

## Effect of Hydrogen on Carbon Deposition Catalyzed by Copper-Nickel Alloys

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Carbon deposition from benzene onto cold-rolled sheets of copper-nickel alloys was studied at temperatures ranging from 570 to 700°C, in atmospheres of hydrogen, helium, and their mixtures. The deposition rate onto pure nickel was higher in hydrogen than in helium, whereas that onto 80% nickel alloy was higher in helium-rich atmosphere than in hydrogen. In hydrogen-rich atmospheres, the deposition proceeded at a constant rate, which changed reversibly with the composition of the atmosphere. In helium, the deposition rate decreased gradually. Hydrogen seems to affect the catalytic deposition in two ways: (i) by removing surface carbon film which hinders the catalytic action of metal surface, and (ii) by removing the chemisorbed species which are the precursor of the deposition.

### INTRODUCTION

In the course of a study of the deposition of carbon catalyzed by nickel and its copper alloys, it was observed that hydrogen suppressed deposition onto copper-rich substrates, whereas it accelerated deposition onto nickel-rich ones (1, 2). It was subsequently found that the effect of hydrogen depends critically on the temperature and the composition of the substrates, as will be seen below.

The suppression of carbon deposition by hydrogen has been observed in cases of deposition on some inert surfaces such as glass and platinum (3-5). The accelerative effect of hydrogen on the catalytic carbon deposition has often been reported (6-9), but not well understood. The present study was undertaken to explain the role of hydrogen in the catalytic deposition process. The results will be presented together with a possible explanation based on a mechanism of the deposition discussed in an earlier report (1).

### EXPERIMENTALS

Carbon was deposited from benzene, at a partial pressure of 8 kPa, onto a cold-rolled sheet of metal specimen, suspended in a quartz reactor, and the weight change of the specimen was measured by means of a quartz spring balance. The experimental arrangement and the procedures were the same as before (1), with the exceptions given below.

The reactant, benzene vapor, was carried by an atmospheric flow of hydrogen-helium mixture at a total flow rate of  $30 \pm 0.5$  cm<sup>3</sup> (STP)/min. The composition of the carrier was calculated from the predetermined flow rate of hydrogen which was controlled by a flow controller.

High purity metal powders of 99.99% grade were used to prepare the metal specimens. In the metallurgic process, manganese (0.3%) was added for deoxidization. The impurities will be ignored and the specimens will be referred to by the weight fraction of nickel to the sum of

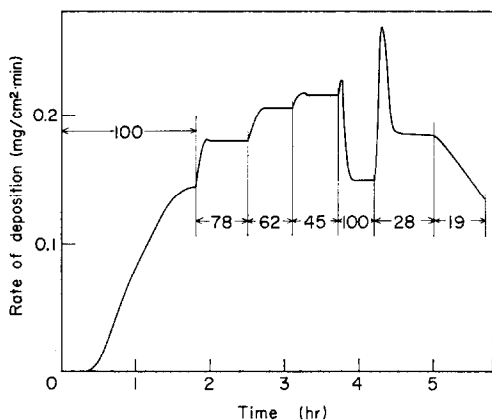


FIG. 1. Rate of carbon deposition onto 90% nickel at 608°C. Numerals in the figure denote volume fraction (in %) of hydrogen in carrier.

copper and nickel. The specimens were heated in hydrogen at 700°C for 2 hr for conditioning before deposition runs, unless otherwise noted.

### RESULTS

A typical variation of the deposition rate is illustrated in Fig. 1 for a case onto a 90% nickel sheet. In hydrogen, carbon

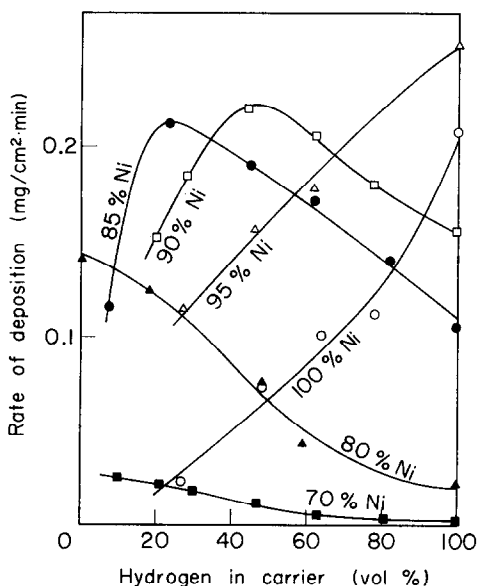


FIG. 2. Comparison of the deposition rates on copper-nickel alloys at 606 to 608°C.

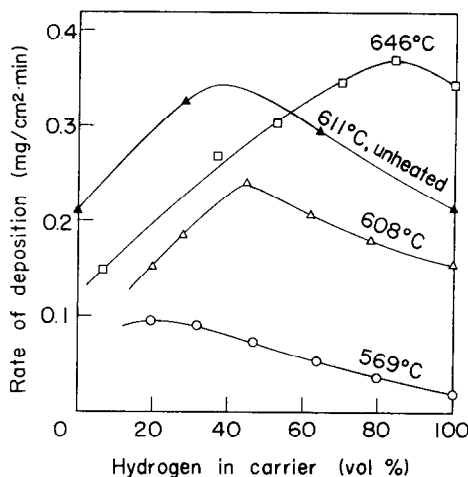


FIG. 3. Temperature dependence of the deposition rate on 90% nickel.  $\blacktriangle$ : On the specimen without pretreatment in hydrogen at 700°C.

deposition took place after an induction period of about 20 min and the rate increased gradually until a steady state was attained. Steady states were obtained successively by changing the composition of the carrier and they were reversible unless a helium-rich carrier was used. In helium-rich atmospheres, the rate decreased with time and a very rapid deactivation was seen in pure helium.

The rates of deposition at around 600°C in mixed carriers are compared in Fig. 2, in which the data on one specimen are presented for each substrate. The rates are reproducible within 10% among different specimens of the same composition. Interestingly, only a 5% difference in alloy composition makes the reactivity pattern markedly different. The deactivation in helium-rich carriers seemed to occur in the region where the rate had a negative dependence on hydrogen content.

The reactivity patterns at different temperatures were sought for 90% nickel sheet which showed a maximum in the pattern at 608°C. As shown in Fig. 3, the maximum shifted toward higher concentration of hydrogen as the temperature was raised. Included in Fig. 3 is a result for a

specimen tested without annealing in hydrogen. This indicates that the surface and bulk state of the substrate does affect the rate itself as discussed before (1), but does not affect the position of the maximum. Arrhenius type plots for the deposition in hydrogen are given in Fig. 4. Both 100 and 80% nickel showed maxima in the rate versus temperature profile.

To check the possibility that the above behavior is inherent in the cold-rolled sheet, carbon depositions onto powder specimens were carried out in mixed carriers. On an alloy powder of 85% nickel, the ratios of the rates in carriers of 100, 65, and 30% hydrogen were roughly 1:3:5 at 610°C. On a 100% nickel powder, the rate in pure hydrogen was no less than eight times the rate in 20% hydrogen. These results indicate that the dependence of the deposition rate on the atmosphere is not associated with a particular form of the metal.

The exhaust gas left during the deposition in hydrogen was found, by gas chromatography, to contain a considerable amount of methane. For example, the relative rate of methane formation to that of carbon

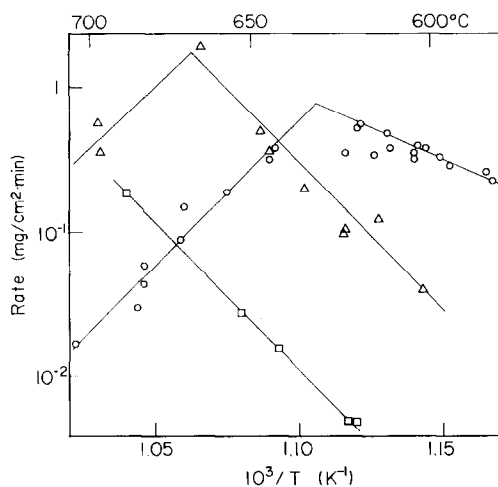


FIG. 4. Arrhenius plots of the deposition rate in hydrogen. ○: 100% nickel; △: 80% nickel; □: 70% nickel.

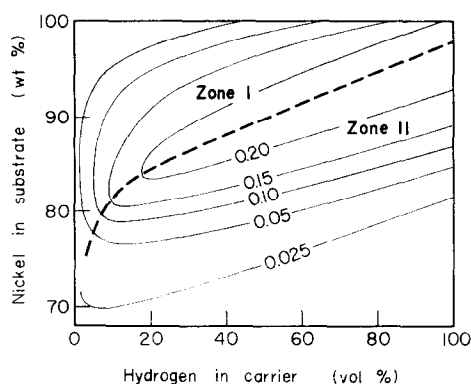


FIG. 5. Contour map of the deposition rate at around 607°C. Numerals denote the rate in mg/cm<sup>2</sup>·min. Broken line represents the ridge which divides two zones.

formation was 0.2 and 0.06 (in mole unit) at 590 and 646°C, respectively, on 90% nickel. The relative rates on other substrates were about the same.

#### DISCUSSIONS

The carbon formation catalyzed by metals, especially by nickel, has been investigated by several workers. There are a few types of deposit (10-12) among which a fibrous form of carbon containing metal particles is the main product under the present conditions (1). The following mechanism has been proposed for the formation of fibrous carbon (9, 11). Gaseous hydrocarbon molecules adsorb dissociatively on a metal surface and form adsorbed carbon atoms. These atoms dissolve into metal and aggregate at a site where they condense to form a nucleus of bulk carbon. When this nucleus grows beneath the metal surface, the carbon so formed pushes out metal particles from the sheet and takes the form of a filament. The dissociation, or carbon atom formation, should occur at a site separated from the condensation site for a lasting catalytic formation of bulky mass on the catalyst itself. In addition to the above, we have suggested that a concurrent reaction in which adsorbed carbon atoms form surface film

competes with the main process, to explain the rate-decrease at higher temperatures and the rapid deactivation of nickel-rich substrates in helium (1, 2). It has also been reported that the growth of carbon filaments terminated when the metal surface was covered by carbon film (13, 14).

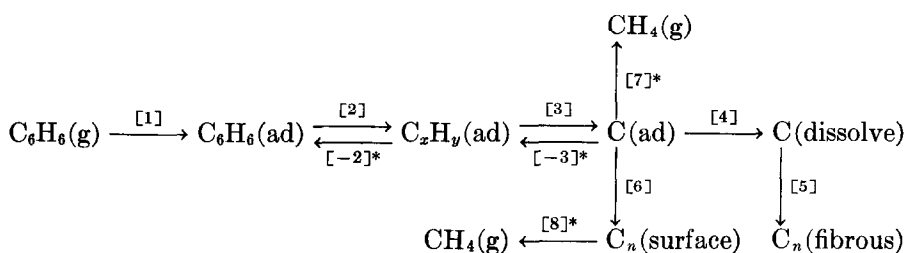
Before examining the present results as to whether they can be shown to be consistent with the above mechanism, we will recast the data in Fig. 2, with some degree of smoothing, into a contour map (Fig. 5). The map has a ridge and this divides the studied region into two zones as defined in the figure. In zone I, a higher nickel content or a lower hydrogen concentration tends to reduce the deposition rate, while an inverse relation is observed in zone II.

One of the kinetic features in zone I is that the deposition rate decreases irreversibly with time when helium-rich carrier is used. This seems to be caused by the formation and development of surface carbon film, which covers the active sites for chemisorption. If this is the case, the accelerative effect of hydrogen in zone I is due to the removal of such a carbon film or its precursors, perhaps through the formation of methane. This is similar to

a case of dehydrogenation of hydrocarbons with metal catalysts, where hydrogen maintained the metal surface active by removing the hydrocarbon residues (15). The effect is expected to be more pronounced when carbon atoms are formed rapidly, i.e., in cases of deposition on nickel-rich substrates.

The suppressive effect of hydrogen in zone II can be connected with the inhibition of the deposition onto alloys containing more than 69% copper (1), and, therefore, with the effects observed in cases of noncatalytic depositions (3-5). The effect can be best understood as a decrease in the concentration of adsorbed carbon atoms caused both by the reverse reactions of surface dehydrogenation and by the gasification of surface carbon atoms to form methane.

A scheme for the present interpretation is given below, where the asterisks denote the reactions with hydrogen. In both zones, hydrogen is supposed to eliminate the adsorbed species, but it mainly works in step [8] as a "cleaning agent" in zone I, whereas it acts mainly in steps [7], [-2], and [-3] in zone II.



Thermodynamically, higher temperatures favor the surface decomposition of hydrocarbons rather than the hydrogenation reactions, though the temperature dependences of the individual steps are not known. If the equilibrium consideration is applied as a rough approximation to the temperature dependence of the rate, a rise in the temperature would lead to an extension of

zone I, i.e., a shift of the ridge in Fig. 5 to lower right, in accordance with the observed trend in Fig. 3. The negative temperature dependence of the deposition rate at higher temperatures (Fig. 4) can be attributed to a rapid formation of surface carbon which hydrogen can only partly eliminate.

There may be other types of action of hydrogen which can be related to the

observed behavior. Hydrogen may alter the rate of adsorption of benzene, in a similar manner to the coadsorption of ethylene and hydrogen (16), or it may modify the property of the catalyst itself (17). Adsorbed hydrogen atoms can assist the dissociation of benzene by abstracting hydrogen atoms from adsorbed molecules (18). Lobo *et al.* suggested an acceleration mechanism due to a surface dehydrogenation by adsorbed hydrogen atoms for the case of deposition from olefins (19). Dissolved hydrogen in nickel is reported to have no effect on the diffusion of carbon atoms through the metal (20), but it may loosen the grain boundaries of the metal, from where the detachment of nickel particles occurs. In metallurgy, the hydrogen embrittlement of iron base alloys is a familiar phenomenon and a "decohesion" of metal-metal bond has been proposed for it (21). These factors could contribute to the deposition process, but are not sufficient by themselves to explain the whole kinetic behavior.

Hitherto, we have neglected the effect of the surface state of metal, i.e., possible influences of crystallite size distribution and surface enrichment of an alloy component, or its impurity. Some of these were discussed in the preceding report, though not conclusively (1). The surface enrichment of manganese could have occurred, but the deposition behaviors on specimens with less manganese were not greatly different from the present ones. We believe that the surface state of metal affects the rate of deposition more or less, but does not significantly affect the dependence of the rate on the composition of the atmosphere.

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