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## MECHANISM OF THE SYNTHESIS OF AMMONIA ON IRON CATALYSTS

EX AEDIBVS ACADEMICIS IN CIVITATE VATICANA

## MECHANISM OF THE SYNTHESIS OF AMMONIA ON IRON CATALYSTS

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SUMMARIVM — Dubia quaedam, quae adhuc post quinquagenarias investigationes exstant, Auctor exponit et examinat, de hammoniacy synthesy per chalybisy catalysim.

Ammonia synthesis involves the breaking of nitrogen-nitrogen ( $N\equiv N$ ) and hydrogen-hydrogen, H-H, bonds and the making of nitrogen-hydrogen, N-H, bonds in ammonia,  $NH_3$ . With the advent of deuterium it was possible for JUNGERS and TAYLOR (1935) to show that both the breaking and making of hydrogen-hydrogen and nitron-hydrogen bonds occur readily at room temperatures on iron synthetic ammonia catalyst. This suggested that the breaking of nitrogen bonds might be the slow step in the synthesis process. Studies of nitrogen adsorption on iron catalysts by EMMETT and BRUNAUER (1934) showed indeed that nitrogen chemisorption was a measurably slow process at synthesis temperatures ( $>200^\circ C$ ). TEMKIN and PYZHEW (1940) formulated a kinetic expression for the synthesis process in which slow chemisorption of nitrogen was the rate-

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determining step, and this theory found general acceptance until 1953.

At that time, ENOMOTO and HORIUTI in Japan performed experiments which indicated that both nitrogen and hydrogen must be involved in the slow step of the reaction. Their conclusion has been tested by a group of Dutch investigators (1960) whose results strongly conflict with the results from Japan and support the original thesis of EMMETT and BRUNAUER.

In an attempt to resolve the conflict, OZAKI, TAYLOR and BOUDART (1960) measured the relative rates of synthesis of nitrogen and hydrogen and nitrogen and deuterium on iron synthetic ammonia catalysts under similar temperature and pressure conditions. Their experimental finding that the reaction with deuterium was four-fold greater than that with hydrogen suggested initially that hydrogen was involved in the rate-determining process. A more penetrating analysis led to the conclusion that the nitrogen-adsorption step could still be retained as the slow process provided the surface was principally covered with  $-NH$  or  $-ND$  complexes, the former in considerable excess under given conditions.

These results have prompted TAMARU (1962 and experiments still unpublished) to measure the adsorption of nitrogen and hydrogen on the surface *while the reaction is in progress*. He has found a marked acceleration of nitrogen adsorption by hydrogen (co-operative adsorption). TAMARU showed that the hydrogenation step of the chemisorbed nitrogen is not as fast a process as has been presumed. He observes that nitrogen chemisorption undergoes no appreciable rapid change when ammonia is removed from an equilibrated mixture of nitrogen, hydrogen and ammonia. He has shown that chemisorbed nitrogen reacts much more rapidly with deuterium than with hydrogen. His present conclusion is that two steps may be rate-determining. At higher temperatures and lower hydrogen pressures, the hydrogenation of chemisorbed nitrogen is rate-deter-

mining, while, at lower temperatures and higher hydrogen pressures, nitrogen chemisorption is rate-determining.

Many years ago HALSEY (1949) pointed out that the concept of a rate-determining step was only applicable to a *uniform* catalytic surface. On a non-uniform surface one should not speak of a *single* rate-determining process. The iron ammonia synthesis catalyst is an excellent example of a non-uniform catalyst surface. Its extreme sensitivity to traces of water vapor as poison is one evidence of this. Other evidence comes from the work of the Dutch school, which has shown that extended reduction of iron catalysts with hydrogen of great purity, introduced into the system through palladium membranes, with reducing times of the order of 1000 hours produces a catalyst on which ammonia can be made *at room temperatures* rather than at the technical temperature of  $\sim 400^{\circ}\text{C}$ . Man, therefore, has finally achieved what the azotobacter and the leguminous nodules have been doing for millennia, fixing nitrogen at room temperature!

