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Ammonia adsorption and decomposition on several faces of platinum

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This paper is part of an ongoing study of the structure sensitivity of ammonia adsorption on platinum. In the work here, the adsorption of ammonia on Pt(111) and Pt(210) are compared using temperature programmed desorption (TPD), single-reflection infrared (IR), electron energy-loss spectroscopy (EELS), and molecular-beam techniques. In addition, the adsorption of ammonia on Pt(111), (5×20)Pt(100), (2×1)Pt(110), Pt(210), and Pt(211) are compared with TPD. It is found that the TPD spectrum of ammonia is similar on Pt(111), Pt(100), Pt(110), Pt(210), and Pt(211). There was always a molecular peak between 310 and 370 K, another peak at 170 K, and a multilayer peak at 120 K. The sticking probability was found to vary by a factor of 10 from Pt(210) to Pt(111). However, the infrared spectrum of ammonia adsorbed on Pt(111) is virtually identical to the EELS of ammonia on Pt(210) after accounting for a difference in the sensitivity of IR and EELS. Analysis of the TPD data indicates that the surface concentration of ammonia is a factor of 100–200 higher on Pt(210) than on Pt(111) at 670 K. By comparison, Pt(210) was found to be at least a factor of 100 more active than Pt(111) for ammonia dissociation at 670 K. There is more work to be done. However, the results so far indicate that the variations in sticking probability and residence time play an important role in the variations in rate.

I. INTRODUCTION

Over the years, there have been several papers which have used surface spectroscopy to examine ammonia adsorption on single-crystal platinum.^{1–5} This work has shown that the adsorption of ammonia is molecular on Pt(111). There are two kinds of ammonia in the first monolayer, called α_1 and α_2 ammonia. The α_1 ammonia desorbs around room temperature while the α_2 ammonia desorbs around 170 K. The α_1 ammonia is thought to be bound through the line pair on the nitrogen while the α_2 ammonia is thought to be held with a hydrogen bond to the α_1 ammonia. Ammonia does not dissociate below 400 K on Pt(111). However, there is some evidence that it can dissociate at higher temperatures.^{5–7}

The purpose of the work reported here was to determine to what extent the adsorption of ammonia was structure sensitive. In previous work, Lofler and Schmidt⁶ examined ammonia decomposition near atmospheric pressure on Pt(111), Pt(100), Pt(110), and Pt(210). They found that Pt(210) and Pt(110) were much more active than Pt(111) or Pt(100) for ammonia dissociation. Guthrie, Sokol, and Somorjai⁷ and Gland and Kollin⁵ examined ammonia decomposition on Pt(557) and Pt(577), respectively, using molecular-beam techniques. They found that Pt(577) and Pt(557) were much more active than Pt(111) for ammonia decomposition. Unfortunately, at present, no one has reported any work which shows how the binding of the ammonia varies with surface structure. Hence, it is unclear how the observed differences in reactivity are related to differences in the processes which occur on the various faces of platinum.

The purpose of the work here was to examine the adsorption of ammonia on a series of faces of platinum. An attempt was made to relate differences in the ammonia dissociation activity of the various crystals to differences in the behavior

of the ammonia on the surface of the crystal. The adsorption of ammonia on several faces of platinum was examined with temperature programmed desorption (TPD), electron energy-loss spectroscopy (EELS) or single-reflection infrared (IR), and molecular-beam techniques. So far we have done a detailed comparison of ammonia adsorption on Pt(111) and Pt(210) and a less complete examination of ammonia adsorption on Pt(100), Pt(110), and Pt(211). While there is more work to be done, the data are starting to produce a coherent picture of the structural sensitivity of ammonia adsorption on platinum.

II. EXPERIMENTAL

The experiments were done by using the apparatus and procedures described previously. Pt(100), Pt(111), Pt(100), Pt(210), and Pt(211) samples were cut from the same single-crystal rod. Each sample was mechanically polished, washed, and mounted in the vacuum system. The sample was then cleaned by repeatedly heating in oxygen, sputtering, and annealing until no impurities could be detected.

During a TPD experiment, the crystal was cooled to 90 K. The crystal was then dosed with ammonia through an uncalibrated capillary array. Next, the crystal was heated linearly under computer control. The heating rate was varied from 3 to 30 K/s. However, it was found that individual features could only be resolved at heating rates between 10 and 20 K/s. The Pt(110) TPD data were taken in one of our vacuum systems, while all of the other spectra were taken in another one.

The EELS work was done in the same apparatus as was used for most of the TPD work. The sample was cleaned until no impurities could be detected by AES. The sample

was then dosed with a varying amount of ammonia at 100 K. An EELS spectrum was then recorded with a LK2000-DAC EELS spectrometer purchased from LK Technologies, Bloomington, IN. Next, the sample was annealed to various temperatures and cooled back to 100 K. Then another EELS spectrum was recorded. A typical scan took about 50 min. The background pressure of ammonia was typically below 4×10^{-10} Torr for most of that time.

The molecular-beam work was also done in the apparatus as was used for the TPD work. The EELS spectrometer was not present at that time. Ammonia from a differentially pumped pulsed valve source was directed toward a hot crystal at a fixed incidence angle of 15° from the surface normal. The desorbing products were detected with a Riber QX100 quadrupole mass spectrometer set at a fixed detection angle of 65° . A boxcar averager was used to record the data. The pumping speed of the chamber was such that detailed waveform analysis was not meaningful. However, work in progress will attempt to correct that difficulty.

The IR work was done in a separate apparatus described elsewhere.⁹ The procedures were virtually the same as those described above. The only exception was that the dosing system on the single-reflection IR apparatus had a calibrated leak. Hence, the dosing could be done quantitatively.

Previous work has shown that an adsorbed ammonia layer is subject to electron beam damage.⁸ Hence, in all the experiments above care was taken to never expose the ammonia to

an electron beam other than the EELS beam. All of the other experimental techniques were standard. One is referred to our previously published work for more details.

III. RESULTS

Figure 1 shows a series of TPD spectra for ammonia desorption from Pt(111), Pt(100), Pt(110), Pt(210), and Pt(211). The (111) spectra are very similar to those reported previously. At low exposure there is a single broad peak centered at 310 K. This peak has been labeled α_1 . The peak grows and broadens with increasing exposure. Simultaneously a new peak appears at ~ 170 K. The new peak has been labeled α_2 . The new peak grows with increasing exposure and shifts to lower temperatures. Eventually the new peak saturates at a nominal exposure of ~ 16 L. In addition, there is a multilayer peak at ~ 120 K which grows continuously at high exposures.

The TPD spectra of ammonia desorbing from (5×20) Pt(100) are almost the same as those for ammonia desorbing from Pt(111). Again, at low exposure there is a single broad peak centered at 310 K. This peak has been labeled α_1 . The peak grows and broadens with increasing exposure. Simultaneously a new peak appears at ~ 170 K. The new peak has been labeled α_2 . The new peak grows with increasing exposure and shifts to lower temperatures. Eventually the new peak saturates at about a nominal exposure of 16 L. In addition, there is a multilayer peak at ~ 120 K

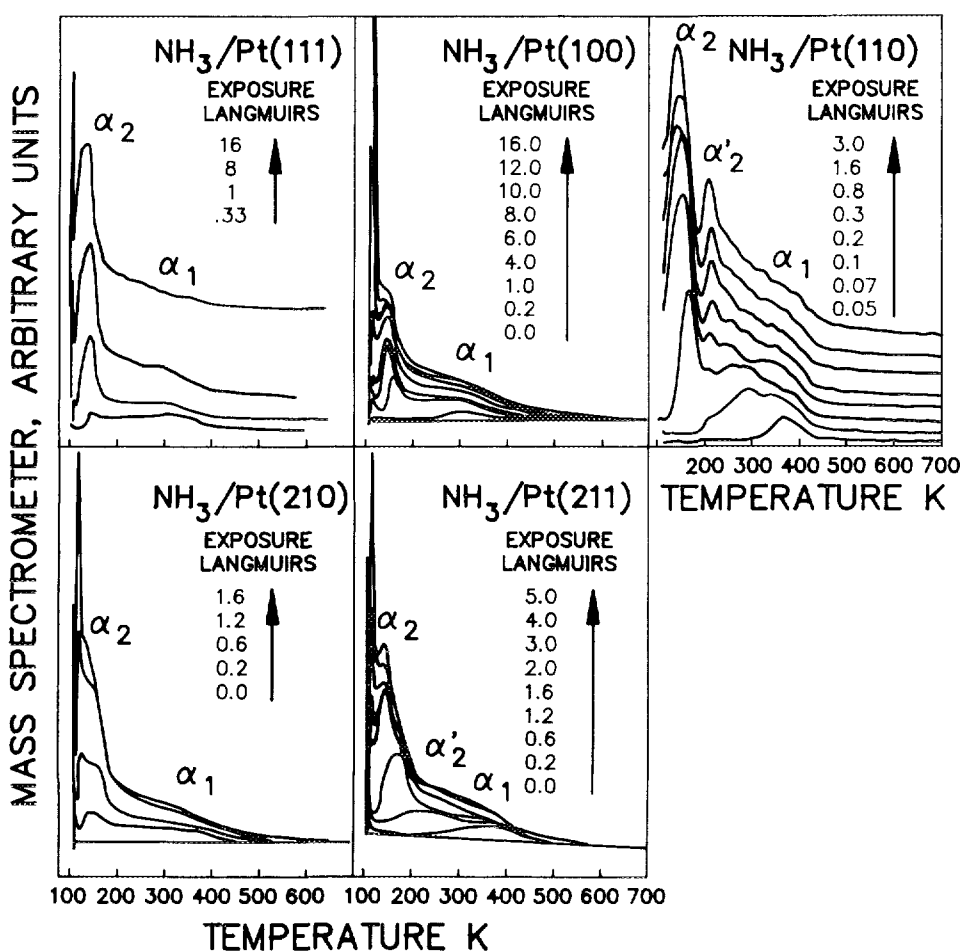


FIG. 1. A set of TPD spectra taken by adsorbing varying amounts of ammonia onto a 100 K (a) Pt(111), (b) (5×20) Pt(100), (c) (2×1) Pt(110), (d) Pt(210), and (e) Pt(211) sample, then heating at 14 K/s.

which grows continuously at high exposures.

Ammonia desorption from Pt(211) shows similar features to those above. At low exposures, one observes a single peak at ~ 370 K. This peak has been labeled α_1 . The peak grows and broadens with increasing exposure, and a new peak appears at ~ 170 K. The new peak has been labeled α_2 . In addition, there is evidence for a distinct intermediate peak at ~ 250 K, labeled α_2' . At high exposures, a multilayer peak grows into the spectrum at 120 K.

Ammonia desorption from Pt(110) also shows similar features to those above. At low exposures, one observes a single peak at ~ 380 K. This peak has been labeled α_1 . The peak grows and broadens with increasing exposure, and a new peak appears at ~ 160 K. The new peak has been labeled α_2 . At high exposures, a multilayer peak grows into the spectrum at 120 K. There is also evidence for a distinct intermediate peak at 210 K. The size of the peaks in the Pt(110) spectra are different than on the other faces because the Pt(110) data were taken in a different machine than the rest.

The Pt(210) spectra are also similar to those on the other faces. There are two monolayer peaks at 370 and 170 K and a multilayer peak at 120 K. The 370 and 170 K peaks seem to grow simultaneously on Pt(210). By comparison, they grow sequentially on Pt(111), Pt(100), Pt(110), and Pt(211). However, the (210) spectra are very similar to those for ammonia desorption from Pt(100), Pt(111), and Pt(211). Hence, we concluded that ammonia adsorption is very similar on Pt(111), Pt(100), Pt(210), and Pt(211).

Note, however, that with Pt(210) and Pt(110) the α_1 and α_2 states of ammonia are largely saturated at a nominal 1.6-L exposure. In contrast, a 5-L exposure is needed to saturate the same states on Pt(211). A 16-L exposure is needed to saturate the states on Pt(100) and Pt(111). Integration of the TPD peaks indicates that the final coverages are similar on Pt(111), Pt(210), and Pt(211). Thus, it seems that the sticking probability of ammonia is about a factor of 10 higher on Pt(210) and Pt(110) than on Pt(111) or (100).

A careful search was made for hydrogen and nitrogen desorption from Pt(111), Pt(100), Pt(110), Pt(210), and Pt(211) using TPD. However, no hydrogen or nitrogen were detected at temperatures below the desorption limit.

Nonetheless, hydrogen and nitrogen are detected at higher temperatures, using molecular-beam techniques. Figure 2 shows how the intensity of the hydrogen and ammonia signals varied with temperature during ammonia decomposition on Pt(210). At temperatures below 500 K only ammonia desorption is detected. However, ammonia, hydrogen, and nitrogen were found to desorb above 500 K. The amount of hydrogen desorbing increases rapidly with temperature, eventually reaching a maximum at 670 K. The desorption rate of hydrogen decreased above 670 K.

It is not clear whether this decrease is real. Gland found that a stepped platinum sample would slowly deactivate during exposure to ammonia at temperatures between 700 and 1000 K. The activity loss was thought to be associated with accumulation of impurities on the sample in the presence of ammonia. Fortunately, the activity was restored upon annealing to 1300 K. The data in Fig. 2 were taken in a random order and the sample was annealed to 1350 K between each

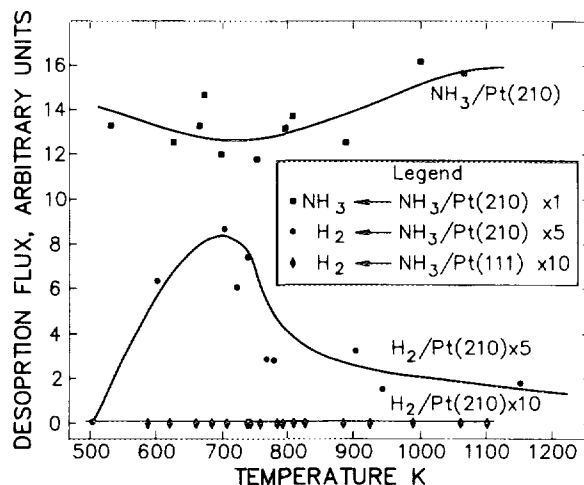


FIG. 2. The relative amounts of hydrogen and ammonia desorbing from a Pt(210) and Pt(111) sample as a function of temperature, when the sample is exposed to a beam of ammonia at an incidence angle of 15° from the surface normal. The measurements were done at a fixed detection angle of 65° .

run. There was no direct evidence for impurities in the work here. Still, Gland did not see the impurities either. Thus, it is not clear whether the effects of impurity segregation at higher temperatures were completely eliminated. Nevertheless, the results here show that the Pt(210) sample is quite effective in dissociating ammonia at temperatures below those where impurity accumulation had previously been found to be a problem.

It is useful to compare the dissociation of ammonia on Pt(210) to ammonia dissociation on Pt(111). The Pt(111) data are also shown in Fig. 2. In contrast to the results on Pt(210), little desorption of hydrogen and nitrogen was detected at any temperature with Pt(111). It would have been difficult to detect a very small amount of ammonia decomposition with our current apparatus. However, analysis of the data show that Pt(210) is at least 100 times as active as Pt(111) for ammonia decomposition.

Vibrational spectroscopy was done to see if this difference in activity is caused by a major differences between the binding of ammonia on the Pt(111) and Pt(210) surfaces. Figure 3(a) shows a single-reflection infrared spectrum of ammonia adsorbed on Pt(111). There are peaks at 3379, 3286, 1654, and 1074 cm^{-1} , respectively. The intensities of the peaks in Fig. 3(a) are different than those in EELS, due to an enhancement of some of the modes in the IR described elsewhere.⁹ However, the peak positions are in close agreement to those observed previously.² By analogy to the previous work, we assign the peaks at 3379 and 3286 cm^{-1} to the NH stretching modes of ammonia and the peaks at 1654 and 1074 cm^{-1} to the NH bending modes of ammonia.

Figure 3(b) shows an EELS spectrum of ammonia adsorbed on Pt(210). There are peaks at 3379, ≈ 3217 , 1616, 1090, 715, and 324 cm^{-1} , respectively. There is also evidence for a shoulder at ~ 1250 cm^{-1} . The peaks at 3379, 3217, 1616, and 1090 cm^{-1} correspond closely to those in Fig. 3(a). The peaks at 3379 and 3217 cm^{-1} are assigned to the NH stretching modes of ammonia by analogy to the as-

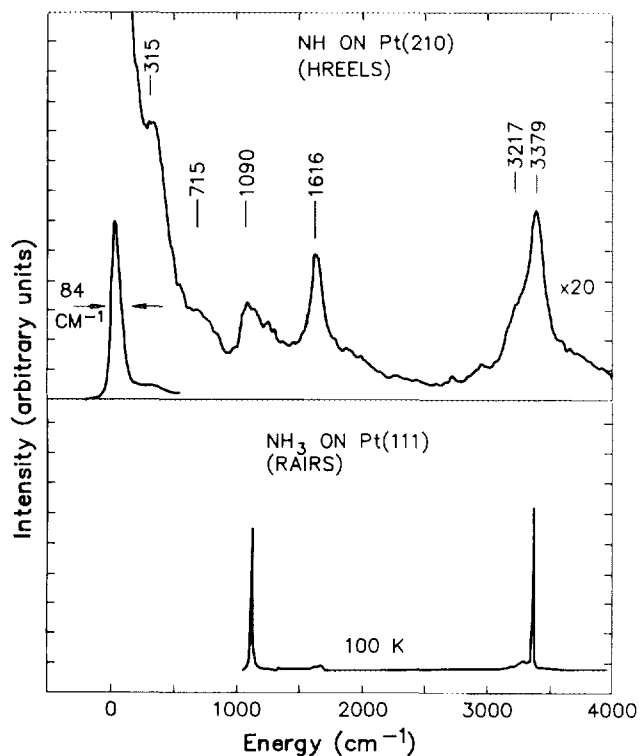


FIG. 3. A comparison of the IR spectrum of ammonia adsorbed on Pt(111) to the EELS spectrum of ammonia adsorbed on Pt(210).

signments above. Similarly, the peaks at 1616 and 1090 cm^{-1} are assigned to the NH bending modes of ammonia. The peaks at 324 and 715 cm^{-1} are below the cutoff frequency of our IR windows. However, they have been observed in a previous EELS study of ammonia adsorption on Ni(110). They are assigned to Pt-N stretching modes and NH_3 rocking modes, respectively. The shoulder at $\sim 1250 \text{ cm}^{-1}$ has also been observed in previous studies of ammonia adsorption on Pt(111); it is thought to be associated with multilayers.

IV. DISCUSSION

It is useful to compare the results in Fig. 3(b) to those in Fig. 3(a). Notice that the vibrational spectra of adsorbed ammonia is very similar on Pt(111) and Pt(210). There are differences in the relative intensities of the peaks in the two spectra. However, the positions of the vibrational bands are very similar on Pt(111) and Pt(210). As a result, it seems that the binding of ammonia does not vary significantly with crystal face.

Note, however, that a metal-nitrogen stretch is seen at 324 cm^{-1} on Pt(210). By comparison, previous EELS work² has indicated that the metal-nitrogen stretch is absent during ammonia adsorption on Pt(111) and Ni(111).¹⁰ The metal-nitrogen stretch is observed on Ni(110). It is not clear why the metal-nitrogen stretch is seen on Pt(210) when it is not seen on Pt(111). Perhaps, the symmetry of the ammonia binding site is different on Pt(210) than on Pt(111). Still, there is no evidence that the form of the ammonia is different on Pt(111) and Pt(210). The observed

differences are of the kind that one would expect for differences in site symmetry.

The TPD data in Fig. 1 give further support to the conclusion that the binding of ammonia does not vary significantly with crystal face. Notice that the structure of TPD spectrum of ammonia is the same on all Pt(111), Pt(100), Pt(110), Pt(211), and Pt(210). There is always a peak between 300 and 380 K, a peak or series of peaks at 170 K, and a multilayer peak at 120 K. All of the peaks are extremely broad, suggesting there are strong interactions within the adsorbed layer. Attempts to resolve the individual peaks by varying the heating rate were not successful on any of the surfaces. There are some differences in the peak temperatures on the various faces, suggesting some small variations in the binding energy of ammonia with crystal face. However, all of the evidence indicates that the binding of ammonia is relatively insensitive to crystal face.

Nonetheless, there are some significant differences in the sticking probabilities of ammonia on the various faces of platinum. While we have not measured absolute sticking probabilities here, the data in Fig. 1 show that ammonia builds up much more quickly on Pt(210) and Pt(110) than on other faces. Analysis of the data indicates there is about a factor of 10 variation in the sticking probability of ammonia with crystal face.

There are also significant variations in the reactivity of the various surfaces for ammonia decomposition. Negligible dissociation of ammonia was detected on Pt(111). In contrast, Pt(210) was reasonably active between 500 and 670 K. We have not done any molecular-beam work on Pt(100), Pt(110), or Pt(211). However, previous work⁵⁻⁷ suggests there are significant variations in the rate of ammonia dissociation on these faces as well.

It is not clear what happens above 670 K. The data in Fig. 2 show a maximum in the reactivity at 670 K. Guthrie, Sokol, and Somorjai⁷ observed a similar maximum during ammonia decomposition on Pt(557). These authors argued that the maximum arises because a new pathway for ammonia desorption opens up at high temperature. We are not sure whether Guthrie, Sokol, and Somorjai's explanation applies to our data or whether the maximum is an artifact due to impurity segregation. However, the data show clearly that Pt(210) is at least a factor of 100 more active than Pt(111) for ammonia decomposition at temperatures where impurity segregation from the bulk is not a problem.

One can speculate why the variations in rate with crystal face arise. First, it is useful to note that while the data are incomplete there appears to be some correlation between the sticking probability of ammonia on the various faces and the reactivity of the faces. In previous work, Lofler and Schmidt⁶ examined the decomposition of ammonia on Pt(111), Pt(110), Pt(100), and Pt(210) at 1 atm. They found that Pt(110) was less active than Pt(210). Pt(111) and Pt(110) were less active still. Here we find that the sticking probabilities follow the same trends. The sticking probability of ammonia is largest on Pt(210) and Pt(110) and smallest on Pt(111) and Pt(100). Hence, we conclude there is some correlation between the variations in sticking probability and the variations in reactivity.

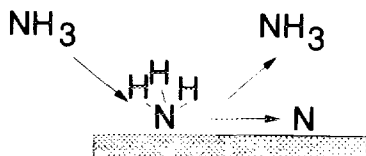


FIG. 4. A simplified picture of the mechanism of ammonia decomposition on platinum.

Still, the variations in sticking probability alone are not sufficient to explain the variations in reactivity. The data in Fig. 2 show that Pt(210) is at least a factor of 100 more active than Pt(111). However, the sticking probability is only different by a factor of 10. Hence, one has to look elsewhere to explain the variations in rate.

For the purpose of further discussion, it will be useful to assume that ammonia decomposition follows the simplified model in Fig. 4. The ammonia will be presumed to stick on the surface, then either react or desorb. The data above show that the sticking probability of ammonia is about a factor of 10 higher on Pt(210) than on Pt(111) at 100 K. The data in Figs. 1 and 3 show that the ammonia is adsorbed nondissociatively on the various faces of platinum. The ammonia is strongly bound at low coverages. There is no evidence for an indirect adsorption process (i.e., a mobile precursor) in the data in Fig. 1. The sticking probability for a direct adsorption process into a strongly bound state is usually relatively independent of temperature. As a result, the sticking probability of ammonia is likely to remain about a factor of 10 larger on Pt(210) than on Pt(111) even when the temperature is raised to 670 K.

There are also likely to be some differences in the rate of ammonia desorption from Pt(111) and Pt(210). The TPD results in Fig. 1 show that the desorption rate of ammonia is smaller on Pt(210) than on Pt(111) at low coverages where only the α_1 state is occupied. If it is assumed that the desorption of ammonia is approximately first order with a preexponential between 10^{10} and 10^{15} s, then one calculates that the activation energy of desorption from the α_1 state is 3 or 4 kcal/mol higher on Pt(210) than on Pt(111) assuming that the preexponential is the same on both faces. This translates into a factor of 10 or 20 variation in the desorption rate at 670 K. The molecular-beam experiments were done where the coverage was low, so only the α_1 state should contribute. Hence, it seems likely that the residence time of ammonia will be about a factor 10 or 20 larger on Pt(210) than on Pt(111).

The sticking probability of ammonia is a factor of 10 higher on Pt(210) than on Pt(111); the residence time of the adsorbed ammonia is a factor of 10 to 20 higher as well. As a result, the steady-state concentration of ammonia will be 100 to 200 times higher on Pt(210) than on Pt(111). It is not surprising then that Pt(210) was found to be at least 100 times as active as Pt(111) for ammonia dissociation.

Admittedly, it is unclear whether the variations in rate are larger than a factor of 100. (A factor of 100 was our mea-

surement limit.) It is also unclear whether sticking probability of ammonia or activation energy for desorption of ammonia vary with temperature. Still, the data here show that one would expect there to be sizable variations in the rate of ammonia decomposition on platinum due to the variations in the sticking probability of ammonia and the variations in the residence time of ammonia on the surface. The expected variations are observed experimentally. Clearly, more work is needed to see if there are additional effects. However, the data here show that the variations in residence time and sticking probability have a major effect on the rate of ammonia decomposition on platinum.

V. CONCLUSION

In summary then, the results here show that the adsorption of ammonia on platinum is *not* structure sensitive. The vibrational spectrum of adsorbed ammonia does not vary significantly from face to face; the basic structure of the TPD spectrum of ammonia is identical on all of the faces examined here. Nonetheless, there are some variations in the binding energy and sticking probability of ammonia with crystal face. These variations produce a large change in the rate of ammonia decomposition with crystal face. There is more work to be done, and there may be other effects. However, it is clear that the variations in residence time and sticking probability have a major effect on the rate of ammonia decomposition on platinum.

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