Kinetics of Liquid-phase Hydrogenation of Aliphatic α,β-Unsaturated Aldehyde over Raney Cobalt Catalyst Modified with Co-, Mn-, Ni-, and $PdCl_2$

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Kinetic studies were carried out on the hydrogenation of the α,β-unsaturated aldehyde, 2-methyl-2-pentenal (UD), over the Raney cobalt catalyst modified with various amounts of Co-, Mn-, Ni- and $PdCl_2$ in *n*-hexane under atmospheric pressure at 40 and 20°C. Initial rates of formation of the saturated aldehyde (r_{SD}), saturated alcohol(r_{SA}) and unsaturated alcohol(r_{UA}) were determined in the concentration range of UD(C_{UD}) 0.018—0.263 mol/*l*. It was found that ($r_{SD}+r_{SA}$) obeyed a Langmuir-type rate equation and r_{UA} a different one. The rate equations are as follows.

$$r_{SD}+r_{SA}=\frac{k_1\cdot b_1\cdot C_{UD}}{(1+b_1\cdot C_{UD})^2},\qquad r_{UA}=\frac{k_2\cdot b_2\cdot C_{UD}}{(1+b_2\cdot C_{UD})^2}$$

where *k* and *b* denote the rate constant of the surface reaction and parameter for the adsorption of UD and hydrogen, respectively, the subscripts 1 and 2 representing the formation of SA and SD and that of UA, respectively. Kinetic parameters k_1, k_2, b_1 and b_2 were found to vary with the amount and kind of modifier. The variation of b_1 and b_2 was irregular. The rate constant k_1 decreased with increasing amount of Co-, Mn- and $NiCl_2$ added; it increased remarkably with the addition of $PdCl_2$. The variation of k_2 was more complicated. Addition of a small amount of the modifiers did not decrease k_2. Further addition of Co- and $MnCl_2$ made k_2 decrease, while that of $NiCl_2$ made it increase. Mechanism of the modification with these metal chlorides is discussed on the basis of the active site hypothesis.

In the course of studies on selectivities of Raney-type catalysts modified with various compounds in the liquid phase hydrogenation of the α,β-unstaturated aldehyde, we have found that the formation of the saturated aldehyde and alcohol over the Raney cobalt catalyst was inhibited by the addition of $FeCl_2$ and that of the unsaturated alcohol was retarded only slightly.[1]

Kishida *et al.* have studied the modifier effect of some organic compounds in the liquid phase hydrogenation of acetone over the Raney nickel catalyst and found that the addition of tripropylamine decreased the rate of hydrogenation at low concentrations of acetone but increased at high concentrations.[2] The effect of the modifier depends on the concentration of the reactant at which the rate measurement was carried out.

Thus in studying the modifier effect on a solid catalyst, it is advisable to determine the kinetic parameters for the adsorption of reactants and for surface reaction, both being independent of the concentration of reactants, and to examine the variation of the two parameters. Such a treatment has seldom been performed on the modifier effect of metal chlorides. In the present paper, kinetics of the liquid phase hydrogenation of the α,β-unsaturated aldehyde, 2-methyl-2-pentenal, over the Raney cobalt catalyst modified with manganese(II)-, cobalt(II)-, nickel(II)- and palladium(II) chlorides are described. Variation of the rate constant and adsorption coefficient with the amount and kind of modifier is examined. Mechanism of uneven poisoning of the catalyst observed when Co- and $MnCl_2$ were added, is discussed on the basis of the active site hypothesis. The promoter effect of $PdCl_2$ on the reaction of the carbon-carbon double bond is also discussed.

Experimental Methods

Catalyst. A Raney cobalt-aluminum alloy(50 wt% Co) was developed with a sodium hydroxide solution and washed with distilled water and then with 2-propanol.[3] The catalyst thus obtained was stirred with specified amounts of anhydrous metal chlorides in 2-propanol for 1 hr in a hydrogen atmosphere. The amount of metal chlorides adsorbed was determined by measuring polarographically the amount of metal ions remaining in 2-propanol solution. It was found that these ions were completely adsorbed on the catalyst when the amount of metal chlorides added was less than 0.10 mmol/g-Co. When metal chloride of 0.15 mmol/g-Co was used, the amount of adsorbed ion was 0.14 mmol/g-Co.

It was observed that the brown color of $PdCl_2$ solution faded by stirring for a few minutes. Absorption of hydrogen was observed, and the blue color of Co(II) ion appeared and then disappeared completely by stirring for 5 min. This indicates that $PdCl_2$ is adsorbed on the catalyst and reduced to the metal according to the following equations

$$PdCl_2 + Co \longrightarrow Pd + CoCl_2$$
$$PdCl_2 + H_2 \longrightarrow Pd + 2HCl$$

and HCl formed reacts with cobalt atom to give $CoCl_2$ and $CoCl_2$ formed is also adsorbed on the catalyst surface.

The modified catalyst thus obtained was washed twice with 2-propanol and 10 times with *n*-hexane and then dried in a hydrogen atmosphere. The resulting catalyst was weighed and stored in the portion containing *ca.* 500 mg of cobalt.[3]

Apparatus, Procedure, and Materials. Hydrogenation was carried out as described previously.[3] Over the catalyst modified with $PdCl_2$, however, it was carried out at 20°C since a too rapid reaction took place at 40°C. Reaction products were analyzed by glc. Adsorbed metal chlorides were not removed during the reaction. Substrate: 2-methyl-2-pentenal, cylinder hydrogen, 2-propanol, and

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[1] K. Hotta and T. Kubomatsu, This Bulletin, **42**, 1447 (1969).

[2] S. Kishida, C. Ko and S. Teranishi, *Shokubai*, **11**, 146 (1969).

[3] K. Hotta and T. Kubomatsu, This Bulletin, **44**, 1348 (1971).

TABLE 1. INITIAL RATES OF THE FORMATION OF SD, SA, AND UA OVER RANEY COBALT CATALYST MODIFIED WITH $CoCl_2$ AT 40°C

$CoCl_2$ (mmol/g-Co)		C_{UD} (10^{-2} mol/l)						
		3.5	7.0	10.5	14.0	19.3	26.3	
0.0	r_{SD}	12.3	15.8	13.4	12.1	11.1	8.8	
	r_{SA}	9.7	8.2	5.5	5.3	4.6	2.4	
	r_{UA}	7.2	8.7	10.0	9.7	8.4	6.9	
0.025	r_{SD}	6.1	6.7	5.7	5.5	5.5	4.9	
	r_{SA}	8.5	6.7	5.0	3.6	2.8	2.0	
	r_{UA}	6.9	9.5	10.5	11.3	10.7	9.5	
0.05	r_{SD}	2.3	2.9	3.3	3.1	2.8	2.3	
	r_{SA}	5.3	3.8	2.5	2.2	1.8	1.2	
	r_{UA}	7.9	9.5	9.4	9.3	8.7	7.2	
	C_{UD}	1.8	3.5	7.0	10.5	14.0	17.5	22.8
0.10	r_{SD}		1.0	1.3	1.5	1.4	1.2	0.92
	r_{SA}		1.2	1.1	0.65	0.38	0.36	0.33
	r_{UA}		4.0	4.1	3.8	3.7	3.6	3.0
0.15	r_{SD}	0.36	0.49	0.66	0.58	0.49		
	r_{SA}	0.53	0.43	0.31	0.24	0.17		
	r_{UA}	1.7	2.3	2.4	2.6	2.5		

Unit of initial rate: 10^{-2} mmol/min·g-Co, C_{UD}: concentration of UD.

n-hexane were the same as those described previouly. Commercial anhydrous metal chlorides of extra pure grade were used without further purification.

Determination of Initial Rate of Formation of Product. The initial rate of formation was determined by extrapolating the plot, rate of formation *vs.* reaction time, to zero.[3]

Results

Initial Rate of Formation of Product. Products of the reaction were found to be the saturated aldehyde 2-methylpentanal(SD), saturated alcohol 2-methylpentan-1-ol(SA) and unsaturated alcohol 2-methyl-2-penten-1-ol(UA). Isomerization of UA to SD, and dehydrogenation of UA to UD and of SA to SD and/or UA were not observed under the conditions studied.

Initial rates of the formation of SD(r_{SD}), SA(r_{SA}), and UA(r_{UA}) are given in Tables 1 and 2 for the catalyst modified with $CoCl_2$, abbreviated as R-Co-(Co), the one with $PdCl_2$ as R-Co(Pd), respectively. R_{UA} decreased by the addition of 0.025 mmol/g-Co of $CoCl_2$ at low concentrations of UD and increased at high concentrations. r_{UA} decreased by the further addition of the modifier. On the other hand, r_{SD} and r_{SA} decreased with increasing amount of $CoCl_2$. A similar behavior was observed for the catalyst modified with Ni- and $MnCl_2$. The behavior of the initial rates mentioned above is not contradictory to that reported by other workers.[4,5]

TABLE 2. INITIAL RATES OF THE FORMATION OF SD, SA AND UA OVER RANEY COBALT CATALYST MODIFIED WITH $PdCl_2$ AT 20°C

$PdCl_2$ (mmol/g-Co)		C_{UD} (10^{-2} mol/l)				
		3.5	7.0	10.5	15.8	21.0
0.0	r_{SD}	5.7	8.0	8.0	7.5	7.0
	r_{SA}	3.7	3.2	2.7	2.2	2.0
	r_{UA}	2.2	3.1	4.3	4.4	4.3
	C_{UD}	5.3	8.8	14.0	19.3	26.3
0.025	r_{SD}	35	38	29	26	21
	r_{SA}	6.0	3.6	3.3	3.0	1.9
	r_{UA}	3.7	3.8	4.0	4.5	3.9
0.050	r_{SD}	44	50	52	55	54
	r_{SA}	5.9	4.4	3.2	2.4	1.1
	r_{UA}	2.8	3.6	2.8	2.5	2.3
0.10	r_{SD}	60	68	70	79	80
	r_{SA}	5.3	3.8	3.2	2.6	1.5
	r_{UA}	+	+	+	+	1.9

r_{UA} increased by the addition of 0.025 mmol/g-Co of $PdCl_2$ at low concentrations of UD and decreased at high concentrations, and decreased by the further addition of the modifier. r_{SD} increased by the addition of $PdCl_2$ more remarkably than r_{SA}.

Rate Equation and Kinetic Parameters. The data in Table 1 were analyzed by means of the equation

$$r=\frac{k\cdot b\cdot C_{UD}}{(1+b\cdot C_{UD})^2} \tag{1}$$

where k denotes the rate constant, C_{UD} the concentration of UD, and b is the ratio of the adsorption equilibrium constant of UD to that of hydrogen, divided by the liquid phase concentration of hydrogen *i.e.* $b=K_{UD}/$

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[4] Z. Csuros and J. Petro, *Acta Chem. Acad. Sci. Hung.*, **20**, 129 (1959).

[5] Y. Takagi and T. Yamanaka, *Sci. Papers Inst. Phys. Chem. Res.*, **55**, 105 (1961).

TABLE 3. KINETIC PARAMETERS

		With respect to the formation of SA+SD		UA	
	(mmol/g-Co)	k_1 (mmol/min·g-Co)	b_1 (l/mol)	k_2	b_2
$CoCl_2$	0.0	1.0	25	0.38	11
	0.025	0.25	21	0.43	7.5
	0.050	0.28	22	0.39	11
	0.10	0.094	20	0.20	16
	0.15	0.040	25	0.11	13
$MnCl_2$	0.025	0.44	18	0.39	7.2
	0.050	0.26	24	0.33	8.4
	0.10	0.091	20	0.17	14
	0.15	0.032	22	0.13	13
$NiCl_2$	0.025	0.54	15	0.38	12
	0.050	0.53	23	0.39	12
	0.10	0.44	27	0.40	12
$PdCl_2$	0.0	0.44	11	0.17	6.1
	0.025	1.4	17	0.17	20

$K_H \cdot C_H$ and called adsorption coefficient. As the rate measurement was carried out under the constant pressure of hydrogen, and the solubility of hydrogen is assumed to be independent of the composition of reaction mixture, C_H is constant at a given temperature, and b depends only on the adsorption equilibrium constants of UD and hydrogen.

Rearranging Eq. (1), we obtain: $(C_{UD}/r)^{1/2}=1/(k\cdot b)^{1/2}+(b/k)^{1/2}\cdot C_{UD}$. This gives a linear relation between $(C_{UD}/r)^{1/2}$ and C_{UD} when $(C_{UD}/(r_{SD}+r_{SD}))^{1/2}$ *vs.* C_{UD} for R-Co(Co) are plotted (Fig. 1), and $(C_{UD}/r_{UA})^{1/2}$ *vs.* C_{UD} (Fig. 2). From these plots, the values of kinetic parameters k and b were determined (Table 3). The values of the kinetic parameters for R-Co-(Mn), R-Co(Ni) and R-Co(Pd-0.025) determined similarly are also given.

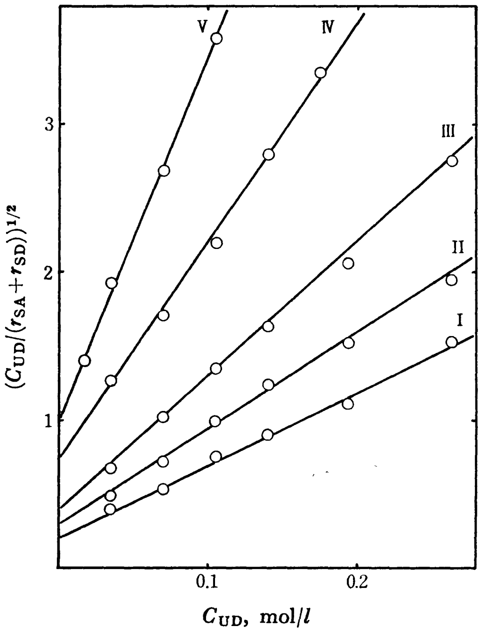

Fig. 1. $(C_{UD}/(r_{SA}+r_{SD}))^{1/2}$ *vs.* C_{UD} plots for R-Co catalyst modified with $CoCl_2$ of 0.0 mmol/g-Co, I; 0.025, II; 0.050, III; 0.10, IV; 0.15, V.

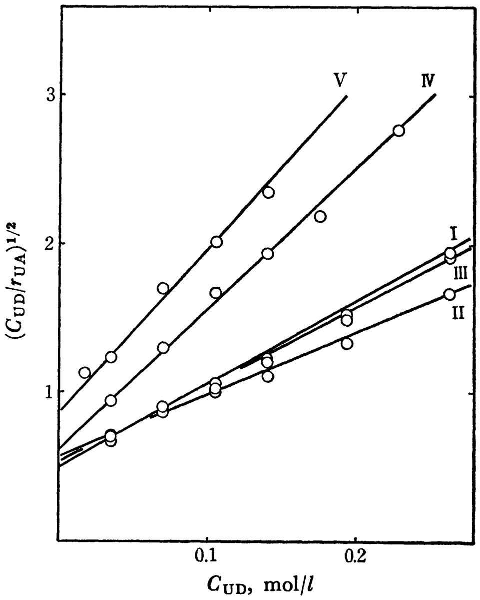

Fig. 2. $(C_{UD}/r_{UA})^{1/2}$ *vs.* C_{UD} plots.

The rate data over R-Co(Pd-0.050 and 0.10) were not analyzed by the same method since SA was supposed to be formed through both SD and UA. Variation of the values of b_1 and b_2 is irregular (Table 3). Variation of the rate constant with the amount of metal chlorides is shown in Fig. 3. The rate constant for the formation of SA and SD (k_1) decreases with increasing amount of Co-, Mn- and $NiCl_2$, but it increases with the addition of $PdCl_2$.

Addition of a small amount of these modifiers does not decrease the rate constant for the formation of UA (k_2). Further addition of Co- and $MnCl_2$ decreases k_2, while that of $NiCl_2$ makes it increase.

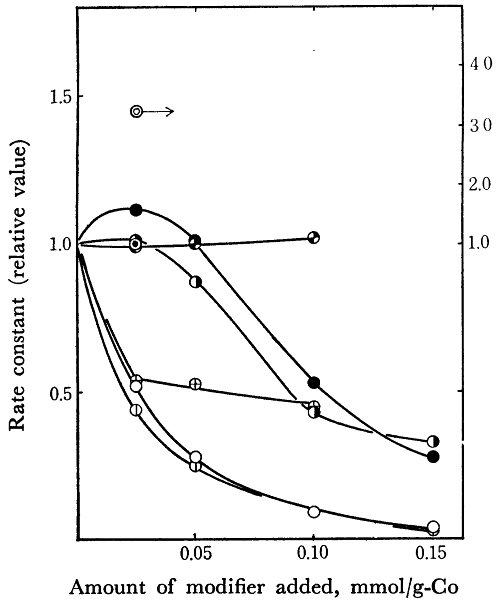

Fig. 3. Variation of rate constant with amount of modifier added, for k_1 with $CoCl_2$, ○; $MnCl_2$, ⦶; $NiCl_2$, ⊕; $PdCl_2$, ◎; k_2 with $CoCl_2$, ●; $MnCl_2$, ◑; $NiCl_2$, ◕; $PdCl_2$, ⊙

Discussion

It has been reported[1] that, in the hydrogenation of a mixture of SD and UA (mole ratio 1 : 1) over the Raney cobalt catalyst in the absence and in the presence of $FeCl_2$, SD was preferentially hydrogenated. Since the initial rates of formation of the three products varied with the addition of Co-, Mn- and $NiCl_2$ in a similar way to that observed when $FeCl_2$ was added, it can be considered that the hydrogenation of UA to SA does not occur over the catalyst modified with Co-, Mn-, and $NiCl_2$ in the period in which the concentrations of SD and UA are comparable. Thus, the reaction scheme,[3] in which the formation of UA and that of SA and SD were separately treated, can also be valid for the present systems over the catalyst modified with Co-, Mn-, and $NiCl_2$.

When the mixture of UA and SD was hydrogenated over the Raney cobalt catalyst modified with $PdCl_2$ (0.050 and 0.10 mmol/g-Co), both SD and UA were hydrogenated simultaneously. Thus in the hydrogenation of UD over the $PdCl_2$-modified catalyst the reaction path of the hydrogenation of UA to SA has to be considered, and the formation of SD and SA and that of UA can not be treated separately. This is considered to be due to the formation of metallic palladium which is active for the hydrogenation of the carbon-carbon double bond. This is supported by the result where r_{SD} over the $PdCl_2$-modified catalyst increased remarkably. Promotion in the activities of the Raney nickel and cobalt catalysts by the addition of platinum-metal compounds was reported by several workers.[6-8]

The decrease of k_1 over R-Co(Co) and R-Co(Mn) (Fig. 3), can be explained as being due to the poisoning of active sites. The variation of k_2 over R-Co(Mn) might indicate that the formation of UA, SA and SD takes place on different sites of catalyst surface and the site responsible for the formation of UA is not occupied with $MnCl_2$ when 0.025 mmol/g-Co of the modifier was used.

Modification of the catalyst with $CoCl_2$ of 0.025 mmol/g-Co caused the increase of k_2. Promotion in the rate constant can not be explained by a simple active site hypothesis. As the number of active sites responsible for the formation of UA can not be considered to increase with the addition of 0.025 mmol/g-Co of $CoCl_2$ although k_2 was found to increase, the specific rate constant defined as the rate constant per unit active site must increase. This suggests a promoting effect which is induced onto a site by the modifier adsorbed on another site. The fact that k_2 begins to decrease can be explained by considering that further addition of the modifier causes the adsorption of $CoCl_2$ even on the site responsible for the formation of UA and, hence, the increase in the number of sites covered by the modifier overcomes an increase in the specific rate constant. A similar behavior of rates has also been observed in acetone hydrogenation over the Raney nickel catalyst by the addition of a small amount of triethylamine.[2]

The ratio k_2/k_1 increased with the amount of Co- and $MnCl_2$, and decreased with the addition of $PdCl_2$. Although behaviors of k_1 and k_2 over R-Co(Ni) differ somewhat from those over R-Co(Co) and R-Co(Mn), the ratio k_2/k_1 over R-Co(Ni) increased with the amount of $NiCl_2$ added, as found for the modification with Co- and $MnCl_2$. It can therefore be considered that $NiCl_2$ acts as the modifier in the original form and is not reduced to the metal on the catalyst surface.

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

[7] M. Delepine and A. Horeau, *C. R. Acad. Sci. Paris*, **201**, 1301 (1935), *ibid.*, **202**, 995 (1936).

[8] B. V. Aller, *J. Appl. Chem.*, **8**, 492 (1958).