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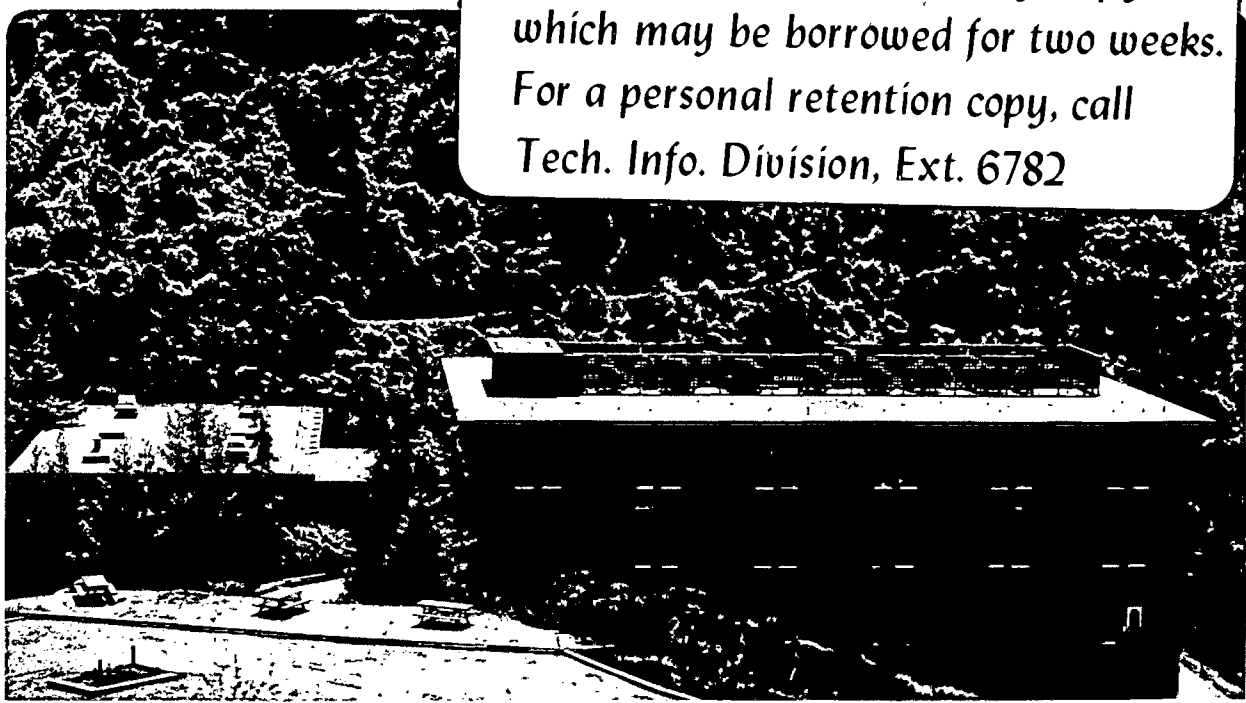
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STRUCTURE SENSITIVITY IN THE IRON SINGLE  
CRYSTAL CATALYSED SYNTHESIS OF AMMONIA

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Since the beginning of this century, the kinetics of the iron-catalysed synthesis of ammonia has been subject to many investigations, and there has been considerable uncertainty concerning details of the mechanism of the reaction [1-3]. We report the first direct and therefore unambiguous measurement of the surface structure sensitivity of the iron-catalysed ammonia synthesis reaction using the (111), (100), and (110) crystal faces of iron and operating at pressures approaching those used industrially (20 atmospheres). The Fe(111) face was found to be the most active, the activity ratio being 450:28:1 for the Fe(111), Fe(100), and Fe(110) planes. We have also observed the formation of a strongly bound nitrogen species during the reaction, in the presence of which ammonia continues to be produced.

The apparatus [4] consisted of a stainless steel ultrahigh vacuum chamber equipped with a 3-grid retarding field analyser for Auger and LEED measurements of the surface composition and structure, a residual gas analyser, an ion gun for specimen cleaning and a high pressure cell connected to an external loop. Reactant and product gases at a total pressure of 20 atmospheres were continuously circulated over the heated iron crystal specimen by a positive displacement pump; samples, periodically withdrawn using a gas chromatograph type sampling valve, were passed via a nitrogen carrier through a photoionisation detector in order to determine the amount of ammonia in the loop. Ammonia was the only species present which could be detected by the photoionisation detector obviating the need for a separating column.

Circular ion specimens with crystal faces (111), (110), and (100) were spark-cut from a high purity (4N) single crystal rod and diamond polished, the final dimensions being approximately 6 mm diameter and 1 mm thickness. Sulphur and carbon were found to be the principal contaminants after this procedure,

but could be removed by several days of heating at 800°C in 1 atmosphere of hydrogen, followed by many cycles of argon ion bombardment and annealing at 700°C. In order to minimise the catalysis occurring on ill-defined iron surfaces, platinum foil was spot-welded to the rough edges of the specimens.

Results of measurement of structure sensitivity are shown in Table I from which it can be seen that the (111) surface of iron catalyses the synthesis of ammonia from hydrogen and nitrogen at a rate which is at least 450 times faster than that of the ordered (110) surface and 16 times faster than that of the ordered (100) surface. Our result is consistent with the low pressure chemisorption studies of Ertl and coworkers [2] where it was reported that the rate of dissociative chemisorption of nitrogen is greatest on the (111) plane of iron and least on the (110) plane, and also with previous suggestions [1-3,5] that this step is rate-determining in the ammonia synthesis reaction.

The (111) plane of iron contains both seven-coordinated ( $C_7$ ) and four-coordinated ( $C_4$ ) atoms, whereas the (110) and (100) planes contain only six-coordinated ( $C_6$ ) and  $C_4$  atoms, respectively. The large variation in rates of ammonia synthesis on the various planes (Table I) and the anomalously high catalytic activity that we have also detected on the (110) and (100) planes when deliberately disordered by ion bombardment, lend considerable support to the proposals of Boudart [3] and others [6,7] regarding the importance of clusters and  $C_7$  iron atoms as components of the active site on the catalyst surface.

Although bulk nitrides of iron are thermodynamically unstable under the conditions of these experiments, we have observed the formation of a long-lived, strongly-bound nitrogen species during the synthesis reaction on both Fe(111) and Fe(100) crystal faces in the presence of which ammonia continued to be produced at an undiminished rate. The catalytic significance of this somewhat surprising observation has yet to be determined.

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Table I: Ammonia Synthesis-Surface Structure Sensitivity

<u>Catalyst Surface</u>	<u>Area (cm<sup>2</sup>)</u>	<u>Rate(a). (moles NH<sub>3</sub> cm<sup>-2</sup>x<sup>-1</sup>)</u>
Fe(111)	0.63	4.6 x 10 <sup>-8</sup>
Fe(100), ordered	0.80	2.8 x 10 <sup>-9</sup>
Fe(110), ordered	0.57	0(b)
Fe(100), disordered (c)	0.80	4.5 x 10 <sup>-9</sup>
Fe(110), disordered (c)	0.57	9.7 x 10 <sup>-10</sup>

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(a) Total pressure, 20 at.;  $P_{H_2}/P_{N_2} = 3/1$ ; temperature = 798 K

(b) Detection limit  $\sim 1.1 \times 10^{-10}$  moles NH<sub>3</sub> cm<sup>-2</sup>s<sup>-1</sup>

(c) Argon ion bombardment ( $1.5 \times 10^{-5}$ ) Acm<sup>-2</sup> for 10 minutes at 500 V)



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