

EFFECT OF NUCLEAR IRRADIATION
ON THE ACTIVITY OF
IRON METHANATION CATALYSTS

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INTRODUCTION

As part of a program to determine the place of nuclear energy and related technology in the utility gas industry, reports were prepared for the Gas Operations Research Committee of the American Gas Association by the Vitro Corporation of America and Arthur D. Little, Inc., on the feasibility of specific nuclear applications.⁸ The Little report,¹⁰ "Effects of Radiant Energy on the Synthesis of Gaseous Fuels," suggested three subjects for experimental study: 1) irradiation of catalysts prior to use, with the objective of enhancing their activity for desirable reactions by producing crystal disorders and/or inducing radioactivity, 2) irradiation of catalysts during use to attain objectives similar to 1 above, and to possibly effect beneficial radiochemical reactions, and 3) use of high-frequency discharges or other radiation to produce gas-phase reactions in the absence of catalysts.

A specific study based on the first of these suggestions was initiated at the Institute of Gas Technology in January 1958 to investigate the effects of nuclear irradiation on the activity and selectivity of iron methanation catalysts.

Bombardment of solid materials by nuclear radiation is known to produce a number of physical changes commonly called "defects". A description of the nature of these defects has been given by Dienes,³ Harwood,⁹ and others. Gamma rays, when losing their energy by absorption in a solid, produce primarily three effects: the photoelectric effect, the Compton effect, and positron-electron pair production. In addition, gamma radiation has been observed to produce displaced atoms in solids, but this effect is very small. Heavier particles, such as neutrons, inflict more serious damage to a solid. Neutron bombardment may result in crystal lattice defects, neutron capture, ejection of a charged particle, or nuclear fission. Several types of lattice defects may be produced which include vacancies, interstitial atoms, and impurity atoms. Other effects observed are replacement collisions, thermal spikes, and displacement spikes. Fission of an atomic nucleus or neutron capture, which result from impact with neutrons, produce isotopes or new elements.

All of the radiation effects described are similar in that they affect the electronic configuration in solids. Although much work has been done to relate the electronic structure of solids to their catalytic behavior,⁶ most work has been concerned with electronic effects related to factors other than those due to nuclear irradiation. Only a few investigators have studied the effects of nuclear irradiation, primarily X-ray and gamma-ray, on catalyst behavior. Depending on the catalytic system investigated, nuclear irradiation has been observed to result in an increase in activity in some cases, and a decrease in others.

The work of Clarke and Gibson¹ with the Fischer-Tropsch reaction is of special interest in relation to the present methanation study. They observed significant increases in the activity of iron mill scale catalysts which had been treated before reduction with 1 to 5×10^7 roentgens of gamma radiation. The increased activity persisted for the durations of their tests, which ranged from 48 to 300 hours. A considerable effect of particle size was established, with increases in activity varying from nil with 400- to 600-micron particles, to 40 to 60 percent with 0.2- to 5-micron particles. These investigators also report that no change in catalyst activity was obtained in a test with a neutron-irradiated catalyst of large particle size (1.2 to 2.4 mm.).

An extensive A.G.A.-sponsored study of the methanation process has been underway at the Institute for some time, in which a highly active Raney nickel catalyst has been brought to advanced stages of development.^{4,5} Several types of iron catalysts had been studied earlier, but their use in the development of the methanation process was abandoned, since it was not possible to overcome the tendency of these catalysts to cause high rates of carbon formation at the severe operating conditions favoring methane production.¹² Results similar to those obtained at the Institute with iron methanation catalysts have also been obtained by other investigators, principally the U.S. Bureau of Mines⁷ and the British Gas Research Board.²

The favorable results obtained by Clarke and Gibson indicated that improvement in iron catalyst properties may be feasible by use of a suitable irradiation procedure. If sufficient activity for methane production in the absence of carbon deposition and higher hydrocarbon formation could be achieved by such treatment, advantage could then be taken of the high sulfur resistance and low cost of iron catalysts. This might make these catalysts attractive alternates to the presently used nickel catalyst. Cobalt catalysts, which have many properties similar to those of iron catalysts, might also benefit from irradiation.

EQUIPMENT AND PROCEDURES

Three types of iron catalyst were used in this study. A skeletal iron catalyst was prepared by partial caustic leaching of a crushed, 50% aluminum-50% iron Raney alloy. A catalytically active reduced iron surface was prepared on National Controlled "T" chilled iron shot obtained from the National Metal Abrasives Company. Commercial ammonia synthesis catalyst, sold under the

designation of Aero Catalyst FM-2 by the American Cyanamid Company, was also used.

Gamma irradiation of catalysts was done in the High Level Irradiation Facility of Argonne National Laboratory. Total dosage for each batch was 10^8 roentgens at an intensity of approximately 10^4 roentgens per minute. Both irradiated and unirradiated Raney iron catalysts were stored at 0°F . to minimize annealing. Other catalysts were stored at room temperature. The maximum time elapsed between irradiation and use did not exceed one week for the catalysts stored at room temperature, and was less than one month for the refrigerated samples.

The CP-5 Nuclear Reactor at Argonne National Laboratory was utilized for the neutron irradiations. Total dosage for each sample was approximately 10^{19} neutrons per sq. cm. at a neutron flux of about 2×10^{13} neutrons per sq. cm.-sec. Irradiated samples were stored before use at room temperature for approximately one month, to allow the level of induced radioactivity to decay to a safe value.

Catalyst Testing Apparatus

Both fluid- and fixed-bed reactors were used. Initial tests were made with fluid-bed units, but the reproducibility obtained with this equipment was not sufficient to permit accurate measurement of changes in catalyst activity caused by gamma irradiation. A fixed-bed reactor was therefore constructed and used for all subsequent tests. Flow diagrams of both types of reactors are shown in Figure 1.

Fluid-Bed Unit. The fluid-bed unit, as shown on the left in Figure 1, was constructed in duplicate, except for the purification section, to permit simultaneous testing of unirradiated and irradiated catalysts. Each reactor consisted of an 18-in. high pyrex catalyst section, 30 mm. O.D. by 26.4 mm. I.D., surmounted by a 103-mm. O.D. by 15-in. high catalyst separation zone. A 6-in. long by 25-mm. O.D. section below the catalyst section, packed with 3-mm. O.D. pyrex tubing, served as an inlet gas preheater. A porous glass disk separated the preheat and catalyst sections, and acted as a catalyst bed support and a feed gas distributor. Product gas was withdrawn through an 8-in. long, tubular, porous glass filter which retained the catalyst fines. The reactor and preheat section were completely enclosed in a single Hevi Duty electric furnace. Temperatures were measured with five 20-ga. chromel-alumel thermocouples inserted in a 10-mm. O.D. thermowell axially located in the reactor. Power to the electric furnace was controlled manually.

Synthesis gas and purge nitrogen were fed from high-pressure cylinders through activated carbon to remove sulfur compounds. Dry test meters were used for metering of feed gases, and wet test meters for the product gases.

Fixed-Bed Unit. The fixed-bed unit was essentially the same as the fluid-bed, except for the reactor itself, shown at the right in Figure 1. The reactor consisted of a 16-3/4 in. long, 1-1/2 in. IPS, Schedule 80, stainless steel pipe press-fitted into a 12-in. long by 5-in. O.D. aluminum bronze block.

The block was spirally wrapped with resistance heating wires. A 3/8-in. O.D., 20-ga. stainless steel thermowell was mounted axially in the reactor and extended its full length. Feed gases entered at the top of the reactor and flowed downward through the catalyst bed. The bed was confined between two 24-mesh type 304 stainless steel screens. The space above the catalyst bed was packed with reagent grade copper shot to facilitate inlet gas preheating. The lower part of the reactor was packed with -18, + 20 mesh size, refined glass beads instead of copper shot to minimize heat losses. The bottom of the reactor was flanged to facilitate catalyst charging.

When radioactive catalysts were tested, a thin stainless steel liner was used to prevent reactor contamination. The liner, which was 16 in. long, 1.375 in. O.D. and 1.278 in. I.D., was closed at the bottom by a perforated stainless steel plate, and was held in the reactor by means of a 1-in. long threaded section at its top.

Test Procedures. Synthesis gas consisting of hydrogen and carbon monoxide in a 3:1 mole ratio was purchased in high-pressure cylinders. Electrolytic grade hydrogen was blended with this mixture for tests in which higher H₂/CO ratios were used for the feed. Feed and product gas compositions were determined by mass spectrometer.

With all of the catalysts studied, some preliminary treatment was required after the catalyst sample was placed in the reactor and before the methanation test was started. The Raney catalysts were reduced in the catalyst-preparation procedure and transferred to the reactor under methanol. The bed was then heated and a stream of nitrogen was passed through it, to thoroughly dry the catalyst prior to the methanation test. Iron shot and ammonia synthesis catalysts were charged to the reactor in the oxidized state and were reduced with hydrogen prior to the methanation tests.

There was little difference in test procedure between the fluid- and fixed-bed units except for the size of catalyst samples, and gas flow rates. In the fluid-bed reactor, the catalyst charge was approximately 100 c.c., occupying about 11 in. of the reactor height when fluidized. A 1-1/8-in. deep bed, with a volume of 30 c.c., was used in the fixed-bed reactor tests on gamma-irradiated Raney and ammonia synthesis catalysts. In tests of neutron-irradiated ammonia synthesis catalyst, where the reactor liner was used, the depth of the 30 c.c. sample was 1-9/16 in. A 100 c.c., 3-3/4 in. deep, bed was required for the tests with iron shot because of its low activity.

DISCUSSION

Operating conditions for evaluation of the relative methanation activity of irradiated and unirradiated iron catalyst samples were limited to a narrow range because 1) iron catalysts have a lower activity for the methanation reaction than nickel catalysts, 2) methane formation is greatly exceeded by higher hydrocarbon formation at the lower temperatures, and 3) methane formation is accompanied by considerable carbon formation at the higher

temperatures. Carbon deposition was most detrimental in these tests, since rapid buildup of carbon on the catalyst surface made detection of changes in catalyst performance resulting from other causes, such as irradiation, exceedingly difficult. Under some conditions, carbon deposition was so severe that the catalyst bed was almost completely blocked to gas flow. It was determined experimentally to be impractical, for this reason, to feed synthesis gas having a hydrogen to carbon monoxide ratio of less than 6:1 to the fixed-bed reactor, or less than 9:1 to the fluid-bed reactor. The resulting product gases consequently contained large concentrations of excess hydrogen, which is undesirable in the methanation process, but should not affect the validity of the activity tests. Although other investigators have shown that steam dilution can be used effectively to control carbon deposition, steam feed was not practical in these tests because of possible reduction of the already low carbon monoxide content by the water-gas shift reaction.

Since increases in catalyst temperature will 1) increase carbon deposition, 2) increase the rate of methane formation, and 3) decrease the equilibrium methane concentration in the product gas, the selection of a suitable temperature level was of major importance. Reactor temperatures (and thus catalyst activities) were kept as low as possible within the limits of accurate gas flow and gas composition measurements. The fluid-bed reactor was particularly inflexible in this respect, since gas velocity had to be maintained within narrow limits to keep the catalyst fluidized. Therefore, low catalyst activity could not be independently compensated by a low synthesis gas space velocity to obtain a specific degree of carbon monoxide conversion.

Effects of Gamma Irradiation

To determine the effect of prior gamma irradiation of the catalyst on the conversion of carbon monoxide to methane, conditions of synthesis gas space velocity and catalyst bed temperature were selected for each type of catalyst tested so that the resulting product gas composition was considerably removed from the equilibrium value. Sets of comparison tests were made with irradiated and control samples from the same catalyst batch at equal operating conditions. Differences in catalyst activity were noted by comparison of the methane-equivalent space-time yields (the rate of production per unit volume of catalyst of the total gaseous hydrocarbons times their average carbon number) from each set of tests.

Results of three runs made with Raney iron catalyst in the fluid-bed methanation unit are given in Table 1. In these tests a space velocity of approximately 1000 SCF (standard cubic foot of gas at 60°F., 30 in. Hg, saturated with water vapor) per cubic foot of catalyst per hour was employed, with a 9.5-9.7:1.0 H₂/CO ratio synthesis gas. The reactor temperature was maintained at 500°F. Under these conditions, carbon recovery as gaseous products varied between 72 and 93 wt. %, corresponding to carbon deposition on the catalyst between 7 and 17 wt. % of the carbon fed.

Table 1.-FLUID-BED REACTOR TESTS
WITH RANEY IRON CATALYST (75% ALUMINUM CONVERSION)

Run No.	12A	13	12B
Reactor No.	1	2	2
Catalyst No.	6A	6A	6B
Catalyst Treatment	Control	Control	Irradiated
Carbon Recovery, wt. %	83	85	93
Methane/Higher Hydrocarbon Mole Ratio	2.0	2.1	2.2
Methane Equivalent Space-Time Yield, SCF/cu. ft. cat.-hr.	32	19	64

The results of these tests, which were made with samples from the same catalyst batch, indicate that the gamma-irradiated catalyst produced more than twice as much methane equivalent per unit of catalyst and time as the unirradiated catalyst. However, no firm conclusions could be justified regarding the actual degree of catalyst improvement, because of the limited reproducibility of results from the fluid-bed reactor. The poor reproducibility was attributed to the large number of operating variables (not necessarily related to intrinsic catalyst activity) which could not be controlled within sufficiently narrow limits. Control of temperature gradients in the bed was especially difficult.

To minimize the effect of extraneous variables in the methanation test procedure, further comparisons between irradiated and unirradiated catalyst were made in the fixed-bed reactor. In addition to better control of process variables with the fixed-bed unit, the elimination of fluidization requirements made possible the selection of catalyst particle size, sample size, bed temperature, and space velocity to give the desired degree of conversion with catalysts having widely different activities, without alteration of the reactor or feed and product gas trains.

The results of three runs made with Raney iron catalyst in the fixed-bed reactor are given in Table 2. This catalyst differed from that used in the fluid-bed tests in particle size range, and in that only 30% of the aluminum was reacted during catalyst activation, as compared with 75% with the fluid-bed catalysts.

Table 2.-FIXED-BED REACTOR TESTS
WITH RANEY IRON CATALYST (30% ALUMINUM CONVERSION)

Run No.	19	16	24
Catalyst No.	13A	13B	15
Catalyst Treatment	Control	Irradiated	Alloy Irradiated
Carbon Recovery, wt. %	86	88	88
Methane/Higher Hydrocarbon Mole Ratio	5.2	4.6	3.2
Methane Equivalent Space-Time Yield, SCF/cu. ft. cat.-hr.	41	46	39

Runs 16 and 19 were made with irradiated and unirradiated samples, respectively. Run 24 was made with a catalyst prepared from Raney alloy which had been irradiated prior to catalyst activation, in contrast to irradiation of the activated catalyst in each of the other Raney catalyst tests. A feed gas space velocity of approximately 2000 SCF/cu. ft. catalyst-hr of 6.4-6.9:1.0 H₂/CO synthesis gas was employed, with a catalyst bed temperature of 700°F. Carbon recovery as gaseous products ranged between 86 and 88 wt. % at these conditions. Comparing the results from Runs 16 and 24 with those from Run 19, it can be seen that the methane-equivalent space-time yield was about 12% higher with the irradiated catalyst, whereas it was about 5% lower when the Raney alloy was irradiated prior to catalyst activation. These variations in catalyst activity are relatively small, and approach in magnitude the reproducibility of the test. However, the increase in the activity of the irradiated Raney iron catalyst was consistent with the results obtained earlier in fluid-bed operation.

Two runs were made with iron shot catalyst. However, the level of activity of this catalyst was so low, and concentrations of hydrocarbons in the product gas were so small, that no significance could be placed on the comparative data from these runs.

The only commercial catalyst employed in this study was the ammonia synthesis catalyst, which had a level of activity comparable with that of Raney iron. Test conditions were the same as those for the fixed-bed tests with Raney iron, except that the catalyst bed temperature was maintained at 500°F. As shown in Table 3, an increase of approximately 10% in methane-equivalent space-time yield was observed with the gamma-irradiated sample; this is similar to the increase found with Raney iron.

No evidence was found to indicate that the synthesis reaction mechanism was significantly affected by prior gamma irradiation of the catalyst. Carbon deposition and distribution of products between methane and higher molecular weight hydrocarbons did not vary in any systematic manner which could be attributed to catalyst irradiation. All of the tests were of short duration, so it could not be determined whether the initial effects observed would persist with longer use of the catalyst.

Since the results were obtained with catalysts which had been irradiated at least one day prior to test, they are not indicative of the possible effect of irradiation immediately prior to or

Table 3.-FIXED-BED REACTOR TESTS
WITH AMMONIA SYNTHESIS CATALYST

Run No.	25	26
Catalyst No.	22	23
Catalyst Treatment	Control	Irradiated
Carbon Recovery, wt. %	86	87
Methane/Higher		
Hydrocarbon Mole Ratio	0.5	0.4
Methane Equivalent Space-Time		
Yield, SCF/cu. ft. cat.-hr.	39	43

during the methanation reaction, where short-lived effects might be significant.

The residual effects of high-intensity gamma radiation on solids are limited to ionization and possibly slight crystal lattice defect production. X-ray diffraction examination of an irradiated sample of Raney iron catalyst failed to disclose any evidence of crystal lattice deformation by the radiation dosage of 10^8 roentgens employed in this study. This does not mean that defects were not produced during the gamma treatment, but that any physical effects on the crystal were too small or too short-lived to be detected by subsequent X-ray diffraction analysis.

Effects of Neutron Irradiation

Four comparative tests with samples of ammonia synthesis catalyst were made to determine the effect of thermal neutron irradiation on catalyst activity. A summary of the results of these tests is given in Table 4.

Runs 27 and 30 were made with samples of untreated ammonia synthesis catalyst; Runs 28 and 29, with irradiated samples. The run conditions employed were the same as those used in comparative tests of gamma-irradiated ammonia synthesis catalysts: 2000 SCF/cu. ft. catalyst-hr feed gas space velocity, 6:1 hydrogen/carbon monoxide feed gas ratio, and 500°F. catalyst bed temperature.

One sample of irradiated catalyst (No. 25, Run 28) showed an activity that was about 30% higher than the average of the activities of the two untreated samples. A second sample of neutron-irradiated catalyst (No. 26, Run 29) showed an activity substantially the same as that of the unirradiated samples. This difference in activity between the two samples of irradiated catalyst cannot be attributed to any apparent differences in test conditions or method of catalyst reduction. However, in spite of the close control of experimental procedures, the neutron-irradiated sample showing the high catalytic activity (No. 25) appeared to undergo a greater degree of reduction during activation; from the three samples showing similar activity (Nos. 24, 26 and 27), 49.0 to 51.4% of the oxygen content of the iron oxides was removed, whereas with Sample 25 oxygen removal was 71.0%. Work reported by Simnad¹¹ showed that the rate of reduction of nickel oxide by hydrogen at 250°-350°C is increased by a factor of three when the oxide has been irradiated with high-energy protons.

Table 4.-FIXED-BED REACTOR TESTS OF THERMAL NEUTRON-IRRADIATED AMMONIA SYNTHESIS CATALYST

Run No.	27	28	29	30
Catalyst No.	24	25	26	27
Catalyst Treatment	Control	Irradiated	Irradiated	Control
Carbon Recovery, wt. %	87	79	79	80
Methane/Higher Hydrocarbon Mole Ratio	0.34	0.44	0.44	0.42
Methane Equivalent Space-Time Yield, SCF/cu. ft. cat.-hr.	29	36	26	27

Catalysts 25 and 26 were irradiated simultaneously; however, No. 25 was exposed to a neutron flux of 2.6×10^{13} neutrons/sq.-cm.-sec., whereas No. 26 was exposed to a flux of 2.0×10^{13} neutrons/sq.-cm.-sec. The total dosage for Catalyst 25 was therefore 30% greater. The half-lives of the radioactive isotopes of iron present (Fe^{55} and Fe^{59}) are 2.94 years and 45.1 days, respectively, with Fe^{55} comprising approximately 70% of the total radioactive isotopes present. Since only three days elapsed between the tests with the treated samples, the differences in their catalytic activity should not be due simply to a decrease in radioactivity or to annealing of defects in this period.

The results of these tests indicate that thermal neutron irradiation of ammonia synthesis catalyst prior to use may have an effect on its activity. There was no measurable change, however, in carbon deposition and distribution of products between methane and higher molecular weight hydrocarbons.

Since an increase in catalytic activity was observed with the irradiated sample which had received the higher neutron dosage, it is possible that higher dosage levels than employed in these tests might result in substantially increased catalytic activity. Irradiation by fast neutrons might also increase activity, since a higher ratio of crystal lattice defects to induced radioactivity would be produced.

CONCLUSIONS

It can be concluded from the experimental results that gamma irradiation or thermal neutron irradiation prior to use may have a beneficial effect on the activity of iron methanation catalysts. The scope of this program was not sufficient, however, to define the radiation requirements to obtain optimum beneficial effects. The observed degrees of catalyst improvement resulting from irradiation can be considered small from a practical standpoint, in view of the generally low activity and poor product distributions obtained with the iron methanation catalysts studied.

The nature of the improvement due to irradiation seemed to be limited to increased activity with no apparent change in the product selectivity (methane/higher hydrocarbon ratio). No significant decreases in carbon deposition were obtained. Although direct analogy cannot be drawn, the observed results with gamma-irradiated catalysts do not appear to differ greatly from the findings of Clarke and Gibson with iron mill scale catalyst.¹

Although this study was limited to tests of short duration, and to limited ranges of radiation intensity and dosage levels, the results show that a more detailed fundamental investigation in this area would be warranted. Further study should include the testing of other types of methanation catalysts, other catalyst particle sizes, other forms of nuclear radiation, and other radiation dosage and intensity levels.

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ACKNOWLEDGMENT

Guidance of this work by the Project Supervising Committee of the American Gas Association, under the chairmanship of A. D. Harrison is gratefully acknowledged. The counsel of H. R. Linden and the assistance of H. A. Dirksen and J. E. Epperson is greatly appreciated. Analytical work was carried out under the supervision of J. E. Neuzil and D. M. Mason.

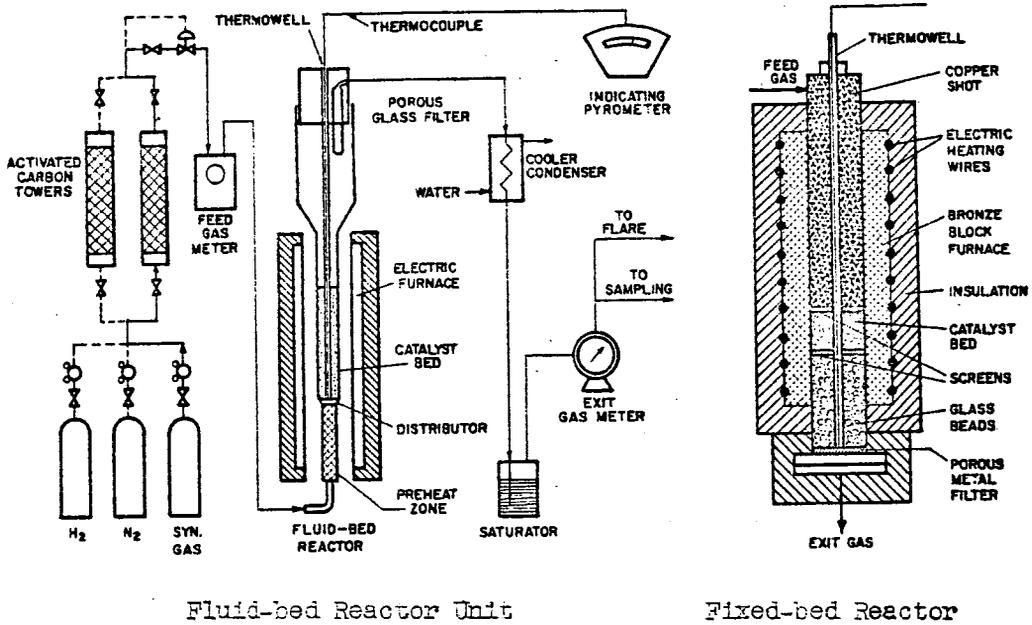


Figure 1. Methanation Catalyst Testing Equipment