JOURNAL OF CATALYSIS 47, 328–332 (1977)

Catalytic Decomposition of Carbon Monoxide on Single Crystalline Ruthenium

KAMAL J. SINGH AND HELEN E. GRENGA

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Received August 30, 1976; revised February 7, 1977

Single crystalline bulk spheres of ruthenium were treated with carbon monoxide at 550°C and 760 Torr for times varying from 6 to 96 hr. After reaction the spheres were examined by reflection high energy electron diffraction (RHEED) and by optical microscopy. It was found that carbon monoxide had decomposed catalytically to produce graphite, which deposited as streamers centered about $\langle 0001 \rangle$, $\langle 10\bar{1}0 \rangle$ and $\langle 10\bar{1}1 \rangle$ poles on the ruthenium surface. The results indicated that surface steps surrounding low index poles were active sites for this reaction, as has been previously observed for nickel.

INTRODUCTION

Knowledge of the role of the catalyst surface is of primary importance in understanding heterogeneous catalysis. It has long been known that relatively few surface sites participate in many of these reactions, and considerable effort has been made to identify the active sites.

In the case of the catalytic decomposition of carbon monoxide on nickel, which deposits graphite on the surface, the active sites have been identified (*1*, *2*) as steps on surfaces oriented near $\{111\}$. Iron and cobalt are also known to decompose carbon monoxide (*3*); and, while ruthenium is known to behave similarly to iron, cobalt and nickel in many reactions involving carbon monoxide (for example, methanation), the decomposition of carbon monoxide on ruthenium has not been previously reported.

If carbon monoxide decomposes on ruthenium, the carbon may be in the form of carbides, as reported for the most active regions of iron (*4*), or it may be in the form of graphite, as reported for the most active regions of nickel (*1*, *2*). A carbide of ruthenium with unknown composition has been claimed to result from the reaction of ruthenium oxide with graphite at 2500°C (*5*). Molten ruthenium reportedly dissolves appreciable amounts of carbon, which precipitates as graphite upon cooling (*5*).

The purpose of the present study was to determine whether or not carbon monoxide decomposes catalytically on ruthenium and, if so, the nature of the products and active sites for the reaction.

METHODS

A ruthenium single crystal rod, obtained from Materials Research Corp., was machined by spark erosion technique to a spherical shape about 0.25 in. in diameter with a stem on one side to facilitate handling. The machined specimen was mechanically polished with successively finer grades of abrasive polishing paper and then with an aqueous suspension of 0.3 μm alumina on a felt cloth. The crystal was then electropolished at about 0°C in an aged (24 hr) solution of 5 g potassium hy-

ISSN 0021-9517

droxide, 6 ml glycerine, and 80 ml distilled water. Electropolishing required 5 to 10 min at 8 to 9 V, dc. After rinsing with distilled water and drying in nitrogen, the specimen was placed in the reaction chamber of the high vacuum system.

The vacuum system, which was capable of about 10^{-7} Torr (1 Torr = 133.3 $N\ m^{-2}$), was constructed primarily of Pyrex glass with a quartz reactor tube. The system was equipped with an oil diffusion pump, liquid nitrogen trap and other standard high vacuum accessories, including bake-out facilities.

After evacuation and bake-out of the system, the specimen was annealed in research grade hydrogen for 1 hr at 550°C. The specimen was then outgased at 550°C for 1 hr and subsequently treated with research grade carbon monoxide at 550°C and 760 Torr for times varying from 6 to 96 hr. The specimen was cooled to room temperature in a vacuum.

After removal from the system, the specimen was examined visually and with optical microscopy. Reflection high energy electron diffraction (RHEED) was used to identify the solid products of the reaction. Efforts to examine the specimen and extraction replicas by electron microscopy, both scanning and transmission, were unsuccessful due to lack of contrast for products (scanning) and difficulties in obtaining replicas from the highly curved surface (transmission).

RESULTS

Reflection high energy electron diffraction revealed only graphite after carbon monoxide treatment; i.e., no oxides or carbides were identified. Table 1 gives RHEED results for two experiments along with *d* spacings of various graphite planes for comparison.

TABLE 1

RHEED Results on Specimens from Reactions IV (6 hr CO Treatment) and VI (48 hr CO Treatment)

Observed *d* spacing		Graphite *d* spacing (*hkl*)
Expt IV	Expt VI	
3.35	3.345	3.35 (002)
—	—	2.13 (100)
2.01	2.044	2.04 (101)
—	—	1.801 (102)
—	1.752	1.675 (004)
1.546	—	1.541 (103)
1.206	1.227	1.230 (110)
—	1.15	1.154 (112)
—	—	1.117 (006)
—	—	1.014 (202)

After a 6 hr treatment with carbon monoxide, only a small amount of graphite deposition located around the $\langle 0001\rangle$ pole was observed by optical microscopy. After reaction times of 12 hr and longer, graphite deposits became heavier and covered larger areas of the ruthenium surface. Comparison of the graphite deposition pattern on the bulk sphere after reaction times of 6, 12, and 48 hr indicated that deposition began near the $\langle 0001\rangle$ poles, then occurred near $\langle 10\bar{1}1\rangle$ and $\langle 10\bar{1}0\rangle$ poles and finally spread outward along the surface from each of these regions to produce the pattern shown in Fig. 1. (The black spot near the center of the sphere is due to light reflection during photography). The basal plane at the center of the light hexagonal region in Fig. 1 appeared to have only a light amount of graphite deposition, even after a 48 hr reaction time; these hexagonal shaped regions centered about the basal planes were present after reaction times of 12 and 48 hr. Farther from the $\langle 0001\rangle$ poles, the graphite deposition became increasingly heavier. The dark graphite deposits on the crystal were separated by narrow bands of lighter deposition. These bands were along the planes of $\langle 11\bar{2}0\rangle$ zones lying between $\langle 0001\rangle$ poles and along planes lying between $\langle 10\bar{1}1\rangle$ poles via the $\langle 11\bar{2}2\rangle$ poles.

Optical microscopy revealed that the graphite near low index poles appeared to be in the form of somewhat poorly defined streamers, which varied in density, shape

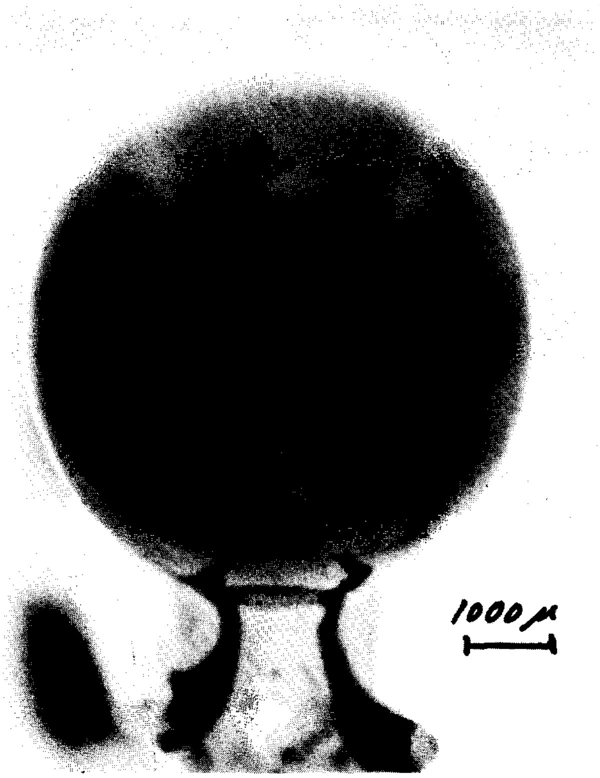

FIG. 1. Ruthenium single crystal sphere after treatment with carbon monoxide for 48 hr at 550°C. The center of the light hexagonal region is a $\langle 0001\rangle$ pole and the light bands radiating from the $\langle 0001\rangle$ pole are $\langle 11\bar{2}0\rangle$ zones.

and size depending upon the ruthenium orientation. The streamers appeared to have heavier graphite deposition at the "head" followed by a trail of lighter deposition. An example of streamers near a $\langle 10\bar{1}0\rangle$ pole is shown in Fig. 2. Some of the streamers in this micrograph appear to have flat heads while others are more pointed.

Examination of numerous micrographs revealed that the streamers were formed in circles about $\langle 0001\rangle$, $\langle 10\bar{1}0\rangle$, and $\langle 10\bar{1}1\rangle$ poles with their heads pointing to the respective low index poles; going away from each of these low index poles, the heads of the streamers became increasingly darker, the trail shorter and less distinct, until finally the graphite appeared as narrow bands.

The graphite was very strongly adherent to the ruthenium surface and could not be removed by wiping with a cloth or by ultrasonic cleaning.

DISCUSSION

The expectation that ruthenium would show a behavior similar to iron, cobalt and nickel for the catalytic decomposition of carbon monoxide was confirmed; graphite was deposited on the surface of ruthenium.

Graphite was first observed on ruthenium $\{0001\}$ regions. This behavior is similar to that shown by nickel in several studies (*1, 6–8*) in that the close packed nickel $\{111\}$ regions were found to be most active. However, after long time reactions graphite deposited equally in all directions around the Ni $\langle 111\rangle$ poles, whereas for ruthenium the planes along $\langle 11\bar{2}0\rangle$ zones in the vicinity of Ru $\langle 0001\rangle$ poles had relatively lighter graphite deposition. Another major difference between Ru and Ni was that there were three very active crystal regions on ruthenium, $\{0001\}$, $\{10\bar{1}0\}$, and $\{10\bar{1}1\}$, compared to only one on nickel, $\{111\}$.

It was anticipated that the morphology of the graphite deposits could be related to the active sites for this catalytic reaction on ruthenium by comparison with graphite deposit morphology previously reported (*9*) on single crystal nickel spheres. The observation that (i) graphite deposited in circular patterns around the low index poles, $\langle 0001\rangle$, $\langle 10\bar{1}0\rangle$, and $\langle 10\bar{1}1\rangle$, and (ii) the density of the graphite streamers increased going away from the poles were similar to observations on graphite deposition about the $\langle 111\rangle$ poles on single crystal bulk spheres of nickel. Thus it appears that surface steps on low index regions of ruthenium are active sites for this reaction, as has been previously reported for nickel (*1*, *2*).

For a spherically shaped single crystal, a flat low index plane is located directly at the pole with the same index, while going away from the pole there are terraces of this plane separated by steps between the terraces. Since the crystal is spherical, the steps form a circular pattern centered about the pole; and the distance between the successive steps will decrease as the distance from the pole increases. Thus, deposition at such steps leads to the pattern of streamers cited above.

Certainly, a number of questions are not answered by this study; for example, the size of graphite crystallites, epitaxial relations between graphite and ruthenium, whether or not carbides are formed during the reaction and whether the graphite contains any ruthenium. Additional studies on flat surfaces oriented near the three low-index poles are currently underway and should provide suitable electron microscopy specimens which are necessary to answer some of these questions.

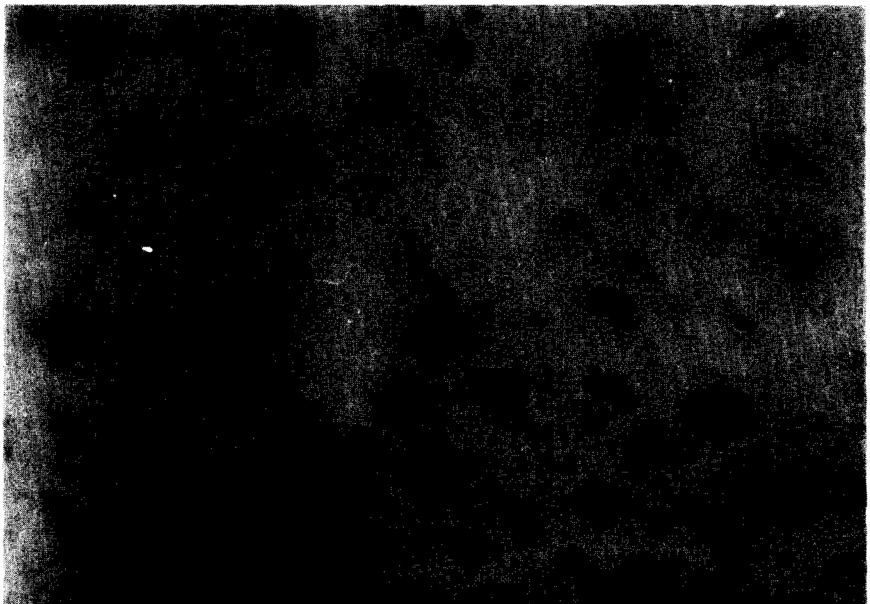

FIG. 2. Optical micrograph of graphite streamers near $\langle 10\bar{1}0\rangle$ pole. Double arrow points toward $\langle 10\bar{1}0\rangle$ pole; single arrows indicate several streamer "heads."

ACKNOWLEDGMENT

The authors gratefully acknowledge support of this work by the National Science Foundation.

REFERENCES

1. Grenga, H. E., and Lawless, K. R., *J. Appl. Phys.* **43**, 1508 (1972).
2. Grenga, H. E., PhD dissertation, Univ. of Virginia, 1967.
3. Kehrer, V. J., Jr., and Leidheiser, H., Jr., *J. Phys. Chem.* **58**, 550 (1954).
4. Ratliff, J. T., PhD dissertation, Georgia Tech. 1968.
5. Hansen, M., "Constitution of Binary Alloys," p. 378. McGraw-Hill, New York, 1958.
6. Gwathmey, A. T., and Cunningham, R. E., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 10. Academic Press, New York, 1958.
7. Gwathmey, A. T., and Cunningham, R. E., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky, and P. B. Weisz, Eds.), Vol. 9, p. 25. Academic Press, New York, 1957.
8. Gwathmey, A. T., *Rec. Chem. Progr.* **14**, 117 (1953).
9. Cox, E. *et al.*, *Actes Congr. Int. Catal., 2nd, 1960* p. 1605 (1961).