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VAPOR PHASE HYDROCARBONYLATION OF METHANOL WITH COBALT-PALLADIUM ON ACTIVE CARBON CATALYSTS

Kaoru FUJIMOTC,* To-oru SETOYAMA, and Hiro-o TOMINAGA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Acetaldehyde was formed from methanol by vapor phase reaction with synthesis gas over supported cobalt-palladium catalysts in the presence of methyl iodide, at temperatures between 180 and 240°C and at pressures between 10 and 65 atm. Active carbon carrier was found essential for bringing about the catalytic activity of cobalt. Addition of soft alkali metal salts and palladium accelerated the rate of acetaldehyde formation.

Since 1951, 1) extensive study has been done on the hydrocarbonylation of methanol with homogenous catalytic system utilizing solubilized cobalt complexes 2) or cobalt-ruthenium bimetallic complexes. 3) Authors have found that nickel on active carbon is an excellent catalyst for the vapor phase carbonylation of methanol to give methyl acetate and acetic acid 4) or of methyl acetate to give acetic anhydride 5) under mild conditions. In the heterogeneous catalytic systems mentioned above active carbon carrier is essential for exhibition of the carbonylation activity of nickel 4) or rhodium. 6) In the present work we tried to explore a new solid catalyst for vapor phase hydrocarbonylation of methanol.

Catalysts were prepared by an impregnation method from aqueous solutions of chlorides of the active components and were activated by reduction in hydrogen at 450°C for 3 h before reaction. Reaction tests were conducted by using a pressurized flow type reactor (with inner diameter of 14 mm, and length of 400 mm) which contained granular catalysts. The products were analyzed by a gas chromatograph.

Table 1 shows the activities for methanol hydrocarbonylation of the several catalysts in the presence of methyl iodide. The major products are acetaldehyde, methane, dimethyl ether and methyl acetate, but little ethanol was obtained in contrast with the case of liquid phase hydrocarbonylation utilizing the cobalt complex catalysts.[1,7,8] It should be noted that cobalt is active to some extent and that its activity is promoted by adding palladium, although palladium itself is essentially inactive. Another point to be noted in Table 1 is that activated carbon (A.C.) is most superior while silica and almina are less effective as the carrier of the Co-Pd hydrocarbonylation catalyst. Supposedly this results from the character of activated carbon as an electron donor-acceptor as we have pointed out for the carbonylation of methanol.[4]

Table 1. Catalytic Activities of Methanol Hydrocarbonylation

Pressure, 41 kg/cm^2; Temperature, 210°C; W/F, 4.0 g-h/mol
CO/H_2, 1/1; P_{CH_3OH}, 4 kg/cm^2; CH_3I/CH_3OH, 1/200 mole ratio

Catalyst	Yield of product (%, methanol base)			
	CH_3CHO	CH_4	CH_3OCH_3	CH_3COOCH_3
Co(4.0^a) on A.C.	1.9	1.6	1.3	0.6
Pd(4.0^a) on A.C.	0.3	4.9	2.0	1.2
Co(2.0^a) + Pd(2.0^a) on A.C.	2.9	2.1	0.6	0.9
Co(2.0^a) + Pd(2.0^a) on SiO_2	0.1	0.2	0.2	0.3
Co(2.0^a) + Pd(2.0^a) on Al_2O_3	0.6	2.8	10.8	1.3

a) Metal loading in wt%.

Added alkali metal salts affect the activity of the Co-Pd/A.C. catalyst as illustrated in Table 2. The order of the promotional effect per mole of alkali metal added is in the following order:

$$Rb > Cs > K > \text{none} > Na > Li$$

This order is precisely the reverse of that of electronegativity of the alkali metals. It indicates that the cobalt rich in electron favores the hydrocarbonylation, which coincides with the reported ligand effect on the homogeneous metal complexes.[9] Under the present reaction condition, palladium seemingly activates the molecular hydrogen as palladium-hydride which might participate in one of the elementary steps which determine the reaction rate. Thus, it is supposed that hydridic character of hydrogen atom on the catalyst is promoted by the added palladium or alkali metal salts resulting in the acceleration of the reaction rate.

Table 2. Effects of Added Alkali Carbonate on the Catalytic Activity

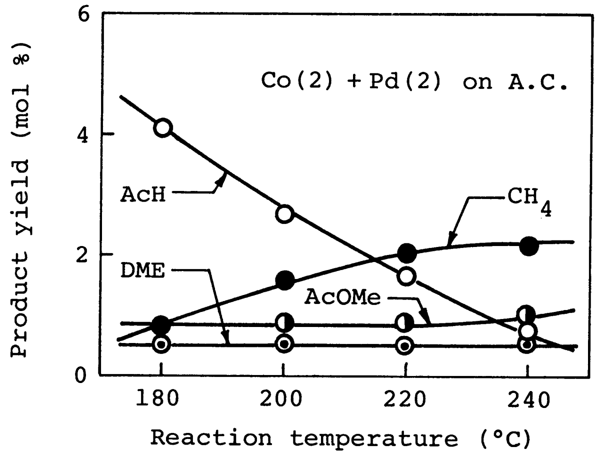
Catalyst, Co 2 wt%-Pd 2 wt%-alkali metal 1 wt% on A.C.; Pressure, 41 kg/cm^2; P_{CH3OH}, 4 kg/cm^2; CO/H_2, 2/1; Temperature, 210°C; CH_3I/CH_3OH, 1/200 mole ratio

Additive	Yield of product (%, methanol base)			
	CH_3CHO	CH_4	CH_3OCH_3	CH_3COOCH_3
None	2.9	2.1	0.6	0.9
Li	1.9	4.9	1.4	1.9
Na	2.3	2.0	0.9	1.3
K	3.5	2.5	0.8	1.4
Rb	6.4	5.2	1.8	2.6
Cs	4.9	3.1	0.7	1.6

In the range from 180 to 240°C, the formation of acetaldehyde decreases with the increase in the reaction temperature (Fig.1) as against the case of liquid phase reaction.$^{2)}$ Hydrocarbonylation of methanol with synthesis gas is substantially free from the thermodynamic limit of conversion, for example, the equilibrium constants are 9.2×10^4 at 180°C and 1.9×10^3 at 240°C.$^{2)}$ Accordingly, the adsorbed amount of some reactant such as carbon monoxide is one of the important factors which control the reaction rate.

Contrary to the yield of acetaldehyde, that of methane increases with increasing temperature suggesting that methyl species, which is formed through the addition of methyl iodide to catalyst (reaction (1) in Fig.2), is hydrogenated quickly (reaction (2)) without being carbonylated (reaction (3)) at higher temperature.

It was indicated that about 0.04 atm of methyl iodide is enough to promote the reaction, and it suppresses the rate of acetaldehyde formation at higher partial pressure whereas methyl acetate, another carbonylated product, increases

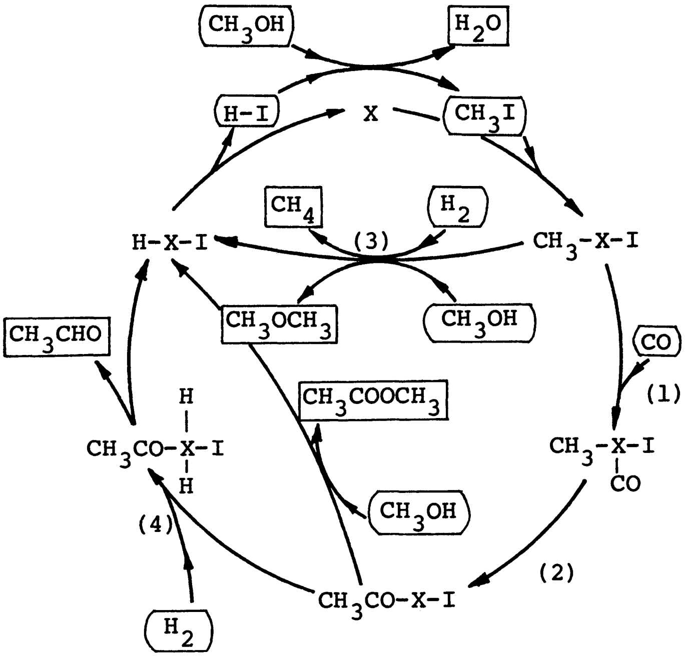


Press., 40 kg/cm^2; Syngas/MeOH, 9.0; P_{CO}/P_{H2}, 2/1; W/F, 4.0 g-h/mol; CH_3I/MeOH, 1/200

Fig. 1. Effect of reaction temperature on hydrocarbonylation of methanol.

almost linearly to the partial pressure of methyl iodide.

It was found that the cobalt-active carbon catalyst which contained palladium and soft alkali metal salts, could be an excellent catalyst for the vapor phase hydrocarbonylation of methanol to acetaldehyde in the presence of methyl iodide promoter. The reaction net work of products formation, which is assumed to be analogus to that catalyzed by cobalt carbonyl complexes, is postulated as illustrated in Fig. 2. In the net work the reaction path which include the formation of acyl complex and the hydrogenolysis of it to acetaldehyde is the main route.



(X : Active site of the catalyst)

Fig. 2. Reaction path of product formation.

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