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A Comparison of Nitric Oxide Decomposition on Pt(210) and Pt(410): An Example Where an Increase in Step Density Has Produced a Decrease in Reactivity

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TPD is used to compare the dissociation of NO on Pt(210) and Pt(410). Flash of a NO-saturated Pt(210) sample produces a single N_2 peak at 500°K and two NO Peaks at 440 and 485°K, with about 70% of the NO dissociating. By comparison, flash of an NO-saturated Pt(410) sample yields a single N_2 peak at 440°K and negligible NO. These results show that Pt(410) is considerably more active than Pt(210) for NO dissociation even though the step geometry is identical on the two surfaces and the step density is higher on Pt(210). Thus it appears that the active site for NO decomposition on platinum consists of a specific arrangement of atoms and is not just a step on the surface.

INTRODUCTION

This paper is a continuation of an ongoing project whose objective is to compare the rate of NO dissociation on a variety of faces of platinum. Previous work has shown that Pt(111) and Pt(110) are inactive for NO dissociation (*1*), while Pt(100) and Pt(511) are active (*1*, *2*), but only at temperatures above 400°K. Pt(410) is active below room temperature (*3*, *4*), and seems to show some dissociation activity at 100°K (*5*, *6*).

This paper considers which site on Pt(410) is especially active for NO decomposition. Figure 1A shows the arrangement of the atoms on the surface of Pt(111), Pt(100), Pt(110), Pt(410), and Pt(511). Pt(410) is a stepped surface with terraces of 8-fold coordinated (C_8) atoms, and steps containing 6-, 9-, and 11-fold (C_6, C_9, and C_{11}) coordinated atoms. Pt(511) is similar, except that the steps contain 7- and 10-fold coordinated atoms. Pt(110) contains 7-, 9-, and 11-fold coordinated atoms, Pt(111) contains only 9-fold coordinated atoms, and Pt(100) contains only 8-fold coordinated atoms. Previous investigators (*7*, *8*) have asserted that the active sites on heterogeneous catalysts can be identified with atoms (i.e., sites) of special coordination. Notice that there are 6-fold coordinated atoms on Pt(410). There are no 6-fold coordinated atoms on the other faces shown in Fig. 1A. Pt(410) is especially active for NO dissociation. Thus, one possibility is that the most active site for NO dissociation is the C_6 atom.

This is not the only possibility, however. Banholzer *et al.* (*9*) proposed a model for NO decomposition on platinum, which considered the symmetry of the orbitals available for reaction. In their model, an active site is a complicated structure. There are several atoms, arranged in a way to produce a set of surface orbitals which are conducive to the reaction.

Figure 2 shows a diagram of one of the active sites for NO decomposition on Pt(410), according to the model of Banholzer *et al.* (*6*). It consists of an assembly of eleven surface atoms. There are three central atoms which do most of the bonding and eight others that establish the

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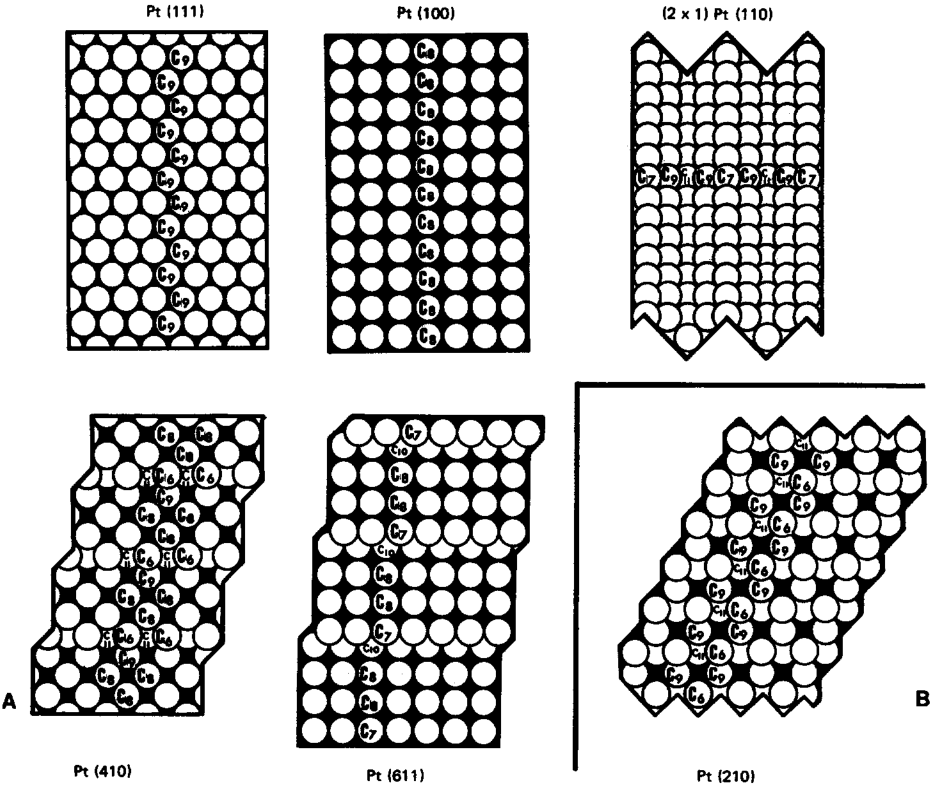

FIG. 1. The coordination number of various sites on (A) Pt(111), Pt(110), Pt(100), Pt(511), Pt(410) and (B) Pt(210). Note that several of these faces reconstruct. The atomic arrangements shown are the ones observed after adsorption of NO where LEED patterns are available (if not, (1 × 1) structures were assumed).

correct local symmetry. According to the model, an NO molecule bound to the atom labeled A in Fig. 2 could bend toward atom B and break; an NO on B could bend toward A. Similarly, an NO at C could bend toward D and vice versa, while an NO at E could bend toward F. According to the Banholzer *et al.* model, the A → B transition is the most favorable due to enhanced overlaps, but B → A, C ↔ D, and E ↔ F transitions could also occur.

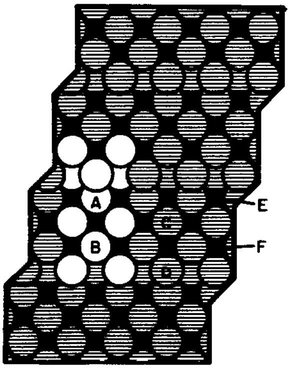

FIG. 2. The most active site for NO decomposition on Pt(410) according to the model of Banholzer *et al.* (9).

It is interesting to consider what would happen with Pt(210). Figure 3 is a diagram of a (1 × 1) Pt(210) surface. Notice that Pt(210) contains almost twice as many C_6 sites per unit area as Pt(410). Thus, if the C_6 sites are the active sites for NO decomposition, Pt(210) should be more active than Pt(410). However, a perfect Pt(210) surface does not contain any sites with a configuration like that of the unshaded region in Fig. 2. According to the Banholzer *et al.* model, an NO bound to site A can still bend over toward site B. However, as there is no

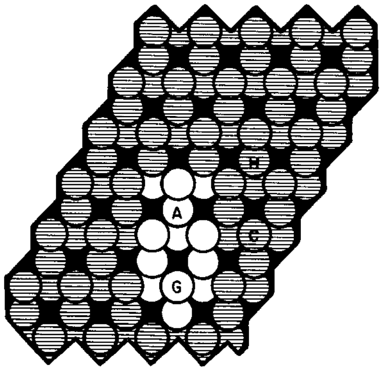

FIG. 3. The atoms involved in NO decomposition on Pt(210) according to the model of Banholzer *et al.* (*9*).

atom at site B, no bond can form. Instead, the most likely pathway according to the model (i.e., the pathway that conserves the most bonding), is for a bond to form with atom G. Similarly, atom D is missing, so that the C → D transition cannot occur. According to the model, the most likely pathway is for an NO at C to bend over to H. Both these transitions involve a significant stretching of the NO bond, so that neither is as likely as the A → B transition on Pt(410). Thus, if Banholzer's model is correct, one would expect Pt(210) to be less active than Pt(410) for NO dissociation. One would expect the opposite if the C_6 sites are active. Therefore, a comparison of the catalytic activity of Pt(210) and Pt(410) would show which of these models is correct. The purpose of this paper is to compare the NO dissociation activity of Pt(210) and Pt(410) using TPD.

EXPERIMENTAL

The experiments were done using the apparatus and procedures described previously by Banholzer *et al.* (*3*). A vacuum system of standard design was used for the work. It had a base pressure below the X-ray limit of the ion gauge, and a measured time-constant for NO and N_2 desorption below 0.05 sec.

Two samples, one with (210) orientation, the other with (410) orientation were cut from the same single crystal rod. They were mechanically polished on both sides, then mounted in the vacuum system on a pair of manipulators. Each sample was cleaned as described previously, (*3*) then dosed with NO, and flashed. An LSI-11 computer was used to control the heating rate and acquire the data. Care was taken to ensure that the two samples were treated identically throughout the experiments. Pt(210) and Pt(410) runs were interspersed so that changes in the vacuum system did not produce an artificial difference between the results from the two samples. A Pt(410) sample was run in the manipulator used for the (210) runs to ensure that the results were not manipulator-dependent.

RESULTS

Figure 4 shows a set of TPD spectra taken with the two samples. The Pt(410) results are nearly identical to those described by Banholzer *et al.* (*3*). There is a single Mass 28 (N_2) peak which shifts from 485 to 440°K with increased exposure. There is also a tiny Mass 30 (NO) peak which appears to be associated with desorption from the support rods. By comparison, the Pt(210) results show a Mass 28 (N_2) peak at approximately 500°K and two Mass 30 (NO) peaks at approximately 440

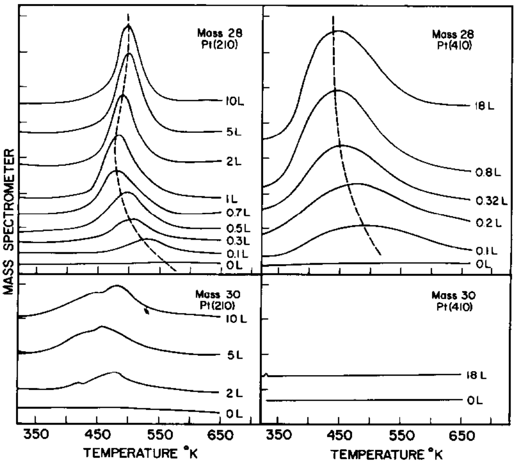

FIG. 4. A set of Mass 28 and Mass 30 TPD spectra taken by exposing a Pt(210) and Pt(410) sample to various amounts of NO, then heating at 27.5°K/sec.

and 485°K. Each of these peaks shift in a complicated way with coverage. Dissociation fractions calculated as described previously (*5*) are 70% on Pt(210) and close to 100% on Pt(410). This compares to a previous report (*1*) of 50% dissociation on Pt(100).

The data also show that the kinetics of N_2 desorption from Pt(410) and Pt(210) are quite different. On Pt(410) the Mass 28 peak decreases monotonically with increasing coverage. A detailed examination of the peak shift described by Banholzer *et al.* (*3*) shows that N_2 desorption from Pt(410) follows a simple second-order kinetics. The Pt(210) data are more complicated. With increasing coverage the N_2 peak first shifts to lower temperatures, then to higher temperatures. Similar shifts have been seen during NO desorption from Pt(100), and it has been argued (*2*) that the shifts are a result of the NO dissociation that occurs during the heating cycle. It is likely, therefore, that NO dissociation is also occurring during the heating cycle on Pt(210). The kinetics of the N–O dissociation process can be inferred from the variations in the N_2 peak temperature with the heating rate. The results of this experiment showed that the activation energy for N–O dissociation is about 25 kcal/mole on Pt(210). This compares to 6 kcal/mole on Pt(410) (*6*). Thus, it is clear from both the kinetics, and the fractional dissociations, that Pt(410) is much more active than Pt(210) for NO dissociation.

DISCUSSION

It is interesting to consider what the results presented in this paper tell us about the active site for NO decomposition on platinum. As noted previously, there are more C_6 sites on Pt(210) than on Pt(410). If the C_6 site were active for NO decomposition, the activity of Pt(210) would be higher than Pt(410). Yet, the data show that Pt(210) is less active than Pt(410). There are C_8 sites on Pt(410) which are missing on Pt(210). However, Pt(100) contains more C_8 sites than Pt(410). If the C_8 sites are especially active, Pt(100) should be more active than Pt(410). Previous results show Pt(100) to be less active than Pt(410). It appears, therefore, that the relative activity of Pt(210), Pt(410), and Pt(100) cannot be explained based solely on the concentrations of C_6, C_8, C_9, and C_{11} sites.

Of course, the Banholzer *et al.* model predicts that the active site is more complicated. The most favorable site is predicted to consist of C_6, C_9, and C_8 atoms arranged in a line with eight additional surface atoms and nine subsurface atoms to establish the correct local symmetry. The current data do not permit one to check whether this site or some other site on Pt(410) is especially active for NO dissociation. However, it is clear that the active site is not just an individual C_6, C_8, C_9, or C_{11} atom on the surface; rather it must involve some more complicated arrangement of atoms such as the site in Fig. 2.

CONCLUSIONS

In summary, the NO dissociation activity of Pt(210) and Pt(410) was compared using TPD. It was found that Pt(210) has a lower catalytic activity than Pt(410), even though it has a higher step density and an identical step geometry. Yet, steps are clearly quite important to the rate; Pt(410) is much more active than any other previously studied face. It is clear, therefore, that it is not the steps themselves, but rather the detailed arrangement of atoms around the catalytic site, that cause Pt(410) to be unusually active.

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REFERENCES

1. Gorte, R. J., Schmidt, L. D., and Gland, J. L., *Surf. Sci.* **109**, 367 (1981).

2. Bonzel, H. P., Broden, G., Pirug, G., *J. Catal.* **53,** 96 (1978).
3. Banholzer, W. F., Masel, R. I., *J. Catal.* **85,** 127 (1984).
4. Park, Y. O., Masel, R. I., Stolt, K., *Surf. Sci.* **113,** L385 (1983).
5. Park, Y. O., Banholzer, W. F., Masel, R. I., *Appl. Surf. Sci.* **19,** 145–160 (1984).
6. Park, Y. O., Banholzer, W. F., Masel, R. I., *Surf. Sci.* **155,** 341 (1985).
7. Boudart, M., Djega-Mariadassou, G., *in* "The Kinetics of Heterogeneously Catalytic Reactions." Princeton Univ. Press, Princeton, N.J., 1985.
8. Somorjai, G. A., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 26, p. 1. Academic Press, New York, 1977.
9. Banholzer, W. F., Park, Y. O., Mak, K. M., Masel, R. I., *Surf. Sci.* **128,** 176 (1983).