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Effect of hydrogen on carbon deposition from carbon monoxide on nickel catalyst

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The role of hydrogen in carbon deposition on Ni has been studied at $H_2/CO < 1$ and 698 K by determining the respective rates of the carbon-forming reactions: (1) $CO + H_2 \rightarrow C + H_2O$ and (2) $2CO \rightarrow C + CO_2$. The steady-state rate of reaction (1) increases in proportion to H_2 pressure. On the other hand, reaction (2) is facilitated by the addition of an extremely small amount of H_2, so that the rate becomes about eight times that for pure CO but hardly varies as more H_2 is added. Similarly, there is a great difference in catalytic activity for ethylene hydrogenation between spent catalysts obtained in the deposition with and without H_2. These findings suggest that hydrogen, even in a small amount, makes free Ni surface area larger than for pure CO.

Keywords: Carbon deposition; hydrogen effect; nickel

1. Introduction

In the studies of carbon deposition from hydrocarbons or CO on transition metals, it has been frequently found that the presence of hydrogen in a reacting atmosphere enhances the deposition rate [1–5]. For the deposition from mixtures of CO and H_2, the first detailed studies were made on Fe/Al_2O_3 by Walker et al. [1]. Recently, Bianchi and Bennett [5] reported that the rate enhancement resulting from the presence of a small amount of hydrogen ($H_2/CO = 1/10$) on an iron surface is due to the hydrogen-assisted CO dissociation process in which surface OH species are proposed to be formed as an intermediate for both of the following carbon-forming reactions:

$$CO + H_2 \rightarrow C + H_2O\,, \tag{1}$$

$$2CO \rightarrow C + CO_2\,. \tag{2}$$

Another factor which has so far been pointed out [6–9] is that excess hydrogen acts to keep metal surface free from carbonaceous deposits by reacting them away. At low concentrations of H_2, however, uncertainty still exists as to the contribution of such a geometric factor. Thus, in the present study, the role of hydrogen in carbon deposition has been investigated by determining the respective rates of reactions (1) and (2) on Ni catalyst at $0 \leqslant H_2/CO \leqslant 0.6$ and 698 K. In addition to these kinetic data, catalytic activity for ethylene hydrogenation has been measured after interrupting the deposition reaction to estimate the number of free Ni surface atoms as active sites.

2. Experimental

Polycrystalline Ni ribbon, 0.1 mm thick and 2.5 mm wide (Nilaco Co., 99.95%) was cut to convenient sizes to be used as catalysts. The catalysts with apparent areas of about 2.8 and 6.5 cm^2 were polished, degreased with acetone vapor, and then reduced with 100 Torr of H_2 at 723 K before use. Carbon deposition reactions were carried out in a static system at 698 K, by varying H_2/CO ratios at a fixed initial pressure of CO (50 Torr). The following two apparatuses were used: one was a Cahn electrobalance (reaction volume: 3200 ml) and the other a closed-circulation apparatus (260 ml) equipped with a Baratron capacitance manometer and a sampling tube for GC analyses with an active carbon column. In the experiments with the latter apparatus the products, H_2O and CO_2, were removed continuously by cooling a U-shaped trap locating in a circulation path at 77 K in order to avoid the possible occurrence of their secondary reactions, such as the water–gas shift reaction and the reverse reactions of (1) and (2). Thus, the materials actually detected during the reaction were H_2, CO and a byproduct CH_4. H_2 is, however, much less sensitive than the others in a He carrier, and hence gas compositions were determined by calibrating GC-peak intensities for CO and CH_4 with 10 Torr of N_2 which was premixed with the reactants as an internal standard. In several runs, relative amounts of H_2O and CO_2 condensed in the trap were analyzed with a Porapak QS column. All these GC data were collected with an electronic integrator (SIC Chromatocorder). The rates of reactions (1) and (2) were determined from the amounts of CO and H_2 consumed, in which CH_4 is conveniently assumed to be formed through the reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O\,. \tag{3}$$

Ethylene hydrogenation was carried out with 10 Torr of equimolar mixture at 323 K in the circulation apparatus, after interrupting the deposition reaction by evacuation for 15 min. High purity gases (Takachiho Chem. Co., H_2 99.9999%, CO 99.95%, C_2H_4 99.9%) were used without further purification.

3. Results and discussion

Fig. 1 shows the results obtained with the electrobalance. In this series of experi-

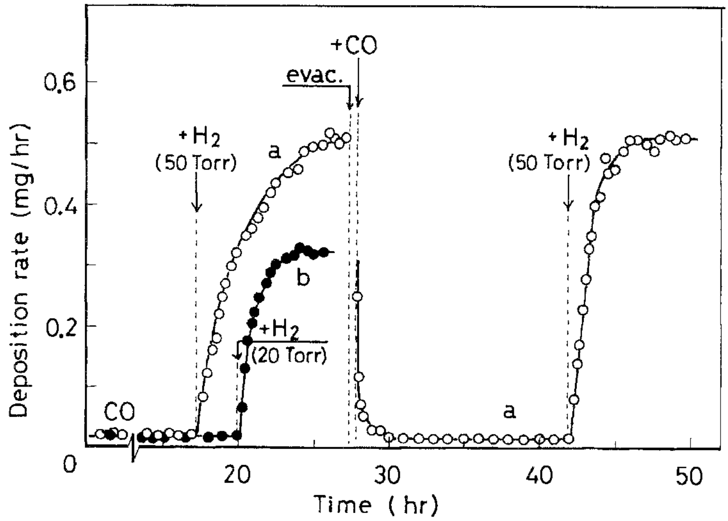

Fig. 1. Effect of the addition of H_2 on carbon deposition from CO (50 Torr) at 698 K. Initial area of catalyst: 5.6 cm^2.

ments, H_2 was suddenly admitted to the catalysts (6.5 cm^2) when the reaction with 50 Torr of CO proceeded to a small extent. The deposition is very slow with pure CO, but after the addition of H_2 accelerates to a constant value (R_c) which was found to continue to heavy deposition. Such an accelerative phenomenon can be attributed to a gradual increase of active sites. The possible explanation of this increase lies in either the partial removal of carbon layers covering catalyst or progressive separation of Ni particles from the catalyst surface. The fact that run (a) is repeated with a similar pattern and with almost the same value of R_c indicates that Ni particles have been already broken away to some significant extent in the first run with pure CO, and hence that the latter factor seems to be unimportant. On the contrary, the former factor is demonstrated by the variation of deposition rate in the second run with pure CO. That is, the rate is fast at the very beginning but declines quickly to almost the same level as in the first run, showing a severe reduction of active sites in the absence of H_2. Another point to note is the fact (not shown) that R_c increased with increasing H_2 pressure, attained a maximum in the range 40–50 Torr, and then decreased.

Calculation of the amount of CO taken up by each of reactions (1)–(3) is based on the assumption that other secondary reactions could be ignored. Unexpected changes in gas compositions due to these reactions were examined by measuring the relative amounts of H_2O and CO_2 condensed in the trap. The results are summarized in table 1, together with those predicted from the calculation. Observed H_2O/CO_2 ratios are markedly different from the values of less than 0.1 which should be obtained when the water–gas shift reaction is in equilibrium at 698 K in the range $P_{H_2}/P_{CO} < 0.6$. This fact and the close agreement between the predicted

Table 1
Comparison of calculated and observed H_2O/CO_2 ratios

Pressure (Torr)		Time (h)	Calc. CO-uptakes (μmol) by react.			H_2O/CO_2	
H_2	CO		(1)	(2)	(3)	calc.	obs.
5.63	50.74	5	11.3	11.2	–	2.0_2	2.2_8
10.06	50.79	4	9.5	6.0	0.9	3.4_7	3.6_6
14.94	49.64	6.5	30.8	18.5	4.7	3.8_4	3.7_2
26.07	50.09	5	29.1	11.8	4.7	5.7_3	5.5_2

and observed ratios indicate that the secondary reactions have little effect on distorting gas compositions under the present conditions. Fig. 2 shows typical results of CO uptakes obtained with initially fresh catalysts (2.8 cm^2) for different H_2/CO ratios including pure CO (dotted line 2′) for comparison. CH_4 is formed at a H_2/CO ratio of 0.58 (a), but not at 0.10 (b). In both cases, the three reactions proceed linearly with time after a certain initial period during which their rates increase gradually, as clearly shown in fig. 2a. When these catalysts were used for subsequent runs performed with identical mixtures, the linear progresses were reproduced without the identical period. Thus, it seems quite likely that with H_2 present the number of active sites increases with the progress of the separation of Ni particles, which takes place effectively in the initial period, and is kept almost constant in a steady-state. Alternately, the lack of the initial period for pure CO

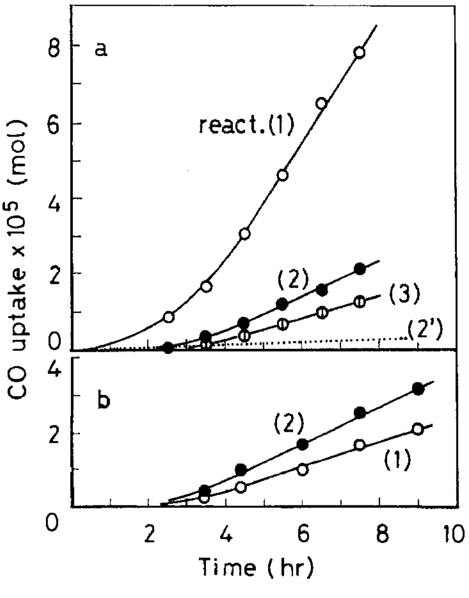

Fig. 2. The amounts of CO taken up by reactions (1)–(3) against time. Initial area of catalyst: 2.6 cm^2, (a) $P_{CO} = 49.70$ Torr, $P_{H_2} = 28.89$ Torr, (b) $P_{CO} = 50.23$ Torr, $P_{H_2} = 5.20$ Torr. Dotted line (2′) shows the result with pure CO (49.92 Torr).

(dotted line 2′) probably shows the deactivation of the particles. These considerations suggest that a steady-state rate should be used for evaluating the effect of H_2 on each of the reactions. It is interesting to note that H_2 promotes reaction (2) by a factor of about 8 independently of its pressure, while reaction (1) shows a faster rate at a higher pressure of H_2.

In order to avoid ambiguous results caused by differences in surface properties among samples, detailed rate data were acquired from deposition reactions carried out successively on a catalyst with 2.1 mg of pre-deposited carbon. A summary of the results is shown in fig. 3 as steady-state rates in μmol-C/h for reactions (1) and (2) and in μmol-CH_4/h for reaction (2) versus H_2 pressure. It is confirmed that the rate of reaction (2) rises sharply due to the presence of H_2 of 5 Torr or less but then changes very little up to the pressure as high as 30 Torr. Another carbon-forming reaction (1) exhibits near first-order behavior, suggesting the dissociation of H_2 to be rate-determining. As a result, deposition rate increases almost linearly with increasing H_2 pressure (curve C), in accord with the result obtained using the electrobalance. It seems necessary to correct the rate data for reactions (1) and (2) by the quantity of CH_4 formed, since it has been recognized [10–12] that CH_4 is formed through carbon adspecies. However, such error is negligible below 10 Torr.

Among the features of fig. 3, rate enhancement in reaction (2) is important for elucidating the role of H_2, in the sense that it is remarkable in a low pressure range. Bianchi and Bennett stated that this reaction is assisted by hydrogen on Fe/Al_2O_3, and proposed a mechanism involving surface OH as an intermediate for

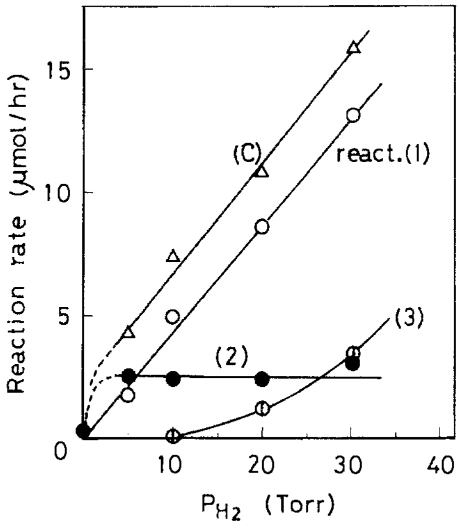

Fig. 3. Steady-state rates of reactions (1)–(3) against H_2 pressure. Initial area of catalyst: 2.8 cm^2, $P_{CO} \approx 50$ Torr. Curve (C) shows overall deposition rates evaluated from the data for reactions (1) and (2).

both formations of CO_2 and H_2O. However, this mechanism cannot explain the characteristic pressure-dependence of the rate of reaction (2). Another factor to be considered is a geometric effect of H_2 which causes active sites to increase, as mentioned in the discussion of the results of figs. 1 and 2. The disproportionation of CO is known to involve ensembles of Ni atoms [10,13–17] as active sites, the number of which has been determined to be 5–6 [15] or 4 [17] by means of a high-field magnetic method. Therefore, it can be assumed that in a steady-state of carbon deposition with H_2 the number of free Ni surface atoms would be more than 30 times that for pure CO. Such a difference, if exists, should result in a large difference in catalytic activity for a reaction taking place on metallic Ni. This was examined by adopting ethylene hydrogenation as a test reaction, which was carried out on a spent catalyst containing initially 4.4 mg of carbon according to a cyclic procedure; carbon deposition (698 K, 2h)–evacuation (698 K, 15 min)–ethylene hydrogenation (323 K). The hydrogenation reaction was followed by manometric measurements within initial 15% conversion, over which linear and reproducible progresses were observed. Table 2 summarizes the results in the sequence of events. Hydrogenation activity of the catalyst decreases sharply after the deposition from pure CO (run 5) but recovers after the subsequent deposition with H_2, in accord with the expectation and also with the results of fig. 1. It is also interesting that the number of free Ni surface atoms appears to vary in a similar manner as observed in the rate of reaction (2) with increasing H_2 pressure. These findings confirm the geometric effect of H_2 to be a principal factor for enhancing the rate of reaction (2), even when its amount is very small. Consequently, it can be concluded that the rate of this reaction is determined by the number of active sites, or the number of adsorbed CO molecules. On the other hand, the first-order behavior of reaction (1) can be explained by high surface coverages of CO which suppresses the dissociation of H_2. Therefore, the hydrogen-assisted CO dissociation process [5,18] can be excluded under the present conditions.

The geometric effect of a small amount of H_2 is supported by electron microscopic observations made by Lamber et al. [19], who have studied the aggregation of Ni supported on amorphous carbon. According to their results, significant aggre-

Table 2
Deposition condition and catalytic activity for ethylene hydrogenation at 323 K

Run No.	Predeposition[a] H_2/CO (Torr)	Hydrogenation rate (mol/min)
1	40.27/50.11	4.57×10^{-8}
2	10.05/50.15	3.59×10^{-8}
3	24.46/50.74	3.59×10^{-8}
4	5.12/50.03	2.30×10^{-8}
5	0 /50.48	$\leq 0.05 \times 10^{-8}$
6	36.45/49.56	3.91×10^{-8}

[a] 698 K; 2 h (Nos. 1–5), 6 h (No. 6).

gation takes place when heated in a H_2 atmosphere (4.5×10^{-4} Torr), but not in vacuum because of the encapsulation of Ni particles with graphitic carbon layers. They also observed that only the particles partially covered are able to move across the substrate surface. Thus, the difference in aggregation behaviors may arise from the difference in free Ni surface area. For a large excess of H_2, it has been established [6] that the reaction of carbon adspecies to form CH_4 leads to an increase of free Ni surface area. Although CH_4 is formed to a slight extent or not at all below 10 Torr of H_2, some steps for CH_4 formation must be concerned with the geometric effect. One possibility is the formation and decomposition of hydrogenated carbon adspecies, CH_x.

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