_{total} is the total coverage of species, and K is related to the proton affinity by

$$K = \exp[(\mathrm{PA}_{\mathrm{base}} - \mathrm{PA}_{\mathrm{surface}})/kT]. \tag{2}$$

In equation (2), $\mathrm{PA}_{\mathrm{surface}}$ is the proton affinity of the surface, $\mathrm{PA}_{\mathrm{base}}$ is the proton affinity of the pyridine or substituted pyridine, k is Boltzmann's constant and T is temperature. Figure 2 is a plot of the data. Lines calculated for the Langmuir model with $\mathrm{PA}_{\mathrm{surface}}$ of 903.5 kJ/mole, and the Bethe approximation with $\mathrm{PA}_{\mathrm{surface}}$ of 910.4 kJ/mole, $h = 4$ kJ/mole and $n = 6$ ($nn = 6^2 - 1 = 35$) are also included in the figure. Note that equation (1) explains the qualitative features of the data, *i.e.*, a decrease in the cation concentration with decreasing $\mathrm{PA}_{\mathrm{base}}$. Still, equation (1) predicts that the concentrations of cationic intermediates should drop off suddenly as the proton affinity of the adsorbate decreases, but the data show a much more gradual decline. Figure 2 is in fact a titration curve, and we find that the titration curve is much broader than one would expect from the Langmuir model.

Fortunately, the modified Bethe approximation described on page 287 in Masel [1] does a reasonable job of fitting the data. The key assumption in the Bethe approximation is that the adsorbate is held in an ordered lattice, and that there are pairwise interactions between adsorbate molecules out to n-nearest-neighbor lattice positions and that equilibrium is maintained. The average strength of interactions is presumed to be a constant, h kJ/mole. Masel derives the Bethe approximation for the case of adsorption onto a clean surface. However, the same derivation applies to the case of starting with an ordered arrangement of pyridine on a surface and converting some of the pyridines to pyridinium cations. In that case h would correspond to the change in the pairwise interactions when a pyridine is converted to a pyridinium cation n nearest neighbors away from another pyridinium cation. $\mathrm{PA}_{\mathrm{surface}}$ is the titration point in the model. By definition, it is the point where K in equation (2) is unity. Under those conditions, half of the molecules are ions.

Figure 2 shows that the Bethe approximation fits the data assuming $\mathrm{PA}_{\mathrm{surface}}$ of 910.4 kJ/mole, $n = 6$ and $h = 4$ kJ/mole. In other work we have found that the quality of fit is almost independent of h, provided h is between 2 and 20 kJ/mole. The best fit comes with n between 5 and 7. Physically, an $n = 5$–7 implies that there are long-range repulsive interactions between the pyridinium cations extending out 5–7 nearest neighbors.

The analysis in figure 2 assumes that the concentration of protonated species reaches equilibrium at 140 K, so the differences in the degree of protonation of pyridine 2-fluoropyridine and 3-fluoropyridine are associated with a thermodynamic, not a kinetic limitation. While it is possible that the differences in the degree of protonation are associated with a kinetic *versus* a thermodynamic limitation, this seems less likely. The data in Lee and Masel [10,11] shows that the pyridinium production process is reversible: the concentration of ionic species grows when either hydrogen or pyridine are added to the surface, and decreases again when the hydrogen desorbs at 180 K. The fact that the process is reversible suggests that equilibrium is achieved. We cannot be 100% sure that no kinetic limitation exists. Still, the bulk of the evidence is that an equilibrium analysis is appropriate.

4. Discussion

The results here provide further evidence that a hydrogen-covered Pt(110) surface is a weak Brønsted acid. In a previous paper, we provided kinetic and spectroscopic evidence that cations form when bases such as pyridine or fluoropyridine adsorb on a hydrogen-covered Pt(110) surface. Desorption of the ions has also been observed [12–14]. Here we observe the same spectroscopic results, but we also have additional evidence that the species are ionic from the results in figure 2. In particular, note that there is a change in the pairwise interactions when an adsorbed pyridine molecule is converted to a pyridinium cation 5–7 nearest neighbors (∼30 Å) away from another pyridinium cation. It is very unusual to observe pairwise interactions extending out 5–7 lattice positions. Neutral species would not be expected to show such long-range repulsions, *i.e*., a pyridinyl radical (C_5H_5NH) could never tell whether a species 30 Å away was an adsorbed pyridine or another pyridinyl radical. Charged species, however, would be expected to show long-range Coulomb repulsions. Two pyridinium cations should repel each other even when the two ions are 30 Å apart. The fact that we observe long-range repulsions between the species is strong evidence that the species are charged. Such a result provides additional evidence that the adsorbed species are cationic.

One can also use figure 2 to quantify the MSAEL of the surface. In previous work, Gorte proposed that one can use the proton affinity to quantify the acidity of a zeolite. We propose a similar quantification here. That is, we fit the data to a model and use the model to infer the MSAEL. According to the Bethe model, the data best fit is with a $PA_{surface}$ of 910.4 kJ/mole. According to the Langmuir model the data best fit is with a $PA_{surface}$ of 903.5 kJ/mole. A linear interpolation of the data to the titration point where $\theta_{cation}/\theta_{total} = 0.5$ gives a $PA_{surface}$ of 911 kJ/mole. Overall, we conclude that $PA_{surface}$ is between 903 and 911 kJ/mole.

One detail here is that an implication of our data is that the proton affinity of the surface is coverage-dependent. That is, we see strong repulsive interactions between the adsorbed cations, so that the stability of the cation should decrease with increasing coverage. Unfortunately, at this point, we do not have the data to quantify the variation in the proton affinity with coverage. We have tried to measure EELS spectra at low coverage but could not resolve the N–H stretch with 2-fluoropyridinium. Therefore, we do not know the magnitude of the variation in the proton affinity with coverage. Still, we have direct evidence for strong repulsive interactions, so the proton affinity must be coverage-dependent.

5. Conclusions

In summary, then, the objective of our paper was to measure the MSAEL of Pt(110) spectroscopically using pyridine, 3-fluoropyridine and 2-fluoropyridine as indicators. We find that the technique works. The stability of corresponding pyridinium cations ($C_5H_4XNH^+$) varies with the proton affinity as expected theoretically. There are some unexpected features in the data. The titration curve is much broader than one would expect if the ions were independent. Fortunately, we can fit the titration curve with the Bethe model, provided we assume that there are Coulomb interactions between adjacent cations, out to 6 nearest neighbors. Overall, the MSAEL on the proton affinity scale has been determined to be 907 ± 4 kJ/mol.

6. Implications

The implication of this result is that a hydrogen-covered Pt(110) surface is mildly acidic. To put this result in perspective, Pt(110) is a reasonable fuel cell anode; we already knew that a Pt(110) surface was acidic since Pt(110) produces protons during the electro-oxidation of hydrogen [34,35]. However, here we quantify the acidity. Meanwhile, the absolute enthalpy of hydration for proton ion is 1094 kJ/mol exothermic [36]. Previously, the heat of adsorption of pyridine on Pt(110) was determined to be 55.8 kJ/mol [10]. According to the measurements here, the reaction

$$H_{(ad)} + H_2O \rightarrow H_3O^+_{(aq)} + e^-_{(ad)} \tag{3}$$

is $(-1094 + 55.8 + 907) = -131$ kJ/mole (exothermic) so that proton formation is a favorable process on Pt(110).

7. Appendix A

As noted in the introduction, many recent papers [1–15] have shown that hydrogen-covered metal surfaces can be acidic. Hydronium cations ($H_3O^+(H_2O)_x$) [2–5], methoxonium cations ($CH_3OH_2^+$) [6–9] and pyridinium cations ($C_5H_4XNH^+$) [10–11] have been identified spectroscopically, when multilayers of bases such as water, methanol, pyridine or substituted pyridines adsorb on hydrogen-covered platinum surfaces. Pyridinium cations have also been observed to desorb from the surfaces [12–14].

Previous work has also shown that the thermodynamics of ion formation are favorable on platinum [5–7] and that the secondary kinetic isotope effect characteristic of ionic species [15] is observed. Also, in a larger way, currents are observed in fuel cells and other related devices. Such currents are possible only if ions form in multilayer films above metal surfaces.

One of the reviewers asked how ion formation is possible given the abundance of electrons on metal surfaces. Physically, ions are stable on surfaces whenever the electron affinity of the ion is lower than the electron affinity of the surface. Pyridinium cations [$C_5H_5NH^+$] have a lower electron affinity than platinum [36] so they form easily on platinum [10]. The ions even desorb at higher temperatures [12–14]. Bare hydroniums and methoxoniums are not stable on platinum, but when the cations are solvated, by water or methanol, the resultant complexes have a lower electron affinity than platinum [2,5–7,31,32], so ions can form. References [2,3,5,6,10] expand this idea in greater detail. These references show that ion formation is thermodynamically favorable on Pt(110).

The evidence for the formation of pyridinium ions is particularly strong. Pyridinium cations desorb at elevated temperatures when pyridine and hydrogen are dosed onto clean metal surfaces [12–14]. The fact that the ionic species desorb means that the ionic species must form on the surface. Indeed, spectroscopic evidence also shows evidence for pyridinium cation formation [10]. There are some differences between the spectra of pyridinium on platinum, and pyridinium in zeolites, as discussed elsewhere [11]. In particular, some of the framework vibrations in pyridinium in zeolites are not seen on Pt(110). However, the missing peaks are also missing from the IR spectra of pyridinium cations in the solution [37,38]. The spectroscopy coupled with the observation of desorption of ions is strong evidence that the ions form.

Acknowledgments

This material is based upon work supported by the U.S. Department of Energy under grant DEGF-02-99ER14993. Any opinions, findings and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the Department of Energy.

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