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The Catalytic Dehydrogenation, Dehydroxylation, and Dehydroxymethylation of Benzyl Alcohol. III. The Effect of Metal Chlorides as Additives

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This paper will describe the reaction of benzyl alcohol in the presence of various kinds of modified stabilized nickel catalysts, which had been prepared from the mother catalyst by treating it with solutions of appropriate metal chlorides. The catalytic activities of each modified catalyst for the formation of benzene, toluene, and benzaldehyde were compared in terms of the f_H, f_{CH_3}, and f_{CHO} values; the selectivities for the formation of benzene and toluene against that of benzaldehyde, S_H and S_{CH_3}, were also evaluated. In general, the formation of toluene and benzene was greatly affected both by the kind and by the amount of metal chlorides used as additives. The reaction was promoted by the addition of a proper quantity of alkali metal chloride. In the cases of the reactions by lowly-modified catalysts, the decreasing order of the f_H and f_{CH_3} values according to the kind of metal ion adsorbed on the catalyst was as follows: $Na^+ \geqq K^+ > Co^{2+} > Ca^{2+} > Cd^{2+} > Ba^{2+} > Hg^{2+} > Cu^{2+}$. On the other hand, in the higher degrees of modification, the corresponding order of the f_H and f_{CH_3} values was altered to be as follows: $K^+ > Na^+ > Co^{2+} > Cd^{2+} > Ba^{2+} \geqq Ca^{2+} > Cu^{2+} > Hg^{2+}$. With regard to the modified nickel catalysts treated with 0.08 N solutions, it was found that the sequence of the f_H and f_{CH_3} values due to the kind of metal ion was roughly correlated with that of the atomic numbers of the corresponding metals. The results are discussed in connection with the general concept of catalytic chemistry.

Preceding papers[1,2] have described the catalytic reactions of benzyl alcohol in the presence of various nickel catalysts and of modified stabilized nickel catalysts treated with solutions of sodium compounds. The reaction products mainly consisted of benzaldehyde, toluene, and benzene, sometimes accompanied by the formation of small quantities of certain hydrocarbons and carbon dioxide. The composition of the product was found to be variable under the influence of the chemical nature of the catalysts employed. Numerous papers on the hydrogenation of benzyl alcohol over various metal catalysts[3] have described the formation of toluene as a hydrogenolysis product of the alcohol. The palladium and nickel catalysts were proved to be especially preferable for the hydrogenolysis of benzyl alcohol to toluene. On the other hand, it has been shown that benzyl alcohol is converted to benzaldehyde, toluene, and benzene in the redox reaction of unsaturated organic compounds, with benzyl alcohol as the hydrogen donor and in the presence of nickel catalysts.[4]

In general, the behavior of benzyl alcohol adsorbed on the catalyst surface is so complex that this catalysis cannot be simply comprehended. Garbisch *et al.*[5] have discussed the mechanism of the hydrogenolysis of benzyl alcohols. Mitsui *et al.*[6] have reported that the hydrogenolysis of optically-active benzyl-type alcohols proceeds either with the retention or the inversion of the configuration through sterically-different adsorbed transition states of substrates, depending upon the kind of catalyst metal. On the other hand, Khan *et al.*[7] have offered another proposal regarding the configurational behavior in the catalytic hydrogenolysis of benzyl alcohols.

However, relation between the behavior of benzyl alcohol and the surface nature of the catalysts has not yet been explored clearly. In order to get further information on the operative factor of the catalytic reactions of benzyl alcohol, the present investigation was carried out into the reaction of benzyl alcohol catalyzed by modified nickel catalysts, which had been prepared by the treatment of the surface of a nickel catalyst with solutions of various metal chlorides.

Results

In all the experiments, we employed a stabilized nickel catalyst (hereafter abbreviated as S–Ni)(S 10),[8] from which various kinds of modified nickel catalysts were prepared by treating it with solutions of proper metal chlorides. By a procedure similar to that described in the preceding paper, the degree of modification for each modified S–Ni was controlled by using metal chloride solutions of varying concentrations.

When a given amount of the S–Ni catalyst was treated with aqueous NaCl, KCl, and $CaCl_2$ solu-

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[1] Part II: M. Ishige, K. Sakai, M. Kawai, and K. Hata, This Bulletin, **44**, 1095 (1971).

[2] M. Ishige, K. Sakai, M. Kawai, and K. Hata, *ibid.*, **43**, 2186 (1970).

[3] H. Adkins and L. W. Covert, *J. Phys. Chem.*, **35**, 1684 (1931); N. S. Tikhomirova-Sidrova, *Zh. Obshch. Khim.*, **25**, 1504 (1955), *Chem. Abstr.*, **50**, 4825h (1956); J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962); S. Nishimura and K. Mori, This Bulletin, **32**, 103 (1959); S. Nishimura, *ibid.*, **32**, 1158 (1959); **34**, 32 (1961); S. Nishimura and M. Hama, *ibid.*, **39**, 2467 (1966).

[4] K. Sakai, T. Ito, and K. Watanabe, This Bulletin, **39**, 2230 (1966).

[5] E. W. Garbisch, Jr., L. Schreader, J. J. Frankel, *J. Amer. Chem. Soc.*, **86**, 4233 (1967).

[6] S. Mitsui, S. Imaizumi, and Y. Esashi, This Bulletin, **43**, 2143 (1970), and the references cited therein.

[7] I. Jardine and F. J. McQuillin, *J. Chem. Soc., C*, **1966**, 458; D. A. Denton, F. J. McQuillin, and P. L. Simpson, *ibid.*, **1964**, 5535; A. M. Khan, F. J. McQuillin, and I. Jardine, *ibid.*, *C*, **1967**, 136; *Tetrahedron Lett.*, **1966**, 2649.

[8] *Cf.* a footnote of the preceding paper[1]; T. Yamanaka, *Kagaku Gijutsu*, **2**, 57 (1958).

tions of given concentrations, the amount of metal chlorides adsorbed on the catalyst surface was measured by the titration of the residual solution with a standard solution of silver nitrate. The amount of adsorbate determined in a 0.16N solution was found to be 0.15 meq per 1 g of the catalyst; this value was independent of the kind of metal chloride within about a 4% error: a linear relation between the amount of adsorbate and the initial concentrations of the metal chloride solutions was also observed.

The modified-nickel-catalyzed reaction of benzyl alcohol was practiced in a sealed tube by heating it at 162°C for 24 hr, then, the composition of the reaction mixture was evaluated by gas chromatography. It was previously found by kinetic observation[2] that the reaction proceeds as a first-order one, with the diminution of benzyl alcohol during the initial period of the reaction, but becomes complicated when more than 30% of benzyl alcohol is transformed. Thus, in order to avoid the difficulty of the kinetic analysis, the calculation of the rate was generally based upon the time required within the period before 30% of the alcohol reacted.

The f_H, f_{CH_3}, and f_{CHO} values, which had previously been defined as representing the catalytic activity for the formation of benzene, toluene, and benzaldehyde respectively, were calculated both from the observed rate constant of the alcohol, k_{alc}, and from the composition of the reaction products. The S_H and S_{CH_3} values, which indicate the selectivity factors for the formation of benzene and toluene with regard to that of benzaldehyde, were also estimated much as in the preceding report. The results obtained are summarized in Table 1. The plots of the f and S values *vs.* the degrees of the modification[9] for each modified S–Ni are also given in Figs. 1 and 2 respectively.

Table 1. Catalytic reactions of alcohol in sealed tubes in the presence of various modified S–Ni

Additive		Benzyl alcohol eacted (%)	Composition of products (mol %)			Rate constant $k_{alc}\times 10^2$ (hr^{-1})	Activity			Selectivity	
Compound	Conc. of solution (N)		PhH	$PhCH_3$	PhCHO		f_H	f_{CH_3}	f_{CHO}	S_H	S_{CH_3}
None		30.9	39.8	37.9	22.3	1.44	57.3	54.6	32.1	25.2	23.1
NaCl	0.02	31.5	42.2	29.8	28.0	1.57	66.2	46.8	44.0	19.4	2.8
	0.04	28.9	38.7	31.0	30.3	1.42	55.0	44.1	43.0	10.6	1.0
	0.08	26.4	42.3	27.4	30.3	1.28	54.2	35.1	38.8	14.5	−4.3
	0.16	25.0	44.2	25.7	30.1	1.20	53.0	30.8	36.1	16.6	−6.8
KCl	0.02	30.9	42.9	35.8	21.3	1.44	61.8	51.6	30.7	30.6	22.6
	0.04	24.4	40.2	46.3	13.5	1.16	46.6	53.7	15.7	47.3	53.4
	0.08	26.0	39.2	40.8	20.0	1.25	49.0	51.0	25.0	29.3	31.0
	0.16	26.7	43.1	37.8	19.1	1.29	55.6	48.8	24.6	25.8	29.7
$CaCl_2$	0.02	21.8	22.6	46.6	30.8	1.02	23.1	47.5	31.4	−19.7	11.8
	0.04	22.0	21.9	43.4	34.7	1.04	22.8	45.1	36.1	−19.9	9.7
	0.08	24.5	19.6	42.0	38.4	1.08	21.2	45.4	41.5	−29.1	4.2
	0.16	21.6	17.6	44.0	38.4	1.01	17.8	44.4	38.8	−33.8	5.7
$BaCl_2$	0.02	21.5	22.3	43.3	34.4	1.01	22.5	43.7	34.8	−0.2	0.1
	0.04	20.5	22.4	44.9	32.7	0.96	21.5	43.1	31.4	−0.2	0.1
	0.08	20.7	19.8	46.4	33.8	0.97	19.2	45.0	32.8	−0.2	0.1
	0.16	21.8	18.8	44.5	36.7	1.03	19.4	45.8	37.8	−0.3	0.1
$CoCl_2$	0.02	24.7	28.2	41.9	29.9	1.17	33.0	49.0	35.0	−2.4	18.8
	0.04	26.4	29.1	44.0	26.9	1.28	37.2	56.3	34.4	3.4	21.5
	0.08	25.8	27.9	45.0	27.1	1.24	34.6	55.8	33.6	1.3	22.0
	0.16	28.9	31.0	35.1	33.9	1.42	44.0	49.8	48.1	−3.8	14.6
$CuCl_2$	0.02	18.6	18.9	43.5	37.6	0.85	16.1	37.0	32.0	−30.0	6.5
	0.04	20.8	22.7	41.3	36.0	0.97	22.0	40.1	34.9	−20.3	6.1
	0.08	19.4	19.1	41.7	39.2	0.89	18.0	39.2	36.9	−31.2	2.6
	0.16	18.5	23.2	38.4	38.4	0.85	19.6	32.4	32.4	−21.7	0.0
$CdCl_2$	0.02	22.2	25.3	45.0	29.7	1.04	26.3	46.8	30.9	−7.0	17.9
	0.04	20.1	24.5	44.2	31.3	0.93	22.8	41.1	29.1	−10.8	15.0
	0.08	16.8	14.8	46.0	39.2	0.76	11.2	34.9	29.8	−42.6	6.8
	0.16	23.5	24.2	46.5	29.3	1.11	26.9	51.6	32.5	−8.3	19.9
$HgCl_2$	0.02	20.3	21.6	43.9	34.5	0.94	20.3	41.3	32.4	−10.7	14.4
	0.04	22.4	25.5	43.3	31.2	1.06	27.1	45.9	33.1	−8.8	14.4
	0.08	15.5	11.9	14.5	74.0	0.69	8.0	10.0	51.1	−80.6	−71.0
	0.16	14.4	21.6	40.2	38.2	0.64	14.9	25.9	24.6	−24.8	2.2

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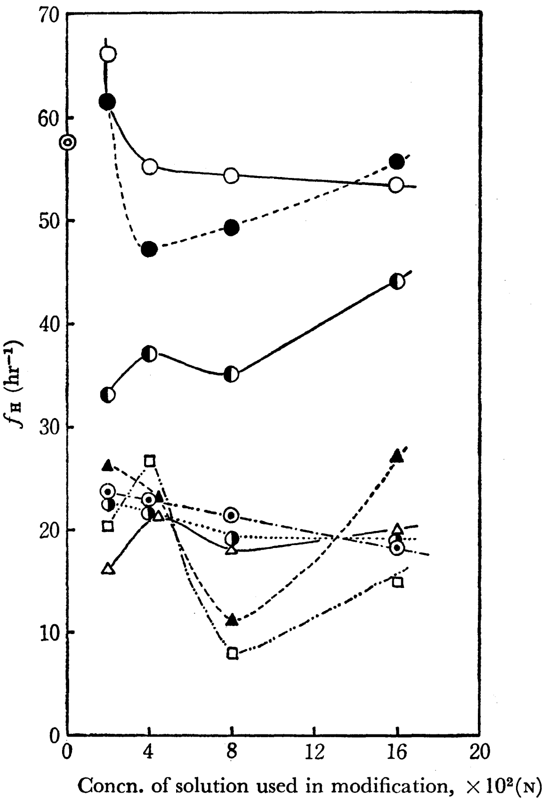
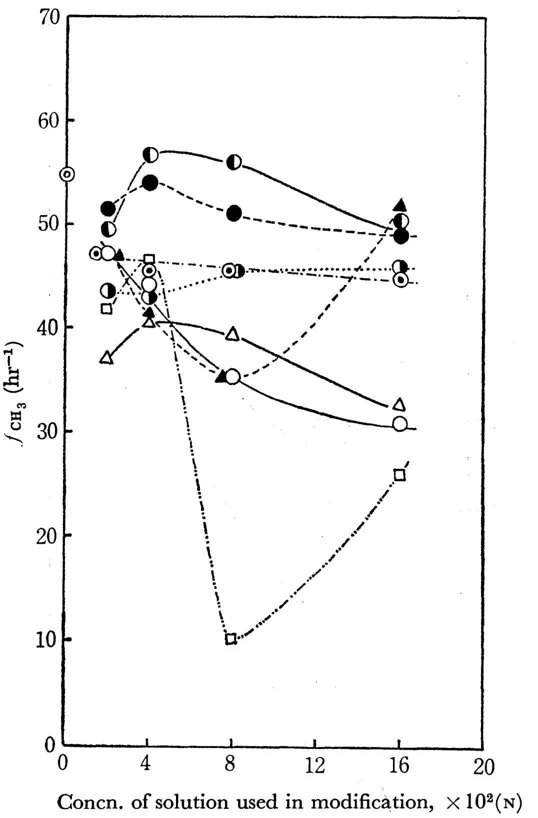
[9] The degrees of the modification are tentatively represented by the initial concentrations of the solution used on treatment.





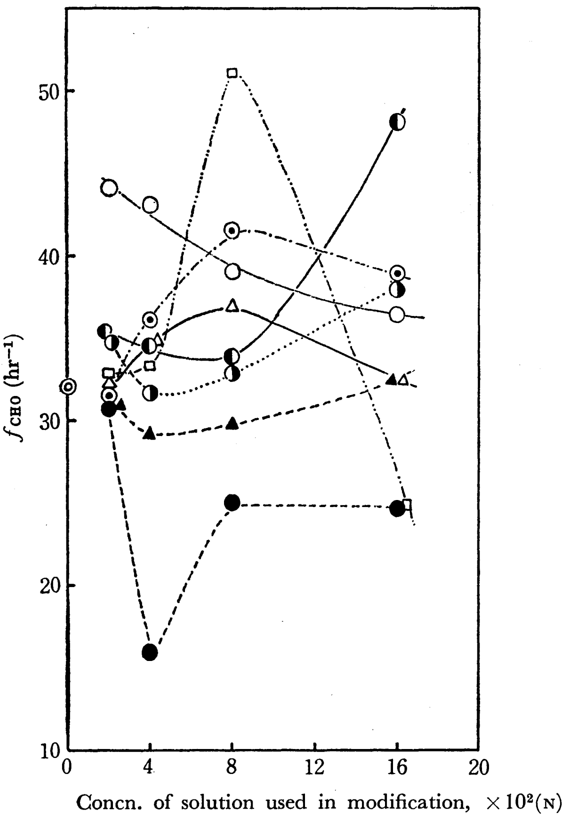


Fig. 1. The activities of modified catalysts for the formation of benzene, toluene, and benzaldehyde.
○ NaCl, ● KCl, ⊙ $CaCl_2$, ◑ $BaCl_2$, ◐ $CoCl_2$, △ $CuCl_2$, ▲ $CdCl_2$, □ $HgCl_2$, ◎ Control (unmodified S–Ni catalyst)

As may be seen in Fig. 1, the effects of metal chlorides as additives appear somewhat complicated; yet we can find some features of the additives in the catalysis: (1) A proper amount of alkali metal chloride acts as a promotor. (2) Alkaline earth metal chlorides are less influential than alkali metal chloride on the f value change with the increase in the amounts of the metals adsorbed on the catalyst. (3) The formation of toluene and benzene is largely influenced by both the kind and the amount of the adsorbate. (4) A remarkable change in the f values is observed when a varied amount of mercury(II) chloride is used as the additive.

On the basis of the f values for various modified S–Ni, it is noticeable that the effect of the additives is in a remarkably different order on lowly modified catalysts from that on more highly modified ones. In the reations with lowly modified catalysts, the f_H and f_{CH_3} values decrease generally according to the kind of metal cation used as additives in the following order: $Na^+ \geqq K^+ > Co^{2+} > Ca^{2+} > Cd^{2+} > Ba^{2+} > Hg^{2+} > Cu^{2+}$. This order is somewhat like the decreasing order of the heat of hydration of a metal complex.[10]

On the other hand, when modified catalysts with the same metal chlorides but in higher degrees were used, the f_H and f_{CH_3} values were observed to decrease in the following order on the average: $K^+ > Na^+ > Co^{2+} > Cd^{2+} > Ba^{2+} \geqq Ca^{2+} > Cu^{2+} > Hg^{2+}$. The correlation between the f values and the normal electrode potentials of corresponding metals was examined;

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[10] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd Ed. John Wiley & Sons, Inc. N. Y. (1967), p. 81; $-\Delta H$, (kcal): $K^+(79) > Na^+(100) > Ba^{2+}(316) > Ca^{2+}(382) > Cd^{2+}(437) > Hg^{2+}(441) > Co^{2+}(497) > Cu^{2+} \approx Ni^{2+}(507)$.

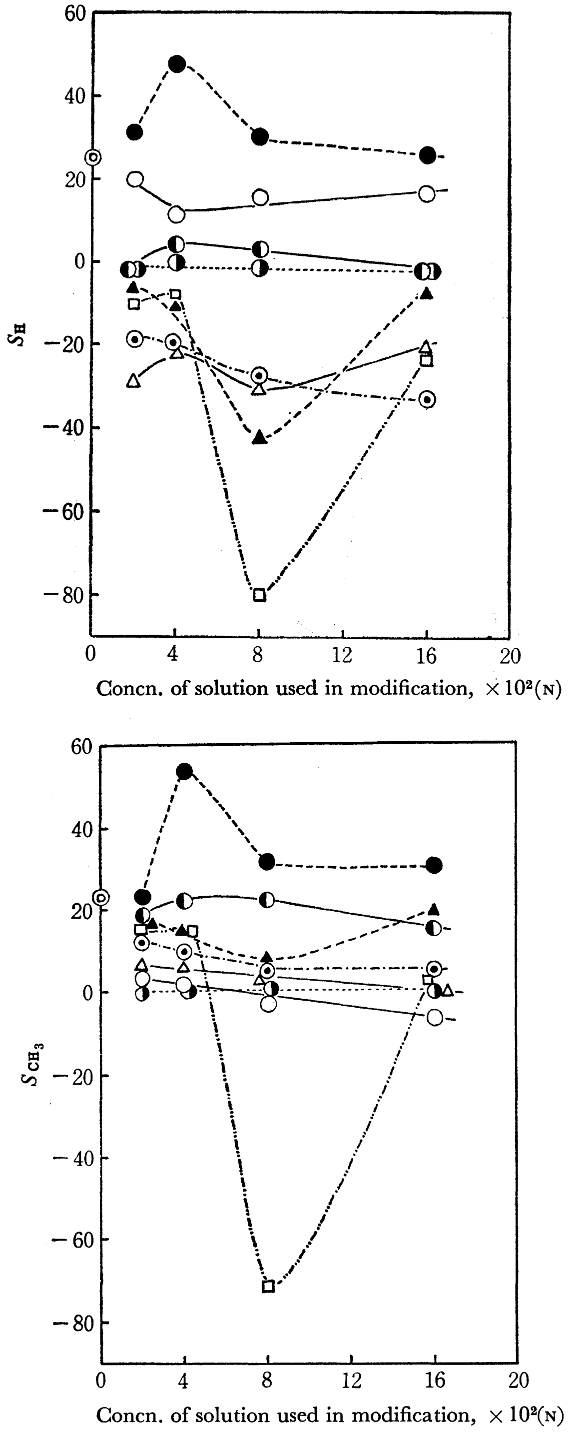

Fig. 2. The selectivities of modified catalysts for the formation of benzene and toluene against that of benzaldehyde. (The notations are the same as in Fig. 1).

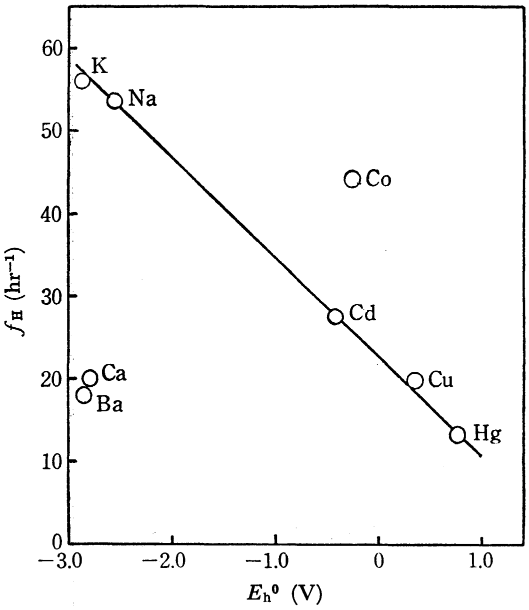

Fig. 3(a). The plots of f_H in the higher modification degree *vs.* the electrode potential of metal ($M^0 \rightleftarrows M^{n+} + ne^-$, 25°C).

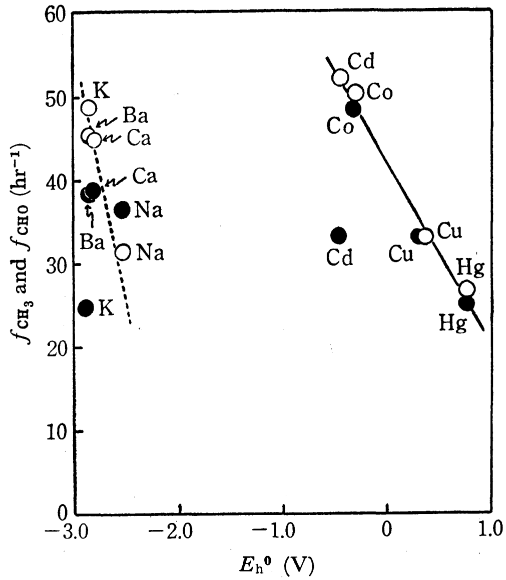

Fig. 3(b). The plots of f_{CH_3} and f_{CHO} in the higher modification degree *vs.* the electrode potential of metal ($M^0 \rightleftarrows M^{n+} + ne^-$, 25°C).
○ toluene, ● benzaldehyde

the results are shown in Fig. 3. As may be seen in Fig. 3, the formation of benzene is assumed to be approximately correlated with the potential change in the catalyst surface caused by the addition of metal chlorides to the catalyst. However, it was found that the cobalt ion promotes the formation of benzene exceptionally, more than would be predicted from its electrode potential, whereas calcium and barium ions have the opposite effect on the reaction. The relation of the formation of toluene and benzaldehyde is not so clearly correlated with the electrode potential of metal as it is in the case of benzene. We can readily recognize that the relations between the f value and the electrode potential of the metal used as the additive may be roughly divided into two groups: the lower-electrode-potential group and the higher-electrode-potential group. The alkali and alkaline earth metals belong to the former group, whereas the transition metals belong to the latter one. Within each group, there is a tendency for the f values to vary in correlation with the electrode potential of the metals adsorbed on the catalyst.

With regard to the modified nickel catalysts treated with a 0.08N solution of each metal chloride, it is found that the decreasing sequence of the f_H and f_{CH_3}

values due to the kind of metal chloride is roughly associated with that of the atomic number of the corresponding metals. This finding leads to a consideration that the promoting and poisoning effects by metal chlorides may partially result from the polarizability of the metals as additives.

It is interesting that the general order of the decrease in the f_{CHO} values observed in the presence of the modified catalysts treated with 0.08N solutions of metal chlorides is roughly reversed for the formation of benzene and toluene (f_H and f_{CH_3} values). This observation implies that highly polarizable metal ions adsorbed on the catalyst are preferable to the dehydrogenation of benzyl alcohol.

The tendency of the changes is S_H and S_{CH_3} values brought about by the addition of metal chlorides is generally similar to that of the changes in f_H and f_{CH_3} values respectively. The general features of the change in selectivity caused by the adsorption of metal chlorides may be summarized as follows: (1) KCl can characteristically serve to increase the selectivity for the formation of benzene and toluene. (2) The S-value changes due to NaCl, $CaCl_2$, $BaCl_2$, and $CoCl_2$ are almost independent of their amounts. (3) A considerably large variation in S value is observed as a result of the addition of the mercury(II) ion.

Discussion

It is assumed that the change in selectivity for the formation of toluene and benzene in the presence of each modified S–Ni may come from the change in the catalytic activity for the formation of the corresponding products. Thus, with the purpose of examining the correlation between f and S values for the formation of toluene and benzene, log f was plotted against the S values. The results are shown in Fig. 4. In the case of the formation of benzene, the plots are distributed on nearly a straight line. For the production of toluene, the relation is not so clear as in the case for benzene, thought a faint linear relation is also observed.

A large amount of experimental evidence has already revealed the non-uniformity of the surface of the nickel catalyst.[11] A properly-devised poisoning experiment can often provide information on the possible presence of areas or centers on the catalyst surface possessing different degrees of catalytic activity. This consideration can be demonstrated when a suitable catalyst poison is selectively adsorbed first on the sites of greater activity and then upon less active sites. However, the reaction of benzyl alcohol catalyzed by modified S–Ni catalysts treated with metal chlorides cannot be explained simply by such a poisoning effect of the metal chlorides, because there is a promoting effect on the reaction from a proper kind and amount of metal chlorides,[12] and also because a regular variation in the catalytic activity is brought about on the modified S–Ni, depending on the property of the added metal cation. It is reasonable to conclude that the electrode

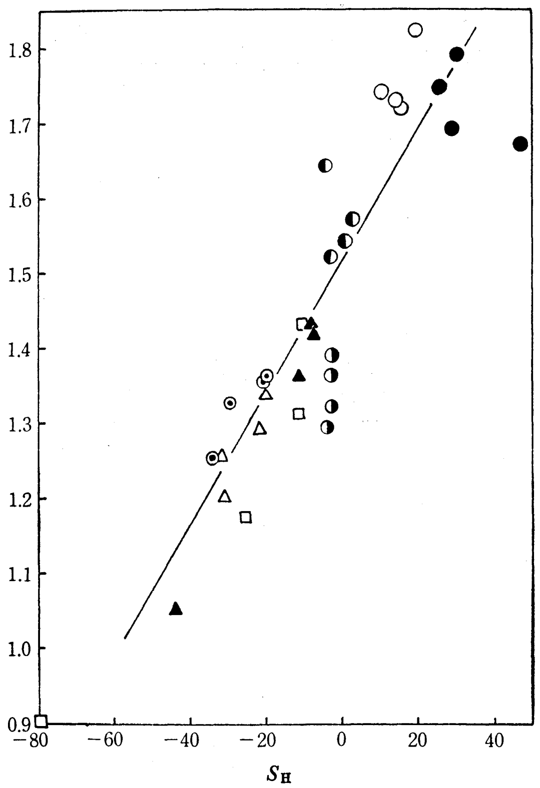

Fig. 4(a). The plots of log f_H vs. S_H. (The notations are the same as in Fig. 1).

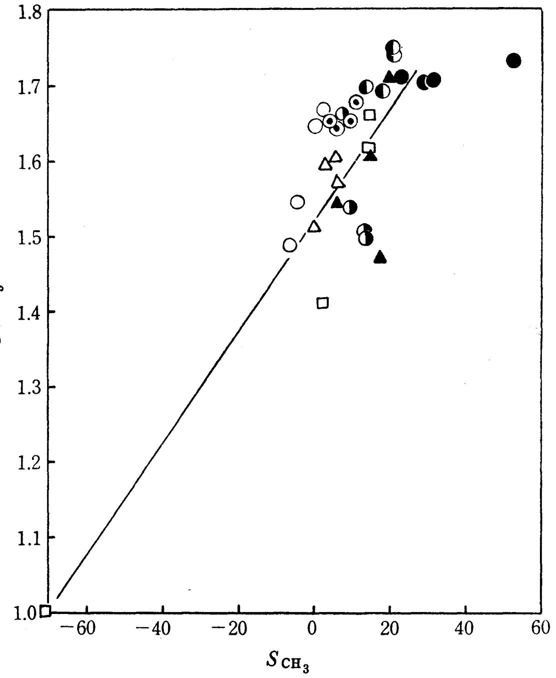

Fig. 4(b). The plots of log f_{CH_3} vs. S_{CH_3}. (The notations are the same as in Fig. 1).

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[11] W. W. Russell and W. V. Loebenstein, *J. Amer. Chem. Soc.*, **62**, 2573 (1940); A. T. Gwathmey and R. E. Cunningham, *Advan. Catal.*, **IX**, 25 (1957); **X** ,57 (1958); P. Emmett, *J. Phys. Chem.*, **63**, 1162 (1959); K. Hirota and S. Teratani, *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), **57**, 206 (1963); I. Uhara, *Shokubai*, **9**, 127 (1967).

[12] We have previously reported on the accelerating effect of NaCl on the reaction; *Cf.* Ref. 1; K. Sakai, M. Ishige, K. Watanabe, and K. Hata, This Bulletin, **43**, 1172 (1970).

potentials of the additive metals may play an important role in the promoting and retarding effects on the reaction, and that the polarizability of the metal ions adsorbed on the catalyst surface may be partially responsible for the change in f and S values. These observations suggest that this catalytic reaction of benzyl alcohol takes place in association with the acid and base functions of the catalyst surface.

It is known that the catalytic activity and selectivity are considerably correlated with the acid strength of heterogeneous metal catalysts,[13] and that the heterogeneous catalysis can be extensively elucidated by means of the acid-base concept.[14] In the formation of toluene and benzene from benzyl alcohol, it was found that the larger f values are mainly brought about by the addition of a hard metal ion, such as Na^+ and K^+, whereas the smaller f values are associated with the addition of a soft metal ion, *e.g.*, Hg^{2+}. Furthermore, the medium f values often result from the metals which belong on the borderline of the soft-hard classification. In the formation of benzaldehyde by dehydrogenation, the relation between the f_{CHO} values and the hardness of metal ions as additives tends to be opposed to that in the cases of the formation of toluene and benzene. Though a plausible explanation for this cannot yet be proposed, it seems that either the reaction path or the rate-determining step in the formation of benzaldehyde is different from that in the formation of toluene and benzene; that is, the more favorable formation of benzaldehyde is related to the change in the acid strength of the nickel catalyst by the addition of soft metal, whereas the formation of toluene and benzene is unfavorable under the same conditions.

Since the surface structure of the nickel catalyst is not sufficiently clear, it is very difficult to consider in what manner the substrate interacts with the active sites on the catalyst. However, according to the rule of the SHAB concept[13–15] that hard acids prefer hard bases and soft acids prefer solft bases, the hydroxyl group of the alcohol possessing a hard-base character will interact more strongly with the harder acid sites, and the phenyl group, as a soft base, will favorably coordinate to the softer acid sites. If the newly-formed coordination bond of each group to a metal is sufficiently strong, this should contribute to the cleavage of the C–O and C–C bonds of benzyl alcohol.

It can reasonably be inferred that the C–C bonds is more durable than the C–O bond in the catalytic fission, because the former bond is in a stable soft-soft combination, while the latter one is in a unstable hard-soft combination. This consideration is consistent with the finding of the present experiments that the f_{CH_3} values are generally larger than the f_H values.

Experimental

Material. *Benzyl Alcohol*: Benzyl alcohol used in all the experiments was purified by the previously-described procedure.[2] Its purity was confirmed by gas chromatography.

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

Preparation of Modified S–Ni. Various kinds of modified S–Ni catalysts were prepared by treating the S–Ni with aqueous solutions of various metal chlorides in the same manner as was described previously.[1] The degree of modification was controlled by adjusting the concentration of the aqueous solutions of each metal chloride to 0.02, 0.04, 0.08, and 0.16 N.

Reaction. Benzyl alcohol (2.00 m*l*) and a modified S–Ni catalyst (0.333 g) were heated at 162°C for 24 hr in a sealed tube. After the reaction was over, the tube was cooled with ice, then 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] *Cf.* M. Misono, *Shokubai*, **9**, 252 (1967), and the references cited therein.

[14] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963); *Science*, **151**, 172 (1966).

[15] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967); *Chem. Eng. News*, **31**, 90 (1965).