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DISPROPORTIONATION OF PROPYLENE ON A SUPPORTED MOLYBDENA-ALUMINA CATALYST WITH FLOW SYSTEM IN THE LIQUID PHASE

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The disproportionation of propylene with flow system in the gas phase and in the liquid phase has been investigated using a molybdena catalyst supported on alumina. Results show that the catalytic activity decreases rapidly in the gas phase as the reaction proceeds but preserves for longer time in the liquid phase. This should be due to the effect that the heavier materials produced by the side reaction dissolve in the liquefied olefins and are carried away from the catalyst surface.

Research on the catalytic disproportionation of olefins has been reviewed by Bailey$^{1)}$ and Calderon.$^{2)}$ Much of the published work has dealt with heterogeneous$^{3-7)}$ reaction of gaseous olefins and also with homogeneous$^{8-10)}$ reaction in the liquid phase. However, the heterogeneous reaction of liquefied olefins with flow system has not yet been examined in detail. The object of the present work is to compare the durability of catalytic activity by the two methods, in the gas phase and in the liquid phase reactions.

Catalyst was prepared by impregnating γ-alumina (Neobead MS·C, kindly supplied by Mizusawa Industrial Chemicals Ltd.) with water solution of ammonium molybdate at 1/25 atomic ratio of Mo/Al, followed by drying on a water bath. The resulting solid material was calcined in air stream at 550°C for 10 hr, and the catalyst was activated by pretreating in dry nitrogen stream at 600°C for 3 hr just before use. The reaction products were analyzed by gas chromatography.

Most of the published work on the disproportionation of propylene on a supported molybdena-alumina catalysts with flow system in the gas phase has been carried out at temperature above 50°C, where the activity is rapidly decreased.$^{3)}$ The activity of the catalyst below room temperature has not yet been studied.

The results of disproportionation of propylene on a supported molybdena-alumina catalyst with the flow system in the gas phase at 0°C are shown in Figs.1 and 2. As soon as the color of catalyst was changed from light yellow to grayish brown after contacting with olefins, the reacted olefins came out from catalyst bed. About 2×10^{-3} mol/g-cat of propylene was adsorbed at 0°C at the initial stage on reaction stream. In every case, the catalytic activity increased with reaction time at the initial stage, and decreased after reaching the maximum. The increase in activity at the initial stage may be arised from two factors, that is, reduction of the catalyst to activated state of molybdena and slow desorption of butenes along with higher olefins from catalyst surface. The former factor must be more important as judged by products distribution. Fig.1 shows that a larger amount of ethylene than butenes is produced in the initial stage of reaction stream and a long time is required until equal amounts of ethylene and butenes are produced. It also shows that the rate of desorption from catalyst surface decreases in the order of ethylene propylene, 1-butene, trans-2-butene, cis-2-butene, pentenes and hexenes.

Total selectivity to pentenes, hexenes and highers were about 0.2% for the initial several hours, but it decreased with reaction time. After several hours

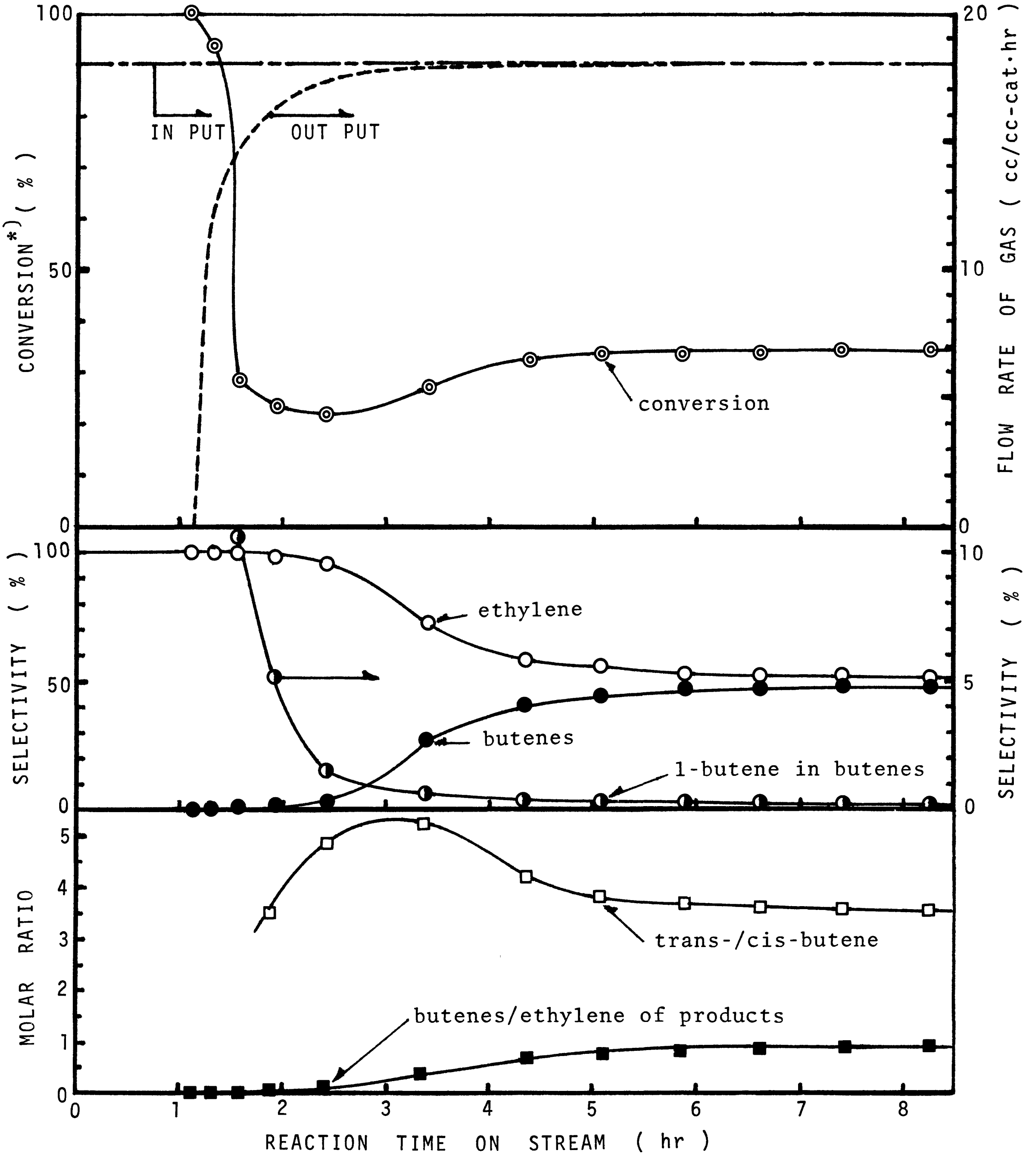

Fig.1 Disproportionation of propylene at 0°C in the gas phase under atmospheric pressure.

*) conversion(%)=[(produced olefins/feed propylene)+(in put-out put)]x100

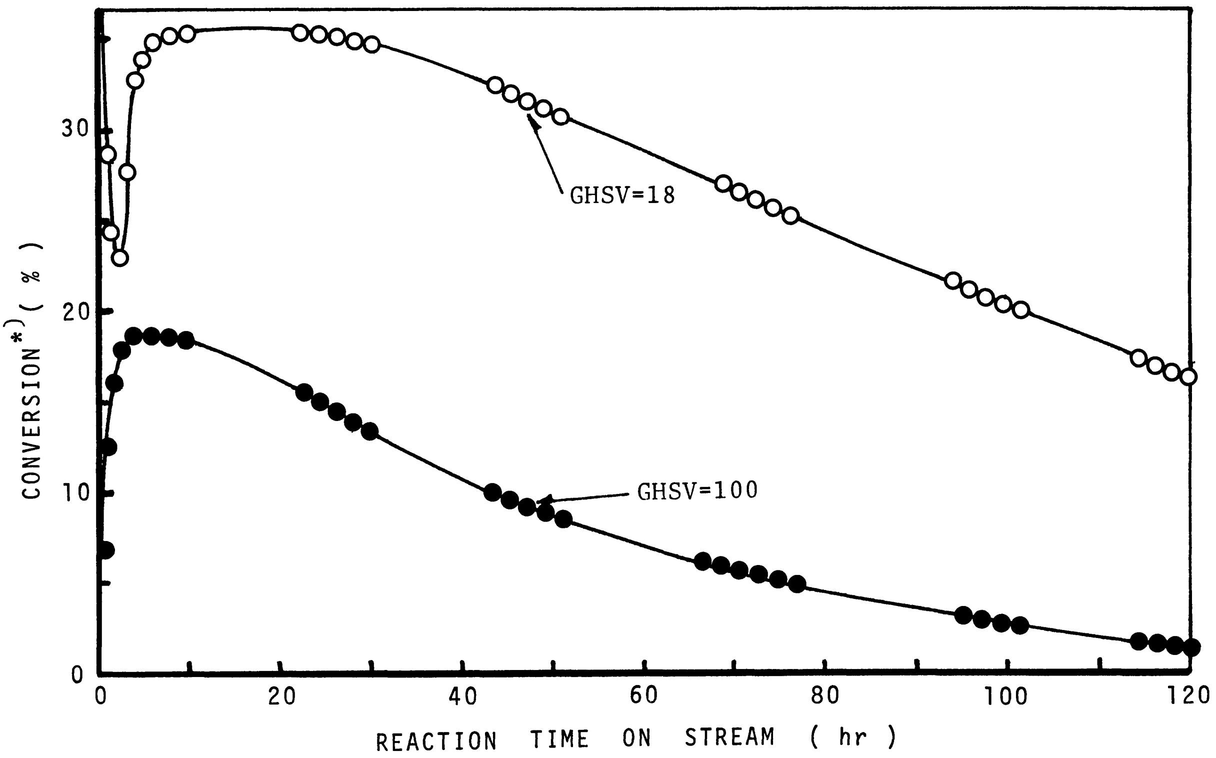

Fig.2 Disproportionation of propylene at 0°C in the gas phase under atmospheric pressure.

*) conversion(%)=[(produced olefins/feed propylene)+(in put-out put)]x100

more than 99.9% of disproportionation products of propylene gave ethylene and butenes . The ratio of butenes to ethylene was less than 1.01. The ratio of trans- to cis-butenes and the yield of 1-butene was less than the equilibrium values in the reaction products of steady state.

Disproportionation on a supported molybdena-alumina catalyst with flow system of liquefied propylene under 50 kg/cm^2 at 0°C is shown in Fig.3. The activity of molybdena-alumina catalyst in disproportionation of propylene increased very slowly and the maximum activity was observed at reaction time on stream from 100 hr to 200 hr. After about 200 hr the catalytic activity decreased very slowly, but the rate of deactivation in flow system of liquefied propylene was very much smaller than in the gas phase reaction. After 460 hr on stream, about 80% of the maximum catalytic activity was preserved. Propylene conversion with space velocity of 18 cc/cc-cat·hr were about 35% in the gas phase and about 3% in the liquid phase under 50 kg/cm^2. This difference of conversion may be caused by the difference in the diffusion coefficient of gas and liquid state. However, the reaction rate of disproportionation of liquid propylene ($7x10^{-3}$ mol/cc-cat·hr) was higher than that of gas phase ($9x10^{-4}$ mol/cc-cat·hr) by a factor of about ten.

At initial stage of reaction in the liquid phase, the selectivity of ethylene and butenes were relatively low, and a higher amount of ethylene than butenes was produced, and 1-butene in butenes was relatively high. Selectivities to ethylene and butenes increased to stoichiometrical values with reaction time on stream after several hours. These results in the liquid phase reaction were similarly observed in the gas phase. The characteristics of the liquid phase reaction can be observed on

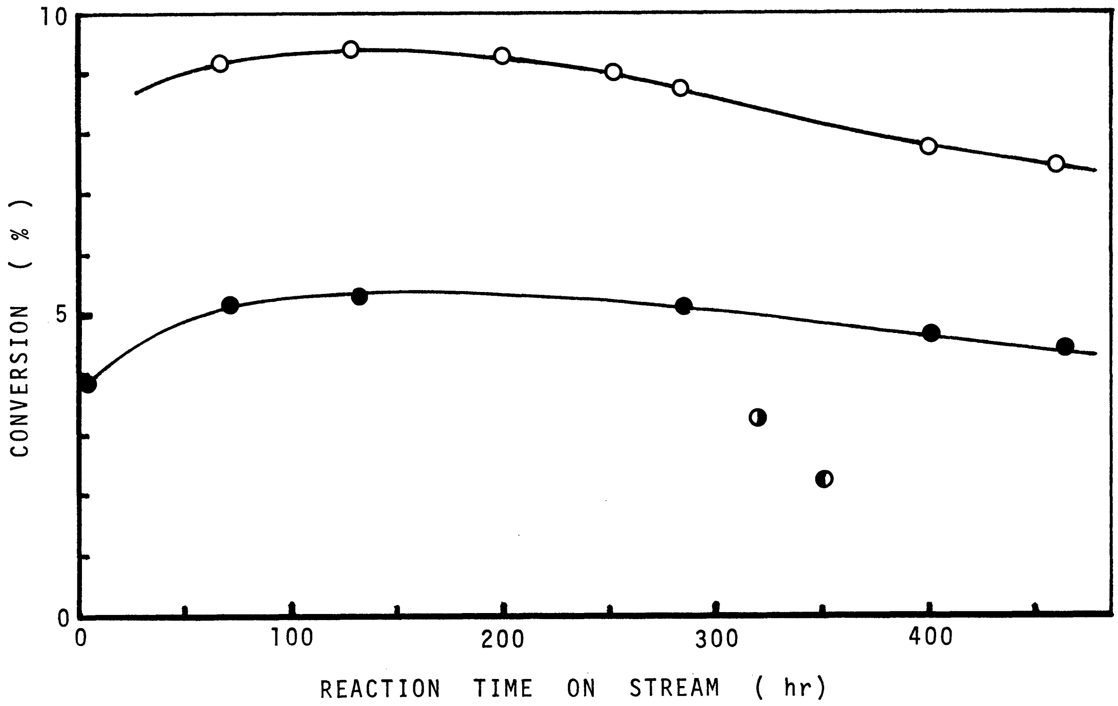

Fig.3 Disproportionation of propylene at 0°C in the liquid phase under 50 kg/cm^2.
○ LHSV=3, ● LHSV=6, ◑ LHSV=12, ◐ LHSV=18.

the formation of small amount of liquid hydrocarbons, which decreased to a trace amount after several hours reaction. After 500 hr reaction a small amount of gummy polymers adhered to catalyst and γ-alumina packed in down stream. The polymers should be insoluble or slightly soluble in the mixed solution of olefin products. The activity of catalyst in the liquid phase reaction can be preserved for longer time because soluble oligomers and polymers in liquefied olefins are carried away from catalyst surface, and so the catalyst is deactivated only little even after long time.

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