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# Synthetic Studies of Cobalt Carbonyl by Noble Metal Catalysts. I.*[1]
## The Effects of the Form of Cobalt Feed and Noble Metal Catalysts

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A novel method of synthesizing cobalt carbonyl was investigated by using noble metal catalysts. It has been observed that the materials containing palladium, *i. e.*, palladium black, palladium chloride, palladium acetylacetonate, bistriphenylphosphine dichloropalladium, and palladium-on-carriers, have a catalytic effect on the cobalt carbonylation reaction, and that palladium-on-carbon (Pd-C) is the most active catalyst. The reactivity of cobalt compounds in the cobalt carbonylation reaction catalyzed by noble metals increases in this order: $CoSO_4 \ll CoO \lesssim Co(OAc)_2 \lesssim \text{Co-oleate} < Co(OH)_2$. When the Pd-C catalyst is used, cobalt hydroxide reacts with synthesis gas of 150 kg/cm$^2$ to give cobalt carbonyl almost quantitatively, even at from 50 to 55°C. The catalytic activities of noble metals were shown to be, in the order of decreasing activity: Pd > Au > Pt ≫ Ag. The effect of the catalyst concentration and the activity of noble-metal catalysts were also compared with those in the case of dicobalt octacarbonyl, as an autocatalyst.

Cobalt carbonyl has been used in various organic synthetic reactions, *e. g.*, in hydroformylation, oligomerization, and the synthesis of acetic acid from methanol, and as a metal source for the synthesis of many organo-metal complexes. Many methods of synthesizing cobalt carbonyl have been proposed.

Making a general classification, the methods of synthesizing cobalt carbonyl may be divided into

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main methods, *i. e.*, with or without an autocatalyst. In the method without an autocatalyst, the cobalt carbonyl is prepared from inorganic cobalt salt and carbon monoxide in the presence of an alkaline substance,[1] or from cobaltous salts of weak acids under a high pressure of carbon monoxide[2] or synthesis gas.[3] On the other hand, the cobalt carbonyl is also prepared by using dicobalt octacarbonyl as an autocatalyst.[4] However, no synthetic method using any catalyst other than the autocatalyst has ever been reported.

In the present investigation, the promoting ability of several noble metals, *i. e.*, palladium, platinum, gold, and silver, which have been known to form the corresponding simple metal carbonyls only with difficulty, has been studied in connection with the cobalt carbonylation reaction.

## Experimental

**Reaction Procedures.** The experimental method will be explained in terms of a typical run. An autoclave (500 m*l*), made of stainless steel and equipped with a magnetic stirrer, was used. *n*-Butyl alcohol (190 m*l*), 0.241 mol of a cobaltous compound, and 2.36 atom% of palladium-on-cobalt were placed in the autoclave. After the air in the autoclave had been replaced with synthesis gas ($H_2/CO=1.2$), the synthesis gas was introduced up to 150 kg/cm$^2$.

The autoclave was heated rapidly until 40°C and then at a rate of 0.6°C per minute until the gauge pressure began to decline. The temperature when the pressure began to drop was defined as the initiation temperature of the reaction, as is illustrated in Fig. 1, and the initiation temperature was used as one of the scales for measuring the reaction activity of cobalt salts and the promoting ability of the materials added. The autoclave was then kept at the initiation temperature for 60 min. Thereafter, the autoclave was rapidly cooled and depressured, and the cobalt carbonyl produced was taken out and analyzed.

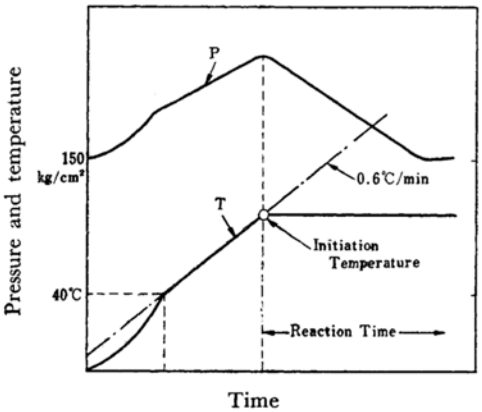

Fig. 1. Definition of the initiation temperature of reaction.

**Analytical Procedures.** The gasometric method reported by Wender *et al.*[5] was employed to determine the content of cobalt carbonyl in the carbonylation products. The crystals obtained from the products were identified as dicobalt octacarbonyl by the gasometric method, by infrared spectrometry, and by cobalt-metal analysis.

The cobalt and palladium were analyzed by the flame-photometric method.

**Materials.** The cobalt compounds and solvents were commercially available and were proved to be sufficiently pure. Materials containing palladium, *e. g.*, palladium chloride, palladium acetylacetonate, and palladium black, were purchased, but bis-triphenylphosphine dichloropalladium was prepared according to the method of Chatt.[6] The palladium-, platinum-, gold-, silver-, and copper-on-carbon (300 mesh up) containing 5 wt% metal were also commercially-available materials.

## Results and Discussion

**The Promoting Abilities of Materials Containing Palladium.** The promoting abilities of various materials containing palladium were investigated in connection with the cobalt-carbonylation reaction. The results are summarized in Table 1. As Table 1 shows, in the absence of palladium, there was an induction period of about 10 min before the initiation of the cobalt carbonylation reaction even at high temperatures, from 213 to 220°C. However, the reaction occurred without any induction period even at extremely low temperatures when a catalytic amount of palladium was present. When the amount of palladium added was fixed at 2 atom%, the initiation temperatures were 155, 103, and 50—55°C for palladium black, palladium chloride, and palladium-on-carbon respectively.

The palladium complexes containing organic ligands, *i. e.*, palladium acetylacetonate and bis-triphenylphosphine dichloropalladium, were less active than the above palladium compounds. These findings seem to indicate that the most efficient form of materials containing palladium is the metal supported on a carrier.

When we compare the activity of dicobalt octacarbonyl as an autocatalyst with the materials containing palladium, we find that the autocatalyst is remarkably inferior to palladium-on-carbon.

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[1] P. Gilmont and A. A. Blanchard, "Inorganic Syntheses," Vol. II, ed. by W. C. Fernelius (Editor-in-Chief), McGraw-Hill Book Company, New York (1946), p. 238.

[2] R. H. Hasek, U. S. Pat. 2865716 (1958).

[3] I. Wender, H. W. Sternberg, S. Meltin and M. Orchin, "Inorganic Syntheses," Vol. V, ed. by T. Moeller (Editor-in-Chief), McGraw-Hill Book Co., New York (1957), p. 190.

[4] J. Kato, H. Wakamatsu and H. Iwanara, Japanese Pat. 265091 (1960).

[5] H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**(1), 174 (1952).

[6] J. Chatt, *J. Chem. Soc.*, **1939**, 1631.

Table 1. The activities of various palladium promoters[*1]

| Catalyst | None | Pd black | Pd-C[*3] | $PdCl_2 \cdot 2H_2O$ | Pd $(acac)_2$ | $PdCl_2$ $(ph_3P)_2$ | $Co_2(CO)_8$[*4] |
|---|---|---|---|---|---|---|---|
| Initiation temp. °C | 213—220[*2] | 155 | 50—55 | 103 | 159 | 189 | 83 |

[*1] Reaction conditions: cobalt hydroxide, 0.241 mol; materials containing palladium (2.36 atom%) on cobalt and *n*-butyl alcohol (190 m*l*); initial pressure 150 atm; $H_2/CO$ ratio of synthesis gas, 1:2.

[*2] An induction period of 9 min was observed.

[*3] Palladium on carbon; 300 mesh up; Pd contents 5%.

[*4] 2.36 atom% on cobalt hydroxide feed was added.

Table 2. The effects of the carriers[*1]

| Carrier | Carbon | Zeolite | $\gamma$-Alumina | Titania | Black[*3] |
|---|---|---|---|---|---|
| SA,[*2] $m^2/g$ | 1200 | 69 | 170 | 10 | 89 |
| Particle size, mesh | 300 | 100 | 300 | 200—300 | — |
| Pd contents,[*4] % | 5 | 7.5 | 3 | 3 | 99.9 |
| Initiation temp. °C | 50—55 | 67 | 124 | 138 | 155 |

[*1] The reactions were carried out under the same conditions as are presented in Table 1.

[*2] The specific surface area of Pd on a carrier catalyst measured by the BET method using nitrogen.

[*3] Palladium black, referential data.

[*4] Pd concentration is fixed at 2.36 mol% on cobalt in each case.

Table 3. The reactivities of various cobalt compounds[*1]

| No. | Cobalt compound | Solvent | Initiation temp. °C | Yield of cobalt carbonyl (mol%) |
|---|---|---|---|---|
| 1 | Cobalt metal powder[*2] | *n*-butyl alcohol | 78 | 18.2 |
| 2 | Cobalt oleate | *n*-butyl alcohol | 76 | 73.9 |
| 3 | $Co(CH_3COO)_2 \cdot 4H_2O$ | *n*-butyl alcohol | 75 | 72.8 |
| 4 | $CoSO_4 \cdot 7H_2O$ | *n*-butyl alcohol | 220 | no reaction |
| 5 | $Co(OH)_2$ | *n*-butyl alcohol | 50—55 | 62.2 |
| 6 | $Co(OH)_2$ | mixed solvent[*3] | 60 | 97.0 |

[*1] Reaction conditions: Feed, 0.241 mol (No. 1 to 5), 0.059 mol (No. 6); Pd on carbon (Pd content 5 wt%), 2.36 atom% on feed (No. 1 to 5), 2.41 atom% (No. 6); Solvent, 190 m*l*. Synthesis gas ($H_2/CO$ 1.2) 150 $kg/cm^2$; Reaction time, 60 min. No carbon monoxide was supplied after the initiation of the reactions in the runs No. 1 to No. 5 but the reaction in No. 6 was carried out under a constant pressure by supplying carbon monoxide.

[*2] Commercially-available material: cobalt content 96.5 wt%, CoO 15.86%.

[3*] 100 m*l* of *n*-butyl alcohol and 90 m*l* of toluene.

This fact is important in considering the reaction mechanism of cobalt carbonylation in the presence of palladium.

**The Effect of the Carrier.** The effect of the carrier of the materials containing palladium on the initiation temperature was also examined.

As Table 2 shows, the carrier remarkably affects the activity of the materials containing palladium. The palladium supported on a carrier is relatively more active than palladium black, which includes no carrier, palladium-on-carbon is the most active material among the palladiums supported on carriers. These results indicate the specific incorporation of palladium and carrier. The relation between the activity of the palladium-on-carrier and the physical properties, *i. e.*, the surface area and the particle size, was also investigated. However, the reactivity seems to be due to key factors other than those properties.

**The Reactivities of Various Cobalt Compounds.** The reactivities of various cobalt compounds in the cobalt-carbonylation reaction were examined in the presence of palladium-on-carbon; the results are shown in Table 3.

When commercially-available cobalt metal powder (300 mesh up) containing 96.5 per cent of cobalt was used, the carbonylation reaction was initiated at 78°C. Afterwards, it was revealed by X-ray analysis that the remarkable activity of cobalt metal powder was due to the cobalt monoxide which was formed on the surface of the cobalt metal powder rather than to the cobalt metal itself. Cobalt acetate and oleate showed similar initiation temperatures of from 75 to 76°C, while cobalt hydroxide showed much lower initiation temperatures between 50 and 55°C. The reactions of those cobalt compounds were carried out at each initiation temperature for 60 min, the yields of cobalt carbonyl were about 60 to 70 mole per cent in each case.

These reaction conditions were unfit for determining the yield at complete conversion because of the following reasons. First, no excess of carbon monoxide was supplied. Second, the accurate analysis of the product was difficult, because large amounts of crystalline dicobalt octacarbonyl were precipitated from the reaction mixture and mingled with the powdery palladium-on-carbon. To determine accurately the yield at complete conversion for the reaction system using cobalt hydroxide, palladium-on-carbon, and butyl alcohol as solvents, the reaction with a lower concentration in cobalt hydroxide by supplying carbon monoxide was carried out in a solvent mixture of butyl alcohol and toluene, which is a good solvent system for the dicobalt octacarbonyl. Cobalt carbonyl was thus obtained in a 97% yield when these was a reaction at 60°C for 60 min, as is shown in Table 3. Moreover, no crystalline cobalt carbonyl was found in the reaction product. In the case of using cobalt sulfate, no reaction occurred until 220°C. These results may be understood easily by considering that the following equilibrium between the formation and the decomposition of cobalt carbonyl is partial to the left side:

$$2CoSO_4 + 8CO + 2H_2 \rightleftharpoons Co_2(CO)_8 + 2H_2SO_4$$

**The Effect of the Palladium Concentration.** The effect of the palladium concentration in the reaction zone on the initiation temperature was investigated by using *n*-butyl alcohol as the solvent. The results are shown in Fig. 2.

The plot of the initiation temperature against the ratio of the promoter metal to the cobalt concentration indicates that the initiation temperature significantly decreases, with only a small increase (less than 1 atom percent on cobalt) in the concentration of palladium, and that less than 5 per cent of the palladium concentration gives rise to an adequate efficiency.

By comparing the effect of the palladium concentration on the initiation temperature with that of dicobalt octacarbonyl as an autocatalyst, as is shown in Fig. 2, the strong promoting activity of palladium-on-carbon is easily evaluated. In addition, no dissolved palladium was detected in the solution of the reaction product by careful analysis using a "Plane Grating Spectrograph Model GE 340." The behavior of palladium in the reaction mentioned above may be considered to suggest that palladium operates catalytically in the cobalt carbonylation reaction.

**Catalytic Activity of Other Noble Metals.** The other metals which are found in the neighborhood of palladium in the periodic table and which are generally considered to form simple metal carbonyls by themselves only with difficulty have also been investigated to see if they promote the cobalt carbonylation reaction.

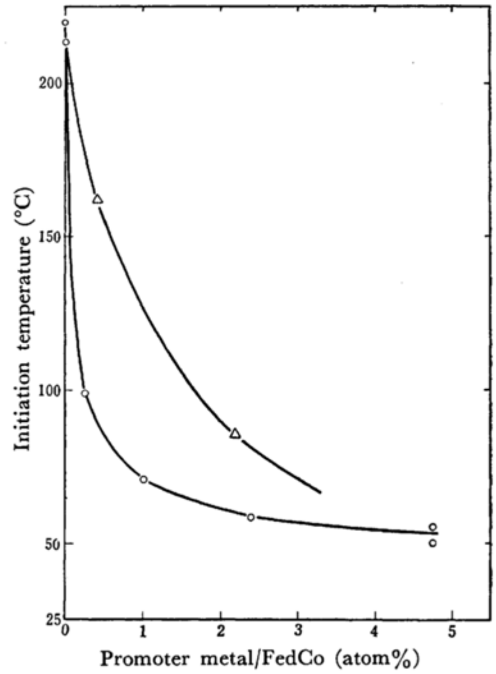

Fig. 2. Effects of the concentrations of promoters on the initiation temperature.
$Co(OH)_2$ 0.241 mol, Synthesis gas ($H_2 : CO = 1.2 : 1$) 150 kg/cm², *n*-BuOH 190 m*l*
⊙ Pd-C ($H_2O$ (7.9 volume% on *n*-BuOH) was added in this series.)
△ $Co_2(CO)_8$

The experiments with the palladium catalyst showed that metal-on-carbon was the most active form. Platinum, gold, silver, and copper were tested as the metal-on-carbon for each metal. The results are shown in Fig. 3.

The initiation temperature in the reaction using the platinum-on-carbon catalyst fell sharply to 100°C when the concentration of platinum was increased to 0.723 atom%. However, little additional effect occurred over 1 atom%.

On the other hand, with gold-on-carbon, the initiation temperature fell gradually along the curve with the platinum catalyst in the low-concentration region, but over 1 atom% it fell dramatically, as was the case with palladium. At the Au/Co ratio of 4.5 atom%, gold-on-carbon can initiate the reaction at temperatures as low as 55°C. Silver-on-carbon showed only a poor activity, and copper-on-carbon had practically no effect on the cobalt-carbonylation reaction.

Thus, the relative activities of carbon-supported metals in the cobalt carbonylation are as follows: $Pd > Au > Pt \gg Ag \gg Cu$.

It is clear from the available data that platinum- and gold-on-carbon are excellent alternative cata-

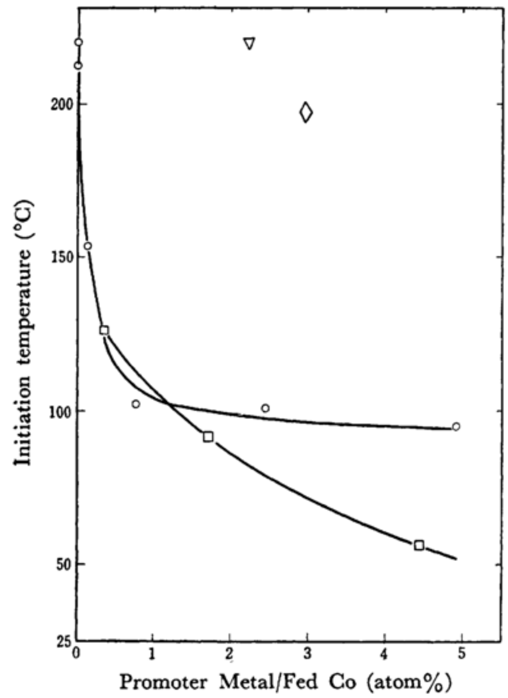

Fig. 3. Promoting activities of various metals in the cobalt carbonylation reaction.
$Co(OH)_2$ 0.241 mol, Synthesis Gas $H_2 : CO = 1.2 : 1$, 150 kg/cm$^2$, *n*-BuOH 190 m*l*
○ Pt-C (5%Pt), □ Au-C (5%Au), ◇ Ag-C (5%Ag), ▽ Cu—C (5%Cu)

lysts, and that palladium-on-carbon is still the best among the five materials examined here.

## Summary

Cobalt carbonyl synthesis with noble metals as promoters has been investigated by using the initiation temperature of the reaction as a measure. The results of this study are as follows.

(1) It has been observed that materials containing palladium, platinum, gold, and silver have promoting effects on the cobalt-carbonylation reaction. The form of the materials containing metal significantly affects the promoting activity. Metal supported on active carbon exhibits an activity superior to that of the corresponding salts or complexes. The promoting activities of the noble metals supported on carbon examined here are in the order of: Pd> Au> Pt≫Ag.

(2) From the plots of the promoter concentration against the initiation temperature, it has been revealed that by adding a small amount of noble metal promoters the initiation temperature of the reaction is markedly lowered; with an increase in the concentration, Pd and Au serve to lower the initiation temperature whereas Pt gives a constant initiation temperature above a certain concentration. Dicobalt octacarbonyl as an autocatalyst shows a concentration effect similar to those of Pd and Au, but the activity is much inferior to theirs.

(3) A cobalt-carbonylation reaction with a Pd-C promoter is also affected by the kind of cobalt compound as in the conventional case. The reactivities are in the order: $Co(OH)_2 >$ Co oleate $\simeq Co(oAc)_2 \simeq CoO \gg CoSO_4$.

Cobalt hydroxide, then, reacts at temperatures as low as from 50 to 55°C.

(4) It has been shown by a careful analysis that no dissolved palladium is present in the product solution. This and other data suggest that noble-metal promoters operate catalytically in the cobalt-carbonylation reaction.