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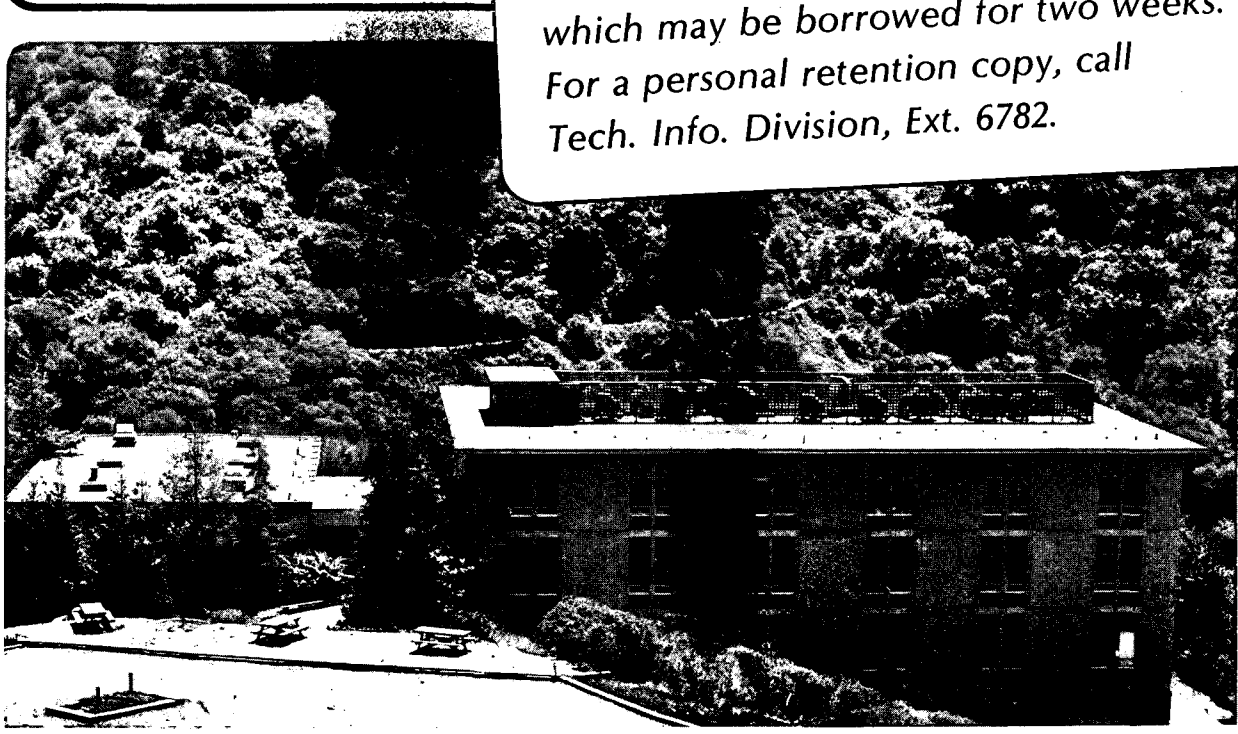

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It was recently reported that a clean polycrystalline Re foil is an efficient catalyst for the synthesis of ammonia from H_2 and N_2 (1,2). As compared with the traditional iron catalyst, the Re foil was found to be more active than the most effective iron single crystal face, e.g., the Fe(111) (3).

In this letter we report the first ammonia synthesis study over rhenium single crystal surfaces, under pressure conditions approaching those used industrially (20 atmospheres). We found an unprecedented structure sensitivity for this reaction on different faces: The Re(0001) basal plane is practically inactive, within our detection limits, while the open Re(11$\bar{2}$0) crystal plane was found to be more active than the most active iron single crystal surface. The Re(10$\bar{1}$0) surface was studied as well and found to be only slightly active. The activity ratio at a crystal temperature of 870 K being 1:50:1700 for the Re(0001), Re(10$\bar{1}$0) and the Re(11$\bar{2}$0) planes respectively. The very small detectable activity of the Re(0001) probably arises from the crystal edges. The activation energies for the NH_3 synthesis on both the Re(11$\bar{2}$0) and the polycrystalline foil were found to be the

same, e.g., 20 ± 1 kcal/mole, which is very close to the value found on the Fe(111) crystal, e.g., 19.4 kcal/mole (3).

The apparatus used (4) consists of a ultra high vacuum (UHV) chamber equipped with a four grid retarding field analyzer for low energy electron diffraction (LEED) and Auger spectroscopy measurements to determine surface structure and chemical composition respectively. A quadrupole mass spectrometer is used for gas analysis and thermal desorption spectroscopy and an ion sputtering gun for sample cleaning. A high pressure cell which enclosed the sample and separated it from the rest of the UHV chamber is connected to an external loop. The 20 atmospheres mixture of reactants and product gases were continuously circulated over the single crystal samples (which were resistively heated), via a positive displacement pump. Gas samples were periodically withdrawn through a sampling valve into a photoionization detector, having 10.2 eV photons, to determine the ammonia partial pressure (nitrogen and hydrogen are not detectable at this photon energy).

The single crystal samples were typically 1 cm^2 discs 1 mm thick, that were oriented and then polished on both sides by standard metallurgical techniques. The only major contamination was carbon but is could be easily removed by Ar^+ ion sputtering (8×10^{-6} A/cm^2 at 500 V) followed by annealing at 1250°C for 7 min and then, if necessary, an additional oxygen treatment at 2×10^{-7} Torr for 2 min with the crystal held at 500°C. Surface structures were then verified using LEED.

The relative structure sensitivity measurements are shown in Fig. 1. These values correspond to absolute rates of 1.8×10^{17} NH_3 molec/$cm^2 \cdot$sec, 5.4×10^{15} NH_3 molec/$cm^2 \cdot$sec and 1.1×10^{14} NH_3 molec/$cm^2 \cdot$sec for the Re(11$\bar{2}$0), Re(10$\bar{1}$0) and the Re (0001) surfaces respectively. The value given for the basal plane e.g., Re(0001) is actually the detection limit of our apparatus, therefore the true rate on this surface is believed to be even smaller. At a temperature of 870 K, some activity could be detected if the Re(0001) crystal surface was previously sputtered at room temperature for 5 minutes with 500 V Ar^+ ions. This activity vanished after annealing the surface at 1200°C for 7 minutes, where a clear hexagonal pattern that is characteristic of the ordered (0001) rhenium crystal surfaces appear in the LEED. Above the relative activity bars in Fig. 1, a schematic presentation of the surface unit cell tructure of each of the studied surfaces is shown. In the least active planes, e.g., Re(0001) and Re(10$\bar{1}$0) the topmost atoms have 9 and 6 coordination numbers (C_9 and C_6 atoms) respectively.

The motivation for choosing the Re(11$\bar{2}$0) single crystal surface as a possible active plane in the synthesis of ammonia, stems from the general similarity of behavior observed between the Re and the Fe catalysts for this synthesis. Detailed studies of the mechanism of ammonia synthesis over iron catalysts (5-10) indicate that the dissociative adsorption of N_2 is the rate limiting step. Related studies on iron single crystals have shown that on the Fe(111) face, nitrogen dissociates with nearly zero activation energy (10), while

the adsorption on the Fe(110) and the Fe(100) faces is activated, therefore much slower. A direct measurement of the reaction rates on these single crystal surfaces for the ammonia synthesis have shown that in agreement with the adsorption studies (10), the Fe(111) face is far more active than the Fe(100) or the Fe(110) faces (3). The importance of the (111) crystal face for NH_3 production was suggested to be related to the C_7 coordination atoms (6,7) which are in the second surface layer.

The high reactivity observed with the Re(11$\bar{2}$0) plane (see Fig. 1) may also be related to the existence of C_7 coordination atoms at the topmost layer of this plane, as shown in Fig. 1. This correlation may imply that as with the iron catalyst, also for Re the rate limiting step involves the dissociative adsorption of N_2, which has yet to be proven. The C_7 atoms are, however, arranged differently in the most active iron face, e.g., Fe(111) than in the most active Re face studied so far, e.g., Re(11$\bar{2}$0). This difference may indicate the possibility that nitrogen bonds differently to these sites on rhenium and iron. Both Fe(111) and Re(11$\bar{2}$0) are very open crystal faces, thus enabling nitrogen atoms to diffuse freely along the troughs, which might be important for the dissociation mechanism of nitrogen on these planes.

It cannot be ruled out, therefore that at least for the Re catalyst, active sites other than the C_7 coordination atoms are more important for the ammonia synthesis. This is supported by the observation of still higher activity on polycrystalline rhenium foil

catalysts than that exhibited by the Re(11$\bar{2}$0) under identical conditions.

A (1 x 1) LEED pattern of the Re(11$\bar{2}$0) is seen if the catalyst is kept at the reaction temperature while evacuating the reactants and products from the high pressure cell prior to opening it to the UHV chamber for the LEED measurements. This may indicate that the Re(11$\bar{2}$0) surface is stable under the reaction conditions and does not undergo reconstruction.

We have also studied the effect of added potassium atoms on the reaction yield. With all the surfaces studied, the polycrystalline foil, the (0001), (10$\bar{1}$0) and the (11$\bar{2}$0) planes of Re single crystals we could not find any change in reaction rates up to K coverages of one-half of a monolayer. The K atoms were stable on the surface during the reaction at the catalyst's temperature range we have studied as indicated by Auger electron spectroscopy. These are particularly interesting results in view of the large effect on the reaction rate observed on iron that was attributed to K atoms adsorbed on the catalysts (9-12).

Finally, during the ammmonia synthesis on both the Re polycrystalline foil and on the Re (11$\bar{2}$0) single crystal plane, a highly stable nitride overlayer was formed, with a post-reaction coverage estimated at about half a monolayer. The synthesis seem to occur on top of this overlayer with undiminished rates. Further studies of

this system and the details of the structure sensitivity, the role of K atoms and the nature of the interaction between nitrogen molecules and atoms on Re single crystals are in progress.

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FIGURE CAPTIONS

Fig. 1. Relative activity of ammonia synthesis for three rhenium single crystal surfaces. 1000 on this relative scale is equivalent to a rate of 4.6×10^{16} NH_3 molec/cm^2 sec and all the rates are measured at crystal temperature of 870 K, and total reactants pressure of 20 atmospheres (H_2:N_2 = 3:1). The solid circles above the relative activity bars represent the topmost atoms while the dotted circles are atoms in the second layer.

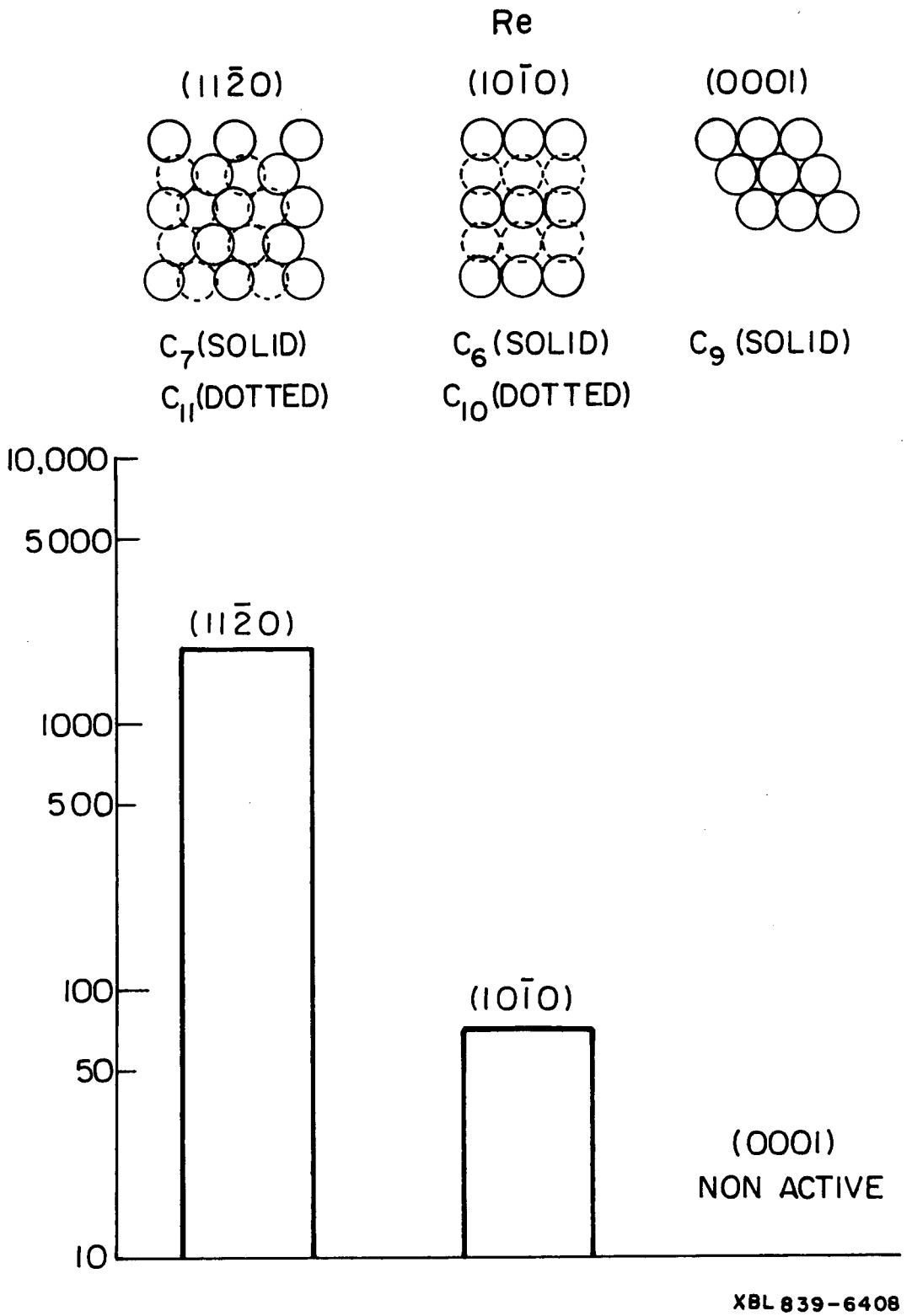
Re
(11$\bar{2}$0)
(10$\bar{1}$0)
(0001)
C_7(SOLID)
C_{11}(DOTTED)
C_6(SOLID)
C_{10}(DOTTED)
C_9 (SOLID)
10,000
5000
1000
500
100
50
10
(11$\bar{2}$0)
(10$\bar{1}$0)
(0001)
NON ACTIVE
XBL 839-6408

Fig. 1

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