Promoting Effect of Zirconium Compound on Catalytic Activity for Oxychlorination of Butadiene

Hiroyuki HAGIWARA and Naoyuki TODO
Government Chemical Industrial Research Institute, Tokyo, Mita, Meguro-ku, Tokyo

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It is generally accepted that certain carriers not only display a large exposed surface of active constituent but also modify the catalytic activity or the selectivity of the active agent. It has been suggested that the surface compound can be formed between the carrier and the supported material giving a complex which has better catalytic properties.[1-2] During the course of studies on the catalyst for the oxychlorination of butadiene to get 1,2- or 3,4-dichlorobutene, a material of chloroprene monomer, it was found that the activities of the catalysts we developed, $CuCl_2$-LiCl-H_3PO_4 supported on sintered commercial alumina-silica carriers, depend considerably on the amount of contaminant zirconium compound on the carriers.

This communication reports on some characteristic effects of the zirconium compound on activity. The carriers used were sintered alumina-silica ($S<1 m^2/g$) of low surface area, obtained from Fujimi Kenmazai Kogyo Co. (SNO3) and Tokai Konetsu Kogyo Ltd. (TA124). Their approximate chemical compositions were Al_2O_3-10 wt% SiO_2 containing zirconium to some extent or practically none. The catalysts were prepared by the usual coimpregnation method. The amounts of $CuCl_2$, LiCl, and H_3PO_4 supported were 1.81 wt%, 0.21 wt%, and 0.08 wt%, respectively. The activity was measured by a conventional flow type apparatus at a space velocity of 210 per hour at temperatures 160—250°C. A stoichiometric reactant mixture was used. Prior to the activity measurement, the catalysts were preactivated at 300°C for 3 hours under the atmosphere of nitrogen. It is shown in Table 1 that the conversion of butadiene depends obviously on the zirconium content in the carriers: the catalyst prepared from SNO3 revealed a much higher conversion than that prepared from TA124. Its ability was modified by treating the carrier with a concentrated hydrochloric acid to reduce the zirconium content. The amount of zirconium is optimum when the activity of the catalyst is maximum. Thus, in order to get the quantitative relationship between activity and zirconium content, we measured the activity of a series of catalysts prepared from a carrier impregnated with various amounts of zirconium oxychloride by calcination at 700°C prior to supporting the active components.

TABLE 1. ACTIVITIES OF THE CATALYST PREPARED BY USING VARIOUS CARRIERS

Carrier	Conversion of butadiene (%)	Selectivity to 1,2- and 3,4-dichlorobutene (%)
SNO3	52.1	94.4
SNO3 treated with HCl	73.0	96.2
TA124	15.8	94.8

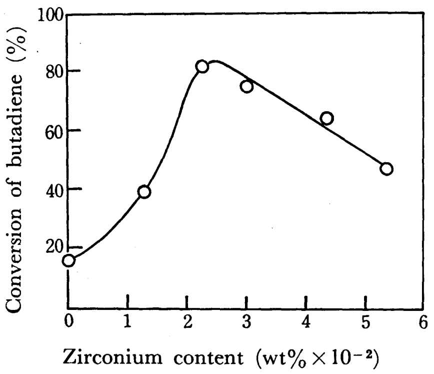

Fig. 1. Effect of zirconium content on the catalytic activity.

We see from Fig. 1 that the addition of an optimum amount of zirconium gave rise to an increase in conversion about five times as high as that obtained without addition of zirconium salts. In contrast, the activity of the catalyst prepared by using silicon carbide as a carrier was not improved by the addition of zirconium salts. The alumina-silica surface might play an important role in cooperation with the zirconium ion for the formation of an active compound composed of $CuCl_2$, LiCl, and H_3PO_4, although neither the structure nor the promoting mechanism of zirconium have been made clear as yet.

1) S. Ogasawara, Y. Nakata, Y. Iwata, and Y. Sato, *Kogyo Kagaku Zasshi*, **73**, 509 (1970).
2) T. Sukeno, M. Mimura and H. Nomura, *ibid.*, **68**, 1838 (1965).