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# The Importance of $C_7$ Sites and Surface Roughness in the Ammonia Synthesis Reaction over Iron

In this note we present data which further supports the contention that $C_7$ sites (Fe atoms with seven nearest neighbors) are those most active in iron ammonia synthesis catalysts. Previous work in our laboratory showed that the synthesis of ammonia from its elements is a very structure sensitive reaction (*1*). It was found that the relative order of activity for ammonia formation was Fe(111) > Fe(100) > Fe(110). Related studies on iron single crystals have shown the same relative order of activity for dissociative chemisorption of nitrogen (*2, 3*), the rate-limiting step in the ammonia synthesis reaction (*4, 5*). The nitrogen dissociation results were explained by the observation of an increasing activation energy for dissociation in the sequence Fe(111) < Fe(100) < Fe(110) (*4*).

It has been suggested that the high activity of the Fe(111) surface is related to the presence of $C_7$ coordination sites, which are in the second and third layers and are exposed to the reactant gases (*1, 6*). A second possibility that could not be excluded from the previous results is that since the Fe(111) surface is very open (second and third layer atoms are exposed), the high catalytic activity is due to the high surface free energy and low work function characteristic of a rough surface. High pressure kinetic results presented here of ammonia synthesis over Fe(210) and Fe(211) surfaces in addition to the Fe(111), Fe(100), and Fe(110) surfaces show that the presence of highly coordinated sites is more important than surface roughness for high catalytic activity.

The apparatus used (*1*) consists of an ultrahigh vacuum (UHV) chamber with a retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) to determine surface structure and composition, respectively. An ion sputtering gun is used for sample cleaning. A high pressure cell which can be closed to isolate the sample from the UHV environment is connected to an external loop. The reactant gases, 15 atm hydrogen and 5 atm nitrogen, were continuously circulated over the single crystal samples via a positive displacement pump. Gas samples were periodically withdrawn through a sampling valve into a photoionization detector with a 10.2-eV lamp to determine the partial pressure of ammonia (nitrogen and hydrogen are not detectable at this photon energy). After reaction the cell is evacuated and reopened to UHV where the sample is analyzed by LEED and AES. The single crystal samples used were on the average 1-$cm^2$ disks about 1 mm thick. They were cut and polished by standard metallurgical techniques. The major impurities in the samples were sulfur and carbon. The sulfur was removed by prolonged sputtering ($4–5 \times 10^{-6}$ $A/cm^2$) while the sample was held at 873 K. Carbon was removed by treating the sample with $10^{-7}$ Torr of oxygen while sputtering. The samples were annealed at 873 K for 2 min after sputtering. Surface structures were verified by LEED. The ammonia synthesis rate was determined under identical conditions over all five different iron single crystal samples in this study (20 atm of a stoichiometric mixture of $N_2$ and $H_2$ at 673 K).

Schematic representations of the five iron crystal unit cells are shown in Fig. 1. The difference in surface roughness between the different planes can be quantified by the use of work function measurements

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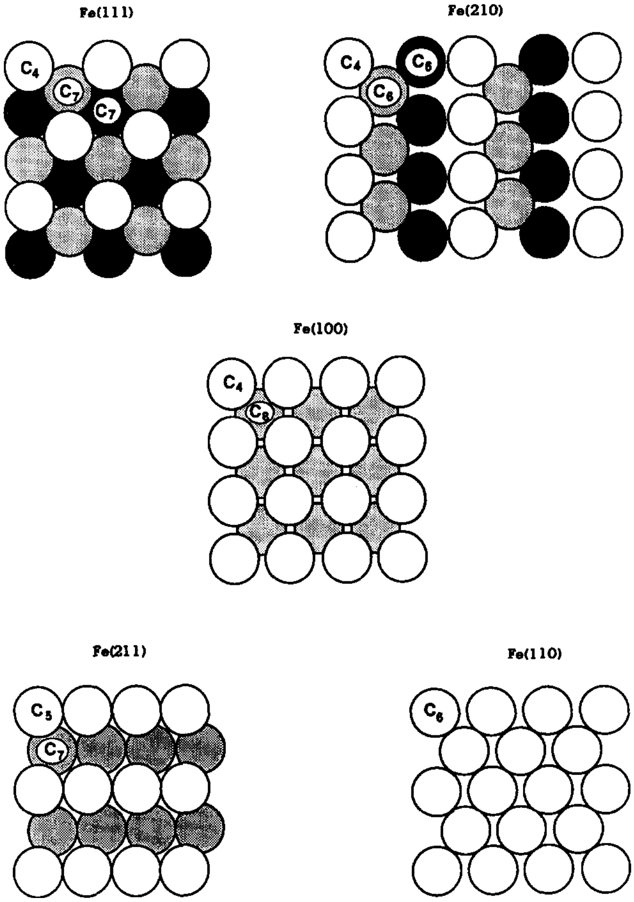

FIG. 1. Schematic representations of the five iron single crystal surfaces. The coordination number for each surface atom is indicated.

(close packed faces have higher work functions then open faces) (*7*). The work functions of all the iron faces we have studied are not available but those of tungsten, another bcc metal which shows structure sensitivity toward the decomposition of ammonia similar to iron (*8*), have been tabulated (*9*). The work function of the tungsten surfaces increase in the following order: $\phi_{210} < \phi_{111} < \phi_{100} < \phi_{211} < \phi_{110}$. The Fe(210) plane contains no $C_7$ sites but it is an open face exposing, second and third layer atoms, much like the Fe(111) plane while the Fe(211) crystal contains $C_7$ sites but it is less open then the Fe(100) face based on the work function measurements. The relative rates of ammonia synthesis shown in Fig. 2 clearly show that the Fe(211) crystal orientation is almost as active as the Fe(111) plane while the Fe(210) face is less active then the Fe(100) plane. If surface roughness was the important ingredient for an active catalyst then we would expect the Fe(210) face to be the most active face and the Fe(211) plane to be less active then the Fe(100) face. Our results are contrary to this and we must conclude that the $C_7$ sites (the most highly coordinated surface site Fe can expose) are more important then surface roughness in the ammonia synthesis reaction.

Theoretical work that correlates high catalytic activity with highly coordinated sites (i.e., the $C_7$ site in Fe) has been performed by Falicov and Somorjai (*10*). Their calculations suggest that highly coordinated

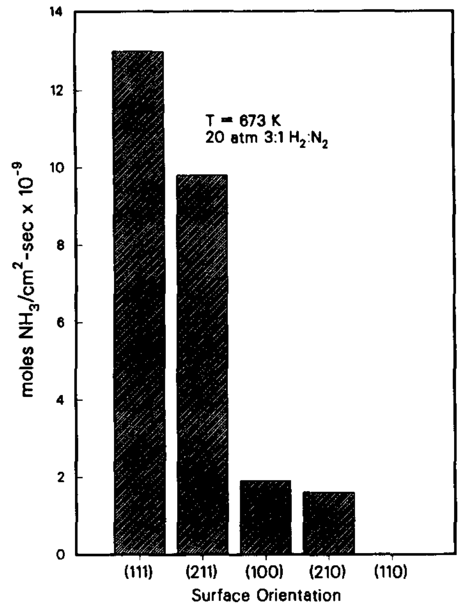

FIG. 2. The rate of ammonia synthesis over the five surfaces studied exhibiting the structure sensitivity of the reaction.

metal atoms will show the greatest catalytic activity because these are the atoms which experience the largest electronic charge fluctuations within the solid. Since the Fe(111) and Fe(211) crystal faces are the only samples used in this study which expose highly coordinated, bulk-like metallic atoms to the reactant gases (nitrogen and hydrogen) they would be expected to show increased catalytic activity. The same conclusions can be drawn from the structure sensitivity of rhenium in the ammonia synthesis reaction (*11*). Here the Re(11$\bar{2}$1) face was found to be the most active crystal orientation studied. Like iron where the Fe(111) and Fe(211) faces contain highly coordinated $C_7$ sites, the Re(11$\bar{2}$1) plane exposes highly coordinated $C_{11}$ and $C_{10}$ sites. Surface roughness on the ammonia synthesis catalyst is only important to the extent that it can expose these highly coordinated surface atoms.

## ACKNOWLEDGMENTS

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D. R. STRONGIN
J. CARRAZZA
SIMON R. BARE
G. A. SOMORJAI

*Materials and Molecular Research Division*
*Lawrence Berkeley Laboratory and Department of Chemistry*
*University of California*
*Berkeley, California 94720*

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