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The Role of Step Atom Density on the Binding and Reaction of Surface Species

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Temperature-programmed desorption was used to examine the adsorption and reaction of CO, H_2, O_2, NO, CH_3OH, and C_2H_4 on several surfaces of platinum to see if there is a correlation between the atom density of step atoms and reactivity. Small variations in the desorption activation energy of hydrogen, oxygen, carbon monoxide, ethylene, and methanol were found the changing crystal face. However, on platinum surfaces, there was no correlation between the desorption activation energy and the step atom density. Reactivity was found to vary greatly with the crystal face. However, no correlation was found between the step atom density and the reactivity for the hydrogenolysis of ethylene to methane, for the decomposition of methanol to carbon monoxide, for the hydrogenolysis of methanol to methane, for the oxidation of methanol to carbon dioxide, for the oxidation of methanol to formaldehyde, or for the decomposition of nitric oxide to nitrogen and oxygen. Only for the self-hydrogenation of ethylene to ethane on platinum surfaces did the reactivity have any correlation with step atom density, and this correlation did not carry through to steady-state experiments. From our study, it appears that the active site for reaction is often not simply a step site. Rather, the active site consists of a special arrangement of step and terrace atoms that are aligned correctly to produce high reactivity.

INTRODUCTION

The idea that catalytic reactions occur on special active sites on a surface was first mentioned by Faraday (1) in 1834. In 1925, Pease and Stewart (2) provided the first direct experimental evidence that active sites exist. Taylor (3–5) expanded this idea to show that molecules react preferentially at special sites on a metal surface.

There are several models for the geometry of the active site. Dowden (6) proposed that a critical ensemble of 5–10 atoms is needed to promote a reaction. Thomas (7) proposed that dislocations, such as scratches, are the active sites for reactions. However, these ideas have not met with wide acceptance. In contrast, Somorjai (8) proposed that the active site is a step or kink atom on the catalyst surface and that proposal has made its way into elementary textbooks on the subject.

Surprisingly, the idea that steps or kinks have anything to do with reactivity has had only limited experimental confirmation. Blakely and Somorjai's (8) original evidence for step and kink atoms as active sites came from a series of experiments on the dehydrogenation of cyclohexene to benzene on single crystal platinum surfaces. During these experiments, the turnover numbers increased to maxima and then tailed off as poisoning covered the entire surface. Blakely and Somorjai plotted the maximum turnover number versus step and kink atom densities and found a correlation between them. The fact that the rate correlated with step and kink atom densities led Blakely and Somorjai to suggest that steps and kinks are active sites.

Unfortunately, subsequent workers from Somorjai's group were unable to reproduce Blakely's results. For example, Davis and Somorjai (9) also studied the dehydrogenation of cyclohexene to benzene on single crystal platinum surfaces. They did not plot their results as maximum turnover number versus step and kink atom density, but this has been done in Fig. 1. Figure 1 shows that Davis and Somorjai's data do not show a correlation between turnover number and step atom density. A comparison of the conditions used by Blakely and Somorjai and Davis and Somorjai is given in Table 1. The reaction conditions are similar. It appears that the difference between the two is the sample cleanliness before reaction.

At this point, there are a lot of data which show that highly corrugated surfaces have a reactivity different from close-packed planes. However, so far no one has determined whether there is a correlation between the variations in reactivity and the step atom density. The objective of this paper is to see if reactivity, as determined with temperature-programmed desorption (TPD), varies with step atom density. Although platinum may not be ideal because it reconstructs, platinum is the only metal with data from enough stepped surfaces for our analysis. We used TPD on a number of faces of platinum to measure heats of adsorption and rates of surface reactions to check whether the variations correlate with step atom density.

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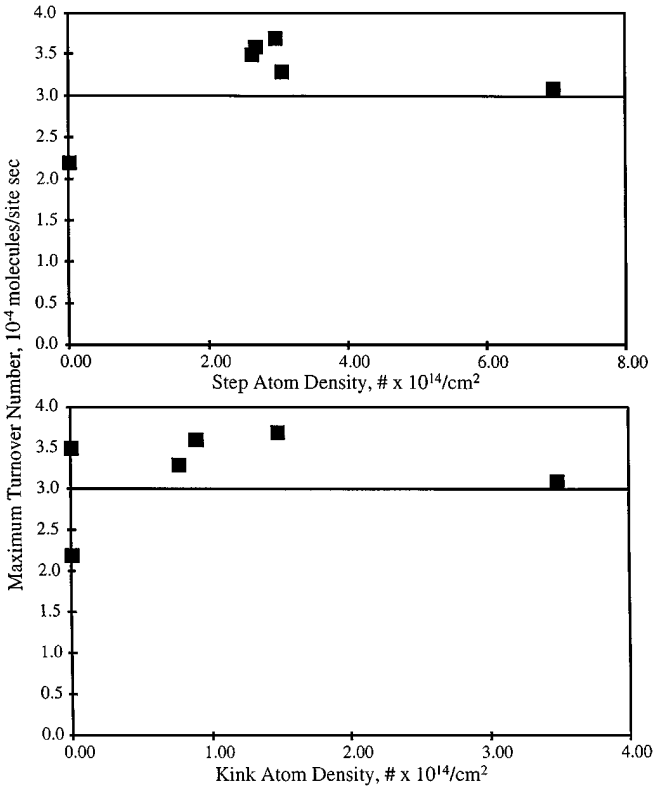

FIG. 1. Maximum turnover number of the dehydrogenation of cyclohexene to benzene on platinum surfaces versus step and kink atom densities. Data from Davis and Somorjai, *Surf. Sci.* **91**, 73 (1980).

METHOD

Most of the data that we are using for this analysis have already appeared in the literature (10–31), and the data were taken in one of four vacuum chambers with base pressures less than or equal to 3×10^{-10} torr. The chambers have ion guns so that the crystals could be cleaned with argon sputtering. Auger electron spectroscopy was then used to check the cleanliness of the crystals. The crystal was cooled through thermal contact with liquid nitrogen and heated resistively. A mass spectrometer monitored the desorption products from the crystal as it was linearly heated. Desorption of oxygen (10, 11, 23), hydrogen (11, 16, 17, 19–21, 31), ethylene (11, 16–18, 25–27), methanol (10, 11, 24, 28), and carbon monoxide (11, 12, 14, 19, 21–23) from platinum surfaces and reactions of ethylene (11, 16–18, 27), methanol (10, 11, 28, 29), and nitric oxide (12–15, 30) on platinum surfaces have been studied in our group. A few data points have been analyzed from other groups' work (32–43). Specifically, these are desorption of oxygen (34, 38–42) and methanol (33, 43) from platinum surfaces and reactions of ethylene (35–37) and methanol (32, 33) on platinum surfaces. These other groups have also used standard ultra-high vacuum systems and techniques.

TABLE 1

A Comparison of Conditions for Blakely and Somorjai (8) and Davis and Somorjai (9)

Blakely and Somorjai	Davis and Somorjai
150°C	150°C
8.4×10^{-7} torr	1.08×10^{-6} torr
$H_2 : HC = 20 : 1$	$H_2 : HC = 16.1 : 1$
Dirty crystal	Clean crystal

TPD spectra were analyzed for desorption activation energy using Redhead's analysis (44). The equation of interest is

$$\frac{E_{\text{act}}}{k_B T_p} = -\ln\frac{\beta_H}{k_o T_p \theta_o^{n-1}} - \ln\frac{E_{\text{act}}}{k_B T_p}, \qquad [1]$$

where E_{act} is the desorption activation energy, k_B is Boltzmann's constant, T_p is the peak temperature, β_H is the linear heating rate, k_o is the preexponential of the rate constant for desorption, θ_o is the initial surface coverage, and n is the reaction order. Values for T_p, β_H, θ_o, and n were found from or given in the TPD spectra. In some of the cases we had previously measured k_o by varying the heating rate. All of these measured k_o values were found to be $10^{13\pm0.5}$/monolayer^{n-1}s. In the cases where k_o was not known, we assumed that k_o was 10^{13}/monolayer^{n-1}s. We also tried varying this assumption. While varying k_o did have an effect on the absolute values of the desorption activation energy, it did not affect the trends.

We always studied the first peak to appear as coverage was increased. This was generally the highest temperature peak. It was assumed that the first molecules adsorbed on the surface moved to the sites where they were the most strongly adsorbed. If the step sites bind the strongest, then the first peak to appear as coverage increases from zero will correspond to desorption from the steps. To avoid confusing adsorption on the surface with adsorption at defect sites, a zero-coverage limit was not used. Desorption peaks at about 10 to 25% of a monolayer were investigated instead. If the steps do bind adsorbates more strongly than terraces, the desorption activation energies from stepped surfaces will be higher than those from flat surfaces.

The reactivity was determined from TPD plots by integrating the areas under the desorption curves. Only the areas under the monolayer peaks were considered. The percent reacted was calculated by Eq. [2],

$$\%\ \text{reacted} = \frac{\text{Area of product of interest}}{\text{Total areas of reactant and all products}}. \qquad [2]$$

This is an atom balance. Appropriate stoichiometric coefficients were used to convert the numbers of product molecules to the numbers of reactant molecules used to

form the products. For ethylene self-hydrogenation, the balance is on carbon atoms, so "all products" includes ethane, ethylene, methane, and adsorbed carbon, but not H_2. The relative sensitivities of the mass spectrometers to a mixture of various gases were measured for nitric oxide reactions (12) and for the hydrogenolysis of ethylene to methane (16,25). These sensitivities were taken into account in finding the areas for Eq. [2].

We used step atom density as our correlating factor because its unit similarity to reaction rates also reported on a per unit area basis. The step atom density was calculated from the number of step atoms per unit cell divided by the area of the unit cell. Equation [3], which is from Nicholas (45), was used to calculate the areas of primitive unit cells for cubic lattices,

$$A = \frac{1}{4}(h^2 + k^2 + l^2)^{1/2} Q a^2 \qquad [3]$$

where A is the area of the primitive unit cell; h, k, and l are the Miller indices; Q is one if h, k, and l are all odd, and it is two otherwise; a is the lattice parameter. We considered (111), (110), and (100) surfaces, as well as surfaces from the three axes of the stereographic triangle. We called (110) a stepped surface because the step density increased monotonically as we moved from either (111) or (100) to (110). The various step constructions are not differentiated because we wanted to investigate the effects of the presence of any step.

RESULTS

Recall that Davis and Somorjai (9) measured the rate of cyclohexene hydrogenation on a number of platinum single crystal surfaces. Figure 1 shows a plot of their maximum turnover numbers versus step and kink atom densities. The rate of reaction is higher on all of the stepped surfaces than on Pt(111). However, they did not find that increases in step atom density lead to increases in the reaction rate among the stepped surfaces. Consequently, it does not appear that the steps *per se* are causing the increase in reactivity. Our interpretation is that other changes are causing the stepped surfaces to be more reactive than Pt(111).

Desorption Activation Energy

Given the lack of correlation between step atom density and reactivity in Fig. 1, we want to know if any properties of the adsorbate correlate with step atom density. In the previous literature, people have often stated that adsorbates preferentially bind to steps and kinks. Therefore, we looked for a correlation between the binding energy of species and the step atom density.

Figure 2 and Table 2 show how the activation energy for hydrogen desorption from a number of faces of platinum varies with the step atom density. Notice that there are variations in the desorption activation energy with changing crystal face. Pt(111) has an intermediate binding energy for hydrogen: some stepped surfaces bind hydrogen more strongly than Pt(111), and other stepped surfaces bind hydrogen more weakly than Pt(111). However, there is no correlation between the activation energy of desorption and the step atom density.

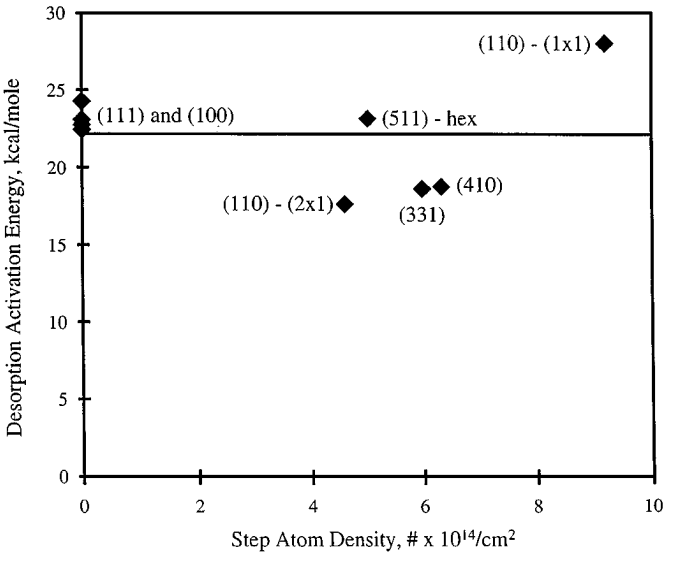

FIG. 2. Desorption activation energy versus step atom density for hydrogen desorption from hydrogen adsorbed on platinum surfaces.

The desorption activation energies for several other compounds desorbing from platinum surfaces are shown in Fig. 3 and Table 2. We observe variations in the activation energies of desorption for ethylene, methanol, and oxygen with respect to crystal face. However, these desorption activation energies clearly do not correlate to step atom density. The activation energy for carbon monoxide desorption seems to correlate with step atom density. CO is a special case in that the binding of CO is highly dependent upon coverage. Experimentally, the variations in the binding energy with respect to coverage are larger than the variations in binding energy with respect to crystal face. At this point there is no evidence that the binding energy of any species certainly correlates to the step atom density, although the binding energy of carbon monoxide might correlate with step atom density. We have also plotted the heat of adsorption as a function of the step atom density for a fixed step geometry. Again, there is no obvious correlation between the heat of adsorption and the step atom density.

Reactivity

Next, we checked to see if the rate of reaction, as measured by TPD, varies with step atom density. Figure 4 and Table 3 show some data for ethylene self-hydrogenation. During the experiments reported in the figure, we adsorbed ethylene onto a cold platinum surface. We then heated the

TABLE 2

Desorption Activation Energies of Ethylene, Carbon Monoxide, Oxygen, Methanol, and Hydrogen from Platinum Surfaces

Adsorbate	Surface	Step atom density # × 10^{14}/cm^2	E_a kcal/mole	Source
Ethylene	(110) - (2 × 1)	4.60	16.43	16, 27
	(331)	5.97	16.43	11
	(110) - (1 × 1)	9.20	11.61	16, 25, 27
	(100) - (1 × 1)	0.00	15.76	17, 26
	(100) - (5 × 20)	0.00	19.39	17, 26
	(210)	11.60	15.22	18, 27
	(511) - (1 × 1)	5.01	17.65	11
	(511) - hex	5.01	15.83	11
Carbon monoxide	(111)	0.00	29.20	19
	(100)	0.00	27.64	22
	(331)	5.97	31.14	23
	(331)	5.97	31.01	11
	(511) - hex	5.01	31.45	11
	(410)	6.31	32.79	21
	(410)	6.31	32.38	12
	(210)	11.60	34.10	14
Oxygen	(110) - (2 × 1)	4.60	51.95	10
	(111)	0.00	42.40	34, 40–42
	(100)	0.00	52.08	38, 39
	(331)	5.97	45.44	23
	(331)	5.97	51.07	11
	(511) - (1 × 1)	5.01	55.03	11
Methanol	(110) - (2 × 1)	4.60	12.51	24
	(111)	0.00	10.96	33, 43
	(110) - (2 × 1)	4.60	7.44	10, 28
	(331)	5.97	14.01	11
	(110) - (1 × 1)	9.20	7.44	10, 28
	(511) - hex	5.01	13.41	11
	(210)	11.60	15.91	10
Hydrogen	(111)	0.00	22.93	19
	(110) - (2 × 1)	4.60	17.65	16, 31
	(331)	5.97	18.62	11
	(110) - (1 × 1)	9.20	28.05	16
	(100) - (1 × 1)	0.00	22.43	17
	(100) - (5 × 20)	0.00	24.26	17
	(100) - (1 × 1)	0.00	22.78	20
	(100) - (5 × 20)	0.00	23.09	20
	(410)	6.31	18.74	21
	(511) - hex	5.01	23.14	11

surface linearly and measured the fraction of the ethylene that was self-hydrogenated to ethane. We then varied the surface and plotted the fraction of the ethylene that was self-hydrogenated versus the step atom density.

The rate does seem to correlate with step atom density. Little self-hydrogenation is seen on Pt(111) or Pt(100). However, the rate increases as the step atom density increases. Interestingly, in previous work we have found two forms of ethylene on the surface during the hydrogenation process: a di-σ form of ethylene and a π-bound form of ethylene. Experimentally, the self-hydrogenation process suddenly turns on when we start to see the π-bound ethylene on the steps, and there is a direct correlation between the π-bound ethylene on the steps and the rate.

Wheeler (46) has measured the rate of ethylene hydrogenation on Pt(111) and Pt(210) in an atmospheric reactor. Based on the results in Fig. 4 one might expect Pt(210) to be much more active than Pt(111). Wheeler's data are given in Table 4. These data were taken at similar ethylene coverages as in the TPD experiments. One finds that initially there is some difference between the catalytic activities of Pt(111) and Pt(210). However, after the system comes to steady state, there is little difference between the rate of ethylene hydrogenation on the two surfaces. Therefore, the correlation with step atom density in Fig. 4 does not seem to carry over to steady-state reactions.

Figures 5 through 8 show how the rates of a number of other reactions vary with step atom density. The percent of methanol that decomposed to carbon monoxide and the percentage of methanol that oxidized to carbon dioxide during TPD on platinum surfaces are shown versus step atom density in Fig. 5. In both cases, some stepped surfaces show higher reactivity than Pt(111). Other stepped surfaces show

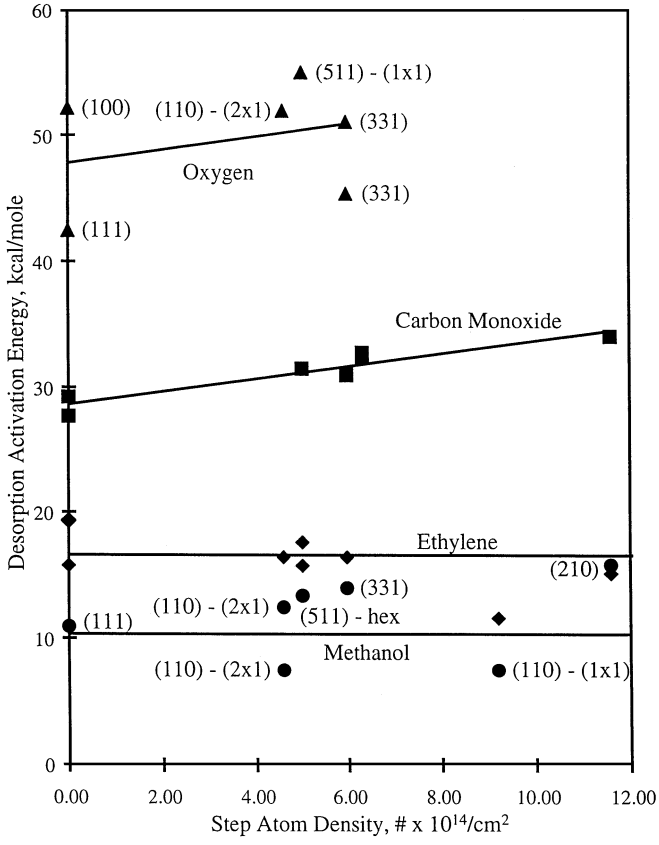

FIG. 3. Desorption activation energies for oxygen, carbon monoxide, ethylene, and methanol from the corresponding compounds on platinum versus step atom density.

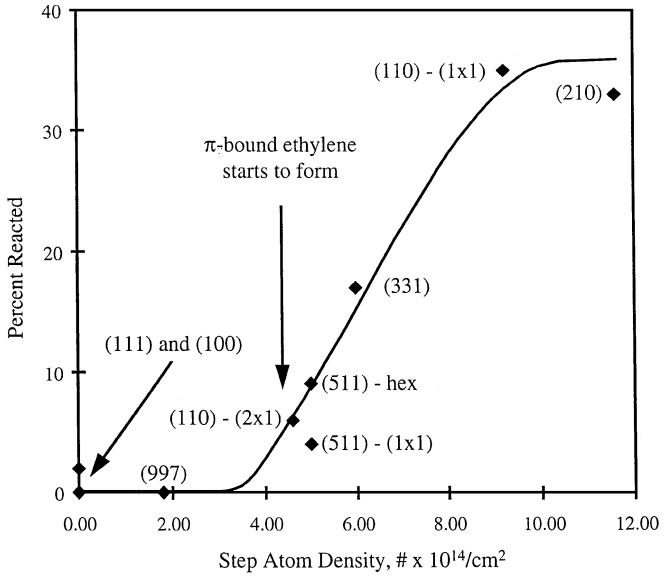

FIG. 4. Percentage of ethylene that self-hydrogenated to ethane on platinum surfaces versus step atom density.

lower activities. There is no correlation between the percentage reacted and step atom density for either methanol decomposition to carbon monoxide or methanol oxidation to carbon dioxide.

Data for the hydrogenolysis of ethylene to methane are shown in Fig. 6. A few stepped surfaces show a high reactivity for this reaction. Figure 7 shows data for nitric oxide

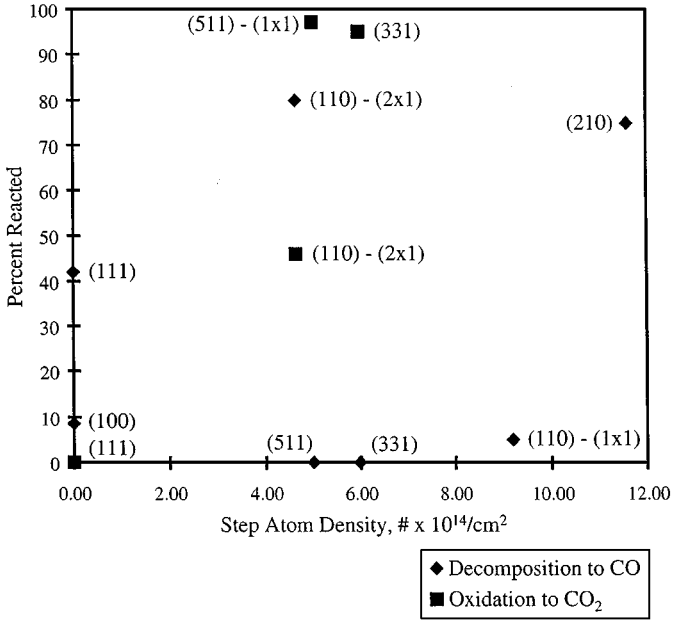

FIG. 5. Percentage reacted for methanol decomposition to carbon monoxide and methanol oxidization to carbon dioxide on platinum versus step atom density.

TABLE 3

Percentage Reacted for Reactions of Ethylene, Methanol, and Nitric Oxide on Platinum Surfaces

Reaction	Surface	Step atom density # × 10^{14}/cm^2	% reacted to product	Source
Ethylene to ethane	(110) - (2 × 1)	4.60	6	16, 27
	(110) - (1 × 1)	9.20	35	16, 27
	(100) - (5 × 20)	0.00	0	17
	(100) - (1 × 1)	0.00	0	17
	(997)	1.79	0	35
	(111)	0.00	2	37
	(511) - (1 × 1)	5.01	4	11
	(511) - hex	5.01	9	11
	(331)	5.97	17	11
	(210)	11.60	33	18, 27
Ethylene to methane	(331)	5.97	0	11
	(511) - hex	5.01	4	11
	(511) - (1 × 1)	5.01	10	11
	(511) - (1 × 1)	5.01	15	11
	(997)	1.79	0	35
	(111)	0.00	0	36
	(111)	0.00	0	37
	(111)	0.00	0	37
Methanol to carbon monoxide	(511) - hex	5.01	0	11
	(511) - (1 × 1)	5.01	0	11
	(331)	5.97	0	11
	(110) - (2 × 1)	4.64	80	10, 28
	(110) - (1 × 1)	9.20	5	10, 28
	(210)	11.60	75	10
	(100) - (1 × 1)	0.00	8.7	32
	(100) - hex	0.00	8.5	32
	(111)	0.00	42	33
Methanol to carbon dioxide	(511) - (1 × 1)	5.01	97	11
	(331)	5.97	95	11
	(110) - (2 × 1)	4.64	46	10, 29
	(111)	0.00	0	33
Methanol to methane	(110) - (1 × 1)	9.20	33	10, 28
	(110) - (2 × 1)	4.60	0	10, 28
	(511)	5.01	0	11
	(331)	5.97	0	11
	(100)	0.00	0	32
	(111)	0.00	0	33
	(210)	11.60	0	10
Methanol to formaldehyde	(110) - (2 × 1)	4.60	35	10, 29
	(511)	5.01	0	11
	(331)	5.97	0	11
	(100)	0.00	0	32
	(111)	0.00	0	33
Nitric oxide to nitrogen	(111)	0.00	2	12
	(110)	9.20	15	12
	(665)	1.32	30	12
	(410)	6.31	98	12
	(210)	11.60	70	13
	(100)	0.00	66	15, 30
	(211)	5.31	66	15, 30
	(411)	3.07	70	14, 30

TABLE 4

Reaction Rates for Ethylene Hydrogenation on Platinum

Surface	Initial reaction rate molecules/Pt atom/s	Steady-state reaction rate molecules/Pt atom/s
(210)	21.8	9.44
(111)	15.8	9.21

Note. 300 K; 50 torr ethylene; 250 torr hydrogen; 450 torr helium (46).

decomposition to nitrogen. Again, some special stepped surfaces show high reactivity. For both Figs. 6 and 7, there is no correlation between the percentage reacted and step atom density.

Figure 8 shows the percentage reacted versus step atom density for the last two reactions: methanol hydrogenolysis to methane and methanol oxidation to formaldehyde. For both, reactions have been observed on only one special stepped surface. All of the other faces that have been examined so far show negligible reactivity. Again, there is no correlation between the reaction rate and the step atom density.

DISCUSSION

The data in this paper provide little support for the idea that steps and kinks have any effect upon catalytic activity. Generally, heats of adsorption are different on stepped surfaces than on close-packed planes. However, the heat of adsorption of a given molecule on a stepped surface might be higher or lower than the heat of adsorption of the same molecule on a close-packed plane. Similarly, we see large variations in reactivity with crystal face. However, a flat surface like Pt(111) often has similar reactivity to a highly corrugated surface like Pt(210). The highest reactivity frequently occurs at intermediate step densities. Very highly stepped surfaces are often unreactive.

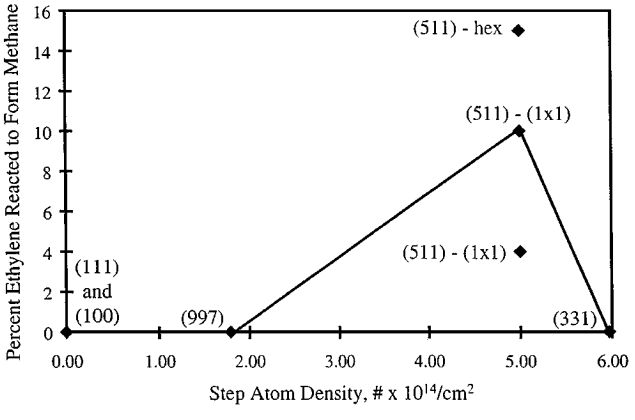

FIG. 6. Percentage reacted for ethylene hydrogenolysis to methane on platinum versus step atom density.

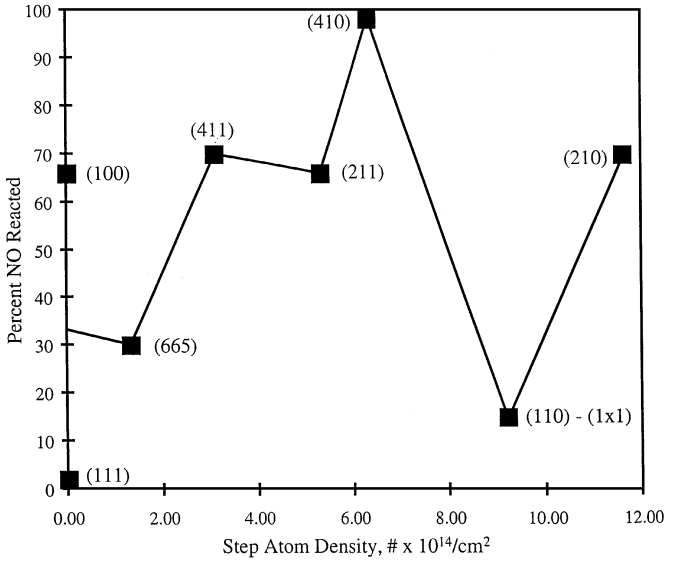

FIG. 7. Percentage reacted for nitric oxide decomposition to nitrogen on platinum surfaces versus step atom density.

From our study of the desorption and reactions of several compounds on flat and stepped platinum crystals, we have found only one case in which the desorption activation energy or reactivity correlates with step atom density: the self-hydrogenation of ethylene. No similar correlation is seen during steady-state ethylene hydrogenation, however.

We think that, in this case, the correlation with step atom density is an artifact of the TPD experiment. Ethylene would like to adsorb into a di-σ state on platinum. However, when ethylene is adsorbed onto a highly stepped platinum surface at 100 K, some of the ethylene molecules are frozen into a π-bound state that can be seen with electron energy loss spectroscopy. The π-bound intermediate

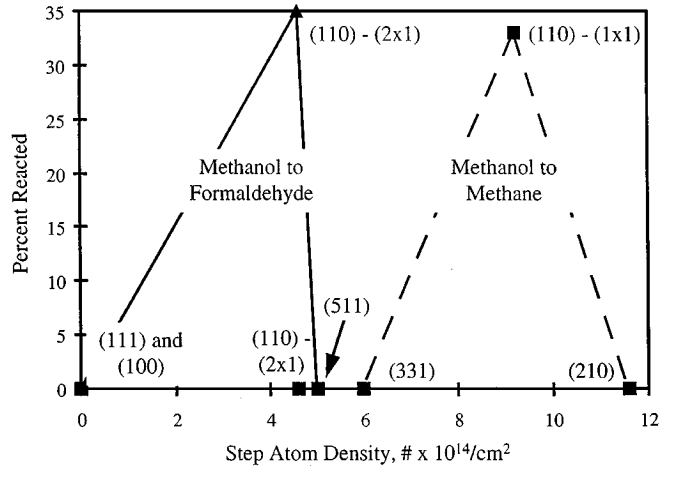

FIG. 8. Percentage reacted for methanol hydrogenolysis to methane and methanol oxidation to formaldehyde on platinum surfaces versus step atom density.

is not observed during ethylene adsorption on Pt(111) at 140 K but is seen during ethylene adsorption on Pt(111) at 80 K. The π-bound ethylene is converted into the di-σ species upon annealing, so the π-bound state is not the preferred state. However, ethylene molecules are trapped into the π-bound state on a 100 K stepped surface. When the surface is heated rapidly, the π-bound ethylene becomes mobile and has an opportunity to react with hydrogen on the surface, to form ethane. The mobile π-bound ethylene could anneal and form di-σ bound ethylene, but a fraction of the π-bound ethylene reacts to form ethane instead of forming di-σ bound ethylene. Most of the ethylene self-hydrogenation reaction goes via the π-bound intermediate.

Experimentally, it seems that the presence of the trapped species is promoting the reaction rather than the steps. We do not observe an effect of step atom density on reaction during steady-state hydrogenation. Nor do we observe a step atom density effect on the self-hydrogenation rate when we dose the ethylene onto a cold platinum surface, anneal the layer to convert the π-bound ethylene into a di-σ state, and then do the TPD experiment. The important factor in ethylene self-hydrogenation is the presence of π-bound ethylene. Steps are important to ethylene self-hydrogenation in that they allow π-bound ethylene to form during dosing at 100 K. However, we have no evidence that steps promote reactivity once the π-bound ethylene forms.

In all of the other cases we have examined, we have no conclusive evidence that steps have any systematic influence on reactivity. In our work, however, we have often found that one special stepped surface has unusual reactivity for a particular reaction. Pt(410) is especially active for NO decomposition. (1×1)Pt(110) is especially active for methanol hydrogenolysis. In both of these cases, surfaces with an intermediate step atom density are the most active. Pt(210), which has a higher step atom density, is less active, as are Pt(111) and Pt(100). Taken together, these phenomena imply that steps by themselves are insufficient to catalyze reactions. Rather, one needs a critical ensemble of atoms. Our best guess is that the active site generally consists of a step plus part of a terrace. Additionally, the site is active only when the terrace atoms are correctly aligned with the step to promote reaction. Experimentally, we find that the reaction rate declines at very high step atom densities since there are too few terrace atoms to complete the critical ensembles. At very low step atom densities, there are few step atoms to combine with terrace atoms to form these critical ensembles, and the reaction rate is correspondingly low. We believe that this critical ensemble of step and correctly aligned terrace atoms explains our reaction data.

Critical ensembles of step atoms with correctly aligned terrace atoms might explain some correlations of reaction rate to defects. Some researchers have noticed that their reaction rates correlate well with the density of defects in their samples. An ad-atom or step defect could easily form a critical ensemble of a step atom with correctly aligned terrace atoms. Each defect could form another critical ensemble, so it would not be surprising for defects to have an effect on the reaction rate. If the defect density stays low enough that the critical ensembles are not broken up by defects, the reaction rate will correlate with the defect density. As the defect density increases, the reaction rate will decrease since the terraces will be broken up by the additional defects, and the critical ensembles will not be found. If the active site needs a step and a terrace, this may be why surfaces with intermediate step atom densities or surfaces with moderate defect densities generally show the highest reactivity.

Still we cannot definitely prove that a critical ensemble of a step atom with properly aligned terrace atoms is the reason for our reaction rate variations. It is possible that some sort of long-range step effect is modifying a terrace site to make it more reactive. It is known that the work function of a stepped surface is lower than the work function of a flat surface (47). Interactions beyond a few nearest neighbors are governed by Friedel oscillations in the electron density (48). Steps also modify the spring constant for vibrations normal to the terrace (49). Any of these effects could modify a terrace site to make it more active. As the step atom density increases, the number of modified terrace sites increases, raising the reaction rate. At very high step atom densities, the effect of the step is diminished because the terrace atoms within modification range of a step are broken up by the additional steps. For example, say that a step atom strongly affects a terrace atom five atoms from the step. As the step atom density increases from zero, there will be more terrace atoms five atoms from a step. As soon as the terraces are narrower than five atoms, there will be fewer terrace atoms that are five atoms from a step. If the reaction rate correlates with these strongly affected atoms, then the reaction rate will increase and then decrease with increasing step atom density. Admittedly, we do not believe that a long range step effect is modifying terrace sites to make them more active, but we cannot rule the possibility out with our data.

One thing that we can say is that steps are much less important to the binding of molecules than previously thought. In the past, people had assumed that step atoms bind molecules more tightly than terrace atoms because the step atoms are less coordinated than terrace atoms. However, that idea ignores surface relaxation. Lee (50) has found through computations that lower coordination does not happen at steps. As surfaces relax, the electronic coordination numbers of step atoms become close to those of the terrace. For example, Table 5 shows some of Lee's results on Pt(210). The electronic coordination numbers of the step atoms are very similar to those of close-packed planes. This means that step atoms are not as uncoordinated as people have previously thought. This higher than expected

TABLE 5

Electronic-Coordination Numbers of Platinum Surfaces [Lee (50)]

Surface	Nicholas's coordination number	Lee's electronic coordination number	Comments
(100)	8	8.9	Flat surface
(111)	9	9.4	Flat surface
(210)	6	8.4	Step atom
(210)	9	9.7	Terrace atom

coordination might be why steps do not bind molecules as tightly as hypothesized.

CONCLUSIONS

From our study of the desorption and reactions of several compounds on flat and stepped surfaces of platinum, we have determined that step atoms are not as important to desorption and reaction as previously thought. While there are small variations in desorption activation energy with changing crystal face, the variations do not correlate with step atom density. There are large variations in reactivity with changing crystal face. However, Pt(111), which is a close-packed surface, often has a higher reactivity than some stepped surfaces. Generally, there is no correlation between step atom density and reactivity. There is one special case where steps do matter: the self-hydrogenation of ethylene to ethane. In this case, a new species is formed at a higher temperature on the steps than on the terraces. Except for this one case, there is no correlation between reactivity and step atom density, which calls into question the idea that steps are active sites.

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