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VAPOR PHASE CARBONYLATION OF METHYL CHLOROACETATE

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The vapor phase carbonylation of methyl chloroacetate (MCA) with rhodium trichloride supported on active carbon was carried out at 200 - 300 °C. Dimethyl malonate (DMM) was obtained in good yield without any side reactions.

It is well-known that carbonylation of MCA was performed in liquid phase with cobalt carbonyl as a catalyst under pressurized conditions.[1-6] Furthermore, alkaline reagent such as sodium alkoxide was necessary to remove hydrogen chloride from the reaction field in a large quantity in order to promote the carbonylation. At present little is known about vapor phase carbonylation in good yield, since the volatility of metal carbonyl is unavoidable at high temperature.

The present investigation was undertaken to carry out the vapor phase carbonylation of MCA to DMM under atmospheric pressure with rhodium trichloride catalyst supported on active carbon. The solution was prepared by dissolving 1 g of rhodium trichloride trihydrate in 100 ml of methanol. 10 g of active carbon (Kanto Kagaku K. K.) was impregnated with this solution and methanol was evaporated to dryness in the air. The flow type reaction system of a previous work was used.[7] The catalyst was placed in the reactor and was heated in carbon monoxide stream at reaction temperature for 1 h. MCA was mixed with methanol in volume ratio of 1 : 5. A mixture of MCA and methanol was fed into the evaporator with a microfeeder and preheated at 200 °C, the vapor being passed to the reactor. The time factor was kept constant at 290 (g of catalyst/mol of MCA/h), while the reaction temperature was kept constant throughout the experiment. Carbon monoxide gas was fed at the rate of 0.13 mol/h and was mixed with the vapor of MCA and methanol at the evaporator. The analysis of the reaction products was investigated by gas chromatography with several columns, because the formation of methyl methoxyacetate as a by-product was expected. However, methyl methoxyacetate was not detected in the reaction products under present reaction conditions. The quantitative analysis of the reaction products was carried out by gas chromatography (PEG 6000, 130 °C). Chlorine liberated from MCA during carbonylation was recovered as hydrogen chloride. This reaction might proceed by a mechanism different from that reported by earlier investigators.[8-10] DMM was obtained in good yield without any side reactions. The carbonylation of MCA catalyzed by rhodium trichloride supported on active carbon was an extremely high selective reaction. Figure 1 shows the effect of the reaction temperature on the catalytic activity.

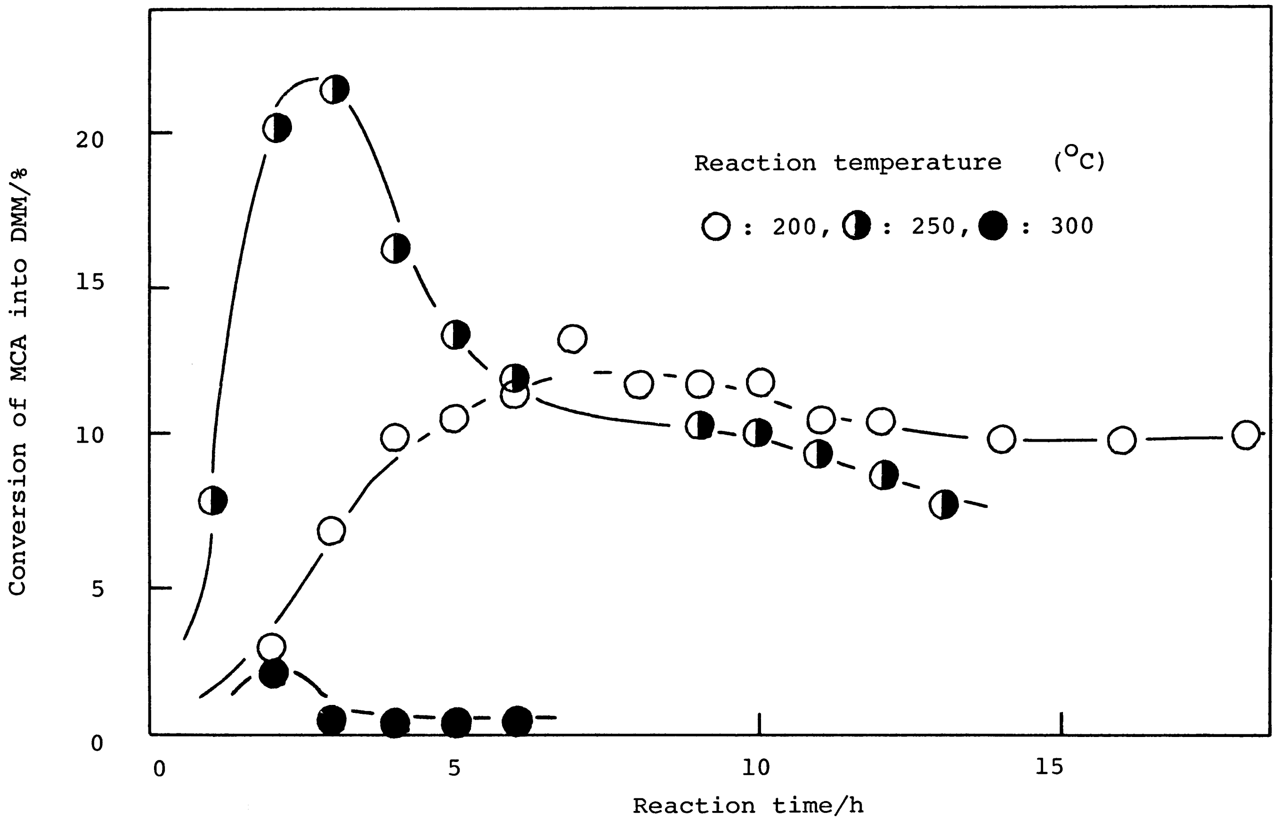

Fig. 1. The effect of the reaction temperature on the conversion of MCA.

All curves have a peak point because of the adsorption of DMM on active carbon. The catalytic activity was decreased with increasing reaction temperature. However, the conversion of MCA into DMM was maintained at approximately constant at 200 °C. That is to say, any indications of the deactivation of the catalyst were not recognized at this temperature. It could be anticipated that the durability of catalytic activity was considerably continued for a long time at the moderate temperature. We would expect this vapor phase carbonylation to be applied to the commercial process.

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