

CHANGES IN THE STRUCTURE OF A CATALYST DURING A CATALYTIC REACTION-DEHYDROGENATION OF CYCLOHEXANOL ON NICKEL OXIDE

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ABSTRACT

Cyclohexanol has been dehydrogenated to cyclohexanone and phenol over nickel oxide. Above 370° C., the electrical conductivity of the solid decreases in the presence of cyclohexanol. It subsequently registers an increase and finally attains a value characteristic of metallic samples. While no hydrogen is adsorbed on nickel oxide at 25° C., the sample after usage in the reaction adsorbs considerable amounts of hydrogen. The adsorption isotherm of hydrogen is quite similar to that observed in the case of metals. It is, therefore, inferred that during the reaction, the catalyst undergoes reduction to the metallic state.

INTRODUCTION

IN any catalytic process, the solid catalyst does not play the role of an inert substance on which the chemical reaction proceeds but the role of an active participant in one of the intermediate stages of the reaction. It is a characteristic and in fact, a distinctive feature of a catalytic process that at the end of the reaction, the catalyst is completely regenerated. However, in some cases, the composition of the catalyst itself does change to some extent in the reaction process. Thus, many reactions catalysed by solid oxides are usually accompanied by oxidation or reduction of the catalysts.¹ As the reaction proceeds, the degree and sometimes the nature as well of the stoichiometric disturbance may change. Boreskov and Matveyev² investigated the decomposition of methyl alcohol to carbon monoxide and hydrogen on zinc oxide. They found that during the reaction process, zinc oxide became enriched in zinc in excess of stoichiometry and thus underwent reduction. In fact, changes in the electrical conductivity clearly indicated the attainment of metallic character by the sample during the catalytic reaction.

In the present study, cyclohexanol has been dehydrogenated to cyclohexanone and phenol over oxidized nickel oxide catalyst in the temperature range 300–410° C. The electrical conductivity of this material as well as changes in the electrical conductivity during the catalytic reactions have been measured. The results throw additional light on the changes in structure and composition that nickel oxide undergoes during the dehydrogenation reaction.

EXPERIMENTAL

Nickel oxide was prepared by the decomposition of nickel carbonate at 500° C. The catalytic reactions were carried out in a fixed bed, vertical, flow reactor. Adsorption studies were carried out in a conventional constant-volume adsorption apparatus. For conductivity measurements, the sample was taken between two platinum electrodes fused in through the sides. The electrical measurements were performed with the aid of d.c. circuits. Potential differences between probes were measured by compensation using a VTVM (Heathkit V-7A/UK) or an oscilloscope as a zero instrument. The value of the activation energy of electrical conductivity for nickel oxide was 13.7 kcal.

RESULTS AND DISCUSSION

Cyclohexanol was dehydrogenated to cyclohexanone and phenol over nickel oxide. In the vertical flow reactor system employed in the present study, cyclohexene was not detected in the catalysate, though Galwey³ has reported its formation while examining the first stages in the reaction of cyclohexanol adsorbed on nickel oxide. The proportion of cyclohexanone and phenol in the catalysate at various temperatures is shown in Fig. 1. At all temperatures, a steady state of conversion was attained only after 40 minutes or so.

The mechanism of dehydrogenation of cyclohexanol below 370° C. appears to be different from that above 370° C. Below 370° C., the amount of unreacted cyclohexanol decreases with increasing temperature. Above 370° C., it shows an increase. On the other hand, cyclohexanone whose concentration in the catalysate increased upto 350° C., registers a fall above that temperature. Phenol follows a similar

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trend though the transition temperature is around 370° C. The apparent activation energy for the total decomposition of cyclohexanol, for the formation of cyclohexanone and phenol in the temperature range 300–350° C. are 11.3, 8.2 and 13.8 kcal/mole respectively.

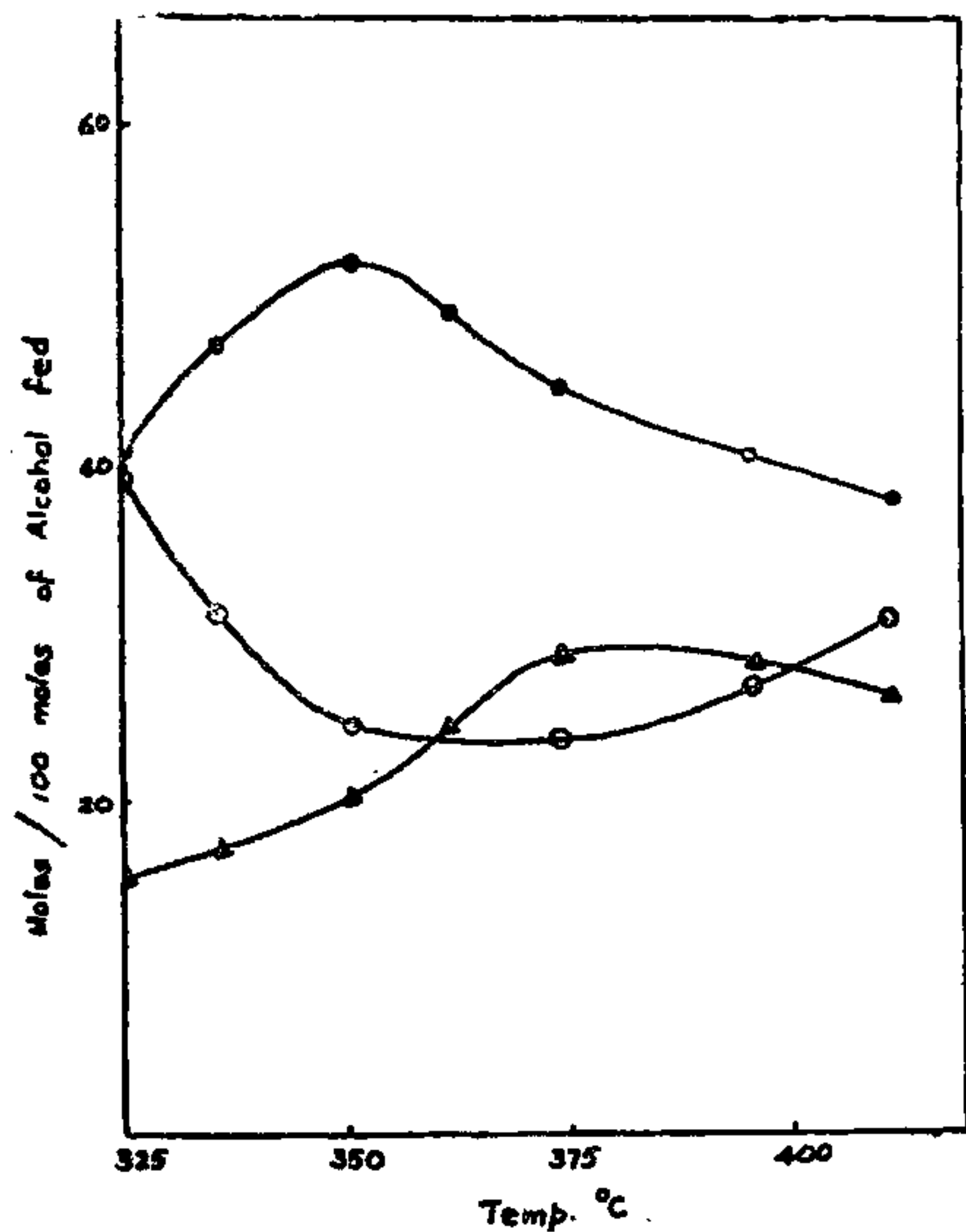


FIG. 1. Influence of temperature on the dehydrogenation of cyclohexanol over nickel oxide. $WHSV^{-1} = 1.0$ hr. ○ Unreacted cyclohexanol; ● Cyclohexanone; △ Phenol.

The effect of contact time on the dehydrogenation of cyclohexanol has been studied at 350° C. and 410° C. The results are shown in Fig. 2. At 350° C., with increasing contact time, the amount of cyclohexanol undergoing reaction increases reaching a value of about 85 mole % at a contact time of 2 hr., with a corresponding increase in the amount of phenol formed. Cyclohexanone reaches its maximum value of 52 mole % at a contact time of 1.0 hr. and then decreases with further increase in contact time suggesting that the cyclohexanone initially formed undergoes further dehydrogenation to phenol. At 410° C., with increasing contact time, the amount of cyclohexanol undergoing reaction increases reaching a value of 73 mole % at a contact time of 2 hr. This is less than that got at 350° C. The amount of phenol at 410° C. is also less than that at 350° C. In the region of very low contact time, the rate of cyclohexanone formation is higher than the rate of

formation of phenol. Since the maximum concentration of cyclohexanone is reached at 0.5 hr., while phenol reaches its maximum concentration only at a contact time of 2.0 hr., phenol should have been formed by the further dehydrogenation of cyclohexanone. From the values of initial rates, however, it may be inferred that phenol is formed simultaneously from either cyclohexanone or cyclohexanol.

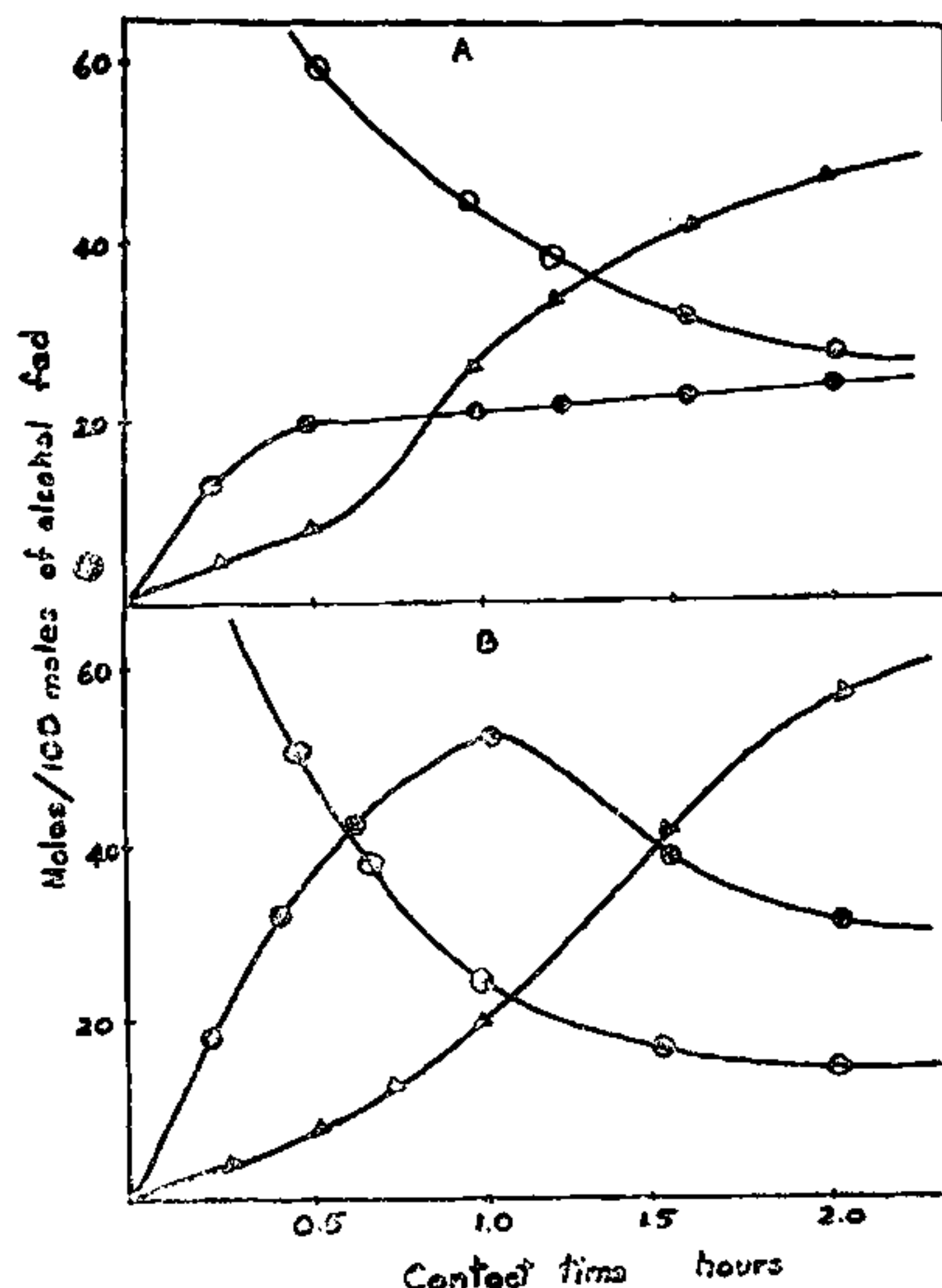


FIG. 2. Influence of contact time on the dehydrogenation of cyclohexanol over nickel oxide. A = 410° C. B = 350° C. ○ Unreacted cyclohexanol; ● Cyclohexanone; △ Phenol.

The changes in the electrical conductivity of nickel oxide in the atmosphere of cyclohexanol are given in Fig. 3. Below 370° C., the conductivity decreases with time and finally attains a constant value. Above 370° C., there is an initial decrease in the conductivity followed by an increase. The $\log \sigma$ value increases above the initial conductivity to reach a constant value of conductivity. This value does not alter during the further course of the reaction. The electrical resistance was of the order of a few ohms in this region.

These results indicate that above 370° C., the catalyst is reduced to metallic nickel. The initial decrease in conductivity shows a surface reduction of Ni^{3+} to Ni^{2+} . The subsequent increase indicates a further reduction of Ni^{2+} to metallic nickel, the conductivity of which is of the order of a few mhos. Even at

380° C., it was observed that the conductivity of the sample decreased first and when the alcohol feed was stopped and oxygen-free nitrogen gas was let in at very low pressures, the desorption of the species brought about an increase in the conductivity which rose above the initial conductivity. This shows that a surface layer of metallic nickel begins to form at this temperature, in the course of the dehydrogenation of cyclohexanol. Such a case was not observed below 370° C.

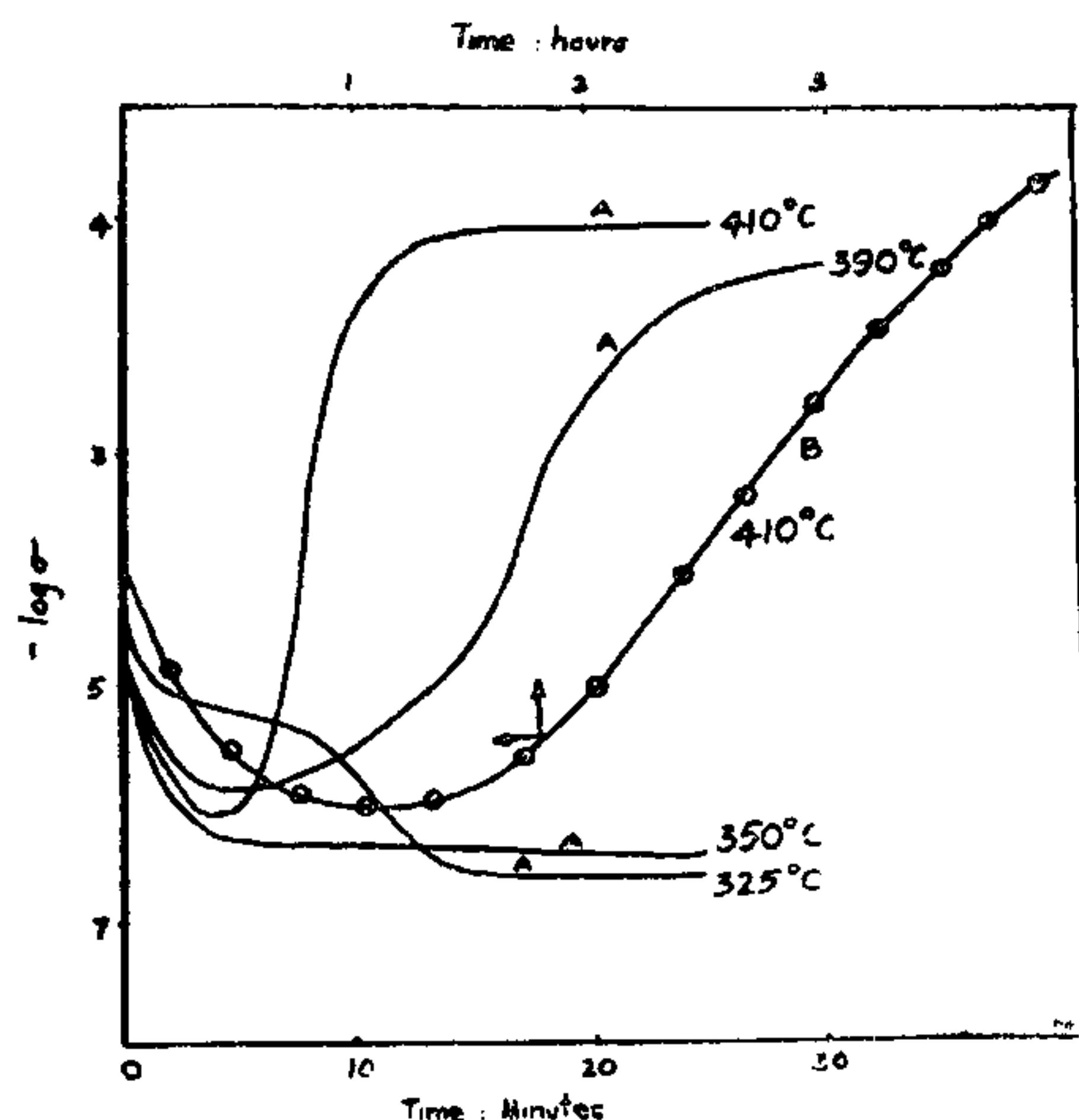


FIG. 3. Changes in the electrical conductivity of nickel oxide. A—In the atmosphere of cyclohexanol vapours; B—In the atmosphere of hydrogen.

The changes in conductivity of nickel oxide at 410° C. while passing dry hydrogen are also shown in Fig. 3. The conductivity decreases first and then increases, the process taking several hours to attain a constant value.

The effect of temperature on the dehydrogenation of cyclohexanol had already showed that above 380° C., the concentration of phenol goes down suggesting the possibility of phenol getting hydrogenated to cyclohexanol (Fig. 1). When phenol and cyclohexanol were mixed in 1:1 ratio and passed over the catalyst, the concentration of phenol was higher in the catalysate. In another series of experiments, phenol was mixed with isopropanol and passed over the catalyst at 410° C. If adsorbed hydrogen, liberated in the course of alcohol dehydrogenation, plays a part and is responsible for such hydrogenation activity, the nature of the catalyst at this temperature being identical,

cyclohexanol should be formed. This was not observed.

Schuit and van Reijen⁴ have successively applied hydrogen chemisorption to measure the surface area of the metallic part of nickel on carrier catalyst. In the present study, such adsorption isotherm studies were undertaken to follow the formation of metallic nickel on nickel oxide resulting from the dehydrogenation of cyclohexanol above 370° C. (Fig. 4).

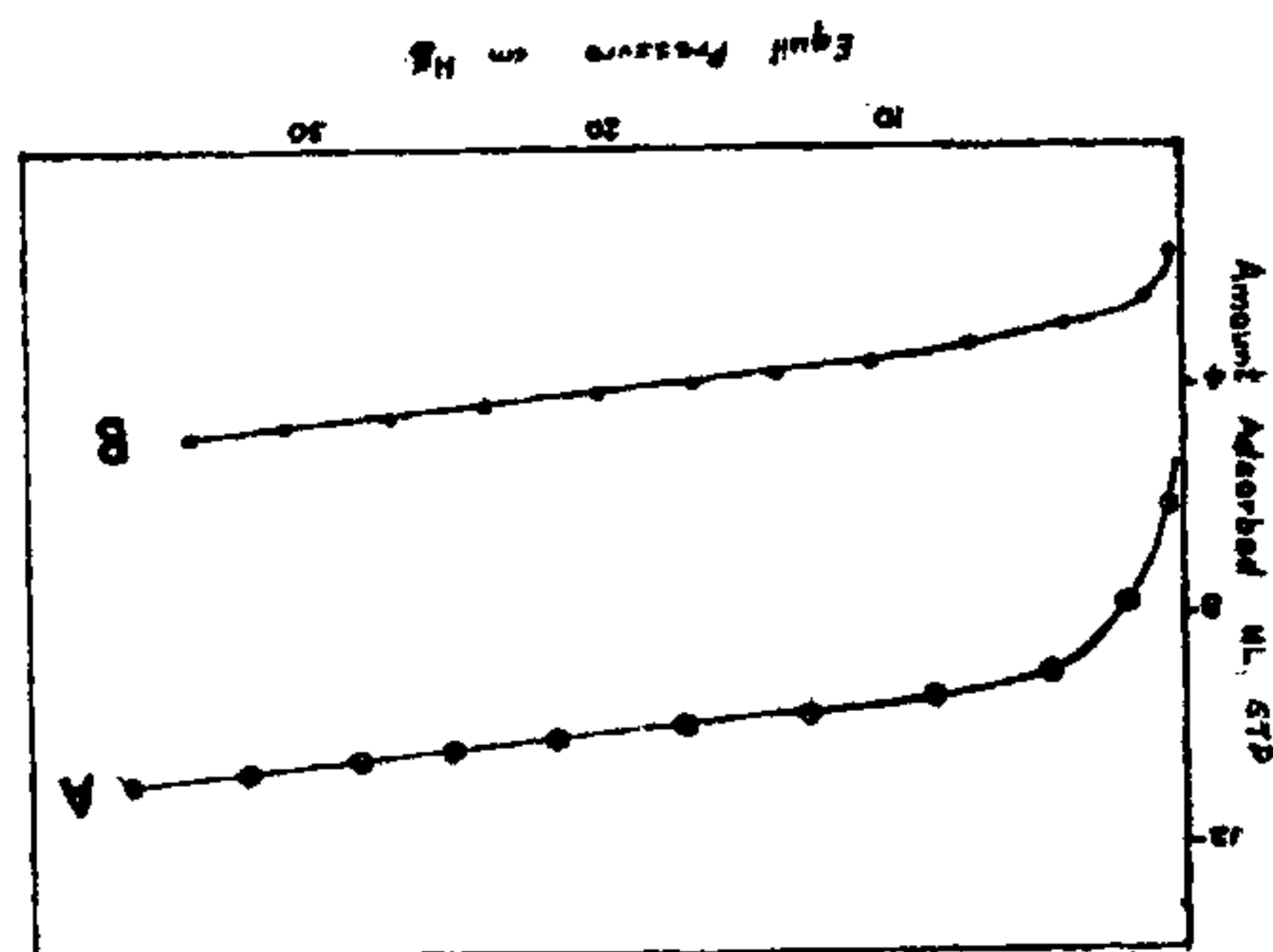


FIG. 4. Adsorption isotherms of hydrogen at 25° C. A: ○ Catalyst treated with cyclohexanol at 400° C. for an hour. B: ●—Catalyst reduced with hydrogen at 400° C. for 3 hours.

In the equilibrium pressure range of 30 to 600 mm. Hg., there was no adsorption of hydrogen on oxidised nickel oxide, the isotherm measurement being carried out at 25° C.

After each run of cyclohexanol dehydrogenation on oxidised nickel oxide at different temperatures, the catalyst was flushed with oxygen-free, dry nitrogen and the catalyst vessel was attached to the adsorption system, evacuated to 10^{-6} cm. Hg., and the hydrogen adsorption isotherms were measured at 25° C. For the catalysts treated upto 370° C., the amount of hydrogen adsorbed was found to be almost negligible, though the colour of the catalyst changed from greyish-black to yellowish-green. The latter observation shows that the chemisorbed excess oxygen on oxidised nickel oxide is desorbed completely by the adsorption of alcohol molecules in the dehydrogenation process.

Considerable amount of hydrogen was found to get adsorbed on the catalyst treated at 410° C. with vapours of cyclohexanol. In Fig. 4, isotherm A shows that the nature of the catalyst is similar to a metal-on-carrier type. The isotherm B is for the catalyst reduced at

400° C. for 3 hours. The similarity of the two curves further reinforces the fact that during the dehydrogenation reaction, the surface of nickel oxide is reduced to the metallic state. Thus starting from a pure metal oxide catalyst, a metal-on-metal oxide is obtained during the reaction. This means that the process of catalyst preparation cannot, strictly speaking, be considered as finished at the moment when the reaction starts. If one may so express it, the final preparation of the catalyst occurs in the process of reaction itself.

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SENSITIVITY TO GIBBERELIC ACID IN RELATION TO DWARFING AND HARVEST INDEX IN BREAD WHEAT

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IT is well known that several genetic dwarfs in crop plants become tall when given an exogenous application of gibberellic acid (GA_3).¹ Allan and his co-workers² have studied the comparative response to GA_3 of dwarf, semi-dwarf and standard short and tall winter wheat varieties. They found that the dwarf and semi-dwarf varieties though responsive to applied GA_3 were not induced to grow to normal height, whereas standard-height varieties were stimulated significantly. All of these were winter varieties and GA_3 was applied after plants were exposed to low winter temperatures. The 'Norin' dwarfing genes introduced from Japan in wheat breeding programmes in the United States, Mexico and other countries after World War II have led to a major yield breakthrough in bread wheat by enabling the repatterning of the plant architecture in a manner suited for high levels of application of fertilizer and water.³ The present study was undertaken to assess the reaction of wheat varieties possessing the 'Norin' dwarfing genes to the application of GA_3 .

The following seven varieties were chosen for the study: two tall Indian varieties (C. 591 and N.P. 824) a γ -ray-induced dwarf mutant of N.P. 824, two semi-dwarf varieties developed in Mexico (Sonora 64 and Lerma Rojo), an experimental strain possessing 3 major genes for dwarfing (Triple dwarf) and an induced amber-grain mutant of Sonora 64 which was released for cultivation in India under the name

Sharbati Sonora.⁴ Monosomic analysis revealed that Lerma Rojo has a recessive gene for dwarfing in chromosome 6D and Sonora 64 and Sharbati Sonora have two such genes in chromosome 2A and 4D.⁵ The triple dwarf had all the three genes with a reducing effect on height. An analysis of the pathway through which the varieties with 'Norin' dwarfing genes give high yields showed that besides being able to utilise more fertiliser because of the favourable morphological frame, they also had a better harvest index (i.e., the ratio of grain to total dry matter, Table I).

TABLE I

Variety	Total dry matter yield (tonnes/hectare)	Harvest index
C. 591	10.30	0.29
N.P. 824	10.60	0.33
Dwarf mutant of N.P. 824	9.00	0.27
Lerma Rojo	11.00	0.50
Sonora 64	11.00	0.55
Sharbati Sonora	11.00	0.55
Triple dwarf	10.50	0.67

The procedure for assessing sensitivity to GA_3 was as follows: Grains were soaked on three layers of filter-paper in petri plates containing five ml distilled water. The seeds