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VAPOR PHASE CARBONYLATION OF METHYL ACETATE, METHANOL, AND DIMETHYL ETHER WITH MOLYBDENUM-ACTIVE CARBON CATALYST

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A molybdenum-active carbon catalyst was found to catalyze the vapor phase carbonylation of methyl acetate and related compounds under pressurized conditions in the presence of methyl iodide promoter. Acetic anhydride was formed from methyl acetate with an yield of 15% and a selectivity of 83% at 250 °C and 45 atm. The molybdenum-active carbon catalyst was active also for the carbonylation of methanol and dimethyl ether to form methyl acetate.

Rhodium complexes are known as excellent catalysts for the liquid phase carbonylation of methanol and related compounds.$^{1)}$ Some of them have been employed in commercial process.$^{2,3)}$ However, rhodium is one of the most expensive metals and its proved reserves are quite limited.$^{4)}$ It is highly requested, therefore, to develop a new catalyst as substitute for rhodium.

The authors have already reported that nickel catalysts supported on active carbon exhibit excellent activities for the vapor phase carbonylation of methanol, dimethyl ether, and methyl acetate.$^{5-8)}$ In the present work, it was found that molybdenum had a catalytic acitivity for the vapor phase carbonylation of methyl acetate when it was supported on active carbon.

The catalyst was prepared by impregnating a commercially available active carbon (Takeda Shirasagi C, 20-40 mesh), with ammonium molybdate aqueous solution, followed by drying in an air oven at 120 °C for 12 h. The molybdenum content in the catalyst was 2.5 wt% as metal. The reference catalysts were prepared by the same procedure but using carbon black (Ketzen Black), silica gel (Fuji Davison ID), and alumina (JRC-ALO-3) as the carriers. The catalysts were activated in situ by hydrogen stream at 450 °C for 3 h before reaction. A continuous flow type reaction apparatus with a fixed catalyst bed was employed at pressurized conditions. Methyl acetate dehydrated with Molecular Sieve 5A was mixed with methyl iodide promoter and was introduced into the reactor with a microfeeder. The reaction conditions were as follows: reaction temperature, 250-300 °C; pressure, 8-45 atm; time factor (W/F), 10 g·h/mol; CO/AcOMe/MeI, 100/9/1 molar ratio. Products were analyzed by a gas chromatograph. Product yields were calculated by the following equation:

$$\text{Yield (\%)} = \frac{\text{(product, mol/h) x (no. of methyl groups in a molecule)}}{\text{(methyl acetate fed, mol/h) x 2}} \times 100 \qquad (1)$$

This implies that all methyl groups in the molecules of acetic anhydride, acetic acid, and methane are derived from methyl acetate.

The main products of this reaction were acetic anhydride and acetic acid. Small amounts of methane and carbon dioxide were formed as by-products. The molar ratio of carbon dioxide and methane in the products was not constant. It has not been clear yet whether carbon dioxide is formed from methyl acetate or from carbon monoxide.

Table 1 shows the results of the methyl acetate carbonylation with molybdenum catalysts supported on active carbon, carbon black, silica gel, and alumina. In the case of molybdenum-active carbon catalyst, the yield of acetic anhydride was 4.5% and it was about a half of the activity of nickel-active carbon catalyst which was previously reported by the present authors.[7,8] The yield of acetic acid was 6.6% and those of methane and methanol were low. On the other hand, silica gel- or alumina-supported catalyst exhibited little carbonylation activity and gave a small amount of methane as a product. In the case of carbon black carrier, the yield of acetic anhydride was smaller than that in the case of active carbon carrier, but gave a high selectivity to acetic anhydride. Similar effect of carbon black carrier has been observed in the case of nickel catalyst for the methyl acetate carbonylation. Taking into account of the fact that the carbonylation activity occurs only when a carbonaceous carrier is employed, some common effect might be induced by the carbonaceous carriers.

Table 1. Effect of carrier materials on product yield in carbonylation of methyl acetate[a)]

Catalyst[b)]	Product yield/%					CO_2/CH_4[c)]
	Ac_2O	AcOH	MeOH	DME	CH_4	
Mo/A.C.	4.5	6.6	0.8	0	1.3	0.4
Mo/SiO_2	0	0	0	0	0.1	-
Mo/Al_2O_3	0	0	0	0.8	tr	-
Mo/C.B.	1.6	tr	tr	0	0.2	2.8
Ni/A.C.	10.8	9.9	2.1	0	2.6	0.5
Ni/C.B.	7.2	2.2	tr	0	tr	-

a) Conditions : 250 °C; 15 atm; W/F = 10 g·h/mol; CO/AcOMe/MeI = 100/9/1 (molar ratio). b) Metal loading : 2.5 wt%. c) Molar ratio.

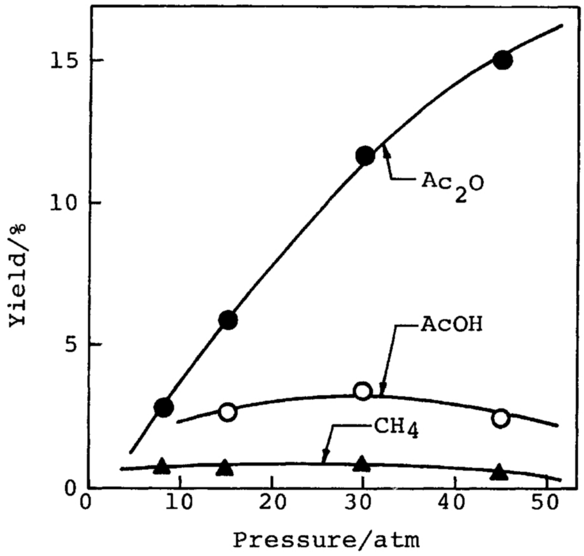

Fig. 1. Effect of pressure on product yield: 2.5 wt% Mo/A.C.; 250 °C; W/F = 10 g·h/mol; CO/AcOMe/MeI = 100/9/1 (molar ratio).

Figure 1 shows the effect of reaction pressure on the carbonylation of methyl acetate with molybdenum-active carbon catalyst. With increasing pressure, the yield of acetic anhydride increased monotonously and that of methane was almost unchanged. The yield of acetic acid increased up to 30 atm and then decreased above the pressure. Acetic anhydride was formed with an yield of 15.1% and a selectivity of 83% at 45 atm, indicating that high pressure was favorable for the selective formation of acetic anhydride on molybdenum-active carbon catalyst.

Table 2 shows the results of the carbonylation of methanol and dimethyl ether with the molybdenum-active carbon catalyst. In the case of methanol carbonylation, the products were methyl acetate and a small amount of methyl formate. Dimethyl ether and methane were also formed. With an increase in the temperature, the yields of methyl acetate, dimethyl ether, and methane increased while the selectivity to methyl acetate decreased. In the case of dimethyl ether carbonylation, the

Table 2. Carbonylation of methanol and dimethyl ether over molybdenum-active carbon catalyst[a)]

Reactant	Temp/°C	Product yield/%				CO_2/CH_4[b)]
		AcOMe	HCOOMe	DME	CH_4	
MeOH[c)]	250	6.0	0.2	29.3	1.6	0.2
MeOH[c)]	275	11.0	0.9	32.0	5.3	0.2
MeOH[c)]	300	17.1	0.5	41.3	15.0	0.3
DME[d)]	250	tr	0	-	0.2	0.3
DME[d)]	275	3.0	0	-	0.6	0.1
DME[d)]	300	5.2	0	-	2.7	0.1

a) Metal loading : 2.5 wt%, Conditions : 11 atm; W/F = 10 g·h/mol. b) Molar ratio. c) CO/MeOH/MeI = 20/9/1 (molar ratio). d) CO/DME/MeI = 240/100/9 (molar ratio).

products were methyl acetate and methane of which yields increased with a rise in the reaction temperature.

In conclusion, molybdenum supported on active carbon was found to be active for the carbonylation of methyl acetate to form acetic anhydride with a high selectivity. Both acetic anhydride yield and selectivity increased with increasing reaction pressure. Molybdenum-active carbon catalyst also exhibited activities for the carbonylations of methanol and dimethyl ether to form methyl acetate as a main product.

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