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NOTE

Relationship of Surface Composition to Enhanced Methanation Activity over Cobalt Single Crystals

The enhanced methane synthesis over cobalt foils previously reported is here related to the surface composition of single crystal cobalt samples activated under the same surface treatments utilized in the previous work. It is observed that the enhanced methanation activity can be related to the presence of a surface cobalt oxide on the activated samples.

Recent mass spectrometric measurements of the kinetics of the methanation reaction over polycrystalline cobalt foils reported by Palmer and Vroom (*1*) have indicated enhanced activity over specifically treated samples. We have undertaken a study of the surface composition of single crystal cobalt samples exposed to the activation treatments of Palmer and Vroom (*1*) in order to more fully understand the basis for the previously observed enhancement. Auger electron spectroscopy (AES), X-ray photoemission spectroscopy (XPS), and low-energy electron-diffraction (LEED) were utilized in this study done under ultrahigh vacuum (UHV) conditions. Reaction kinetics could not, however, be documented in this study due to low pressure exposure conditions ($\sim 10^{-6}$ Torr; 1 Torr = 133.3 N m^{-2}) and poor sample surface area to other metal surface area ratio in the vacuum chamber ($\sim 10^{-4}$).

The cobalt samples used were ultrahigh purity single crystals obtained from the Cornell Materials Science Center (*2*). The samples (17 × 7 × 0.5 mm) were cut and highly polished to expose either the (0001) or the $(10\bar{1}0)$ face. Most of the information reported here has been obtained from studies of (0001) cut crystals, however, limited studies were made on $(10\bar{1}0)$ cut crystals with results similar to those obtained on the (0001) samples.

The samples were mounted on a UHV compatible sample goniometer having the capabilities of both heating the crystals to above 1300°K and cooling to 78°K. The samples were mounted on the end of an electrically grounded molybdenum cup which could be heated from the inside by electron bombardment. This facilitated the AES, XPS, and LEED measurements at high temperatures due to the absence of electric or magnetic fields within the scattered electron monitoring region during heating. Temperatures were monitored by by a chromel/alumel thermocouple spot welded to the crystal sample. The surfaces of the samples were cleaned in the UHV chamber by inert gas ion bombardment. A total of 15 hr of krypton ion bombardment at 300 $\mu A/cm^2$ and 1 keV and intermittant annealing in vacuum to 900°K was required to remove all impurities from the cobalt surface to the 1% of a monolayer sensitivity of AES (Fig. 1a). Once cleaned the crystals were subject to the two cobalt foil activation procedures used by Palmer and Vroom (*1*).

Procedure I. Heating in oxygen at 900°K followed by reduction in hydrogen above 900°K. Use at methanation reaction tem-

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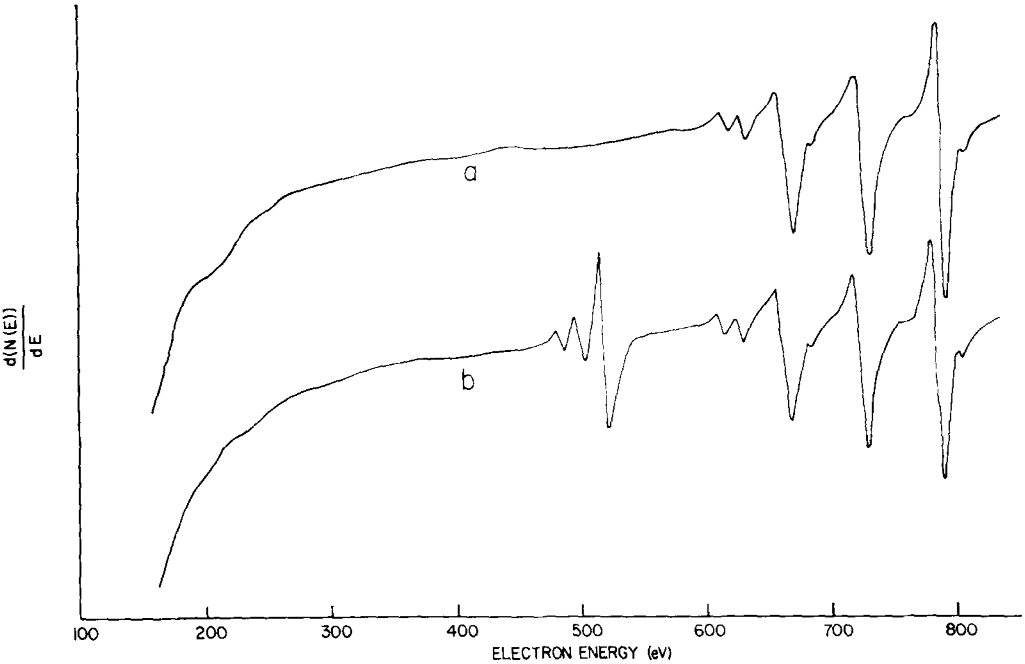

FIG. 1. (a) Auger electron spectrum [$dN(E)/dE$] of the cleaned cobalt crystal. No contaminant lines are present. (b) Auger electron spectrum [$dN(E)/dE$] of the cobalt crystal after exposure to oxygen for 5000 L at 900°K. The features at about 500 eV are due to oxygen.

perature of 525 to 600°K. *No* enhanced methanation activity.

Procedure II. Heating in oxygen at 900°K followed by reduction in hydrogen at 525 to 600°K. Use at methanation reaction temperature of 525 to 600°K. *Enhanced* methanation activity.

To maintain the possibility of *in situ* study by AES, XPS, and LEED, the cobalt samples were exposed to oxygen and hydrogen in moderate doses (5000 to 20,000 L) and at pressures not exceeding 5×10^{-6} Torr; this is in contrast to the 10^9 L or greater exposure and the 1 Torr pressure range used by Palmer and Vroom. However, we believe that our lower exposures and pressures are simply limiting the depth to which our samples have been perturbed by the activation procedures and not altering the chemical or physical basis of the perturbation.

The initial exposure of the clean cobalt surface to oxygen was done at 5×10^{-6} Torr and 900°K to a total exposure of 5000 L. At this point, the AES spectrum revealed large amounts of oxygen present at the surface (Fig. 1b). LEED measurements indicated a diffraction pattern consistent with the formation of CoO (*3*), and XPS measurements corroborated the existence of principally CoO at the surface (Fig. 2). This is consistant with previous XPS studies of the oxidation of cobalt foils (*4*). The small amount of metallic component to the cobalt $2p_{3/2}$ signal in Fig. 2 also indicates that the thickness of the oxide film is significantly greater than about 20 Å (the escape depth of the 657 eV cobalt $2p_{3/2}$ photoelectrons (*5*)). A depth profile of the oxidized surface obtained by monitoring Auger electron spectra as a function of krypton ion bombardment dose in fact indicates that the oxide thickness, or at least significant oxygen penetration into the cobalt lattice, is greater than 1000 Å (Fig. 3). It should also be noted here that

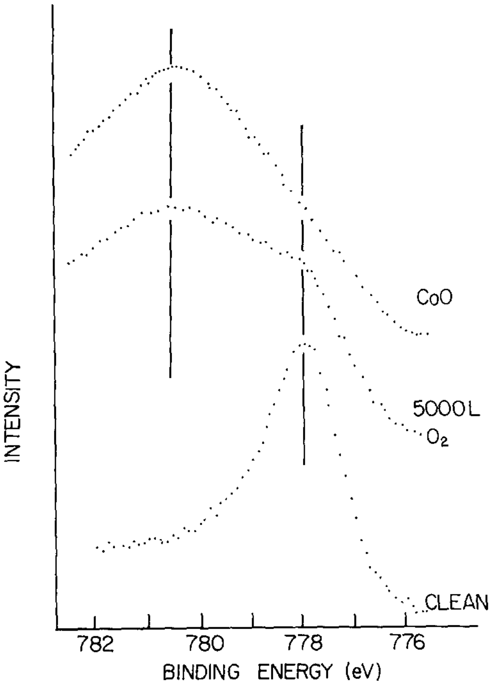

FIG. 2. X-ray photoemission spectrum ($N(E)$) of the $2P_{3/2}$ line of the cobalt crystal after exposure to 5000 L of oxygen at 900°K compared to that of clean cobalt and that of CoO.

such oxygen exposure results in a sample surface that is no longer shiny (originally highly polished) but grey with a matte finish similar to that reported by Palmer and Vroom for their samples. The optical visibility of the change in surface texture and coloration under oxygen exposure is also indicative of a change in surface structure or composition which is of the order of the wavelength of light or more in thickness.

The oxygenated sample was then exposed to hydrogen at 5×10^{-6} Torr and 900°K as required by activation Procedure I. The AES $dN(E)/dE$ peak-to-peak oxygen signal to cobalt signal ratio is plotted as a function of hydrogen exposure in Fig. 4a. It can be seen that the ratio decreases to nearly zero at 9000 L H_2 exposure. In addition, subsequent heating in 5×10^{-10} Torr vacuum at 600°K (the methanation reaction temperature) for 35 min yielded no change in the AES oxygen signal, i.e., little or no oxygen present at the surface. After such a treatment it should also be noted that the surface of the sample had returned to its original shiny condition.

After a subsequent equivalent oxygen–hydrogen treatment, the sample was exposed at 600°K not in vacuum, but in a 40:1 ratio H_2/CO gas mixture at a total pressure of 1×10^{-6} Torr for 30 min. The small size of our sample and the presence of various large area metallic surfaces in our stainless steel UHV chamber prevented any meaningful measurements of the cobalt surface-dependent methanation reaction. However, AES measurements were made of the surface composition of the cobalt sample after the H_2/CO exposure to note whether the cobalt surface was contaminated during the methanation reaction. The only contaminant observed was carbon at a level of approximately 20% of a monolayer and was probably due to the reduction of adsorbed CO to a graphite residue (*1*). Cobalt foils activated by Palmer and Vroom under Procedure I did not show enhanced methanation activity.

After inert gas ion-bombardment cleaning of the surface carbon contamination and reoxygenating the cobalt surface as initially described, the sample was treated as outlined by Procedure II. The oxygenated sample was heated to 575°K in 5×10^{-6} Torr hydrogen for a total exposure of 24,000 L. Figure 4b shows the dependence of the AES peak-to-peak oxygen to cobalt signal ratio on hydrogen exposure. It can be seen that the ratio is very slowly decreasing with exposure (compare to Fig. 4a) and remains at nearly half of the original value even after a 24,000 L exposure. At this point, the sample surface was still matte grey in finish. It is believed that the slow decrease with H_2 exposure in the amount of oxygen at the surface is strongly oxygen diffusion limited at the lower reduction temperature of 575°K. The sharp initial decrease of the ratio (compared to Fig. 4a) indicates a rapid oxygen depletion of the oxygenated surface region by the initial hydrogen exposure, with the decreasing slope of the ratio supporting an oxygen diffusion limited removal rate of the oxygen (*6*). In addition to the high residual surface oxygen content under Procedure II activation, of further interest is the observation that the surface oxygen content significantly increases upon heating in vacuum for 45 min (Fig. 4b). The surface oxygen concentration increases to nearly 80% of the initial oxygenated value and is present in a CoO form as determined by XPS and LEED, with the oxide probably several hundreds of angstroms thick. Heating in the low pressure H_2/CO mixture at 600°K (the methanation temperature) for 45 min results in an initial increase in surface oxygen content with a subsequent decrease as a function of time.

Under activation Procedure II it is seen that unless hydrogen exposures of approximately 10 to 20 times the original oxygen exposure are used, the surface will retain a large amount of CoO which will increase initially when the sample temperature is increased to the reaction operating temperature. CoO or oxygen surface contamination was not observed under activation Procedure I under which no methanation enhancement was reported (*1*). Therefore, the large amount of surface oxide present in the Procedure II activated cobalt sample is believed to be related to the reported enhanced methanation activity of such

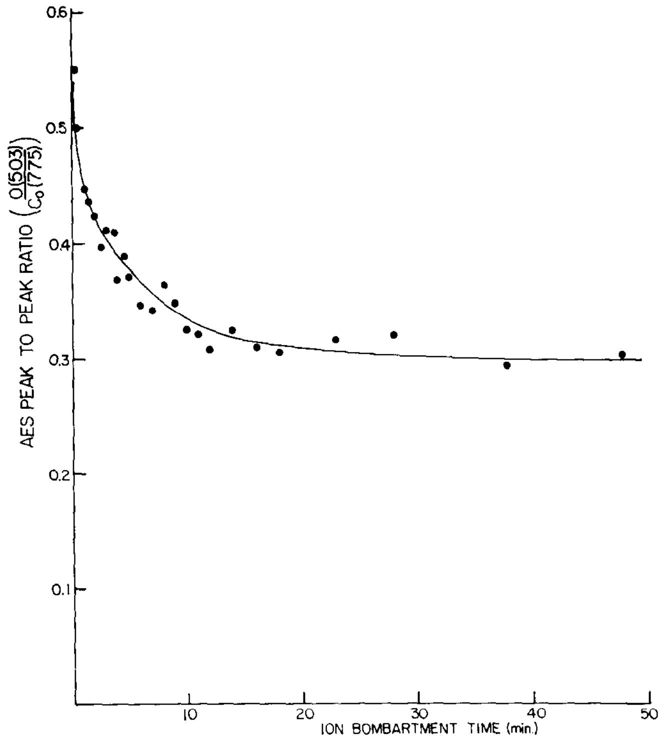

FIG. 3. Ion bombardment depth profile of the AES oxygen (503 eV) to cobalt (775 eV) ratio of the oxygenated cobalt sample (5000 L O_2 at 900°K) at 78°K–900 eV Kr^+ at 300 $\mu A/cm^2$. Ten minutes bombardment time equates in depth to approximately 150 to 200 Å.

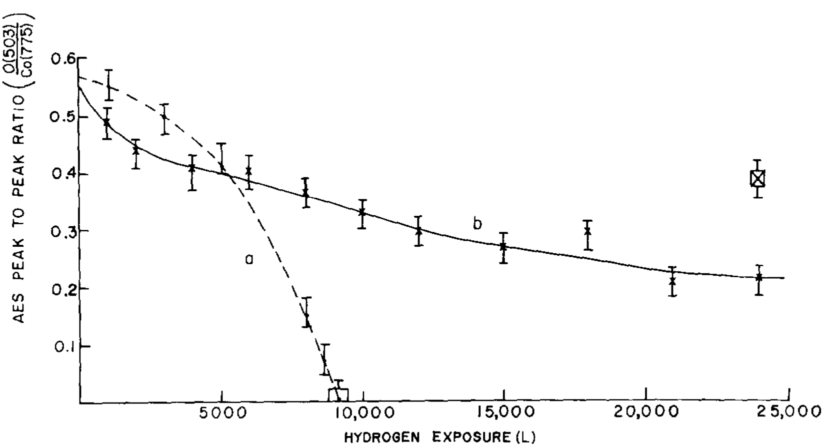

FIG. 4. AES peak-to-peak oxygen (503 eV) to cobalt (775 eV) ratio vs H_2 exposure of oxygenated cobalt surface (5000 L O_2 at 900°K) (a) vs H_2 exposure at 900°K, (b) vs H_2 exposure at 575°K. The square points indicate the O to Co ratio after prolonged heating in 5×10^{-10} Torr vacuum subsequent to the H_2 treatments (see text).

samples. As noted previously, equivalent results with respect to surface oxide formation were obtained for (0001)- and (10$\bar{1}$0)-oriented samples. As a result, there is minimal surface crystallographic specificity in the formation of the surface oxide under activation Procedure II. Our single crystal studies can therefore be directly correlated with the work of Palmer and Vroom done on polycrystalline samples.

CO dissociation with the formation of a residual carbon layer has been noted to be an important step in the methanation reaction (*1*, *7–9*), however, it is generally believed that transition metal oxides are more active in CO oxidation than reduction (*9*, *10*). Our statement of CoO playing an important role in methanation enhancement is not in agreement with this point however, the enhancement of the hydrogenation of CO over iron due to the presence of an oxidized surface has also been recently observed (*9*). The oxide is reduced during the methanation reaction, and it is believed that the reduction process produces small metallic clusters which are very active as compared to the clean metal surface (*9*). It is therefore proposed that the large amount of CoO present at the cobalt surface under activation Procedure II is responsible for the reported enhanced methanation activity over such treated surfaces.

In summary the reason for the methanation reaction enhancement over specifically activated cobalt films has been related to the observation of a large amount of surface CoO present due to the specific activation procedure.

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REFERENCES

1. Palmer, R. L., and Vroom, D. A., *J. Catal.* **50**, 244 (1977).
2. Addis, B., Cornell Materials Science Center, Bard Hall, Ithaca, New York.
3. Ignatiev, A., Lee, B. W., Taylor, J. A., and Rabalais, J. W., *in* "37th Conf. Physical Electronics, Stanford, Calif., June 1977."
4. Brundle, C. R., Chuang, T. J., and Rice, D. W., *Surface Sci.* **60**, 286 (1976).

5. Brundle, C. R., *J. Vacuum Sci. Technol.* **11**, 212 (1974).
6. Kofstad, P., "High-Temperature Oxidation of Metals," Wiley, New York, 1966.
7. Wentrick, P., Wood, B., and Wise, H., *J. Catal.* **43**, 363 (1976).
8. Beecroft, T., Miller, A., and Ross, J., *J. Catal.* **40**, 281 (1975).
9. Dwyer, D., and Somorjai, G., *J. Catal.* **52**, 291 (1978).
10. Rabo, J., Rish, A., and Poutsma, M., *J. Catal.* **53**, 295 (1978).

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