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The Catalytic Dehydrogenation, Dehydroxylation, and Dehydroxymethylation of Benzyl Alcohol. II. The Effects of Sodium Compounds as Additives

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The reaction of benzyl alcohol has been examined over stabilized nickel (S-Ni) catalysts which have been modified by treating the catalyst surface with solutions of sodium compounds; this has been done in order to obtain some information about the relation between the behavior of the molecule adsorbed on the metal catalyst and the chemical nature of the catalyst surface. On the basis of the f_H, f_{CH_3}, and f_{CHO} values, which were defined as representing the catalytic activity for the formation of benzene, toluene, and benzaldehyde respectively, the variation in the activity for each modified S-Ni was evaluated. The general aspects may be summarized as follows: (1) The reaction is generally retarded with an increase in the amount of a sodium compound which is adsorbed on the catalyst during the modification process. (2) When the modification is of a lower grade, the effect of additives on the catalytic activity represented by f values is in the following order: $NaNO_3 < NaOH < Na_2S_2O_3 < NaI < NaBr < NaCl$. (3) A proper amount of NaCl on the catalyst promotes the reaction. The increase in S_H and S_{CH_3} values, which were defined as representing the selectivity factors for the formation of benzene and toluene toward that of benzaldehyde, is roughly associated with the increase in the corresponding f values.

As was reported in the previous paper,[1] the concurrent dehydrogenation, dehydroxylation, and dehydroxymethylation of benzyl alcohol was observed when it was heated at 150—170°C in the presence of various kinds of metal catalysts. The proportions of benzaldehyde, toluene, and benzene in the reaction product were found to be greatly affected by the chemical nature of the catalysts used, and it was assumed that the reaction proceeded through a metal benzyl complex, which was considered to be an adsorbed transition complex on the catalysts.

In order to obtain more detailed information regard-

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[1] Part I: M. Ishige, K. Sakai, M. Kawai, and K. Hata, This Bulletin, **43**, 2186 (1970).

Table 1. The catalytic activities of S-Ni modified by treating with hydroxide solutions of varying concentrations

Concn. of aq. NaOH (N)	Amount of NaOH adsorbed (meq/g)	Rate constant of the decomposition of H_2O_2 $k \times 10^2$ (min^{-1})	Yield of PhCHO (%)
0.0000	—	1.094	46.7
0.02352	>0.0000	0.4885	42.7
0.04824	0.0031	0.4903	21.9
0.09929	0.0844	1.088	10.7
0.1966	0.1860	2.321	10.7
0.2487	0.2620	1.047	10.7

ing the relationship between the behavior of the adsorbed molecule and the chemical nature of the catalysts, an extensive study of the catalytic reaction of benzyl alcohol was carried out in the presence of various kinds of modified nickel catalysts; these catalysts had been prepared by treating their surfaces with various inorganic sodium compounds.

Several observations have been reported on the variation in the catalytic activity and selectivity of the catalysts modified by a variety of additives on the surface of the catalyst: for example, there is the promoting or poisoning effect of a small amount of platinic chloride or amines in hydrogenation on Raney nickel,[2] and that of the pyridine and thiophene which were added to Raney nickel in the reductive dehydroxymethylation of alcohols.[3] There is also the interesting instance of an optically-active alcohol synthesized from methyl acetoacetate by hydrogenation in the presence of modified Raney nickel catalysts; the surfaces of these catalysts had been treated with optically-active carboxylic acids or amino acids.[4] These results suggest that a small amount of an additive on the catalyst surface interacts both with the catalyst metal and with the reactant, thereby bringing about not only a change in the conditions of the catalyst surface, but also a change in the behavior of the reactant molecule on the catalyst. Pines and his collaborators proposed that nickel[3,5] and alumina[6] catalysts possess inherent acid properties, and that the poisoning of active contact sites of the catalysts by sulfur-containing compounds causes an accentuation of the acid properties of the catalysts. However, it is necessary to examine other operative factors of the catalysis in addition to the dual-function mechanism of the reforming catalyst,[7] because the stereospecific property or the reaction selectivity in the catalysis has not yet been sufficiently elucidated.

Results

The Modification of a Stabilized Nickel Catalyst. It has been found that nickel catalysts, such as Raney nickel, Urushibara nickel A, and Stabilized nickel, are useful for the dehydrogenation of benzyl alcohol.[1] Stabilized nickel (abbreviated as S-Ni)[8] was employed in all the following experiments, because it is the most stable in the air and the most convenient of the three catalysts cited. Various kinds of modified S-Ni were prepared by treating S-Ni with sodium hydroxide or various sodium salts. S-Ni was kept soaking for 24 hr in an aqueous solution of the respective sodium compound. Then, the catalyst was separated from the solution and dried at below 80°C. Since the degree of the modification of the catalyst is dependent on the initial concentration of the solution,[9] modified nickels of the

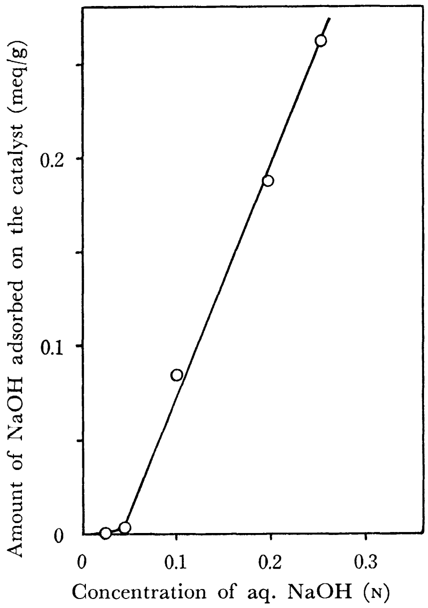

Fig. 1. Relation of the amount of adsorbate *vs.* concentration of aq. NaOH.

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[2] D. R. Levering, F. L. Morritz, and E. Lieber, *J. Amer. Chem. Soc.*, **72**, 1190 (1950).

[3] H. Pines, M. Shamaiengar, and W. S. Postl, *ibid.*, **77**, 5099 (1955).

[4] S. Tatsumi, M. Imaida, Y. Fukuda, Y. Izumi, and S. Akabori, This Bulletin, **37**, 846 (1964); **38**, 1206 (1965).

[5] V. N. Ipatieff, F. J. Pavlike, and H. Pines, *J. Amer. Chem. Soc.*, **75**, 3179 (1953); H. Pines, A. Rudin, G. M. Bô, and V. N. Ipatieff, *ibid.*, **76**, 2740 (1954).

[6] H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960); H. Pines and S. M. Csicsery, *ibid.*, **84**, 292 (1962); K. Watanabe, C. N. Pillai, and H. Pines, *ibid.*, **84**, 3949 (1962).

[7] *Cf.* G. C. Bond, "Catalysis by Metals," Academic Press, London and New York (1962), p. 443.

[8] S-Ni(S 10) is a nickel catalyst made from reduced nickel by treating it with inert gas, such as CO_2. The adsorbed CO_2 can be expelled completely when the catalyst is allowed to coexist with water; T. Yamanaka, *Kagaku Gijitsu*, **2**, 57 (1958); T. Yamanaka and Y. Takagi, *J. Sci. Res. Inst.*, **51**, 168 (1957); T. Yamanaka, K. Taya, and Y. Takagi, *ibid.*, **52**, 143 (1958); *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), **52**, 224 (1958).

[9] K. Mukaida, A. Akiyoshi, and T. Shirasaki, *Shokubai*, **8**, 236 (1966).

same kind but of a different degree of modification were expected to be obtained when solutions of various concentrations were used in treating the catalyst.

The Nature of Stabilized Nickel Modified by Sodium Hydroxide. (a) The Measurement of the Amount of NaOH Adsorbed on S-Ni: The amount of sodium hydroxide on the catalyst surface adsorbed from solutions of various concentrations was measured by the following method. A definite amount of S-Ni was separately soaked in aqueous NaOH solutions of various concentrations and then allowed to stand at room temperature for 24 hr. Then, the diminution in the concentration of each solution was measured by titration with a standard solution of hydrochloric acid. The relation of the amounts of NaOH adsorbed per gram of nickel to the initial concentration of the NaOH solution is shown in Table 1 and Fig. 1. Figure 1 shows an approximately linear relationship between these quantities.

(b) The Measurement of the Activity of the Modified S-Ni to Decompose H_2O_2: Hydrogen peroxide is readily decomposed in first order in the presence of S-Ni.[10] Thus, it is expected that the degree of modification of the modified S-Ni may be represented in terms of the rate constant of the decomposition of H_2O_2. The rate constant of this reaction in the presence of each modified S-Ni cited in the preceding section is evaluated by means of the volumetric measurement of the oxygen generated at 20.03°C. The experimental results are shown in Table 1 and Fig. 2. By referring to the preceding experiment, it was found that the rate constant does not always increase with an increase in the amount of OH^- adsorbed on the surface of the catalyst. However, the intercept of a straight line through the three points in the middle range of the graph provides a value zero for the rate constant at the zero concentration. The slope of this line may represent the relation between the catalytic activity for the decomposition of H_2O_2 and the amount of OH^- on the surface of the catalyst. The deviation of the plots at both ends of the graph clearly suggests the complicated catalytic behavior of each modified catalyst.

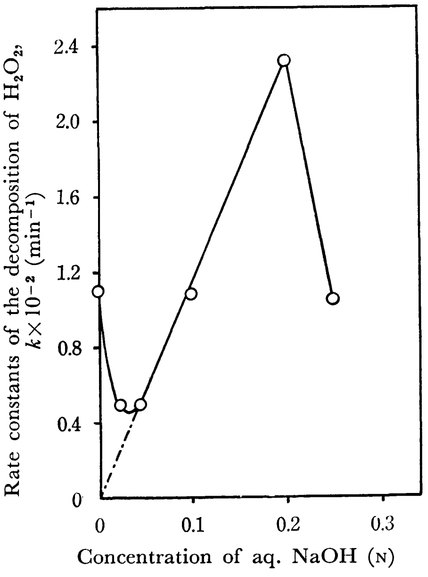

Fig. 2. Relation of the rate constant of the decomposition of H_2O_2 *vs.* concentration of aq. NaOH.

(c) The Relative Catalytic Activities of Modified S-Ni for the Dehydrogenation of Benzyl Alcohol: Benzyl alcohol was dehydrogenated to benzaldehyde by refluxing at 151—156°C for 24 hr in the presence of each catalyst. After 24 hrs' refluxing, the yield of benzaldehyde was estimated by gas chromatography. The yields of benzaldehyde are shown in Table 1 and Fig. 3. In the region of relatively little modification, the reaction was found to be retarded by an increase in the amount of OH^- on the catalyst. However, the yield of benzaldehyde remained almost constant in the presence of the highly-modified catalysts.

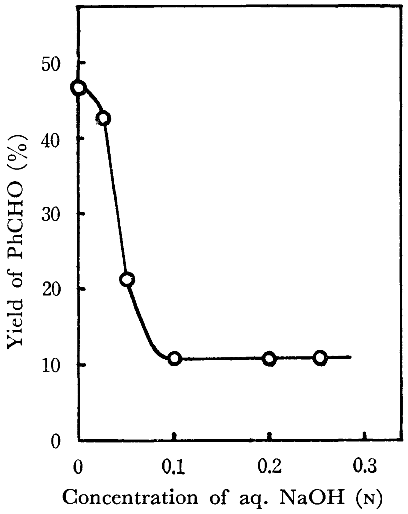

Fig. 3. Relation of relative ratio of the dehydrogenation of benzyl alcohol *vs.* concentration of aq. NaOH.

The Effects of Various Additives on the Catalytic Reaction of Benzyl Alcohol. Different modified nickel catalysts were prepared from S-Ni by treating it with various sodium salts, such as NaCl, NaBr, NaI, $Na_2S_2O_3$, and $NaNO_3$. The same procedure as was used in the preparation of the NaOH-modified S-Ni was employed; variation in the degree of modification was also attained by the use of different concentrations of the salt solution.

The catalytic reaction of benzyl alcohol in the presence of these modified S-Ni catalysts was examined from the point of view of the variation in the catalytic activity and the selectivity of these catalysts. In each of the following experiments, benzyl alcohol was heated in a sealed tube at 154.5—155.0°C in the presence of a modified S-Ni. After the mixture was kept on heat for 24 hr, the sealed tube was cooled to 0°C; the composition of the reaction mixture was then evaluated by gas chromatography. The results are summarized in Table 2. Since it was assumed that the reaction proceeds competitively through an adsorbed transition complex on the

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[10] It is well-known that the catalytic decomposition of H_2O_2 is often utilized to estimate the excess oxygen on the metal oxide surface, which is an important factor of the activity of the oxide catalysts: *Cf.*, S. E. Voltzi and S. E. Weller, *J. Amer. Chem. Soc.*, **76**, 1586 (1954); Y. Matsunaga, This Bulletin, **30**, 984 (1957); I. Mazin and T. Braun, *J. Phys. Chem.*, **24**, 532 (1963).

TABLE 2. CATALYTIC REACTIONS OF BENZYL ALCOHOL IN SEALED TUBES IN THE PRESENCE OF VARIOUS MODIFIED S-Ni

Additive		Benzyl alcohol reacted (%)	Composition of product (mol %)			Rate constants[a] $k\times10^3$ (hr^{-1})	Activity			Selectivity	
Compound	Concn. of solution(N)		PhH	$PhCH_3$	PhCHO		f_H	f_{CH_3}	f_{CHO}	S_H	S_{CH_3}
None		21.2	28.8	46.7	24.5	9.89	28.5	46.2	24.2	7.19	28.3
NaOH	0.02	2.2	3.7	16.1	80.2	0.925	0.313	1.49	7.42	−134	−69.6
	0.05	3.0	8.8	22.2	69.0	1.27	1.12	2.82	8.76	−89.5	−49.2
	0.10	6.3	19.8	31.6	48.6	2.72	5.39	8.60	13.2	−38.9	−18.7
	0.15	6.9	24.7	36.0	39.3	2.98	7.36	10.7	11.7	−20.2	−3.80
	0.20	0.4	0.0	7.5	92.5	0.167	0.00	0.125	1.54	—	−209
	0.25	1.1	15.4	18.2	66.4	0.461	0.710	0.839	3.06	−63.4	−56.2
NaCl	0.02	27.5	26.9	46.6	26.6	13.4	36.1	62.4	35.7	0.40	24.3
	0.04	20.0	31.6	42.6	25.8	9.32	29.4	39.7	25.0	8.80	21.8
	0.08	15.0	30.3	39.2	30.5	6.79	20.6	26.6	20.7	−0.20	10.9
	0.16	11.9	34.6	29.8	35.6	5.28	18.3	15.7	18.8	−1.20	−7.70
NaBr	0.02	17.9	25.0	46.0	29.0	8.25	20.6	37.9	23.9	−6.40	20.1
	0.04	17.0	28.3	44.6	27.1	7.78	22.0	34.7	21.1	1.70	21.8
	0.08	13.0	29.2	41.4	29.4	5.80	16.9	24.0	17.0	−0.26	14.9
	0.16	9.9	35.3	33.6	31.1	4.32	15.2	14.5	13.4	5.40	3.40
NaI	0.02	17.5	28.1	41.9	30.0	8.04	22.6	33.7	24.1	−2.80	14.5
	0.04	13.6	36.0	35.2	28.8	6.08	21.9	21.4	17.5	9.70	8.6
	0.08	8.3	23.1	35.0	41.9	3.60	8.31	12.6	15.1	−25.8	−7.8
	0.16	6.0	28.4	26.0	45.6	2.56	7.27	6.65	11.7	−20.6	−24.4
$Na_2S_2O_3$	0.02	14.0	13.9	45.0	31.1	6.19	8.75	28.3	19.6	−35.0	16.2
	0.04	14.2	27.1	43.3	29.6	6.40	17.3	27.7	18.9	−3.80	16.4
	0.08	11.6	32.2	41.0	26.8	5.14	16.5	21.0	13.8	17.9	18.4
	0.16	11.1	33.9	40.7	25.4	4.93	16.7	20.1	12.3	12.6	20.4
$NaNO_3$	0.02	4.1	8.0	48.9	43.1	0.592	0.474	2.90	2.55	−73.2	5.40
	0.04	4.0	7.1	42.2	50.7	0.575	0.408	2.60	2.92	−85.4	−7.80
	0.08	0.0	0.0	0.0	0.0	0.00	—	—	—	—	—
	0.16	0.0	0.0	0.0	0.0	0.00	—	—	—	—	—

a) Rate constant of the conversion of benzyl alcohol.

catalyst,[1] the activity of each catalyst for the formation of benzene, toluene, and benzaldehyde was expressed in terms of the f_H, f_{CH_3}, and f_{CHO} factors respectively; these factors are proportional to the approximate values of the rate constants for the formation of each product in the early period of the reaction (within the period in which 30% of the alcohol reacted).[11] The f_H, f_{CH_3}, and f_{CHO} were defined as follows:

$$\left.\begin{aligned} f_H &= 100\ k_{alc}\ (\text{mol\% of PhH}) \\ f_{CH_3} &= 100\ k_{alc}\ (\text{mol\% of PhCH}_3) \\ f_{CHO} &= 100\ k_{alc}\ (\text{mol\% of PhCHO}) \end{aligned}\right\} \quad (1)$$

where k_{alc} is the first-order rate constant in the disappearance of the alcohol.

The selectivity factors for the formation of benzene and toluene toward that of benzaldehyde were represented by S_H and S_{CH_3}, which were defined as follows:

$$\left.\begin{aligned} S_H &= 100\ \log\ (f_H/f_{CHO}) \\ &= 100\ \log\ (\text{mol\% of PhH/mol\% of PhCHO}) \\ S_{CH_3} &= 100\ \log\ (f_{CH_3}/f_{CHO}) \\ &= 100\ \log\ (\text{mol\% of PhCH}_3\text{/mol\% of PhCHO}) \end{aligned}\right\} \quad (2)$$

The values of the f and S factors are shown in Table 2.[12] Figures 4 and 5 illustrate the relations of these values *vs.* the approximate degrees of the modification of the catalyst, which were represented by the initial concentrations of the solution used for modifying the catalyst, on the assumption that the degree of modification and the concentration of the sulution are proportional in the region of low concentration.

The results shown in Table 2 indicate that the catalytic activity and selectivity of the catalyst are affected by the nature of the adsorbate on the catalyst surface. The general aspect may be summarized as follows: (1) an increase in the amount of the adsorbate generally brings about a retardation of the reaction; (2) a proper amount of NaCl on the catalyst surface promotes the reaction; (3) variations in the kind and amount of the adsorbate have particular effects on the production of toluene, whereas they have a lesser effect on the formation of benzene; (4) the effect of additives on the catalyst activity, which is expressed by the values f_H, f_{CH_3}, and f_{CHO}, is generally in this order for the S-Ni

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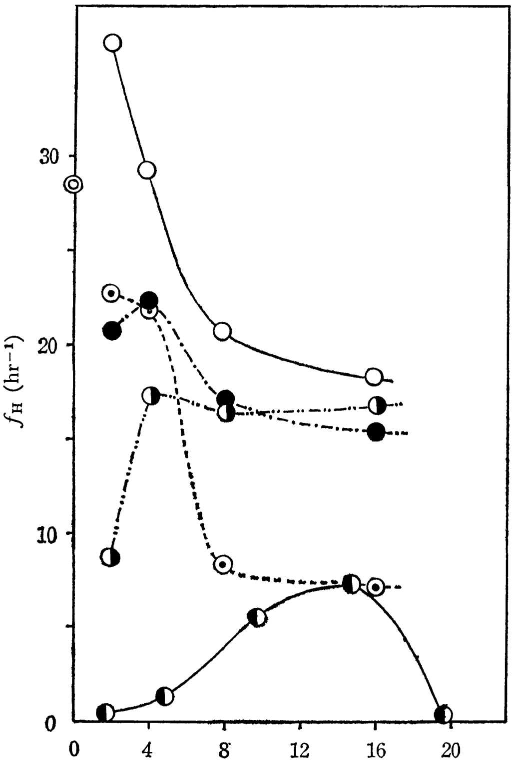
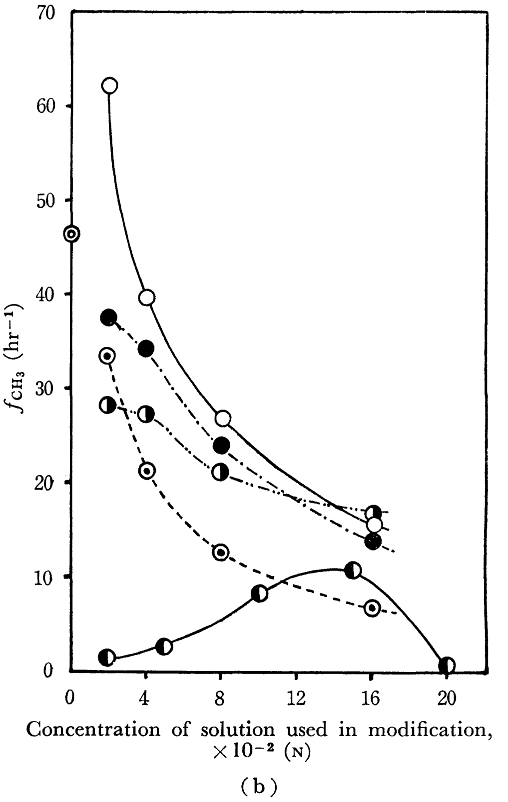
[11] With the further progress of the reaction, the aspect of the reaction becomes complicated and the simple expression adopted here is no more valid.

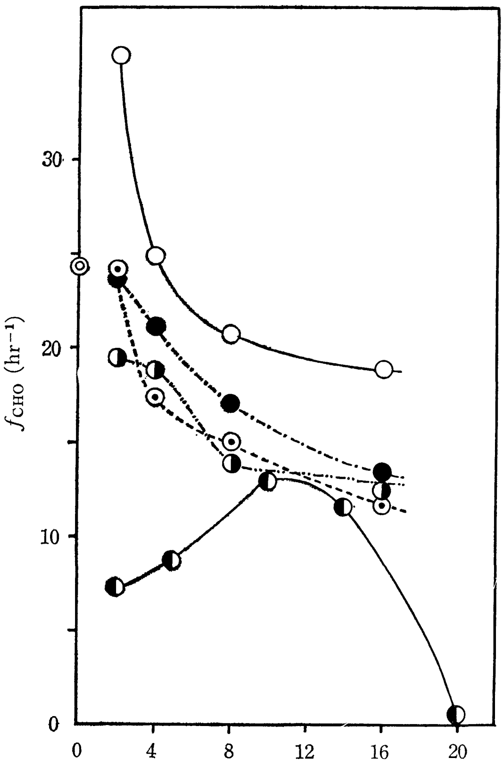
[12] A positive value of S_H and S_{CH_3} indicates that the formation of benzene or toluene is superior to that of benzaldehyde, whereas a negative value means the less formation of benzene or toluene than that of benzaldehyde.



(a)



(b)



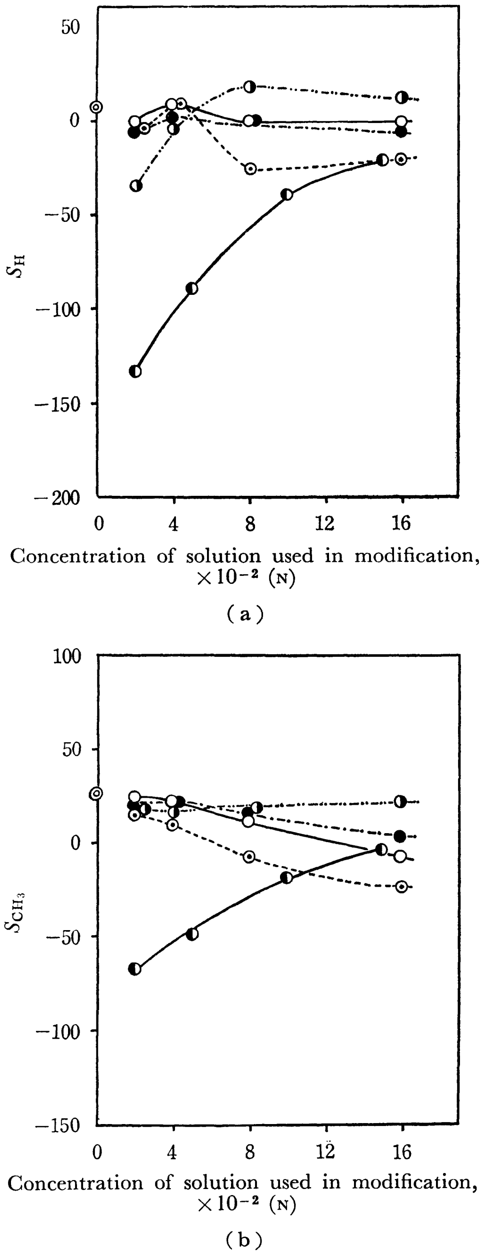
(c)

Fig. 4. The activities of modified catalysts for the formation of benzene, toluene, and benzaldehyde.
○, NaCl; ●, NaBr; ⊙, NaI; ◑, $Na_2S_2O_3$; ◐, NaOH; ◎, control (unmodified S-Ni catalyst)

modified to a lesser degree: $NaNO_3$ <NaOH< $Na_2S_2O_3$ <NaI<NaBr<NaCl; (5) the increase in f values is roughly associated with the increase in S values; (6) with regard to the selectivity change for the formation of toluene when the amount of the adsorbate is increased, the sodium compounds as additives may be classified into two groups: one with decreasing S_{CH_3} values, and the other with increasing S_{CH_3} values. The compounds with larger f_{CH_3} values generally belong to the former group, whereas those with smaller f_{CH_3} values belong to the latter. On the other hand, the effects of various additives on the selectivity for the formation of benzene can not be estimated so clearly as for the formation of toluene. However, an appreciable change in the S_H value is observed with an increase in the amount of the adsorbate in the cases of additives with smaller f_H values.

Discussion

The increasing coverage of the catalyst surface by additive substances might necessarily lead to a decrease in the catalytic activity due to the hindrance of the approach of the benzyl alcohol molecule to the catalyst surface. The data in Table 2 are generally consistent with this consideration, but some of them deviate. Especially, the change in selectivity caused by the additives on the catalyst cannot be simply understood by the coverage, though selectivity does not undergo so great a change as activity as a result of the presence of the additives on the catalyst. It is, however, noteworthy that the observed S values are somewhat influenced by the kinds and the amounts of the additives, and that the



(a)

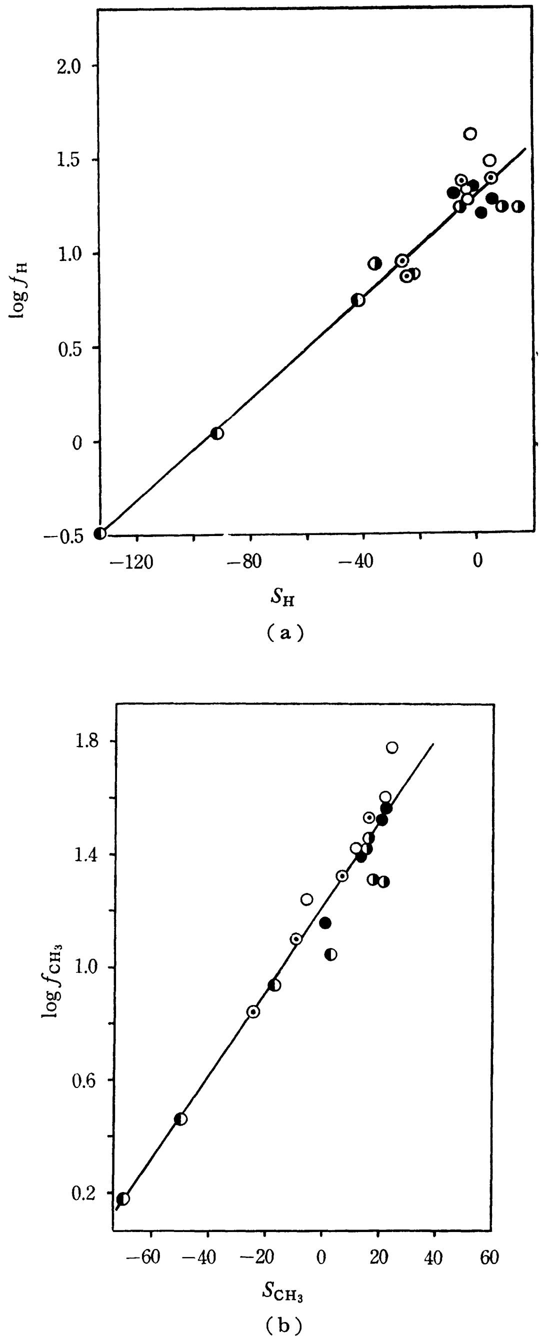
(b)

Fig. 5. The selectivities of modified catalysts for the formation of benzene and toluene toward benzaldehyde. (The notations are the same as Fig. 4.)

influence is related to the f value under the given conditions. This fact suggests the possibility that the change in the catalytic activity for the formation of each product might bring about a change in selectivity for the corresponding product. Therefore, the correlation between f and S values was examined. As is shown in Fig. 6, the plots of $\log f$ *versus* S in each graph were distributed near a straight line, which can be represented by the following equation:

$$\left.\begin{array}{l}\text{for the formation of benzene,}\\ \qquad \log f_H = 0.0137 S_H + 1.31\\ \text{for the formation of toluene,}\\ \qquad \log f_{CH_3} = 0.0147 S_{CH_3} + 1.23\end{array}\right\} \quad (3)$$

However, no such a linerar relation was observed when the reaction proceeded either too fast or too slow.



(a)

(b)

Fig. 6. The plots of $\log f$ *vs.* S for benzene and toluene. (The notations are the some as in Fig. 4.)

It is assumed that the first step in the reaction is the dehydrogenation of benzyl alcohol to benzaldehyde through an adsorbed transition complex on the catalyst, and that the succeeding dehydroxylation and dehydroxymethylation utilize the hydrogen generated by the dehydrogenation. If each product of the reaction is competitively produced from the same transition intermediate at an early stage of the reaction, it is understandable that the selectivity is correlative with the activity of the catalyst. The deviation from the linear relation between $\log f$ and S by the faster reaction can be explained as follows: the faster approach to the pseudo-equilibrium between benzyl alcohol and benzaldehyde brings about a feedback of benzaldehyde to benzyl alcohol, resulting in an increase in the apparent S_H and S_{CH_3} values.

A small amount of sodium chloride was found to promote the reaction. The increase in the activity of the catalyst as a result of the presence of halide ions is found to be in an order consistent with the basicity or inductive effect of halogens.[13] This fact suggests that halide anions on the catalyst surface induce electron transfer around them, thus accentuating the acid property of the catalyst surface.[3,5,14] However, the possibility cannot be excluded that, as has been observed in the catalysts modified by some potassium halides,[15] different amounts of the anion adsorbed from solutions of different halides of the same concentration affect the catalytic activity.[16] Nevertheless, the unique promotion by a proper amount of NaCl as additive indicates that the chloride ion might play an important role in the catalytic reaction.[17] It implies that the change in catalytic activity is mainly dependent on the intrinsic property of the halide ion, rather than being a mere coverage-change.

In the preceding paper, we proposed the intervention of a metal benzyl complex in the reaction. If this is the case, the anions on the catalyst surface might participate as ligands in the complex, thus exerting a certain influence on the activity of the catalyst.

Experimental

Material. Benzyl Alcohol: Benzyl alcohol was purified according to the procedure described previously.[1] The purity was found to be over 99% by gas chromatography.

Catalyst: A commercial stabilized nickel (S 10) (supplied by Nikko Shokai Co., Ltd.), containing 50% of kieselguhr, was used as the catalyst.

Preparation of Modified S-Ni. (i) Sodium hydroxide (10.3 g) was dissolved in distilled water, and then diluted to 1 *l* to make a 0.2487N NaOH solution. The concentration of the solution was determined by titration with a standard solution of oxalic acid. Several portions of the NaOH solution were taken out and separately diluted to prepare 0.1966, 0.09929, 0.04824, and 0.02352N solutions. Every 3.00-g portion of the S-Ni catalyst was soaked in a 30.0-m*l* portion of the NaOH solution, and then left to stand for 24 hr at room temperature. After the adsorption equilibrium had been attained, a 10.0-m*l* portion of the solution was taken out from the upper layer and titrated with 0.1084N hydrochloric acid. The amount of NaOH adsorbed was calculated from the difference in the concentrations.

(ii) Aqueous solutions of NaCl, NaBr, NaI, $Na_2S_2O_3 \cdot 5H_2O$, and $NaNO_3$ were prepared, the concentrations of the solution being regulated to 0.02, 0.04, 0.08, and 0.16N respectively. In an Erlenmeyer flask we then placed a 30-m*l* portion of a solution and a 3-g portion of S-Ni; the mixture was left to stand under a cork-stopper for 24 hr at room temperature. Then, the aqueous layer was removed by decantation, and the catalyst was dried for 12 hr at below 80°C. The catalysts modified by NaOH and $Na_2S_2O_3$ were dried in a desiccator for more than 24 hr at room temperature.

Decomposition of H_2O_2 by Modified S-Ni. Commercial H_2O_2 (30%) was diluted with water to about fifty times the initial volume. In a 30-m*l* flask joined to a gas burette we then placed 20 m*l* of the H_2O_2 solution; the temperature was regulated to maintain 20.03°C. Then, a 0.1210-g portion of modified S-Ni was quickly added; the oxygen generated was measured volumetrically after a proper interval.

Reaction of Benzyl Alcohol in the Presence of Modified S-Ni under Ordinary Pressure. Benzyl alcohol (6 m*l*) and modified S-Ni (1 g) were placed in a 30-m*l*, round-bottomed flask equipped with a reflux-condenser. The content was refluxed for 24 hr in an oil bath, which had been heated at 151—156°C in advance. After the reaction was over, the reaction mixture was analyzed by gas chromatography in order to estimate the amount of benzaldehyde produced.

Reaction of Benzyl Alcohol in the Presence of Modified S-Ni in a Sealed Tube. Benzyl alcohol (2.00 g) and a modified S-Ni catalyst (0.333 g) were heated at 155°C for 24 hr in a sealed tube. After the reaction was over, the tube was cooled with ice, and the composition of the reaction mixture was analyzed by gas chromatography.

The authors wish to express their hearty thanks to Dr. Ken-ichi Watanabe for his helpful encouragement.

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[13] E. Naruko, *Kogyo Kagaku Zasshi*, **67**, 2023 (1964).

[14] I. D. Chapman and M. L. Hair, *J. Catal.*, **2** 145 (1963); C. J. Plank, D. J. Sibbert, and R. B. Smith, *Ind. Eng. Chem.*, **49**, 742 (1957).

[15] L. Michaelis and H. Lachs, *Kolloid Z.*, **9**, 279 (1911).

[16] In the case of reactive adsorbates, such as NaOH and $Na_2S_2O_3$, it might also be considered that a change in quality occurs to some extent as a result of the contact with the air during the preparation of modified catalyst or of the thermal decomposition during the catalytic reaction in the presence of them.

[17] A few studies have been reported on the accelerating effect of NaCl on the reaction: *Cf.*, T. Nakabayashi, *J. Amer. Chem. Soc.*, **82**, 3900 (1960); K. Sakai, M. Ishige, K. Watanabe, and K. Hata, This Bulletin, **43**, 1172 (1970).