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# Liquid Phase Carbonylation with Solid Catalyst. Carboxy Methylation of Dihalo Methane with Group VIII Metals Supported on Active Carbon

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It was found that cobalt supported on active carbon showed an excellent catalytic activity for the carbonylation of dibromo methane in the liquid phase. For example, when the reaction was conducted under the conditions of 140 °C, P(CO)=31 atm, the yields of dimethyl malonate and bromomethyl acetate were 34.4% and 22.2%, respectively. Pd and Rh also showed catalytic activities.

The authors have found that group VIII metals such as rhodium, nickel, iridium and palladium exhibit excellent catalytic activities for the vapor phase carbonylation of organic compounds such alcohols,[1)] dimethyl ether,[2)] methyl acetate,[3)] and methyl chloride[4)] when they are supported on active carbon. It has been already reported by other authors that dialkyl malonate can be formed by the carbonylation of alkyl chloroacetate either in the vapor phase or in the liquid phase.[5)] In the present study, the solid-catalyzed liquid phase carbonylation of dibromo methane and dichloro methane were conducted in order to expand the field for the carbon-supported transition metals as the carbonylation catalyst.

Catalysts were prepared by impregnating metal salts (mostly chlorides) with a commercially available active carbon (AC; Takeda Shirasagi, made of wood, specific surface area: 1200 $m^2/g$) from their aqueous solutions, drying in air at 120 °C for 12 h and then reducing in a hydrogen flow at 400 °C for 3 h. Then it was powdered to fine particles (<200 mesh). The metal loading was 1% by weight. Reactions were conducted in a stainless steel autoclave in which the reaction mixture

Table 1. Carbonylation of $CH_2Br_2$

| Catalyst | Co | Pd | Rh | $Co_2(CO)_8$[a] |
|---|---|---|---|---|
| Product | | Yield /% | | |
| $CH_2(COOCH_3)_2$ | 34.4 | 25.3 | 25.4 | 17.6 |
| $BrCH_2COOCH_3$ | 22.2 | 18.4 | 11.9 | 15.8 |
| $CH_3OCH_2COOCH_3$ | 0.8 | 0.5 | 0.9 | 0.1 |
| $CH_3COOCH_3$ | tr. | 0.5 | 1.1 | 2.4 |
| $CH_2(OCH_3)_2$ | 47.6 | 47.8 | 26.3 | 67.5 |
| $CH_4$ | 0.2 | 2.3 | 1.3 | 1.3 |
| $CO_2$ | 1.2 | 1.5 | 4.6 | 1.2 |

Reaction Conditions:140 °C, 31 atm, 1 h,
$CH_2Br_2$:50 mmol, NaOH:100 mmol, Wcat.:1.0 g,
a) $Co_2(CO)_8$:0.0298 g, NaOH:200 mmol.

composed of methanol, dihalo methane, hydrogen halide acceptor, and catalyst was contained and stirred. After the reaction the product mixture was easily separated from the catalyst by filtration and was analyzed by gas chromatographs.

In Table 1 are shown the catalytic activities of Co, Pd and Rh supported on active carbon and $Co_2(CO)_8$. All the metals tested showed catalytic activities for the formation of dimethyl malonate (DMM). Other carbonylated products were bromomethyl acetate (BMA) and a small amount of methoxy methyl acetate (MMA). Thus the carbonylation reaction on these catalysts are described as follows:

$$CH_2Br_2 + 2CO + 2CH_3OH \longrightarrow CH_3OCOCH_2COOCH_3 + 2HBr \quad (1)$$

$$CH_2Br_2 + CO + CH_3OH \longrightarrow BrCH_2COOCH_3 + HBr \quad (2)$$

$$CH_2Br_2 + CO + 2CH_3OH \longrightarrow CH_3OCH_2COOCH_3 + 2HBr \quad (3)$$

Among the catalysts tested, Co/AC showed the highest activity. Although $Co_2(CO)_8$ showed catalytic activity as already pointed out,[7)] its carbonylation activity was about half of the Co/AC catalyst. Another major product was dimethoxy methane. The formation of dimethoxy methane (DMOM) should be attributed to the methanolysis of dibromo methane by the co-catalysis of supported metals and NaOH. This subject will be discussed later.

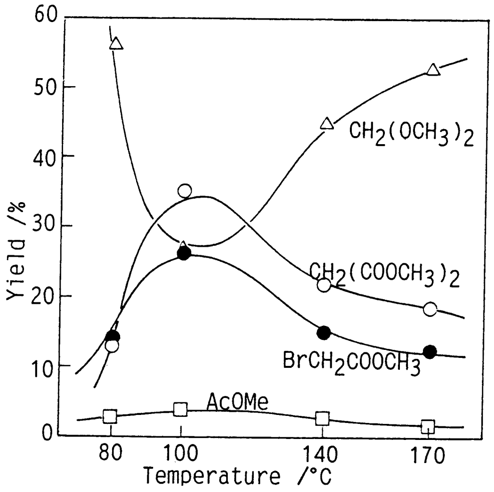

Fig. 1. The effect of reaction temperature, Cat.: Co/AC, 31 atm, 1 h, $W_{cat}$: 1.0 g, $CH_2Br_2$; 50 mmol, NaOH: 200 mmol.

Table 2. Effect of base and reactant on carbonylation of dihalo methane

| Reactant | $CH_2Br_2$ | $CH_2Br_2$ | $CH_2Br_2$ | $CH_2Br_2$ | $CH_2Br_2$ | $CH_2Cl_2$ |
|---|---|---|---|---|---|---|
| HBr acceptor | NaOH | NaOH[a)] | NaOH[b)] | $Na_2CO_3$[c)] | 2,6-Lutidine | NaOH |
| Product | | | Yield /% | | | |
| $CH_2(COOCH_3)_2$ | 13.1 | 35.3 | 20.3 | 16.9 | 23.6 | 28.8 |
| $BrCH_2COOCH_3$ | 14.1 | 26.3 | 34.8 | 27.9 | 35.7 | - |
| $ClCH_2COOCH_3$ | - | - | - | - | - | 0 |
| $CH_3OCH_2COOCH_3$ | 0.3 | 0.3 | 0 | 0.9 | 0.2 | 1.9 |
| $CH_3COOCH_3$ | 0 | 3.9 | 12.4 | 0 | 2.0 | 7.5 |
| $CH_2(OCH_3)_2$ | 56.4 | 27.0 | 0.8 | 0.7 | 0 | 1.2 |
| $CH_4$ | 0 | 0.8 | 0 | 0 | 0.1 | 0 |
| $CO_2$ | 0 | 0.4 | 0.9 | 0.1 | 0.1 | 0 |

Reaction conditions: 80 °C, 31 atm, 1 h, $CH_2Br_2$ or $CH_2Cl_2$:50 mmol, NaOH:100 mmol, Wcat.:1.0 g.
a) 100 °C, 31 atm. b) 100 °C, 16 atm. c) $Na_2CO_3$: 50 mmol.

In Fig.1 are demonstrated the effects of reaction temperature. The formations of DMM and BMA reached maximum, while that of DMOM showed minimum at 100 °C. The reason of this temperature effect is not clear yet.

Table 2 shows some of the factors which control the reaction characters. When NaOH as the hydrogen bromide acceptor was substituted by $Na_2CO_3$ or 2,6-lutidine, the formation of carbonylated products increased (especially in the case of 2,6-lutidine), whereas the formation of DMOM, the methanolysis product, decreased drastically to almost zero. The high selectivity for carbonylated products with 2,6-lutidine has been reported in the case of carbonylation of monosubstituted methyl chlorides with cobalt carbonyl catalyst.5) The high yield of DMOM in the case of the NaOH acceptor, should be attributed to its high basicity which abstract bromide ion from dibromo methane and substitute it with methoxy ion. When the pressure of CO was lowered from 31 atm to 16 atm the yield of DMM decreased and the yield of BMA increased.

The data in Table 2 show that even dichlorometane could be carbonylated on the Co/AC catalyst in methanol to form DMM. The characteristic features of the dichloro methane carbonylation is that the yield of DMM was comparable to dibromo methane, while it gave no chloro methylacetate (mono-carbonylated product) and small amount of dimethoxy methane, regardless of the use of NaOH acceptor. The absence of chloro methylacetate in the product might be attributed to its quick carbonylation to DMM as it has been reported.5)

The carbon-supported cobalt and other group VIII metals could be successfully used for the liquid phase carbonylation of dibromo methane to give dimethyl malonate and bromomethyl acetate. The catalysts were easily separated from the reaction mixture by filtration.

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