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CATALYTIC DEHYDROCHLORINATION OF 1,1,2-TRICHLOROETHANE INTO 1,1 -DICHLOROETHYLENE OVER ALUMINA PROMOTED BY WATER

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It was found by the pulse technique that 1,1,2-trichloroethane was selectively dehydrochlorinated into 1,1-dichloroethylene at 200° over alumina promoted by water before the reaction. Further it was also found that the activity of alumina was retained constant after an initial decrease by first two pulses.

It is already established that the solid base promotes the selective dehydrochlorination of 1,1,2-trichloroethane(TCE) into 1,1-dichloroethylene(VDC), whereas the solid acid does into 1,2-dichloroethylene(DCE).(1)

$$CHCl_2\text{-}CH_2Cl \longrightarrow CCl_2{=}CH_2 + \text{trans/cis } CHCl{=}CHCl \qquad (1)$$

However, catalytic synthesis of VDC over solid bases are often failed because their catalytic activities are lost by formed hydrogen chloride. A patent(2) claims the use of cesium or rubidium chloride as the catalyst. In the present paper, the elimination reaction over alumina is studied for the purpose of surveying catalytic formation of VDC based on the fact that aluminum chloride formed on the surface will be easily converted back to aluminum hydroxide by the addition of water.

$$AlCl_3 \xrightarrow{3H_2O} Al(OH)_3 + 3HCl \qquad (2)$$

Recently, Shinoda(3) reported a high yield of VDC in the copyrolysis of TCE and methanol over alumina. However, methanol may be too expensive for the industrial application of this process, and its recovery is tedious.

The catalytic activity of alumina was observed at 150°-350° by means of the pulse technique. Water was supplied by a microsyringe. The reactant and products were analyzed using a column of 4 m TCP and 1 m PEG 1000. Aluminum hydroxide obtained by precipitation of $Al(NO_3)_3$ with NH_4OH was dried and calcined at 550° or 900°(A-550 and A-900). The content of alkali was very low. A-550 and A-900 had the surface areas of 190 and 50 m^2/g, respectively. The products of the elimination reaction were VDC and trans/cis DCE. The elimination activities of A-550 at 200° are shown in the figure. Although the VDC formation was rather significant for the first pulse compared with the results at the higher reaction temperature,(1) its activity and selectivity were lost severely by successive pulses without the addition of water as shown in the figure. In turn, the selectivity for cis-DCE formation increased very much. The same tendency was observed over A-900 although its activity for VDC formation at the first pulse was lower than that of A-550. The addition

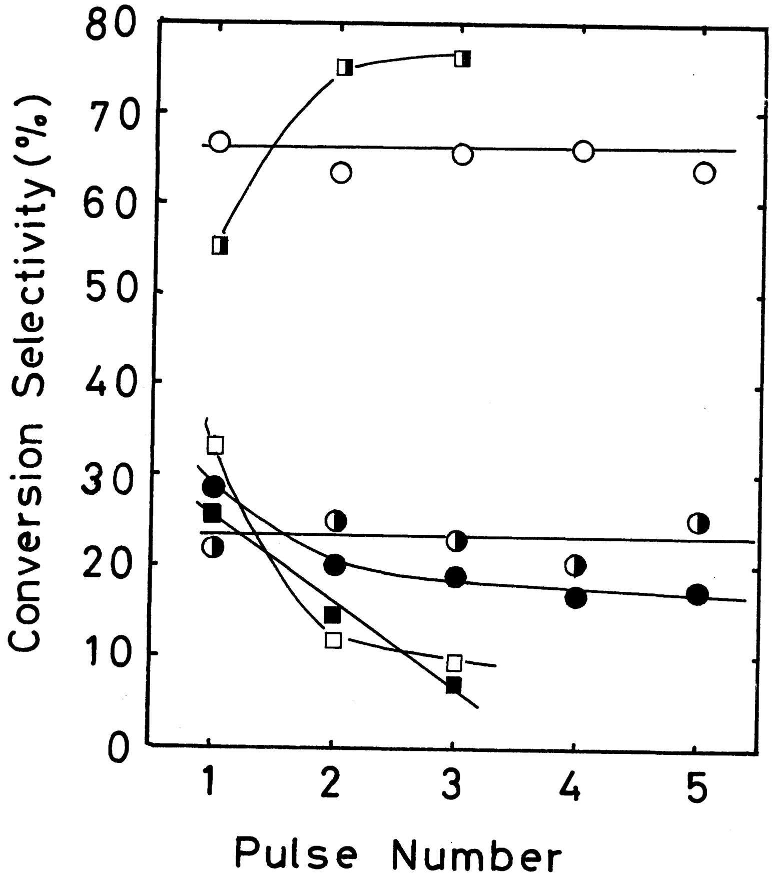

Figure.
Elimination reactions of 1,1,-2-trichloroethane over alumina with and without addition of water before the reaction.

Catalyst; A-550, 51 mg.
Reaction Temp.; 200°.
Flow Rate; 100 ml/min.
Pulse sizes of 1,1,2-trichloroethane and water; 2 μl & 100 μl.
○, □ ; Selectivity of VDC.
◑, ◨ ; Selectivity of cis-DCE.
●, ■ ; Total conversion.
Circles and squares refer to the reaction with or without addition of water.

of water before the reaction brought about not only an increase of the selectivity for VDC formation(65 %) but also its persistence until the fifth pulse. Futhermore, such addition prevented the decrease of activity by the pulse, and kept it constant at 19 % (conversion) after the third pulse.

The improve in the selectivity for VDC formation was much marked over A-900, which showed the selectivity as high as 76 %. Thus, alumina promoted by water was found to accelerate the selective dehydrochlorination of 1,1,2-trichloroethane into 1,1-dichloroethylene by the catalytic reactions. An industrial application of such a process may be possible by using the recycling fluidized-catalyst system. Further mechanistic study is now in progress.

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