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HYDROGENATION OF CARBON MONOXIDE TO OLEFINS CATALYZED BY BIS(2,4-PENTADIONATE)COBALT-LITHIUM ALUMINUM HYDRIDE SYSTEM IN LIQUID PHASE

Take-aki MITSUDO,* Yukiatsu KOMIYA, and Yoshihisa WATANABE
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku Kyoto 606

Bis(2,4-pentadionate)cobalt-lithium aluminum hydride system in tetrahydrofuran-tetralin is active for a catalytic hydrogenation of carbon monoxide to lower linear hydrocarbons, the distribution of which has a maximum at less than C_6 with 85% of selectivity for olefins.

Much attention has been focused on finding novel catalytic systems for the selective reduction of carbon monoxide and several attempts have been reported to control the selectivity by the particle size of the catalyst.$^{1)}$ On the other hand, it is well known that a black 'solution' obtained by the treatment of MX_n [where M = Co, Fe, Ni, etc., X = halogens and 2,4-pentadionate (AA)] in ethers with complex hydrides such as $LiAlH_4$ is very active for catalytic hydrogenation of unsaturated compounds such as olefins and aldehydes.$^{2)}$ Although the character of this black 'solution' is not yet clear, a very small particle of cobalt or cobalt-aluminum species would be highly dispersed in it. We now report that $Co(AA)_2$-$LiAlH_4$-tetrahydrofuran (THF)-tetralin system is active for hydrogenation of carbon monoxide giving lower hydrocarbons, especially olefins whose selectivity is 85%.

Catalysts were prepared by the following two ways: i) Into a mixture of $Co(AA)_2$ (0.77 g, 3 mmol) and $LiAlH_4$ (0.24 g, 6 mmol) in tetralin (20 ml) was added 0.2 ml of THF under an argon atmosphere and the solution was stirred for 2 h at room temperature. The formed black 'solution' was submitted to the reaction (catalyst I). ii) Into a THF solution of $Co(AA)_2$ (3 mmol), a THF solution of $LiAlH_4$ (6 mmol) was added. To the formed black 'solution', silica gel (3.6 g, 300m^2/g) was added and the solvent was distilled off in vacuo at room temperature and then the catalyst was suspended in *o*-terphenyl (16.2 g) (catalyst II).

Typical reaction procedures are as follows. Into a 100 ml stainless autoclave the prepared catalyst (I or II) was placed and synthesis gas (CO/H_2 = 1) was introduced to 14 kg/cm^2 at room temperature and then the autoclave was heated at 260 °C for 30 min (method A). In other method, the pressure was kept constant by supplying the synthesis gas and the reaction was continued till the uptake of the syn gas was not observed (method B).

Typical results are shown in Table. In the reaction by the 'method A' with the catalyst I at an initial pressure 14 kg/cm^2 (CO/H_2 = 1), a rapid uptake of the syn gas occurred at 260 °C. After 30 min, 97 % of the charged carbon monoxide was consumed affording linear hydrocarbons$^{4)}$ (51 %) and carbon dioxide (19 %) (Run 1). The distri-

Table Hydrogenation of Carbon Monoxide Catalyzed by $Co(AA)_2$-$LiAlH_4$ System[a]

Run	P kg/cm^2	CO/H_2	Method	Time min	Temp °C	CO conv.[d] %	Product[b]											
							CO_2	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}^+	total
1	14	1	A	30	260	97 (22.7)[e]	4.42	2.80	1.38 (0)	2.26 (9)	0.941 (10)	0.782 (14)	0.633 (14)	0.526 (14)	0.425 (16)	0.343 (12)	1.11	15.9
2	40	1	A	30	260	59 (38.6)	15.3	5.80	1.44 (16)	1.67 (59)	0.525 (49)	2.63 (66)	2.04 (66)	1.47 (66)	1.24 (68)	0.954 (69)	3.94	37.0
3	21	2	A	30	260	32 (14.3)	7.24	1.15	0.509 (46)	0.556 (75)	0.159 (70)	0.878 (70)	0.566 (86)	0.483 (83)	0.341 (85)	0.239 (87)	0.943	13.4
4	14	1	A	30	230	3 (0.7)	0	trace	0	0	0	0	0	0	0	0	0	-
5	14	1	B	60	260	93 (39.3)	18.7	5.74	2.45 (1)	3.15 (7)	1.01 (11)	1.88 (34)	1.20 (37)	1.03 (39)	0.794 (38)	0.680 (36)	3.61	40.2
6	40	1	B	90	260	95 (137)	47.6	16.8	5.78 (1)	6.53 (13)	3.30 (14)	5.58 (27)	3.92 (30)	3.01 (29)	2.43 (32)	2.05 (33)	8.53	136
7	7[c]	-	-	30	260	-	0	8.60	0.500	2.85	0.240	8.50	0	0	0	0	0	20.2

a) Catalyst I. b) Amounts of C_1 unit (mmol) introduced into the product. Mol % of olefins are given in the parentheses. c) Blank experiment with H_2. d) $\frac{\text{consumed CO}}{\text{charged CO}} \times 100$. e) Amounts of consumed CO (mmol) are given in the parentheses.

bution of the hydrocarbons produced is shown in Figure 1. The hydrocarbon consists of 86 % of paraffins and 14 % of internal olefins.

In a blank experiment with H_2 (Run 7), hydrogenolysis and hydrogenation of THF, 2,4-pentadionate and tetralin gave C_1-C_5, acetone and decalin but none of C_6^+ was detected. This fact shows that C_1-C_5 in Fig. 1 consist of the products derived by the hydrogenolysis of THF and 2,4-pentadionate and the hydrogenation of carbon monoxide. Taking into account the results of the following reaction and the reaction by catalyst II (see below), it would reasonably be concluded that C_6^+ is derived from syn gas.[5] Although the amounts of C_1-C_5 derived by the hydrogenolysis could not be estimated, the distribution of the products derived from syn gas has the maximum at less than C_6.[6]

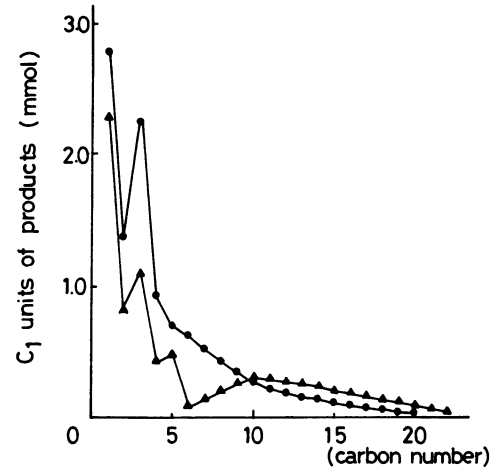

Fig.1 Distribution of products

method A, 260 °C, 30 min, CO/H_2=1, P=14 kg/cm^2. ●; catalyst I, ▲; catalyst I. (5% Co)

In the reaction solution, only a small amount of black precipitate was formed. When syn gas was introduced and the reaction was performed again, the products were almost the same as those in Run 1 and the reaction was repeated six times with a slight deactivation of the catalysis.

In the reaction by 'method B' with catalyst I, the amounts of C_1 units introduced from syn gas into C_6^+ was

7.3 and 19.9 mmol in Runs 5 and 6, respectively, showing that the present system is obviously effective for the catalytic hydropolymerization of carbon monoxide.

The relationship between the selectivity of olefins7) and the P_{CO} (P_{H_2} = 7 kg/cm^2) (method A, catalyst I) is given in Fig. 2. When P_{CO} is 14 kg/cm^2 (CO/H_2 = 2), the selectivity for olefins is 85 % and the olefins contained 76 % of terminal olefins.

Although it is well known that a binary transition metal catalyst of Co-Mn shows high selectivity for olefin,8) there has been no report that a catalyst of cobalt alone induces the high selectivity.

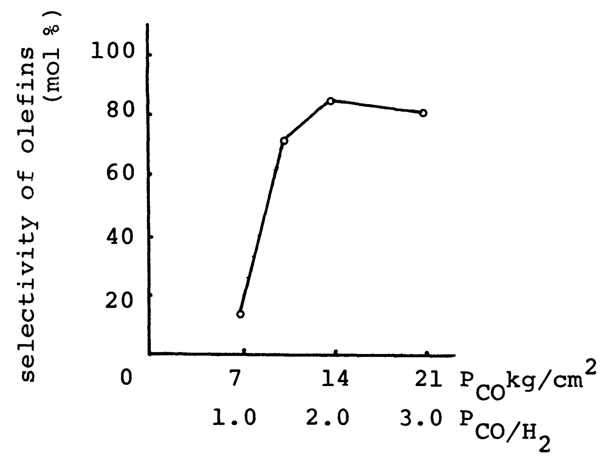

Fig. 2 Effect of P_{CO} on the selectivity of olefins
(P_{H_2} = 7 kg/cm^2, method A, catalyst I)

When this catalyst is supported on silica gel (catalyst II) and the reaction is carried out under the same conditions as Run 1, the reaction rate was slightly slower than that in Run 1, and the reaction products had the conventional distribution with the maximum at C_{10} (Fig. 1). This result shows that the character of the catalyst I dispersed in the liquid phase is changed by the supporting procedure.

To our knowledge this is the first example of the transition metal complex-complex hydride system9) in organic liquid phase which is effective for catalytic reduction of carbon monoxide.

An advantage of this catalyst system would be the facility of its preparation; it takes only 2 h to prepare the catalyst and the activation of the catalyst with H_2 is not required.

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Referrences

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2) For example, Y. Takegami and T. Fujimaki, Kogyo Kagaku Zasshi, 64, 287(1961); Y. Takegami, T. Ueno and T. Fujii, Bull. Chem. Soc. Jpn., 38, 1279(1965); T. Ueno and H. Miya, Chem. Lett., 1973, 39; E. C. Ashby and J. J. Lin, J. Org. Chem., 43, 2567(1978).

3) At 230 °C the reaction hardly occurred. Even at 260 °C hydropolymerization mainly occurred in the present system, while the conventional cobalt catalysts give more than 65 % of methane at 240 °C as the main product; P. Villeger,

J. Barrault, J. Barbier, G. Leclercq and R. Maurel, Bull. Soc. Chim. Fr., 1979, 413.

4) The products were analyzed by GC, GC-MS, ^{1}H and ^{13}C NMR. Analysis of the gaseous products was based on gas chromatography using active carbon (3 mm$^\phi$ x 2.5 m, 50 °C) and Porapak Q (3 mm$^\phi$ x 2.0 m, 80-200 °C). C_5^+ hydrocarbons were analyzed by gas chromatography using OV-101 (0.25 mm$^\phi$ x 45 m, 40-200 °C).

5) The possibility that C_6^+ was derived by the propagation of the products of the hydrogenolysis would be ruled out because the addition of 1-hexene to the reaction system did not cause the change in the distribution of C_7^+.

6) Although all the THF was decomposed in Run 7, more than 90 % of THF used was recovered in Run 3, suggesting that the hydrogenolysis is inhibited by CO pressure. The result of Run 7 shows that the peaks at C_3 and C_5 in Fig. 1 would be due to the hydrogenolysis of THF and 2,4-pentadionate.

7) As the products from carbon monoxide could not be estimated in C_1-C_5, selectivity of olefins is represented as follows;

$$\text{selectivity of olefins (\%)} = \frac{\sum_{i=6}^{9} C_i^{=}}{\sum_{i=6}^{9} C_i} \times 100, \qquad C_i^{=}\text{; olefin}$$

8) J. Barrault, J. C. Menezo and R. Maurel, Bull. Soc. Chim. Fr., 1980, 281; D. Vanhove and M. Blanchard, Nouveau J. Chim., 5, 205(1980).

9) Recently it has been claimed that Co(AA)$_2$-AlEt$_3$ system is effective for catalytic hydrogenation of carbon monoxide affording olefins, however, it appears that the amount of the products reported would not exceed the amount of the catalyst even in 7 h ; M. Blanchard, D. Vanhove, F. Petit and A. Mortreux, J. Chem. Soc., Chem. Commun., 1980, 908.

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