

A Comparative Study of Nickel and Cobalt Catalysts in the Hydrogenation of Substituted Acetophenones. Dependence of Hydrogenation Rate and Adsorption Strength on Substituents and Solvents

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The difference in the nature of nickel and cobalt catalysts has been investigated by a comparative study of the competitive hydrogenation of substituted acetophenones. The electronic and steric effects of substituents and the effects of solvents on the adsorption strength of acetophenones are greater for the reactions over R-Ni than for those over R-Co. On R-Co catalyst acetophenones substituted with electron attracting groups (3-methoxyl, 3-hydroxyl, and 4-fluoro groups with $\sigma^0 > 0$) are adsorbed more strongly than those with electron donating groups (2-, 3-, and 4-alkyl and 4-methoxyl groups with $\sigma^0 < 0$). Over R-Ni catalyst the adsorption of acetophenone is greater than that of any substituted acetophenones. The rates of hydrogenation over R-Ni are more susceptible to the effects of substituent and solvent than those over R-Co. Over both R-Ni and R-Co the rates of hydrogenation of unsubstituted acetophenones are greater than those of substituted acetophenones with either electron donating or electron attracting groups.

Heterogeneously catalyzed reactions involve the adsorption of substrates on the catalyst surface and the reaction on the catalyst surface. Solvents can affect both processes in different ways.

In recent years, it has become possible to examine the adsorption step by a method of competitive reaction. The following systems have been studied by the competitive reaction: cyclohexanone—its 4-alkyl derivatives,¹⁾ cyclohexanone—its alkyl-substituted derivatives,²⁾ acetone—alkyl methyl ketones,³⁾ acetophenone—its substituted derivatives,⁴⁾ benzene—polymethylbenzenes,^{5,6)} cyclohexene—cyclooctene,^{7,8)} 1-hexene—olefinic substrates,^{9,10)} 2-phenyl-3-methyl-2-butene—its substituted derivatives,¹¹⁾ cyclohexene—cycloalkenes,¹²⁾ 1-phenyl-2-propane—4-nitrotoluene,¹³⁾ and nitrobenzene—its substituted derivatives.¹⁴⁾

Reports appeared on the effects of substituents and ring size on the strength of adsorption in the hydrogenation of cycloalkenes⁷⁾ and *p*-substituted nitrobenzenes¹⁴⁾ over various nickel catalysts. Bekkum and his coworkers reported that in the hydrogenation over palladium catalyst the adsorption of acetophenones in an alkaline ethanol solution is influenced to a lesser extent by electronic and steric substituent effects than the rate of hydrogenation and that the hydrogenation is accelerated by electron attracting groups and retarded by electron donating groups.⁴⁾

In this work, the effectiveness of nickel and cobalt catalysts in the individual and competitive hydrogenation of substituted acetophenones in various solvents are compared. In order to confirm that the observed differences are attributable to the difference in metallic properties of nickel and cobalt, the effects of substituents (electronic and steric) on the rate of hydrogenation and on the strength of adsorption were examined mainly over Raney nickel (R-Ni) and Raney cobalt (R-Co) catalysts. The solvent effects were also investigated.

Experimental

Materials and Solvents.

Commercial reagent grade R-Ni

alloy (Ni; 48%), R-Co alloy (Co; 48—50%), zinc dust, nickel(II) chloride hexahydrate, cobalt(II) chloride hexahydrate (Guaranteed Reagent grade; GR), sodium tetrahydroborate (Wako Pure Chemical Industries) were used without further purification.

Acetophenone (GR), 4-methyl-(Extra Pure grade; EP), and 4-carboxyacetophenone (GR) (Wako Pure Chemical Industries Co.) and 4-amino-(GR), 2-methyl-(GR), 3-methyl-(GR), 4-chloro-(EP), and 4-methoxyacetophenone (EP) (Tokyo Kasei Kogyo Co.) were purified by fractional distillation or recrystallization.

4-Ethyl-, 4-isopropyl-, and 4-*t*-butylacetophenone¹⁵⁾ and 4-fluoroacetophenone¹⁶⁾ were synthesized from the corresponding alkylbenzenes and fluorobenzene by Friedel-Crafts reactions. After distillation, 4-methyl-, 4-ethyl-, and 4-*t*-butylacetophenone were purified as the corresponding oximes by fractional crystallization in aqueous methanol. The purified oximes were hydrolyzed in an aqueous solution of 25% hydrochloric acid, the ketones being again purified by fractional distillation.

Commercial reagent grade isopropyl alcohol (*i*-PrOH), methyl alcohol (MeOH), ethyl alcohol (EtOH), propyl alcohol (*n*-PrOH), *t*-butyl alcohol (*t*-BuOH), cyclohexane, benzene, and toluene were purified by the methods given in literature.¹⁷⁾ Each alcohol was dehydrated by refluxing with calcium hydride and then distilled.

Both the ketones and the solvents thus purified were gas-chromatographically pure.

Catalysts. R-Ni and R-Co were prepared by the modified method of Adkins and Billica¹⁸⁾ described in the preceding paper.¹⁹⁾ Urushibara nickel B (U-Ni-B) and Urushibara cobalt B (U-Co-B) catalysts were prepared by the simplified methods.²⁰⁾ Nickel boride (Ni₂B) and cobalt boride (Co₂B) catalysts were prepared as reported by Paul *et al.*, by reducing nickel(II) chloride or cobalt(II) chloride with sodium tetrahydroborate in aqueous solutions.²¹⁾

The catalysts were washed thoroughly with water until the washings were neutral to phenolphthalein. When a solvent immiscible with water was used, the catalysts were further washed with *i*-PrOH to remove water and finally with the solvent.

Urushibara catalysts, metal boride catalysts, and R-Co catalysts each containing 1 g of Ni or Co, and R-Ni containing

0.5 g of Ni were used for hydrogenation.

Hydrogenation. For individual hydrogenation, the substrate (5.2×10^{-3} mol) was hydrogenated with various nickel and cobalt catalysts in 10 cm³ of solvent at 30 °C and under atmospheric pressure of hydrogen in a glass reaction vessel shaken at 350–400 strokes per minute.

For competitive hydrogenation, an equimolar mixture of two substrates (5.2×10^{-3} mol of acetophenone and of substituted acetophenone) was used. Hydrogenation was pseudo zero order with respect to the substrate and first order with respect to catalyst. The rate of hydrogenation is expressed in terms of the initial rate of hydrogen uptake per g catalyst (mol min⁻¹ g⁻¹).

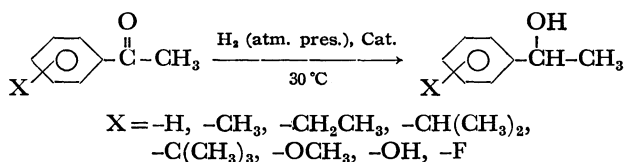
Analysis. The products were identified by comparison of their NMR spectra recorded on a Hitachi R-24 (60 MHz), IR spectra recorded on a Hitachi 215, melting point, boiling point, and retention time in gas chromatography with those of authentic samples prepared by the sodium tetrahydroborate reduction.²²

In the course of competitive hydrogenation, samples of 0.1–0.2 cm³ were withdrawn at appropriate intervals of hydrogen uptake (0–30%) for gas-chromatographic analysis.

Gas-chromatographic analyses of the reaction mixtures were performed with Shimadzu GC6A (detector, FID; carrier gas, N₂) and Shimadzu GC5A (detector, TCD; carrier gas, He) equipped with a column of 5% Silicone OV-17 on Uniport B (80/100 mesh) and of 10% PEG 20M on Celite 545 (60/80 mesh) (Gasukuro Kogyo Co.). The column temperatures employed in the case of OV-17 were 125–150 °C for acetophenone–alkylacetophenones, 170 °C for acetophenone–3-hydroxyacetophenone and acetophenone–4-fluoroacetophenone, and 200 °C for acetophenone–4-methoxyacetophenone.

Results and Discussion

Behavior of Substituted Acetophenones for the Catalytic Hydrogenation with Nickel and Cobalt. Alkyl-, methoxyl-, hydroxyl-, and fluoro-substituted acetophenones were hydrogenated to the corresponding 1-arylethanol in alcohol or hydrocarbon solutions over Ni and Co.



Neither hydrogenolysis of the carbonyl group nor hydrogenation of the aromatic ring was observed at the initial stage of reaction of these substrates.

4-Chloro-, 4-carboxy-, and 4-aminoacetophenone were not studied in detail because of their abnormal behavior during the course of hydrogenation. When 4-chloroacetophenone was subjected to catalytic hydrogenation, the reaction stopped after a slight hydrogen uptake, and the reaction mixture turned green, indicating nickel ion formation. Hydrogenation of 4-aminoacetophenone over nickel catalysts was accompanied by hydrogenolysis.

Kinetics. Kinetic measurements were performed under conditions at which the reaction rates are independent of mass transfer. The rate of hydrogenation was found to be first order with respect to catalysts.

The dependence of the initial reaction rate of hydrogenation of acetophenone on its concentration over R-Ni and R-Co in *i*-PrOH solutions is shown in Fig. 1. The

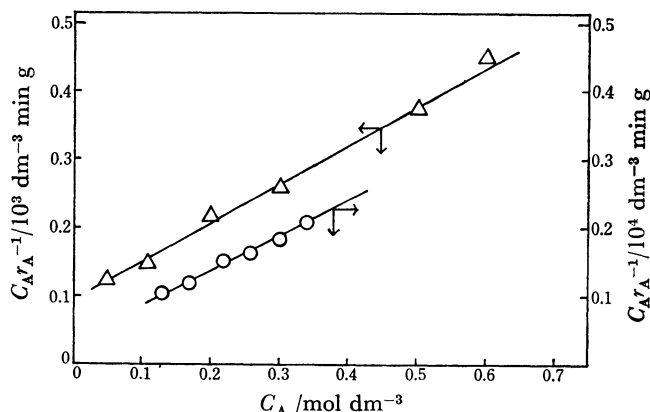


Fig. 1. Langmuir plot for hydrogenation of acetophenone in *i*-PrOH solution over R-Ni and R-Co catalysts. Δ : R-Ni, \circ : R-Co.

linear correlation of the reciprocals of the hydrogenation rate (r_A) vs. the concentration of the substrate (C_A) satisfies the Langmuir isotherm

$$r_A = -\frac{dC_A}{dt} = k_A \theta_A = \frac{k_A K_A C_A}{1 + K_A C_A}$$

where k_A is the reaction rate constant of A, θ_A the fractional surface coverage of A, and K_A the adsorption equilibrium constant of A. In the region of [acetophenone] > 0.2 mol dm⁻³, the rate of hydrogen uptake is zero order with respect to the concentration of acetophenone, thus, $r_A = k_A$. The hydrogenation was carried out by using a solution of [ketone] \geq 0.52 mol dm⁻³ in which the reaction rates are independent of the concentration of substrate.

In the competitive hydrogenation of substrates A and B, assuming that the rate of hydrogenation of A (or B) is proportional to the amount of adsorbed A (or B) and that the adsorption of A (or B) follows the Langmuir isotherm, the following equation is obtained:^{1,4)}

$$K_{B,A} = S_{B,A} / r_{B,A}$$

where $K_{B,A}$ is the relative adsorption coefficient of B to A and used as a measure for the strength of adsorption, $r_{B,A}$ the ratio of the rates in the individual reaction and $S_{B,A}$ the ratio of the product concentration formed in the competitive hydrogenation between A and B. $S_{B,A}$ was determined in the range where the relative rate is independent of time. Thus, $S_{B,A}$ is unaffected by C_A and C_B .

Substituents Effects on the Hydrogenation of Acetophenones over R-Ni and R-Co. The results of hydrogenation (individual and competitive) of acetophenones over R-Ni and R-Co in *i*-PrOH solutions are shown in Table 1. The rate of hydrogenation and the strength of adsorption of acetophenones over R-Ni and R-Co are affected by the nature (electronic and steric effects) of the substituents. In view of substituent effects, the differences in the characteristics of nickel and cobalt catalysts can be summarized as follows:

(1) **Electronic Effects of Substituents.** The electronic effects of substituents on the strengths of adsorption and the rates of reaction over R-Ni and R-Co in *i*-PrOH solution are shown in terms of Hammett's relationship

TABLE 1. SUBSTITUENT EFFECTS ON THE HYDROGENATION OF ACETOPHENONE AND SUBSTITUTED ACETOPHENONE OVER R-Ni AND R-Co CATALYSTS (solv.: *i*-PrOH 10 cm³)

Substituent (X=)	R-Ni		R-Co	
	$K_{X,H}(S_{X,H}/r_{X,H})$	$K_{X,H}(S_{X,H}/r_{X,H})$	$K_{X,H}(S_{X,H}/r_{X,H})$	$K_{X,H}(S_{X,H}/r_{X,H})$
H	1		1	
2-Me	0.21(0.16/0.76)		0.27(0.18/0.66)	
3-Me	0.50(0.44/0.88)		0.95(0.80/0.84)	
4-Me	0.37(0.29/0.78)		0.93(0.71/0.76)	
4-Et	0.36(0.24/0.67)		0.54(0.39/0.72)	
4- <i>i</i> -Pr	0.42(0.21/0.50)		0.58(0.36/0.62)	
4- <i>t</i> -Bu	0.37(0.11/0.30)		0.59(0.33/0.56)	
4-OMe	0 (≈0/0.54)		0 (≈0/0.56)	
3-OMe	0.99(0.83/0.84)		1.52(1.32/0.87)	
3-OH	0 (≈0/0.49)		4.07(2.36/0.58)	
4-F	0.48(0.29/0.60)		1.35(0.97/0.72)	

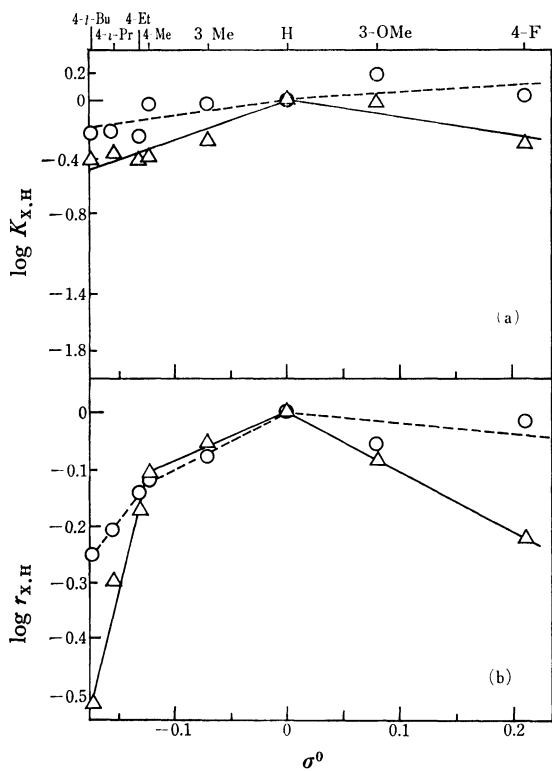


Fig. 2. $\log K_{X,H}$ and $\log r_{X,H}$ plotted against σ^0 values for the competitive hydrogenation of substituted acetophenones in *i*-PrOH solution over R-Ni and R-Co catalysts.

—△—: R-Ni, —○—: R-Co.

using $\sigma^{011,23}$ in Figs. 2a and 2b, respectively.

Strength of Adsorption: Over R-Co the strength of adsorption is greater for the acetophenones with electron attracting groups and smaller for those with electron donating groups than for unsubstituted acetophenone. The ρ value of Hammett plot in the region $\sigma^0 < 0$ is somewhat higher than that in the region $\sigma^0 > 0$.

Over R-Ni the adsorption of acetophenone is the strongest. On the two sides of $\sigma^0 > 0$ and $\sigma^0 < 0$, the Hammett plot forms approximately straight lines with different slopes. The adsorption over R-Co is affected

by substituents to a lesser extent as compared with that over R-Ni.

In the competitive hydrogenation of acetophenone and 3-methoxyacetophenone or 4-fluoroacetophenone, the $K_{X,H}$ values are always larger over R-Co than over R-Ni. The values for 3-methoxyacetophenone over R-Co are much greater than unity (Table 2b). 3-Methoxyacetophenone is more strongly adsorbed on R-Co than acetophenone.

Rate of Hydrogenation: Over both R-Ni and R-Co, the rate of hydrogenation of unsubstituted acetophenone is greater than that of substituted acetophenones with either electron donating or electron attracting groups (Fig. 2b). The Hammett plot for the reaction rates shows greater deviation from the linear relationship than that for the adsorption coefficients. The hydrogenation over R-Ni was affected to a greater extent by substituents than that over R-Co.

TABLE 2. SOLVENT EFFECTS ON COMPETITIVE HYDROGENATION OVER R-Ni AND R-Co CATALYSTS (solv.: 10 cm³)

(a) Hydrogenation of acetophenone and 3-hydroxyacetophenone.

Solvent	$K_{3-OH,H}(S_{3-OH,H}/r_{3-OH,H})$	
	R-Ni	R-Co
MeOH	0(≈0/1.08)	2.05(1.17/0.57)
EtOH	0(≈0/1.00)	2.51(1.53/0.61)
<i>n</i> -PrOH	0(≈0/0.87)	2.80(1.26/0.45)
<i>i</i> -PrOH	0(≈0/0.67)	3.00(1.68/0.56)

(b) Hydrogenation of acetophenone and 4-alkylacetophenones.

Solvent	$K_{X,H}(r_{X,H})$			
	X=4-Me		X=4- <i>t</i> -Bu	
	R-Ni	R-Co	R-Ni	R-Co
MeOH	0.16 (0.89)	1.26 (0.52)	0.063 (0.26)	
EtOH	0.17 (0.80)	0.91 (0.70)	0.070 (0.47)	0.59 (0.68)
<i>n</i> -PrOH	0.31 (0.59)	0.85 (0.72)		
<i>i</i> -PrOH	0.37 (0.78)	0.93 (0.76)	0.37 (0.11)	0.59 (0.56)
Cyclohexane	0.25 (1.00)	0.51 (0.88)	0.40 (0.30)	

(c) Hydrogenation of acetophenone and 3-methoxyacetophenone or 4-fluoroacetophenone.

Catalyst Solvent	$K_{X,H}(S_{X,H}/r_{X,H})$	
	X=3-OMe	X=4-F
	R-Ni	MeOH 0.23(0.10/0.44) EtOH 0.23(0.15/0.65) <i>n</i> -PrOH 0.31(0.24/0.77) <i>i</i> -PrOH 0.99(0.83/0.84) Cyclohexane 0.96(0.74/0.77)
R-Co	MeOH 1.40(1.27/0.91) EtOH 1.73(1.59/0.92) <i>n</i> -PrOH 1.30(1.13/0.87) <i>i</i> -PrOH 1.52(1.32/0.87) Cyclohexane 1.92(1.82/0.95)	1.02(1.26/1.23) 1.01(0.87/0.86) 0.92(0.67/0.73) 1.00(0.92/0.92) 0.80(0.82/1.02)

Concerning the rates of hydrogenation over nickel catalysts, similar effects of substituents have been recently reported in the reaction of substituted acetophenones by Nitta *et al.*²⁴⁾ In the hydrogenation of substituted acetophenones over carbon-supported palladium catalyst, Bekkum *et al.* obtained $\rho=0.74$.

The $S_{X,H}$ values of 3-hydroxyacetophenone and 4-methoxyacetophenone are exceptionally low (Table 1). The deactivating effects of substituents are particularly noticeable with 3-hydroxyacetophenone (over R-Ni in Table 2a) and 4-methoxyacetophenone (over R-Ni and R-Co) which is not hydrogenated at all before acetophenone is completely consumed in alcoholic solutions.

(2) *Steric Effects of Substituents. Strength of Adsorption:* Both over R-Ni and R-Co, the effects of increase in size of alkyl groups at the 4-position of acetophenone on the strength of adsorption are not significant. However, the alkyl group (methyl-) at the 2-position brings about a decrease in the strength of adsorption.

Rate of Hydrogenation: The rate of hydrogenation (Table 1) of 4-alkylacetophenones over R-Ni and R-Co in *i*-PrOH solution decreases in the order: H > 4-Me > 4-Et > 4-*i*-Pr > 4-*t*-Bu. This indicates that the bulkiness of the substituents at the 4-position plays an important role in the reaction rates, which depend on steric effects rather than electronic effects.

The reaction over R-Ni is more sensitive to the steric substituent effects than that over R-Co, with respect to both the hydrogenation rate and the adsorption strength.

(3) *Solvent Effects.* The hydrogenation of acetophenones is strongly affected by the solvent used, particularly on the adsorption strength of acetophenones over Ni catalysts.

From the results (Tables 2b and 2c), the differences between R-Ni and R-Co became apparent by varying the solvents. In general, in the hydrogenation of acetophenones both the rate of hydrogenation and the strength of adsorption over R-Ni are susceptible to solvents to a greater extent than over R-Co.

The adsorption of 4-alkylacetophenones over R-Ni in MeOH and EtOH solvents is very weak, as compared with that of acetophenone (Table 2b). The selectivity of adsorption in MeOH and EtOH solutions is higher for 4-*t*-Bu ($K_{X,H}=0.06-0.07$) than for 4-Me ($K_{X,H}=0.16-0.17$). On the other hand, the adsorption strengths of 4-methylacetophenone and 4-*t*-butylacetophenone over R-Co are hardly affected by solvent, as can be seen from the values of EtOH and *i*-PrOH solvents.

The solvent effects on the rate of hydrogenation and strength of adsorption can be correlated with the relative dielectric constant ϵ_r (Figs. 3a and 3b). In the case of R-Ni, both $r_{X,H}$ and $K_{X,H}$ values decrease with increase in the dielectric constant ϵ_r . In the case of R-Co, both $r_{X,H}$ and $K_{X,H}$ values are affected to a lesser extent by ϵ_r .

Effects of the Method of Catalyst Preparation. In order to know whether the above differences between Ni and Co catalysts are essential or not, the effects of the method of catalyst preparation were studied.

The results of competitive hydrogenation of aceto-

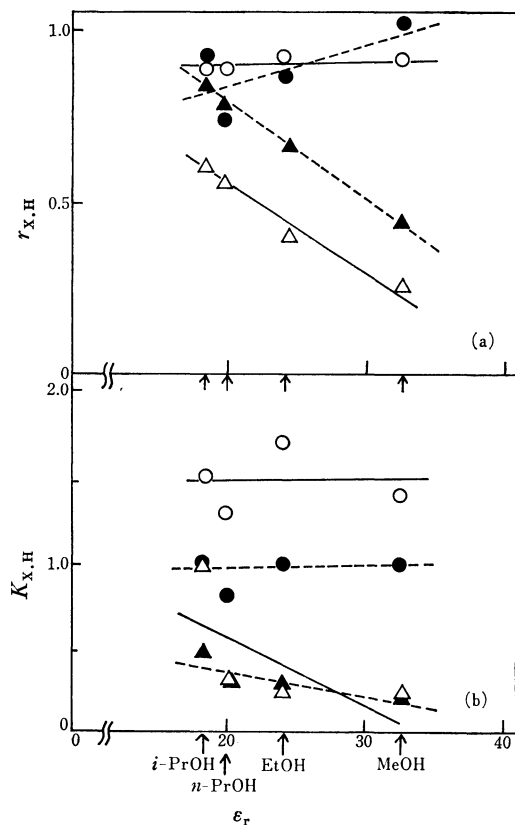


Fig. 3. Relationship between $K_{X,H}$ and $r_{X,H}$ and relative dielectric constants (ϵ_r) in the hydrogenation of 3-methoxyacetophenone and 4-fluoroacetophenone over R-Ni and R-Co catalysts. Δ , \blacktriangle : R-Ni, \circ , \bullet : R-Co, —: X=3-Me, ---: X=4-F.

TABLE 3. COMPETITIVE HYDROGENATION OF ACETOPHENONE AND 4-METHYLACETOPHENONE OVER VARIOUS Ni AND Co CATALYSTS IN EtOH SOLVENT

Catalyst	$K_{4-Me,H}(S_{4-Me,H}/r_{4-Me,H})$
R-Ni	0.17(0.14/0.80)
U-Ni-B	0.17(0.15/0.90)
Ni ₂ B	0.16(0.10/0.61)
R-Co	0.91(0.91/0.70)
U-Co-B	0.94(0.85/0.90)
Co ₂ B	0.63(0.60/0.76)

TABLE 4. $S_{3-OMe,H}$ VALUES ON THE COMPETITIVE HYDROGENATION OF ACETOPHENONE AND 3-METHOXYACETOPHENONE

Catalyst	Solvent	
	MeOH	<i>i</i> -PrOH
Ni ₂ B	0.09	0.86
Co ₂ B	0.86	0.91
R-Ni	0.10	0.83
R-Co	1.27	1.32

phenone and 4-methylacetophenone over the catalysts obtained by three methods are given in Table 3. The $K_{X,H}$ values of R-Ni, U-Ni-B, and Ni₂B catalysts agree

within the range 0.16–0.17, as is the case for the three cobalt catalysts.

A comparison between Ni₂B and Co₂B with respect to the $S_{x,H}$ values in the competitive hydrogenation of acetophenone and 3-methoxyacetophenone shows nearly the same tendency as shown by Raney catalysts (Table 4).

Dependence of $S_{x,H}$ values on the conditions of catalyst preparation was examined in the competitive hydrogenation between acetophenone and 3-methoxyacetophenone. Concerning the effect of aging time in *i*-PrOH solution on the $S_{x,H}$ values, R-Ni is somewhat more susceptible to aging as compared with R-Co (Fig. 3b).²⁵⁾ The digestion time of Raney alloy by 20% NaOH solution has no influence on the $S_{x,H}$ values, despite the presumed gradual decrease in Al content with digestion time. The effect of Al components on $S_{x,H}$ values seems negligible.

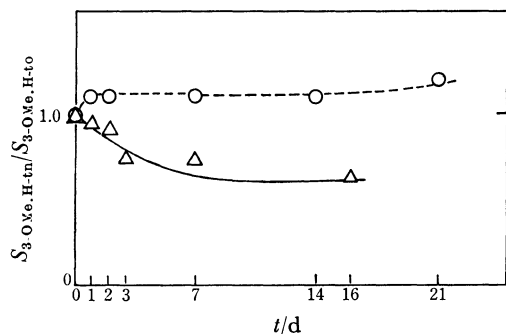


Fig. 4. Relationship between aging time of catalyst in *i*-PrOH solution and relative $S_{3-OMe,H}$ value.
 $-\Delta-$: R-Ni, $-\circ-$: R-Co.

Difference between Ni and Co Catalysts. The above results suggest that the characteristic difference between R-Ni and R-Co can be essentially attributed to the difference between Ni and Co metals. Ni is more susceptible to the effects of substituent groups and solvents as compared with Co. The difference between the two catalysts is in line with our observation that the selectivity over Co catalysts in the selective hydrogenation of 2-naphthol is influenced to a lesser extent by the solvents, as compared with Ni catalysts.¹⁹⁾ In their study of infrared spectra, Blyholder and Shihabi reported that acetone undergoes chemisorption on silica-supported Ni and Co at 25 °C, the amount on Ni being less than that on Co, and that a metal–oxygen bond rather than a metal–carbon bond is responsible for the bonding between acetone and the metal surfaces.²⁶⁾ In the hydrogenation of acetophenones over various Ni catalysts, Nitta *et al.* reported that the rate of hydrogenation is proportional to the surface d-electron density of catalysts, whereas the strength of adsorption of the reactants on the catalyst is inversely proportional to the surface d-electron density of catalysts.²⁴⁾

The reaction over Co catalyst is not very susceptible to the effects of substituents and the strength of adsorption, as compared with that over Ni catalyst. This

suggests that the carbonyl group of acetophenone is adsorbed more strongly over Co than over Ni. The characteristic difference between Ni and Co catalysts can be attributed to the difference of the surface d-electron density between the two metals; the surface d-electron density of Co is smaller than that of Ni. The results support observations concerning the relationship between the strength of adsorption and the surface d-electron density.²⁴⁾ However, the effects of substituents on the strength of adsorption and the rate of hydrogenation are still not completely explained on the basis of only this relationship. The difference between Ni and Co catalysts should be further discussed from the standpoint of their difference in physical properties as related to the mechanisms of hydrogenation.

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