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Effects of Solvents and Added Amines on the Selective Hydrogenation of 2-Naphthol over Urushibara Nickel and Cobalt Catalysts

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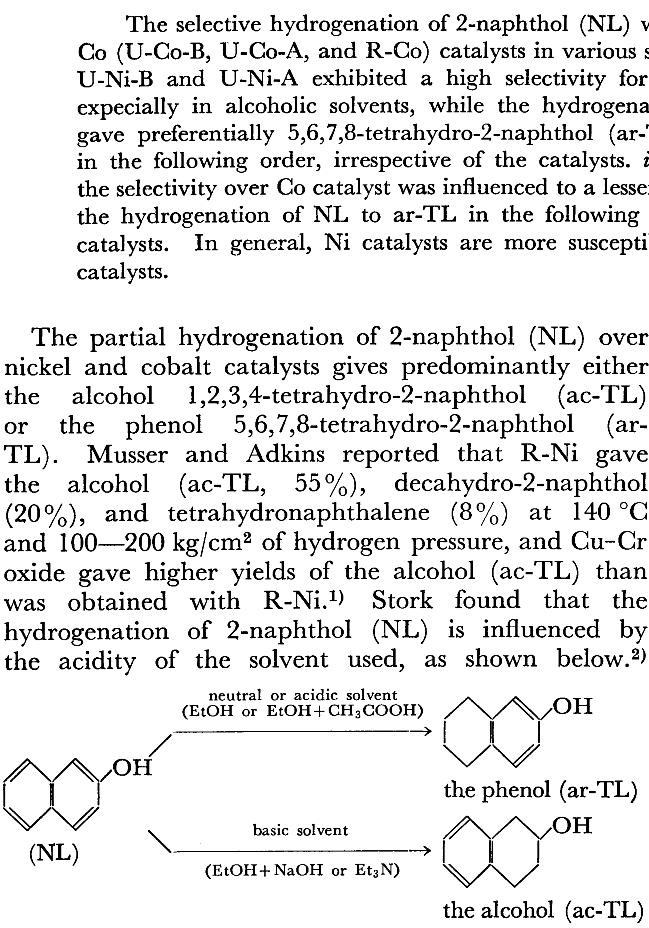
The selective hydrogenation of 2-naphthol (NL) was investigated with Ni (U-Ni-B, U-Ni-A, and R-Ni) and Co (U-Co-B, U-Co-A, and R-Co) catalysts in various solvents at elevated temperatures and pressure (50 kg/cm^2). U-Ni-B and U-Ni-A exhibited a high selectivity for the formation of 1,2,3,4-tetrahydro-2-naphthol (ac-TL), expecially in alcoholic solvents, while the hydrogenation with R-Ni in Et_2O, *i*-PrOH, and benzene solvents gave preferentially 5,6,7,8-tetrahydro-2-naphthol (ar-TL). The ar-TL formation over Ni catalysts decreased in the following order, irrespective of the catalysts. *i*-PrOH>EtOH>MeOH and Et_2O>benzene. However, the selectivity over Co catalyst was influenced to a lesser extent by the solvents. The addition of amines promoted the hydrogenation of NL to ar-TL in the following order: prim->*sec*->*tert*-amine in EtOH over Ni and Co catalysts. In general, Ni catalysts are more susceptible to the effects of solvents and added amines than Co catalysts.

The partial hydrogenation of 2-naphthol (NL) over nickel and cobalt catalysts gives predominantly either the alcohol 1,2,3,4-tetrahydro-2-naphthol (ac-TL) or the phenol 5,6,7,8-tetrahydro-2-naphthol (ar-TL). Musser and Adkins reported that R-Ni gave the alcohol (ac-TL, 55%), decahydro-2-naphthol (20%), and tetrahydronaphthalene (8%) at 140 °C and 100—200 kg/cm^2 of hydrogen pressure, and Cu-Cr oxide gave higher yields of the alcohol (ac-TL) than was obtained with R-Ni.[1] Stork found that the hydrogenation of 2-naphthol (NL) is influenced by the acidity of the solvent used, as shown below.[2]



Adkins and Kusek reported that the use of R-Ni in EtOH gave ac-TL (*ca.* 10%) and ar-TL (*ca.* 80%), but the use of R-Ni in EtOH containing a small amount of NaOH or Et_3N gave ac-TL in more than 60% yield.[3]

Thus, the selective hydrogenation of 2-naphthol has been investigated mainly by changing the solvent acidity, while the solvent effect has been largely ignored.

In this study, the selective hydrogenation of 2-naphthol with Urushibara nickel, Urushibara cobalt, Raney nickel, and Raney cobalt catalysts in various neutral solvents and in ethanol containing various amines was investigated. The characteristic differences between Ni and Co catalysts, especially with respect to the effects of solvents and added amines, are discussed.

Experimental

Material and Solvents. 2-Naphthol (Wako Pure Chemical Industries, GR) was recrystallized from H_2O-EtOH (v/v=1/3). Solvents were purified according to the standard methods described in the literature.[4]

Commercial guaranteed reagent grade amines were used without further purification.

Catalysts. Urushibara nickel and cobalt catalysts were prepared by simplified methods.[5] R-Ni (W-7 type) and R-Co catalysts were prepared by the method of Adkins and Billica:[6] To a well-stirred solution of 2 g of sodium hydroxide in 10 ml of distilled water was added 2 g of Raney nickel or cobalt alloy (Al-Ni or Co, w/w=1/1) at such a rate as to maintain the temperature (for *ca.* 30 min) at 50±2 °C. After the addition was completed the mixture was digested at 50 °C for an additional 50 min with gentle stirring. Ordinarily the W-7 R-Ni catalyst, after digestion, is washed with water three times by decantation, but the Raney catalysts were washed with distilled water until the washings were neutral to phenolphthalein.

When the solvents were immiscible with water, the catalysts were first washed with *i*-PrOH to remove the water and then with the solvent specified.

Each catalyst thus prepared contained about 1 g of Ni or Co metal. Urushibara nickel-cobalt catalyst (U-Ni, Co-B) contained 0.5 g of Ni and 0.5 g of Co.

Hydrogenation. 2-Naphthol (3.6 g; 0.025 mol) was hydrogenated with the catalyst in 25 ml of solvent at an elevated temperature under the initial hydrogen pressure of 50 kg/cm^2 in an autoclave (Nitto Hannoki; 100 ml) at an agitation rate of 450—500 rpm. The reaction temperature was raised from room temperature at the rate of 4±1 °C/min.

Analysis of Reaction Mixtures. After the reaction, the catalyst was filtered off, and the filtrate was analyzed by gas chromatography using the Yanagimoto GC 550T equipped with a column of 5% Silicone OV-17 on Uniport B (Gaschro Kogyo) (ϕ 3 mm×220 cm; glass column, column temp. 180 °C, carrier gas He; 7 ml/min).

Results and Discussion

Selectivity (S value). The main products obtained by the hydrogenation of 2-naphthol (NL) were 1,2,3,4- and 5,6,7,8-tetrahydro-2-naphthols (ac-TL and ar-TL). Since the sums of the yields of decahydro-2-naphthol and tetralin were less than about 5% in most cases, the selectivity in the hydrogenation of 2-naphthol is discussed with respect to the formation of tetralols (ac-TL and ar-TL). The selectivity (*S*) of the hydrogenation is expressed by

$$S = [\text{ar-TL}/(\text{ac-TL}+\text{ar-TL})] \times 100.$$

Solvent Dependence of Selectivity. The results of the hydrogenation of 2-naphthol over Ni and Co catalysts prepared by various methods are shown in Tables 1 and 2.

The different selectivities of U-Ni-B, U-Ni-A, and R-Ni in the various solvents are more clearly seen in Fig. 1.

The selectivities over Ni catalysts changed over a wide range from 22% (U-Ni-B, MeOH) to 81% (R-Ni, *i*-PrOH or Et_2O) with the combinations of catalysts and solvents. In general, the hydrogenation of the phenol ring occurred preferentially over R-Ni and that of the benzene ring over U-Ni-B. The selectivity over U-Ni-A was intermediate between those over U-Ni-B and the R-Ni and *S* values over the catalyst were widely distributed with different solvents, as seen in Fig. 1.

Although the *S* values differed widely with the catalysts, the effects of the solvents with respect to *S* were similar, irrespective of the catalysts, as seen in Fig. 1. Thus, the ar-TL formation over Ni catalysts decreases in the following order: *i*-PrOH>EtOH>MeOH and Et_2O>benzene. The *S* values in ethers were generally greater than those in hydrocarbons.

The hydrogenation over U-Co-B was influenced to a lesser extent by the solvents used than that over U-Ni-B; all the *S* values over U-Co-B were about 50%, as seen in Table 2-1. U-Ni, Co-B catalyst exhibited a greater similarity to U-Ni-B than to U-Co-B. The selectivities by U-Co-A and R-Co catalysts

TABLE 1. SOLVENT EFFECTS ON THE SELECTIVITY OF THE HYDROGENATION OF 2-NAPHTHOL OVER Ni CATALYSTS
2-naphthol(NL): 0.025 mol, solvent: 25 ml,
Ni content of catalysts: 1 g, Selectivity:
S= 100 × ar-TL/(ar-TL + ac-TL).

Table 1-1. Hydrogenation over U-Ni-B

Solvent	React. Time (min)	React. Temp. (°C)	Recov. NL(%)	Selectivity (*S*)(%)
MeOH	60	80—114	43	22
EtOH	90	82—130	0[a]	34
EtOH	35	r.t.—140	0	38
i-PrOH + H_2O[b]	25	—96	21	33
i-PrOH	30	—94	43	43
i-PrOH	13	80—95	74	47
i-PrOH	7	130—152	13[c]	47
Cyclohexane	35	r.t.—96	22	35
Toluene	30	—114	0[d]	37
Toluene	22	—82	49	37
Benzene	30	—118	0	38
Benzene	24	—91	37	39
$(i\text{-Pr})_2O$	35	—100	8	39
THF	35	—136	56	40
THF	30	—104	90	46
Et_2O	40	—140	0[e]	42
Et_2O	30	—96	26	45
Et_2O	30	—100	40	47
Dioxane	30	—116	39	50
$(n\text{-Bu})_2O$	40	—110	68	54

a) Tetralin, 3%; Decalol, 4%. b) H_2O, 2 ml. c) Tetralin, 1%; Decalol, 9%. d) Tetralin, 0.4%; Decalol, 3%. e) Tetralin, 7%; Decalol, 11%.

TABLE 1-2. HYDROGENATION OVER U-Ni-A, ppt-Ni, AND R-Ni

Catalyst	Solvent	React. Time (min)	React. Temp. (°C)	Recov. NL (%)	Selectivity (*S*)(%)
U-Ni-A	MeOH	90	r.t.—152	79	28
	EtOH	30	—118	43	35
	i-PrOH	40	—150	20	44
	Benzene	20	—72	32	53
	$(i\text{-Pr})_2O$	35	—132	25	48
	Et_2O	25	—92	32	62
	$(n\text{-Bu})_2O$	30	—98	95	65
ppt-Ni	EtOH	90	—136	63	41
R-Ni	MeOH	23	—84	25	65
	EtOH	16	—58	20	67
	i-PrOH	17	—60	27	81
	Benzene	15	—53	45	75
	Et_2O	18	—65	43	81

Selectivity: S = 100 × **ar-TL**/(**ar-TL** + **ac-TL**) (%)

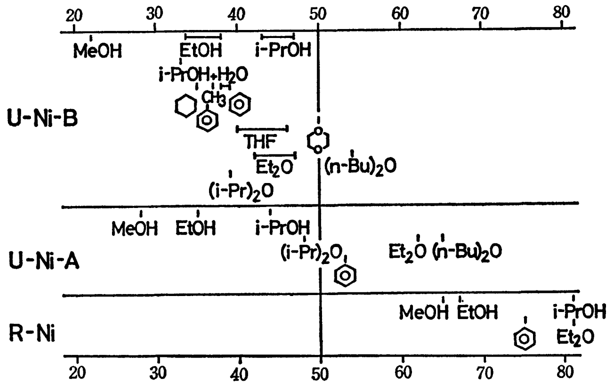


Fig. 1. Solvent effects on the selective hydrogenation of 2-naphthol over Ni catalysts.
ac-TL: 1,2,3,4-Tetrahydro-2-naphthol
ar-TL: 5,6,7,8-Tetrahydro-2-naphthol

TABLE 2. SOLVENT EFFECTS ON THE SELECTIVITY OF THE HYDROGENATION OF 2-NAPHTHOL OVER Co CATALYSTS
2-naphthol(NL): 0.025 mol, solvent: 25 ml,
Co content of catalysts: 1 g, Selectivity:
S= 100 × ar-TL/(ar-TL + ac-TL).

Table 2-1. Hydrogenation over U-Co-B

Solvent	React. Time (min)	React. Temp. (°C)	Recov. NL (%)	Selectivity (*S*)(%)
Cyclohexane	35	r.t.—124	0	44
Benzene	40	—148	0	47
i-PrOH	40	—144	16	50
EtOH	42	—138	0	52
EtOH + H_2O[a]	30	—120	11	54
EtOH	120	110—130	16	55
EtOH	50	150—180	17	56
EtOH	60	80—118	8	57
MeOH	40	r.t.—152	37	56
Et_2O	4	—134	12	55
Dioxane	30	—126	65	56

a) EtOH, 20 ml; H_2O, 5 ml.

Table. 2-2. Hydrogenation over U-Co-A, U-Ni, Co-B, and R-Co

Catalyst	Solvent	React. Time (min)	React. Temp. (°C)	Recov. NL (%)	Selectivity (S)(%)
U-Co-A	Benzene	35	r.t.—142	41	47
	Et_2O	38	—162	34	46
	Et_2O	45	—164	0	49
	EtOH	30	—127	29	54
U-Ni, Co-B[a]	EtOH	60	80—94	35	43
R-Co	Benzene	20	r.t.—73	3	46
	EtOH	25	—90	3	52
	Et_2O	35	—138	41	54

a) Ni, 0.5 g; Co, 0.5 g.

were practically similar to those by U-Co-B. Compared with Ni catalysts, Co catalysts were not very susceptible to the solvent effects on the selectivity.

It is widely recognized that a solvent containing oxygen atoms often acts as a catalyst poison, because of the strong affinity of the oxygen atom to the catalyst surface. Orito and Imai showed that the solvent effect is a critical factor in the hydrogenation of benzene and toluene over Ni catalysts; hydrocarbons are good solvents for rapid hydrogenation, but solvents containing oxygen atoms, particularly primary alcohols and dioxane, strongly restrain the hydrogenation.[7)]

In the hydrogenation of 2-naphthol over Ni catalysts, primary alcohols tended to suppress the hydrogenation of the unsubstituted benzene ring, whereas secondary alcohol, ether, and hydrocarbon solvents gave greater S values than the primary alcohols. However, it is still not clear why the selectivity of hydrogenation depends on the solvents or why the solvent effect of Ni catalyst differs from that of Co catalyst.

The selectivity may depend on the reaction temperature, the amount of hydrogen uptake, or the presence of H_2O. However, it was confirmed that the reaction temperature and the amount of hydrogen uptake influenced the selectivity to only a small extent (less than about 5%), as seen in Tables 1–1 and 2–1. In the hydrogenation over U-Ni-B in i-PrOH containing H_2O, added H_2O tends to promote the formation of ac-TL. The selectivity over U-Co-B was only slightly affectes by the addition of H_2O.

Effects of Added Amine on the Selectivities. The effects of added amine (the amount of amine added: 5 ml) on the hydrogenation in 20 ml of EtOH were investigated. The results with Ni and Co catalysts are shown in Tables 3 and 4, respectively.

It has so far been thought that amines promote the hydrogenation of NL to ac-TL. Stork[2)] and Adkins and Kusek[3)] reported that the addition of Et_3N in EtOH solution over R-Ni catalyst also promotes this reaction.

However, as shown in Tables 3 and 4, the effects of added amines on the selective hydrogenation depend on the nature of the amines: the primary amines tend to increase the yield of ar-TL. On the other hand, the addition of tertiary amines promoted slightly the formation of ac-TL with Ni catalysts and was of little effect in the case of Co catalysts. Thus, the selectivities (S) decreased in the following order: primary amine > secondary amine > tertiary amine.

Table 3. Effects of added amines on the selectivity of the hydrogenation of 2-naphthol over Ni catalysts

2-naphthol(NL): 0.025 mol, solvent: EtOH 20 ml + amine 5 ml, Ni content of catalysts: 1 g, Selectivity: $S = 100 \times \text{ar-TL}/(\text{ar-TL}+\text{ac-TL})$.

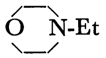
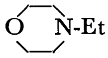
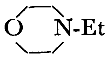
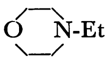
Catalyst	Amine	React. Time (min)	React. Temp. (°C)	Recov. NL (%)	Selectivity (S)(%)
U-Ni-B	Et_3N	30	r.t.—130	41	33
		35	—140	53	40
	Et_2NH	45	—152	40	41
	i-$PrNH_2$	40	—152	28	54
	n-$BuNH_2$	35	—158	75	70
R-Ni	Et_3N	15	—64	13	33
		25	—68	30	46
	Et_2NH	30	—77	12	34
	i-$PrNH_2$	30	—130	10	57
	n-$BuNH_2$	30	—120	54	64
	n-$BuNH_2$	30	—136	8	67

Table 4. Effects of added amines on the selectivity of the hydrogenation of 2-naphthol over Co catalysts

2-naphthol(NL): 0.025 mol, solvent: EtOH 20 ml + amine 5 ml, Co content of catalysts: 1 g, Selectivity: $S = 100 \times \text{ar-TL}/(\text{ar-TL}+\text{ac-TL})$.

Catalyst	Amine	React. Time (min)	React. Temp. (°C)	Recov. NL (%)	Selectivity (S)(%)
U-Co-B	Et_3N	35	r.t.—154	28	57
		40	—132	49	59
	Et_2NH	40	—148	49	62
	i-$PrNH_2$	45	—156	43	63
	n-$BuNH_2$	45	—180	0	65
R-Co	Et_3N	30	—120	21	55
		30	—120	21	52
	Et_2NH	25	—90	47	51
	i-$PrNH_2$	35	—106	14	59
	n-$BuNH_2$	70	—184	22	62

Furthermore, it is noteworthy that the S values over Ni catalysts are influenced in a wide range by the addition of various amines, as compared with Co catalysts: *e.g.*, from 70% with n-$BuNH_2$ to 33% with Et_3N over U-Ni-B and from 65% with n-$BuNH_2$ to 57% with Et_3N over U-Co-B. Thus, concerning the amine effects, the characteristic differences between Ni and Co catalysts are similar to those of the solvent effects discussed above.

The rate of hydrogenation both over Ni and Co catalysts decreased with increasing selectivity (S). The effects of the amines to depress the rate of hydrogenation were in the following order: prim-amine > *sec*-amine > *tert*-amine. The order is parallel to that of the adsorption strength of the amines.

Usually, it has been thought that hydrogenation of a phenol proceeds *via* an intermediate cyclohexanone, which in some cases can be isolated. Stork reported that palladium on charcoal in basic media (*N*-ethylmorpholine) can be used as a good catalyst for the hydrogenation of 2-naphthol to 2-tetralone.$^{8)}$

In the present work, however, the formation of 2-tetralone could not be observed, even when the hydrogenation was carried out in the presence of amine with Ni and Co catalysts, respectively. This may be plausible because the conversion of 2-tetralone to 2-tetralol (ac-TL) would be rapid over Ni and Co catalysts.

Stork has reported that the accelerating effects of Et_3N on the formation of ac-TL might be attributed to the shift of equilibrium toward the ketonic tautomer of 2-naphthol.$^{8)}$ Though this idea may account for the effect of Et_3N, it does not explain how prim- or *sec*-amines promote the formation of ar-TL. Owing to lesser steric hindrance, prim- or *sec*-amines would be more strongly adsorbed onto the catalyst surface than tertiary amines.$^{4)}$ The results obtained suggest that the presence of strongly adsorbed amines on the catalyst surface might inhibit the adsorption of the phenol ring more than that of the benzene ring of 2-naphthol.

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