CANADA

RADIATION EFFECTS ON
p- AND n- TYPE CATALYSTS USED
IN THE THERMAL DISSOCIATION
OF ETHYL ALCOHOL

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MINERAL SCIENCES DIVISION

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RADIATION EFFECTS ON p- AND n-TYPE CATALYSTS USED IN THE THERMAL DISSOCIATION OF ETHYL ALCOHOL

by

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SYNOPSIS

The dissociation of anhydrous ethyl alcohol has been studied over the temperature range 330°-430°C with the employment of catalysts that had been exposed to a range of estimated "integrated" neutron doses of up to 96.6×10^{18} n/cm^2. The catalysts are ZnO, an n-type semiconductor, prepared by decomposition of the carbonate, and Cr_2O_3, a p-type semiconductor, prepared by dehydration of the hydroxide. Measurable changes in yield and decomposition mechanism have been observed as compared with the unirradiated catalysts.

The variation in the behaviour of the catalysts has been related to the various neutron doses received, and the results are discussed in the framework of the electronic theory of catalysis on semiconductors.

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Direction des mines

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EFFETS DE LA RADIATION SUR LES CATALYSEURS DE TYPE "p" ET "n" QUI SERVENT À LA DISSOCIATION THERMIQUE DE L'ALCOOL ÉTHYLIQUE

par

Matteo Donato*

RÉSUMÉ

La dissociation d'alcool éthylique anhydre a été étudiée dans la zone de température 330° - 430°C à l'aide de catalyseurs qui avaient été exposés à une série de dosages "intégrés" de neutrons qui pouvaient atteindre jusqu'à $96.6 \times 10^{18} \text{n/cm}^2$. Les catalyseurs en cause sont le ZnO, semi-conducteur de type "n" obtenu par décomposition du carbonate, et le Cr_2O_3, semi-conducteur de type "p" obtenu par déshydratation de l'hydroxyde. L'auteur a noté des changements mesurables dans le rendement et le mécanisme de décomposition au regard de l'emploi de catalyseurs non irradiés.

La variation dans le comportement des catalyseurs a été attribuée aux diverses doses de neutrons reçues, et l'auteur traite des résultats dans le cadre de l'hypothèse électronique de catalyse relativement aux semi-conducteurs.

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INTRODUCTION

In recent years, there has been an increasing interest in the effect of nuclear radiation on solid inorganic catalysts. This is due to the fact that catalytic behaviour is strongly dependent on the structure and energy conditions of the catalyst and its structure may be modified under nuclear irradiation (1, 2, 3, 4). The object of the present report is to discuss the behaviour, as catalysts, of ZnO, an n-type semiconductor, and Cr_2O_3, a p-type semiconductor, before and after irradiation in the Chalk River reactor. Studies have been made of the well-known thermal dissociation reaction of ethyl alcohol that proceeds along two paths:

$$R\text{-}CH_2OH \begin{cases} \nearrow RCHO + H_2 \quad \text{dehydrogenation} \\ \searrow C_2H_4 + H_2O \quad \text{dehydration} \end{cases}$$
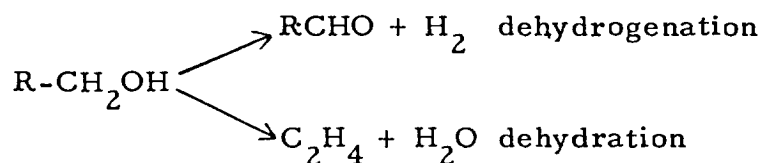
The particular reaction path taken is determined at the first stafe of reaction, the adsorption of the alcohol molecule, and depends on the particular bond broken in the molecule, the OH or C-OH bond; this in turn depends on the nature of the catalyst. With ZnO and Cr_2O_3 catalysts both reactions occur.

It is well known that the reactor irradiation of a solid semiconductor can generally produce the following effects: a) direct ionization; b) change in the degree of disorder in the lattice of the solid irradiated; and c) nuclear reaction in the solid. Each of these effects produces a variation in the number of free carriers in the solid. The first effect is only a temporary effect. The second one can be removed by heating the sample at a high temperature. The third one, which leads to the production of impurities of different chemical character in the lattice of the solid, is a permanent effect and irreversible.

In the past twenty years many authors, such as Hauffe (5), Schwab (6), Garner (7), Wolkenstein (8) and others, have developed an electronic theory of catalysis on semiconductors. According to this theory the nature of the substrate bonding determines the transfer of electrons from the adsorbed molecule to the unfilled electronic levels in the solid catalyst, or from the solid catalyst with an excess of electrons to the adsorbed molecule. This picture of catalysis on semiconductors has been supported by the publications of many research workers. The well-known catalytic activity of the transition metals is thus correlated with their unfilled d-bands, and the different activities of n- and p-type semiconductors with their capability to donate or accept electrons.

In this framework, the gamma and neutron irradiation of a solid catalyst would be expected to alter its catalytic activity, because the products of irradiation include trapped electrons and holes (in non-metals), displaced atoms, and impurities of a different chemical nature, due to the neutron-induced transmutations, all of which influence the electronic structure of the solid catalyst and hence its ability to interchange electrons with the adsorbed molecules on the surface.

It has been reported by Wolkenstein (8) that the relative activity of the catalyst—in this case, for dehydration or dehydrogenation—depends on the position of the Fermi level and that the lowering of this level retards dehydrogenation and accelerates dehydration. Some factors that affect the position of the Fermi level include: acceptor impurities, donor impurities, nuclear radiation.

APPARATUS AND PROCEDURE

The reaction, the decomposition of the ethyl alcohol, was observed at atmospheric pressure and at temperatures within the range 330°-390°C for ZnO and 370°-430°C for Cr_2O_3. The experiments were carried out in a continuous flow reactor made of quartz glass.

The apparatus used in the present study consisted of an
alcohol feeding system, a vaporizing unit, a reactor, an ethanol recovery
system and a gas-measuring device. (Figure 1 shows a schematic diagram
of the apparatus.)   The entire apparatus was made of quartz glass except
for the condenser and the receiver. A Milton-Roy "Minipump", made of
stainless steel, was used for the ethanol feed system to ensure a constant
slow rate of gas flow. A water condenser (0°C) and a dry-ice acetone
trap (-40°C) in series were used to condense the liquid products. The
volume of the gaseous products was measured with a gas volumeter.
The composition of the gas mixture was determined by means of a
temperature-controlled chromatographic system. The samples of gas
were introduced by means of a gas-sampling valve, which provided a
convenient and highly reproducible system for sampling gas streams.
A portion of the gas stream to be analysed was allowed to flow continually
through the valve. The temperature of the catalyst bed during the reaction
was measured and recorded by a chromel-alumel thermocouple placed
in the reactor thermocouple well. Control of the reactor temperature
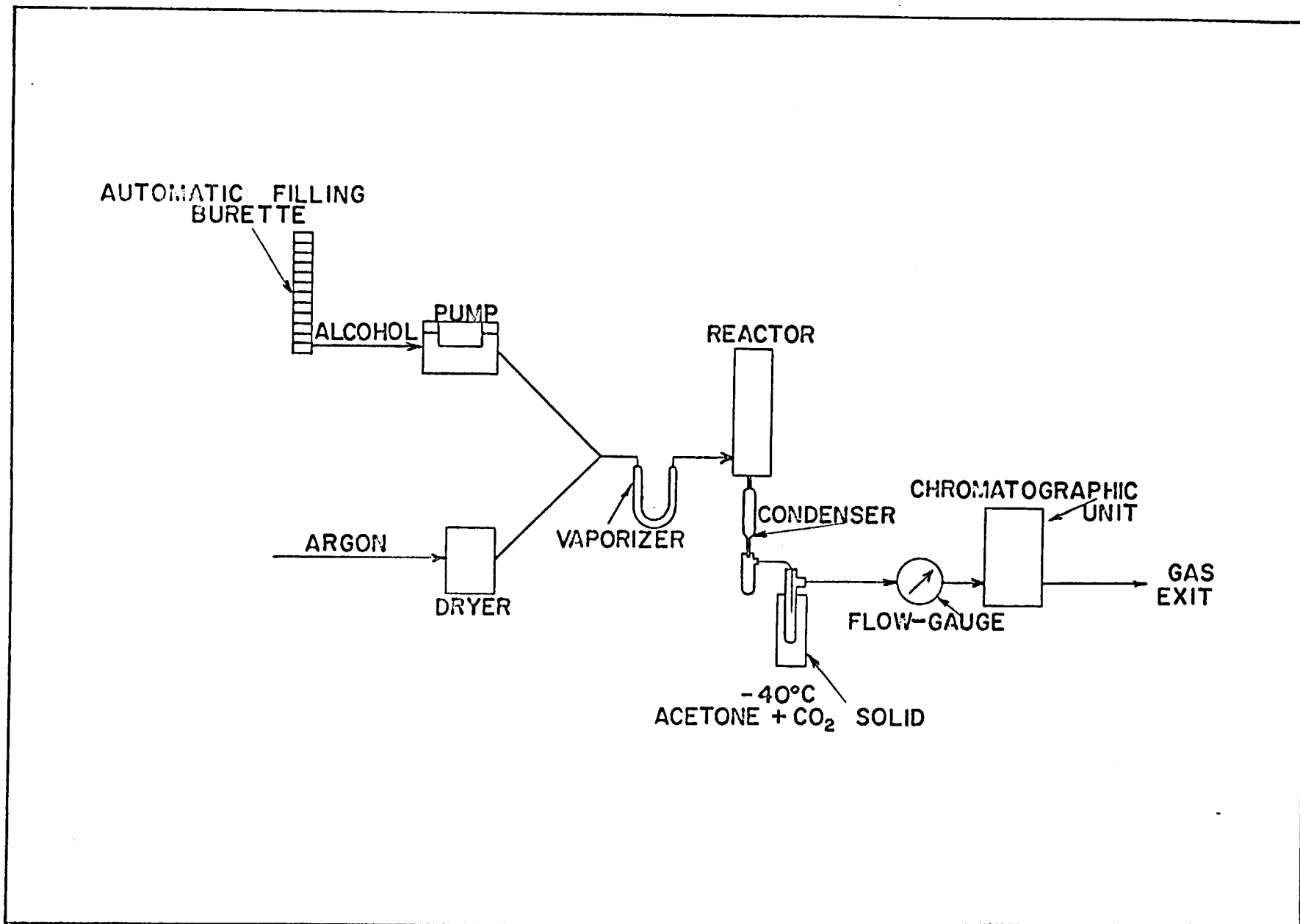was maintained by adjusting the voltage to the reactor heating coil.

FIGURE 1 SCHEMATIC DIAGRAM OF APPARATUS.

PREPARATION OF CATALYSTS

The zinc oxide catalysts were prepared by ignition of $ZnCO_3$ at 450°C in air for 3 hours. The resulting powder was pressed into pellets and the latter were then crushed in order to have granules in the size range of 20-28 mesh. The amount of catalyst used in each test was 0.4 g. The surface area was 23.7 m^2/g.

The chromic oxide catalysts were prepared by precipitation of the hydroxide from a solution of the nitrate, using ammonium hydroxide as the precipitating agent. The reagents used were highly pure Mallinckrodt "Transistar" products. The precipitate was then washed, filtered, and dried. The dry hydroxide was then ground and heated at 450°C for 3 hours in air. The dry Cr_2O_3 was pressed into pellets that were then granulated and screened to yield a 20-28 mesh product. The amount of Cr_2O_3 used in each test was 0.2 g. The surface area was 19.8 m^2/g.

The alcohol feed for both series of catalyst tests was 0.204 ml/min. Properties of the alcohol used are: refractive index n_D^{25} = 1.3600, specific gravity G_{20}^{20} = 0.7955, G_4^{20} = 0.7914, water = 0.10% v/v, b.p. = 78.2°C. Four samples of ZnO and two samples of Cr_2O_3 were irradiated in the Chalk River reactor at various estimated integrated neutron doses up to 10^{20} n/cm^2 at a maximum flux of 5.8 x 10^{13} n/cm^2 sec. The estimated gamma flux was 1 x 10^8 roentgens per hour.

The spectrographic analyses for the ZnO and Cr_2O_3 catalysts
are presented in Table 1.

TABLE 1

Analysis of Catalysts

Catalyst	Surface Area	Elements, per cent									
		Si	Mg	Fe	Cu	Ca	Al	Mn	Pb	Cd	B
ZnO	23.7 m^2/g	0.02	0.005	0.004	0.002	n.d.	n.d.	n.d.	n.d.	0.08	n.d.
Cr_2O_3	19.8 m^2/g	0.07	0.009	0.01	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

The reactor irradiation conditions are presented in Table 2.

TABLE 2

a) Maximum Flux and b) Integrated Neutron Doses

Catalyst	Weight (g)	I	II	III	IV	V
ZnO	0.4	a) Not irradiated b) Not irradiated	2.3×10^{13} 13.9×10^{18}	3.9×10^{13} 23.3×10^{18}	4.6×10^{13} 59.6×10^{18}	4.8×10^{13} 96.6×10^{18}
Cr_2O_3	0.2	a) Not irradiated b) Not irradiated	3.3×10^{13} 20×10^{18}	5.8×10^{13} 34.8×10^{18}		

a) Fluxes in neutrons/cm^2 sec

b) Neutron doses in neutrons/cm^2

The experimental variables determined consisted of feed rate, reaction time, temperature, and amount of gas evolved (hydrogen and ethylene).

From these results, the behaviour of the catalyst, the reaction rates and the percentage of conversion at various temperatures were calculated and curves of percentage conversion versus temperature were plotted. Before and after each series of runs the reactor was flushed with dried argon to ensure that no air or moisture was present.

EXPERIMENTAL RESULTS

After irradiation the zinc oxide catalysts presented a yellow-brown colour; the green chromia catalysts, on the other hand, did not show any change in colour.

In the case of ZnO, the initial experiments indicated that on a fresh catalyst surface the activity of the irradiated catalyst was lower than on the non-irradiated one, but when the catalyst was aged by use at 390°C for a few days the radioactive catalysts were more active and the ratio H_2/C_2H_4, which was changing during the first runs, reached a constant value. Figure 2 shows the reaction rate at a temperature of 390°C for normal and irradiated, stabilized
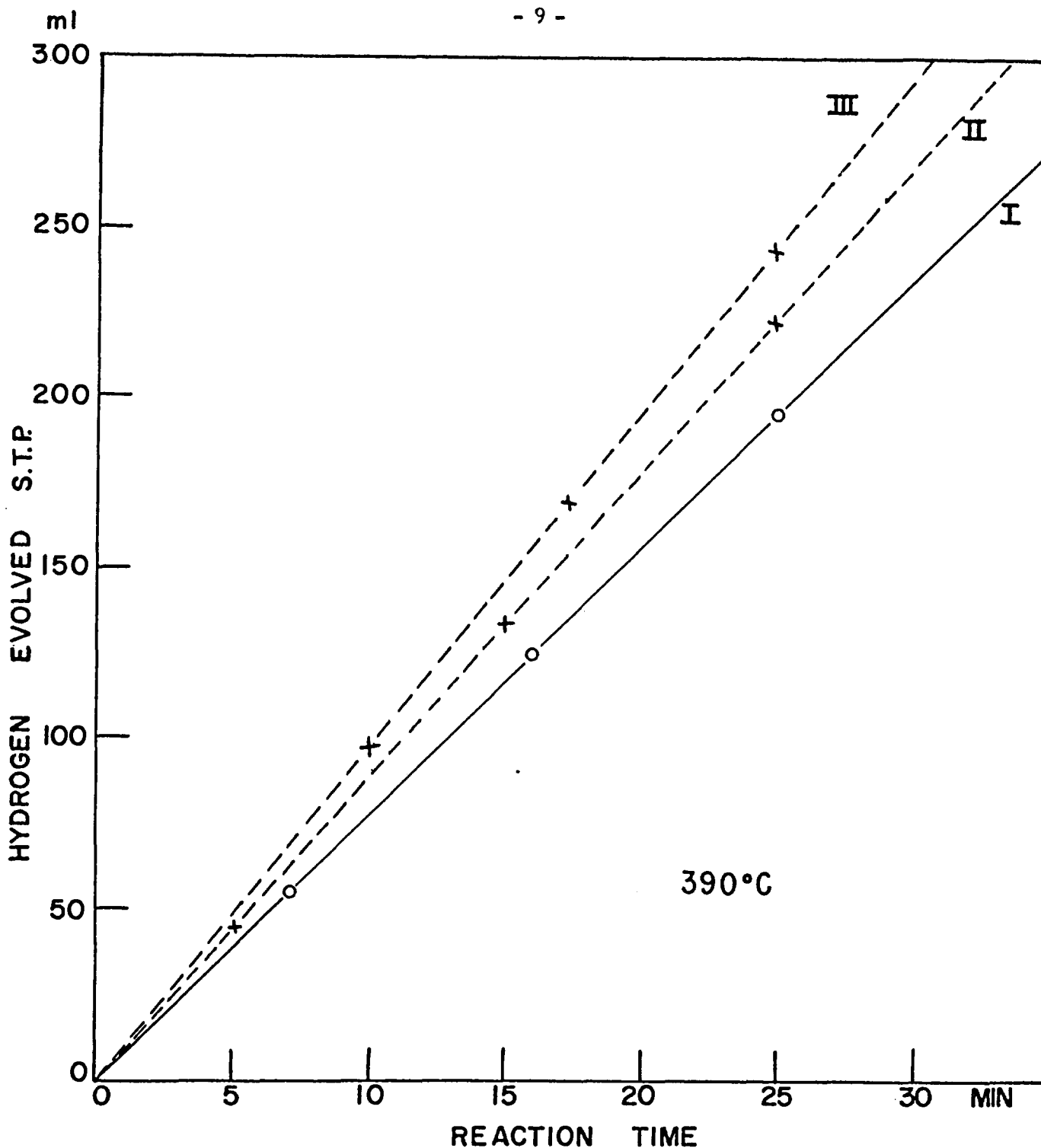
FIGURE 2 REACTION RATES FOR DIFFERENT CATALYSTS - ZnO

ETHYL ALCOHOL FEED -0.204 ml/min

NORMAL CATALYST ———o———

IRRADIATED   II   INTEGRATED NEUTRON DOSE --+--13.9 x 10^{18} n/cm^2

            III   INTEGRATED NEUTRON DOSE --+--23.3 x 10^{18} n/cm^2

catalysts. Figure 3 compares the proportion of hydrogen and ethylene evolved
for normal and irradiated catalysts. Figures 4, 5 and 6 report the per cent
conversion to hydrogen and ethylene, and the total conversion versus the
integrated neutron doses that the catalysts received over the range of
temperatures studied. It is evident that the nuclear irradiation significantly
affects the reaction paths (see Figure 3) and the effect increases with
irradiation times or estimated integrated neutron doses of the solid catalyst,
to reach an asymptotic value of the ratio H_2/C_2H_4, as can be seen in Figure 7.

According to Wolkenstein (8) and Garner (10), the dehydrogenation
of ethyl alcohol is an acceptor or n-type reaction; in other words, this is a
reaction accelerated by the presence of free electrons and it proceeds more
rapidly the higher is the Fermi level (other conditions being equal). In
contrast, the dehydration is a donor or p-type reaction. In the case of ZnO
it is evident that a higher Fermi level has been obtained in the irradiated
catalysts compared with the non-irradiated one and this leads to an increase
in the hydrogen/ethylene ratio in the reaction products. There is also an increase
in the dehydrogenation activity of the same catalysts, which seems to be a function
of the estimated integrated neutron dose of the catalysts (see Figures 2-4)
or of the amount of gallium-69 created. The dotted line in Figure 4 indicates the
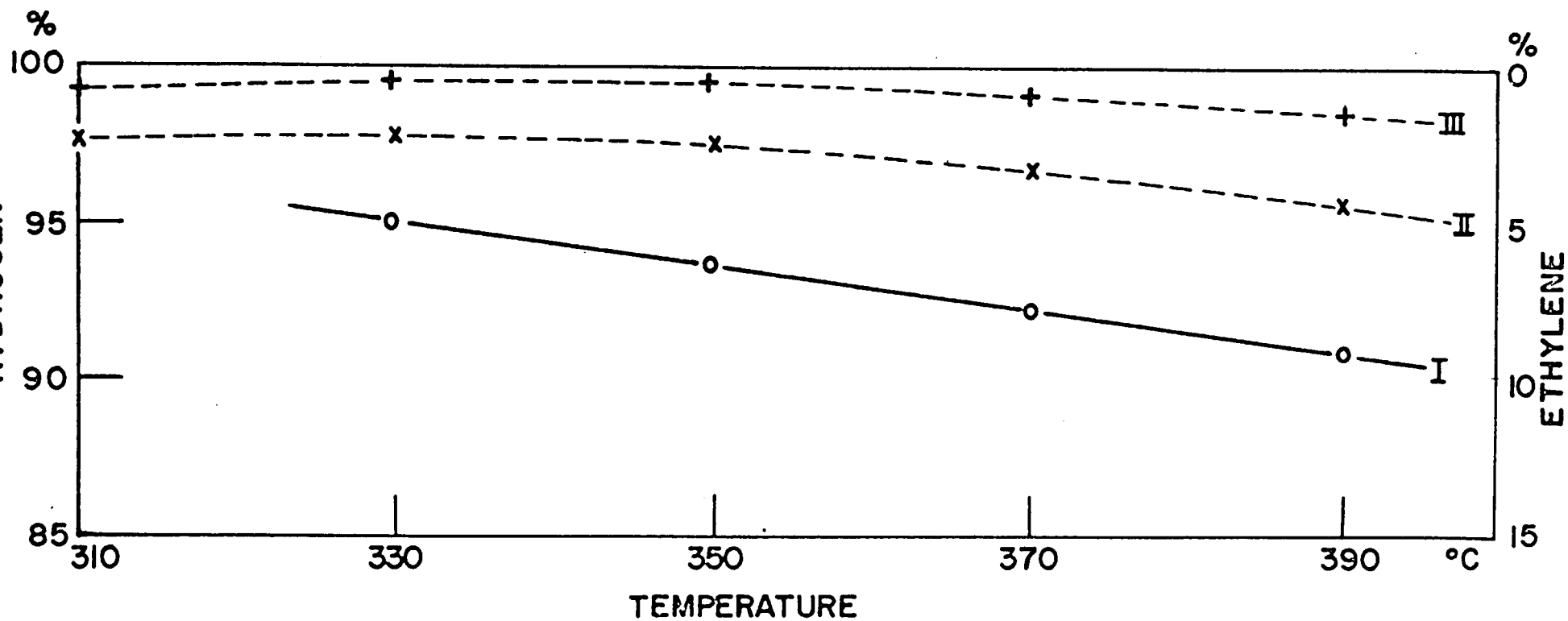shift with temperature in the neutron dose required for maximum hydrogen
conversion.

FIGURE 3 BEHAVIOUR OF ZINC OXIDE CATALYSTS AT VARIOUS TEMPERATURES

ETHYL ALCOHOL FEED = 0.204 ml/min

CATALYST- ZnO TYPE A, 0.4g, 20-28 MESH

NORMAL CATALYST ———o———

IRRADIATED II ———x——— INTEGRATED NEUTRON DOSE 13.9 x 10^{18} n/cm^2

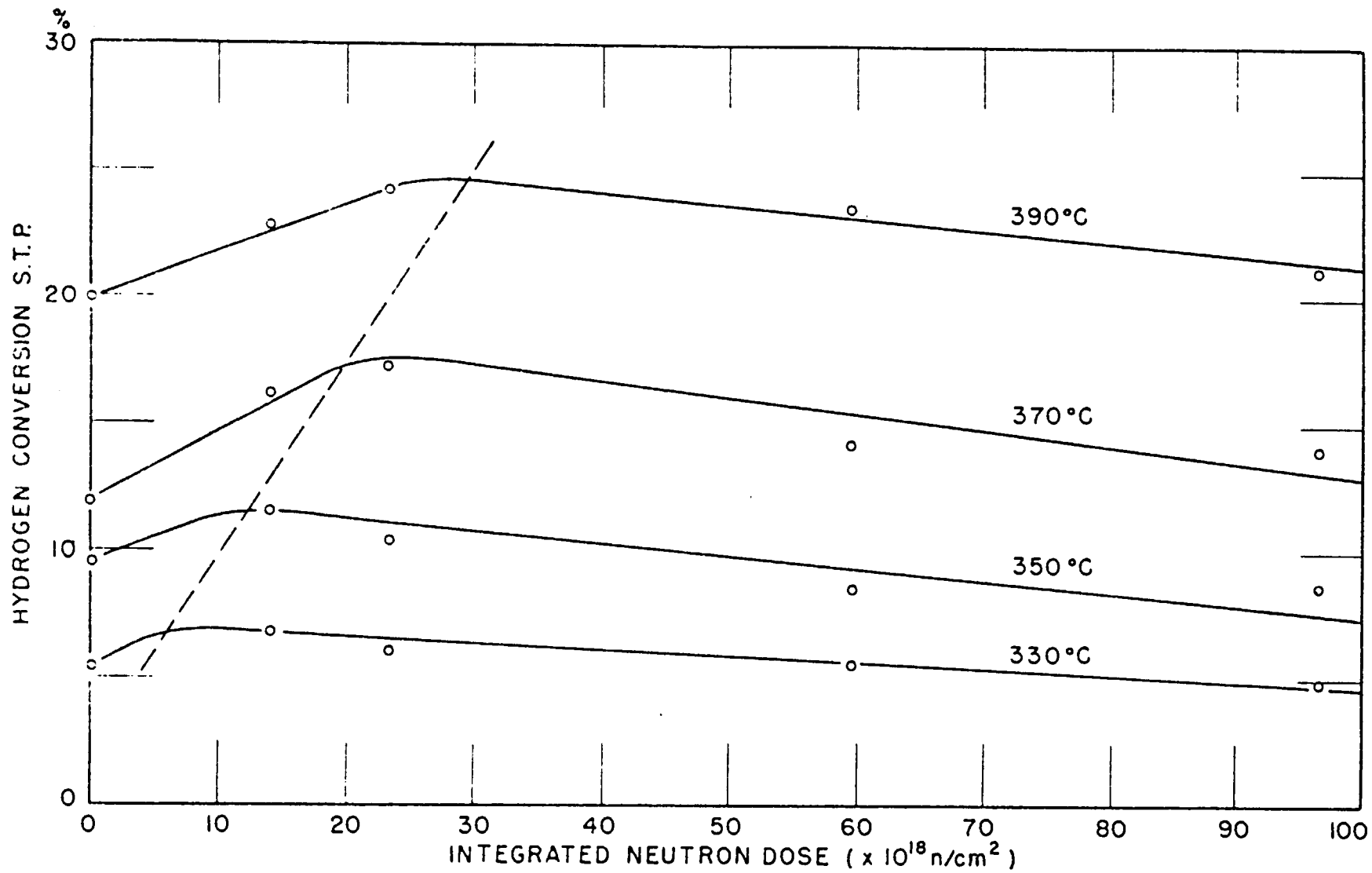III ———+——— INTEGRATED NEUTRON DOSE 23.3 x 10^{18} n/cm^2

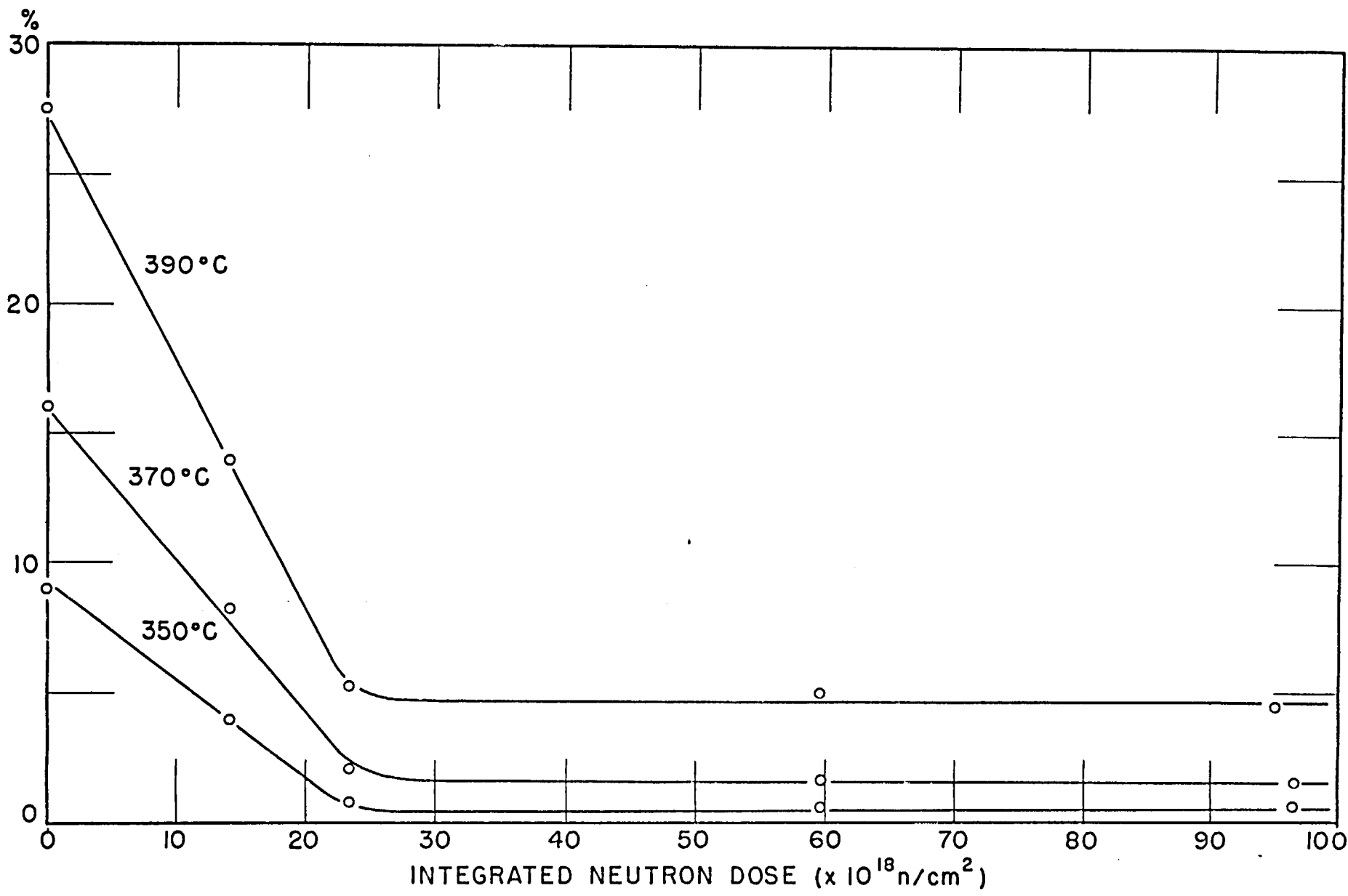FIGURE 4 ZnO CATALYST-EFFECT OF NEUTRON DOSES ON HYDROGEN YIELD

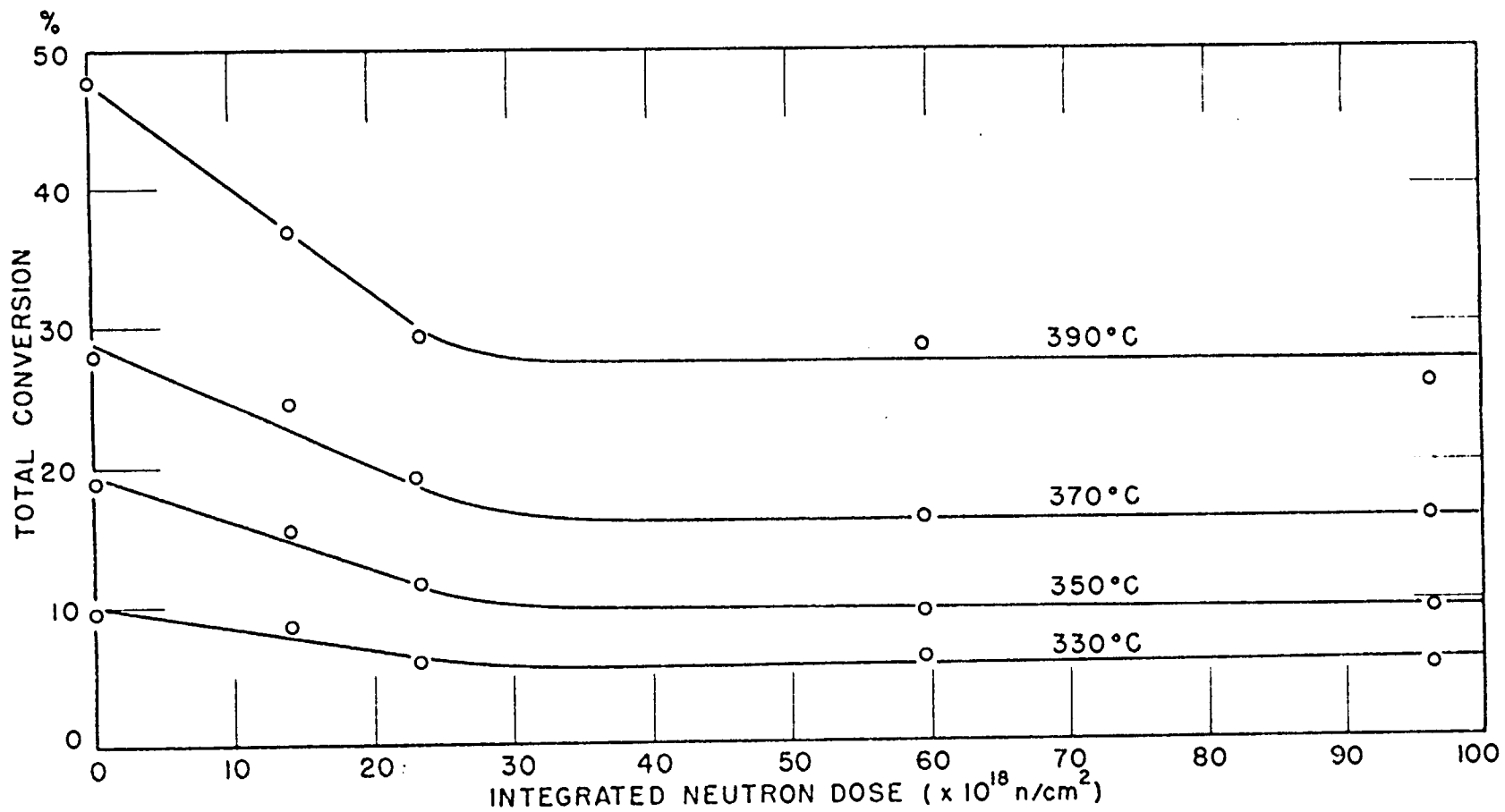FIGURE 5 ZnO CATALYST- EFFECT OF NEUTRON DOSES ON ETHYLENE YIELD.

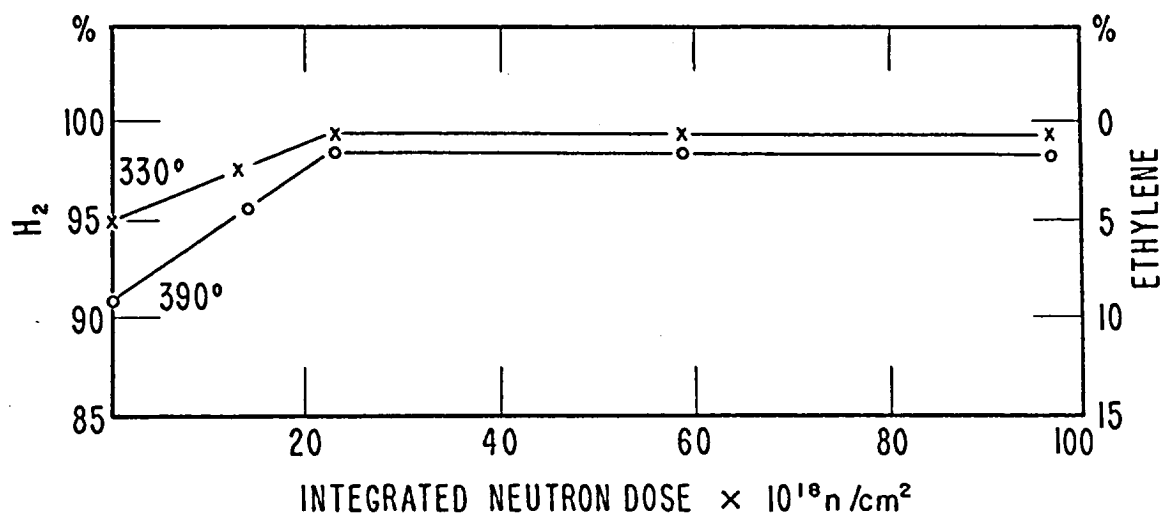FIGURE 6 ZnO CATALYST-EFFECT OF NEUTRON DOSES ON TOTAL CONVERSION

FIGURE 7 BEHAVIOUR OF ZnO AT VARIOUS INTEGRATED NEUTRON DOSES.

The neutron irradiation of ZnO results in nuclear transmutations in the solid, which lead to the production of impurities (mainly gallium-69) of different chemical character in the specimen, and obviously this is an irreversible process.

The natural abundance of Zn-68 is 18.57% in the zinc element, its neutron cross-section is 1.06 barn, and the half-life of Zn-69 is 52 min (11). Because of this short half-life, creation of gallium is practically complete by the time of receipt of the irradiated sample. An approximate calculation of the amount of gallium-69 created by nuclear transmutation of Zn-68 in the catalyst samples used is reported in Table 3.
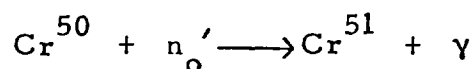
TABLE 3

Production of Ga-69 in Irradiated ZnO

Catalyst: ZnO	Integrated Neutron Dose	Ga-69 (ppm)
I	0	0
II	13.9×10^{18} n/cm^2	2.64
III	23.3×10^{18} n/cm^2	4.84
IV	59.6×10^{18} n/cm^2	12.2
V	96.6×10^{18} n/cm^2	22.0

Gallium is a donor impurity in ZnO.

For the first four catalysts, the amount of copper-65 produced by transmutation of the isotope zinc-64 is of the order of 0.2-1 ppm, about 1/20 of the amount of copper initially present as an impurity in the non-irradiated catalyst, and becomes quite appreciable (2 ppm) at the largest neutron doses and after a long period of decay (Catalyst V). Copper is an acceptor impurity if present in the form of Cu^{++}; in fact it lacks an electron in its closed shell. It may act as donor if present as Cu atom, that is, characterised by one electron in excess in the closed shell, while the Cu^{+} ion possesses a closed electron shell (8).

The exposure to neutron and gamma irradiation of the Cr_2O_3 catalysts did not show any shifting in the reaction path of the catalyst (Figures 8-11) and resulted in a decrease in the activity of the two chromic oxide catalysts, as seen in Figures 9 and 10. Such behaviour of the chromic oxide catalysts was expected. The neutron irradiation of Cr_2O_3 does not result in any nuclear transmutation such as to create significant impurities of different chemical character in the specimen, and the only transmutation created is:

$$Cr^{50} + n_o' \longrightarrow Cr^{51} + \gamma$$

Chromium-51 decays by K-capture with a 27.8-day half-life to vanadium-51, which is stable. The tests described here were done before there was any appreciable decay of chromium-51.
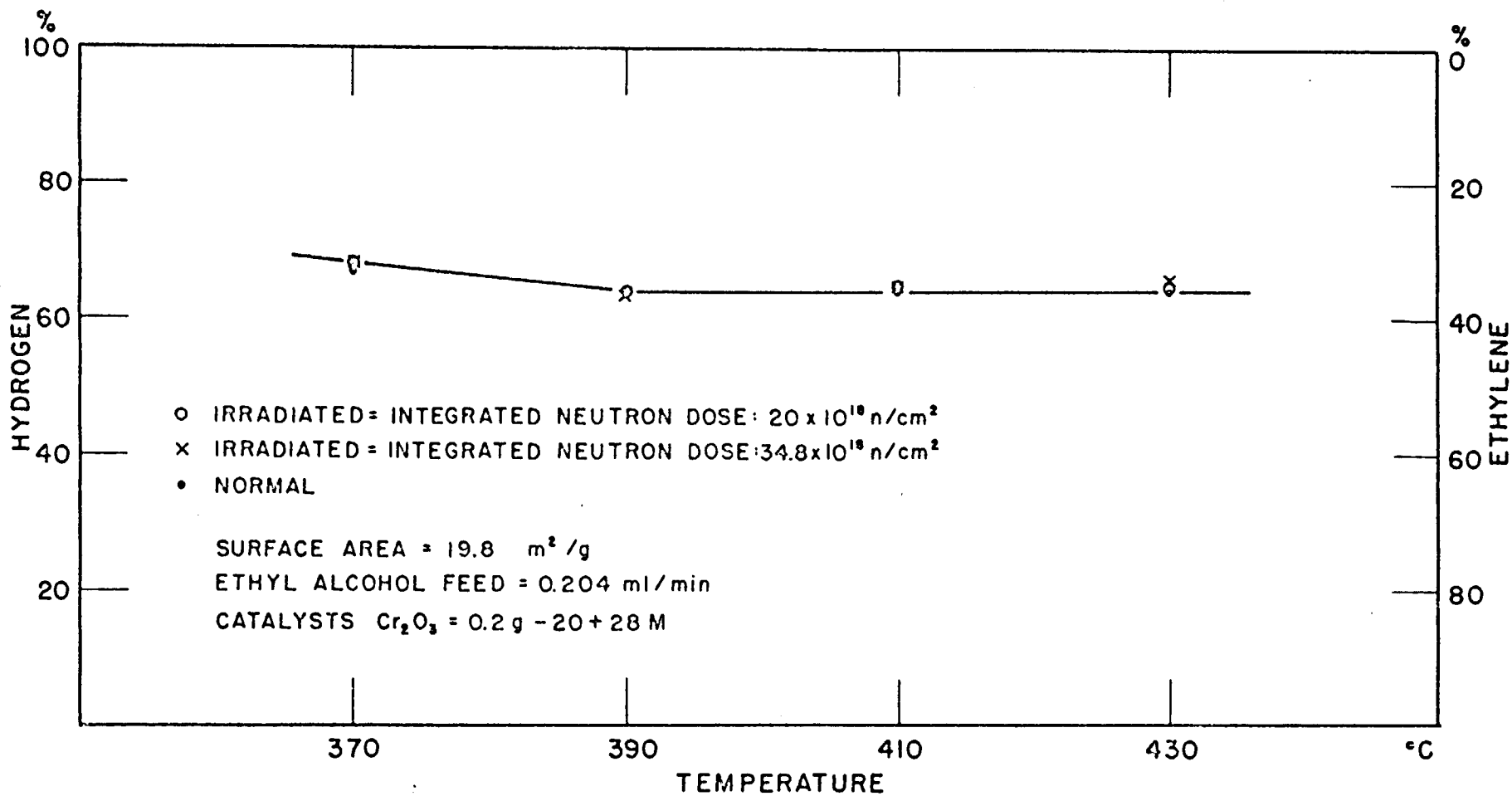
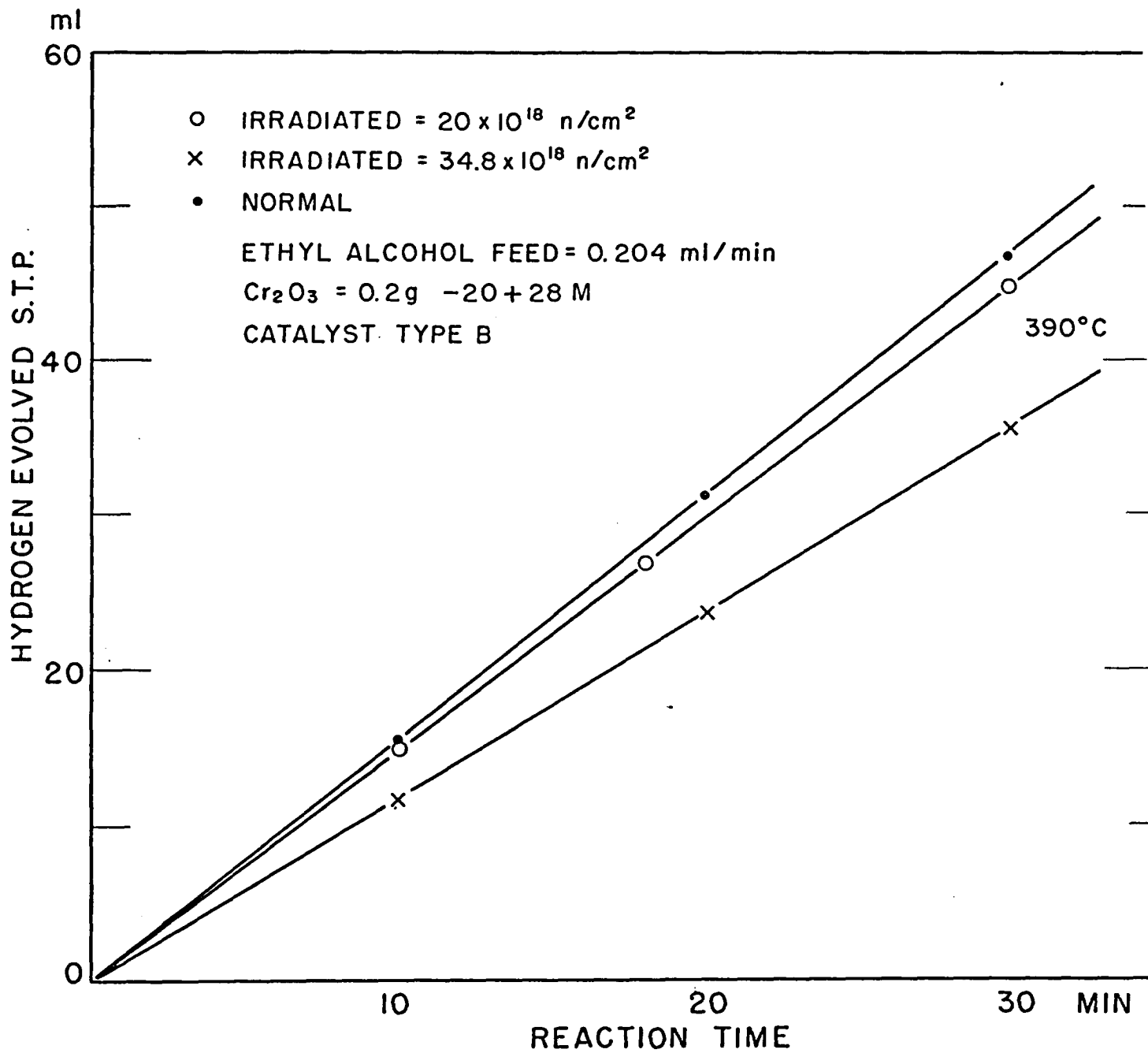FIGURE 8 BEHAVIOUR OF Cr_2O_3 CATALYSTS AT VARIOUS TEMPERATURES

Legend:

○ IRRADIATED = INTEGRATED NEUTRON DOSE: 20×10^{18} n/cm^2
× IRRADIATED = INTEGRATED NEUTRON DOSE: 34.8×10^{18} n/cm^2
● NORMAL

SURFACE AREA = 19.8 m^2/g
ETHYL ALCOHOL FEED = 0.204 ml/min
CATALYSTS Cr_2O_3 = 0.2 g − 20 + 28 M

Axis labels:
- Left: HYDROGEN (%)
- Right: ETHYLENE (%)
- Bottom: TEMPERATURE (°C)

ml

IRRADIATED = 20×10^{18} n/cm^2
IRRADIATED = 34.8×10^{18} n/cm^2
NORMAL

ETHYL ALCOHOL FEED = 0.204 ml/min
Cr_2O_3 = 0.2g −20 + 28 M
CATALYST TYPE B

390°C

HYDROGEN EVOLVED S.T.P.

REACTION TIME

FIGURE 9 REACTION RATES FOR Cr_2O_3 CATALYSTS.
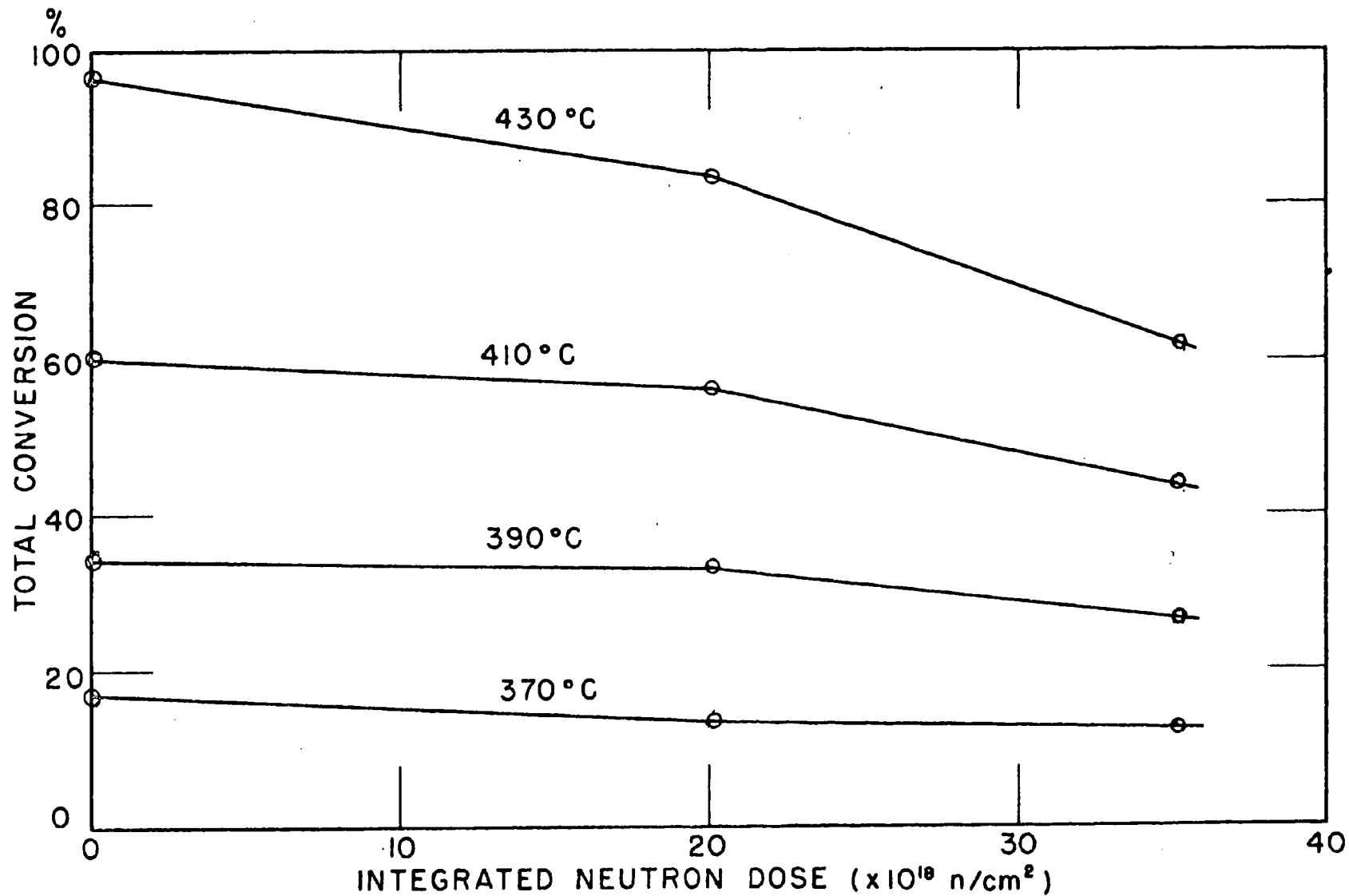
FIGURE 10 TOTAL CONVERSION AT VARIOUS INTEGRATED NEUTRON DOSES—
Cr₂O₃ CATALYST
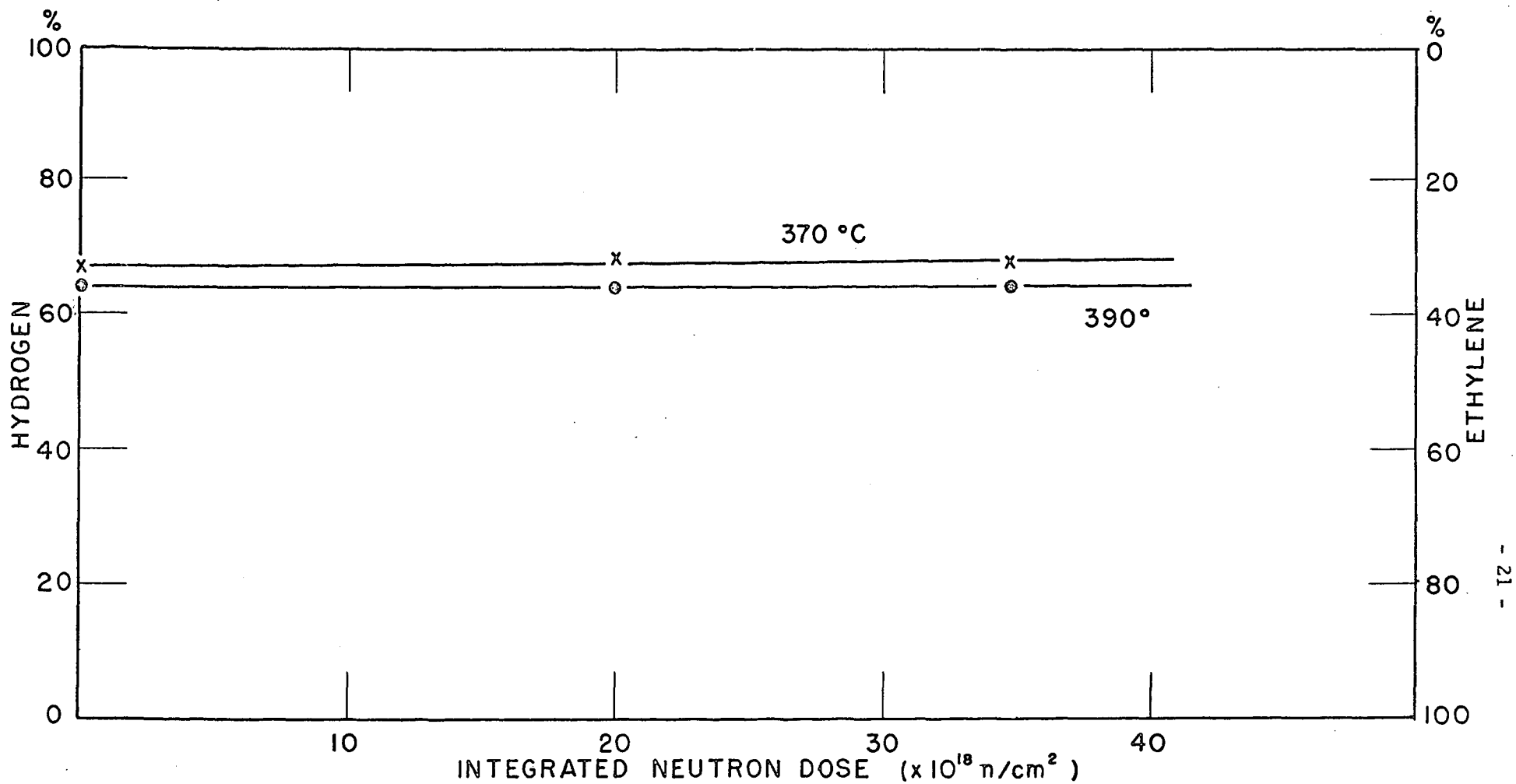
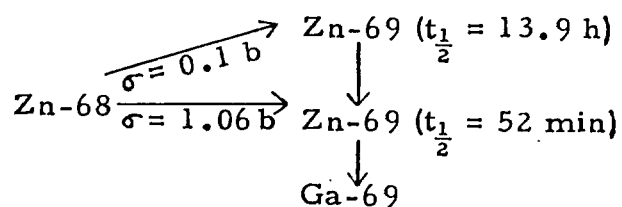FIGURE II   BEHAVIOUR OF Cr_2O_3 CATALYSTS AT VARIOUS INTEGRATED NEUTRON DOSES

CONCLUSIONS

For an n-type semiconductor it has been found by Wagner (12),
Hauffe (13), Schwab (14) and others, that the charge carrier concentration can
be raised by incorporating small amounts ($\sim 0.01\%$) of impurities. Addition of
oxides of trivalent metals, e.g., Al_2O_3 or Ga_2O_3, causes an increase, whereas
oxides of monovalent metals cause a decrease, in the concentration of charge
carriers. In irradiated zinc oxide both zinc and oxygen vacancies, as well as
interstitial zinc atoms, are produced. Interstitial oxygen atoms are unlikely in
stabilized ZnO and the displaced oxygen atoms probably go to vacancies or grain
boundaries, to be freed later. The nuclear reaction

$$Zn\text{-}68 \xrightarrow[\sigma = 1.06\,b]{\sigma = 0.1\,b} \begin{array}{l} Zn\text{-}69\ (t_{\frac{1}{2}} = 13.9\ h) \\ \downarrow \\ Zn\text{-}69\ (t_{\frac{1}{2}} = 52\ min) \\ \downarrow \\ Ga\text{-}69 \end{array}$$

appears to be responsible for the amount of gallium present. In the range of
temperatures investigated so far, it is believed that the lattice defects introduced
by gamma-ray and neutron irradiation are removed slowly, and this could
explain the ageing period during which the catalysts present a lower activity
and a lower H_2/C_2H_4 ratio compared with the non-irradiated one. It may be
mentioned that Kohn, Moore and Taylor (4) had shown that irradiation effects
are relatively stable in refractory oxides. The decrease in catalytic activity

of the chromic oxides as a result of both gamma and neutron irradiation ,
may be attributed to the decrease in the number of conduction-band electrons
by the creation of chromium in interstitial positions that are not completely
annihilated in the temperature range used and in the time these catalysts were
working.

This work has indicated a method for introducing controlled amounts
of impurities into catalysts, by neutron irradiation, that may have important
practical applications.

ACKNOWLEDGEMENTS

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