JOURNAL OF CATALYSIS 61, 543–546 (1980)

Ammonia Oxidation on the Pt(111) and Pt(S)-12(111) × (111) Surfaces

The reactions of oxygen with ammonia have been studied over the low index Pt(111) and the stepped Pt(S)-12(111) × (111) surfaces for pressures in the 10^{-9} Torr range over the temperature range −150 to 700°C. These steady-state oxidation studies were performed on a system equipped with low-energy electron diffraction, Auger electron spectroscopy, and mass spectrometry. On both surfaces the oxidation of ammonia proceeds rapidly in the temperature range 100 to 600°C; the products observed are nitric oxide, nitrogen, and water. The stepped platinum surface is generally more catalytically active than the low index surface for both NO and N_2 formation branches of the reaction system.

INTRODUCTION

As part of a larger program to characterize the surface chemistry of the nitrogen–hydrogen–oxygen system over noble metal surfaces a comparative study of the ammonia–oxygen reaction system has been undertaken on the low index Pt(111) and stepped Pt(S) − 12(111) × (111) surfaces. A study of ammonia oxidation on the Pt(S) − 12(111) × (111) surface has been previously reported by this laboratory (*1*). Catalytic nitrogen formation predominated at low temperature (<300°C) and in excess ammonia and was correlated with the surface concentration of a nitrogen-containing species. Catalytic nitric oxide production predominated above 400°C and in excess oxygen and was correlated with the concentration of absorbed oxygen atoms. The reaction rates for both branches of the reaction leveled off with respect to increased reactant partial pressure as the step edge sites become saturated with adsorbed species. We proposed (*2*), therefore, that the step edge sites are the most active catalytic sites for both reaction branches. The results to be reported in this paper support the conclusion of our earlier work since the stepped surface is more active than the low index surface for both reaction branches.

Pignet and Schmidt (*2*) studied the decomposition of ammonia over polycrystalline platinum wires and found that the decomposition reaction is not significant below about 600°C. Since all of the reactivity studies reported here were performed below 600°C decomposition of ammonia does not contribute to the observed reaction rate. A short review of recent work relating to the mechanism of ammonia oxidation over platinum was presented in an earlier paper dealing with ammonia oxidation on the Pt(S) − 12(111) × (111) surface (*1*).

EXPERIMENTAL

These steady-state reactivity experiments were performed in a stainless-steel ultrahigh vacuum system equipped with several gas inlets, a quadrupole mass analyzer to monitor gas-phase compositions, a cylindrical mirror analyzer for measuring Auger electron spectra (AES), and a low-energy electron diffraction (LEED) unit to determine surface structures. The single-crystal platinum samples were prepared using the usual metallographic techniques. The two samples were mounted on a liquid nitrogen-cooled sample holder which allowed independent temperature control and measurement from −190 to 1100°C. Each sample was supported by two 0.5-mm platinum wires spot welded across the back of the sample. The ends of each of the support

0021-9517/80/020543-04$02.00/0

wires were spot welded to one of the two 3-mm tantalum support bars. The bars were in good thermal contact but electrically isolated from a liquid nitrogen-cooled copper block. Temperatures were measured using 0.08-mm chromel–alumel thermocouples spot welded to the edge of each sample.

Quantitative comparisons of face-specific reaction rates presents a difficult problem for this type of experiment. Typically, sample edges are unoriented, as are sample supports. Refractory materials may be used for sample supports and masks for unoriented exposed surfaces if they are inert. Usual materials such as tantalum and tungsten are *not* inert for reactions involving ammonia and nitric oxide. Due to this materials difficulty, we have used several alternate methods to estimate the reactive surface areas of our samples. The relative areas were determined by adsorbing oxygen atoms to a known surface concentration as measured using Auger electron spectroscopy and confirmed by the appearance of a 2 × 2 LEED pattern. These adsorbed layers were then desorbed and the resulting time traces were integrated to yield relative surface areas. Using this technique, the ratio of the area of the stepped surface to the area of the low index surface was determined to be 0.63 : 1. A geometric estimate of surface area was also made. The total oriented surface for the Pt(S) − 12(111) × (111) was about 1.2 cm^2 and the Pt(111) sample had an oriented surface area of about 1.8 cm^2. This method predicts an area ratio (Pt(S) − 12(111) × (111) : Pt(111)) of 0.67 : 1. The edges of the cylindrically shaped samples and the platinum support wires are not oriented. Geometric estimates indicate that the Pt(S) − 12(111) × (111) sample contained 0.7 cm^2 of randomly oriented surface while the Pt(111) sample contained 0.6 cm^2 of randomly oriented surface. Two experiments suggested that these surfaces may not be catalytically active. During a period when the oriented surfaces were free from impurity, Auger spectra taken of the sample support wires and sample edges revealed large concentrations of calcium oxide and/or oxidized platinum. Calcium oxide contamination or oxidation of the oriented surface area resulted in dramatic poisoning of observed catalytic activity below 500°C (*1*). In order to estimate area specific reaction rates the relative areas determined by the desorption method have been used (0.63 : 1) since this method is direct. Agreement between the relative surface area determined by oxygen desorption and calculation of the relative oriented surface area (not containing edge or wire areas) suggested that the edges did not absorb significant amounts of oxygen. Taken together these observations suggest that the randomly oriented platinum surface was effectively masked by chemical poisoning. The general conclusions drawn from these data do not depend on the specific normalization method used since the raw reactivity data indicated that the stepped sample (total area ~1.9 cm^2) generally displayed larger activities than the low index surface (total area ~2.4 cm^2) even though the total surface area of the stepped sample was about 20% smaller.

Auger spectra were taken periodically thoughout the experiments to assure sample cleanliness. Details of Auger procedures have been published previously (*1*). The steady-state reactivity measurements were made by measuring the change in product partial pressure in this flow reactor. (Details have been presented previously (*1*).) Changes in product partial pressure were determined by subtracting the background determined with a cold platinum sample from the product concentration determined with the catalyst at reaction temperature. Each measurement was repeated three to five times. Flow rates were measured for the products by measuring the exponential decay of pressure following the rapid flash of a filament, while mass spectrometer sensitivities were estimated by calibration with the ion gauge for the gases of interest. Data used for direct comparison of reaction rates on the two samples were taken by interspersing reactivity measurements for the samples. Reactivity measurements were taken so that monotonic increases or decreases in temperature, concentration, or observed reaction rates were avoided.

DISCUSSION AND DATA

The catalytic ammonia oxidation rates presented in Figs. 1 and 2 indicate that specific reaction rates are larger on the stepped Pt(S) − 12(111) × (111) surface than on the low index Pt(111) surface. As discussed previously, the general conclusion that the stepped surface is more reactive does not depend on the area normalization used; the data in Figs. 1 and 2 have been normalized using relative amounts of desorbed oxygen to estimate surface areas. A comparison of the reactivity temperature profiles for ammonia oxidation to molecular nitrogen or nitric oxide indicates that the reactivity temperature profiles are very similar for the low index Pt(111) and stepped platinum surfaces studied. This observation suggests that no marked change in reaction mechanism is occurring as the surface structure is varied from Pt(111) to Pt(S) − 12(111) × (111).

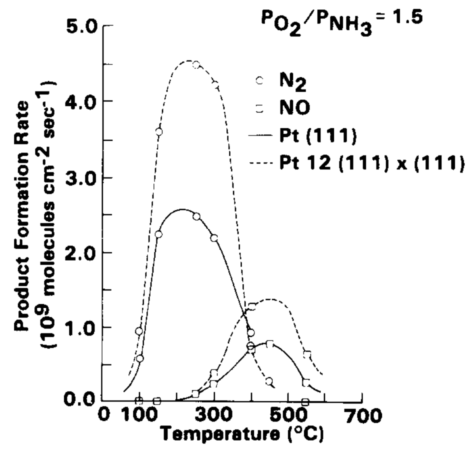

FIG. 1. Ammonia oxidation rates as a function of temperature for a stoichiometric reation mixture. The total pressure is 4 × 10^{-9} Torr.

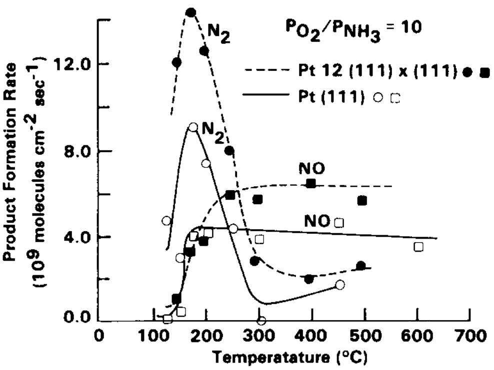

FIG. 2. Ammonia oxidation rates as a function of temperature for a reaction mixture with excess oxygen. The total pressure is 6.0 × 10^{-9} Torr.

The formation rate of nitric oxide in excess oxygen was previously observed to be independent of temperature on the Pt(S) − 12(111) × (111) surface above about 300°C (*1*). The work reported in this paper indicates that the nitric oxide formation rate in excess oxygen is also independent of temperature for the Pt(111) surface, but with a smaller specific reaction rate. The rate-limiting reaction proposed for nitric oxide formation over the Pt(S) − 12(111) × (111) surface (*1*) involved reaction between oxygen atoms on the surface and molecular ammonia. Sticking coefficient measurements made at −75°C indicate that oxygen adsorption (and dissociation) is about ten times slower on the low index Pt(111) surface than on the stepped surfaces (*3*). Therefore it seems reasonable to propose that the coverage of oxygen atoms on the low index surface should be lower, causing the reaction rate to decrease.

Nitrogen formation in excess oxygen was previously studied on the Pt(S) − 12(111) × (111) surface (*1*). By comparing these studies with kinetic studies of the nitric oxide–ammonia reaction over the same surface (*4*) a mechanism was proposed. In excess oxygen, nitrogen formation is thought to occur by a sequential mechanism. Initially ammonia is oxidized to nitric oxide; however, in the low-temperature regime some or all of the nitric oxide remains on the surface long enough to react with another ammonia molecule (or fragment) to

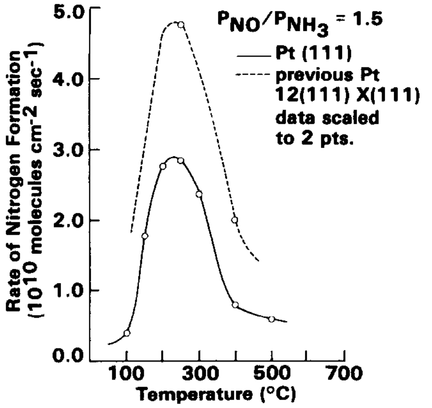

FIG. 3. Reaction rates for the nitric oxide-ammonia reaction as a function of temperature. A temperature reactivity profile from Ref. (*4*) has been scaled to two data points taken during comparative experiments for the Pt(S) – 12(111) × (111) reactivity profile. The total pressure is 6.0 × 10^{-9} Torr.

form molecular nitrogen (*1*). The data taken here indicate that nitrogen formation in excess oxygen is structure sensitive. Data comparing the catalytic activity of the NO + NH_3 reaction on these two surfaces are shown in Fig. 3. (A fairly complete kinetic study of the NO + NH_3 reaction has been published previously (*4*); part of the data for Fig. 3 is taken from those data.) Figure 3 indicates that the NH_3 + NO reaction occurs more rapidly over the Pt(S) – 12(111) × (111) surface than over the Pt(111) surface. This agreement between relative reactivities supports our contention that in excess oxygen nitrogen may be formed sequentially.

CONCLUSION

The introduction of surface step sites increases the rate of ammonia oxidation with a stoichiometric or oxidizing reaction mixture. The difference in the ability of these surfaces to adsorb oxygen atoms can account for the reactivity differences observed. Nitrogen formation in excess oxygen and at stoichiometry is structure sensitive and appears to proceed via an adsorbed nitric oxide intermediate.

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Received May 29, 1979; revised October 18, 1979