CHEMISTRY LETTERS, pp. 877-878, 1973. Published by the Chemical Society of Japan

CO-PYROLYSIS OF 1,1,2-TRICHLOROETHANE AND METHANOL ON ACTIVATED ALUMINA

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The copyrolysis of 1,1,2-trichloroethane (TCE) and methanol on activated alumina was carried out at 250~400°C. 1,1-dichloroethylene (VDC) to 1,2-dichloroethylene (DE) ratio amounted to several times of the ordinary pyrolysis. This reaction proceeded as follows.

$$CH_2ClCHCl_2 + CH_3OH \longrightarrow CH_2{:}CCl_2 + CH_3Cl + H_2O$$

In general, the dehydrochlorination of TCE at high temperature is unfavorable to the formation of VDC[1]. Especially, the elimination from TCE on the solid acids, such as activated alumina, has the poor selectivity for VDC[2),3)]. In this study copyrolysis of TCE and methanol on activated alumina was carried out with the flow technique according to Andrussow's method[4)].

A mixture of TCE and methanol was fed into a joint evaporator by the use of a microfeeder and preheated to 200°C. The reactor and the evaporator were made of glass tube which were heated in electric furnaces. The catalyst was located in the middle of the reactor. Alumina catalysts were fine powder and used together with glass wool. Small temperature gradient was found along a catalyst bed of 25 mm diameter. A thermocouple was placed in the center of the bed. The product gas stream entered a cooler and condensed in a cold trap. The reaction products were analyzed by gas chromatography. Alumina catalysts used are listed in Table 1.

Table 1. Alumina catalysts[a)]

No.	Base amount ($H_0 \geq +9.1$) m mol/g	Acid amount ($H_0 \leq +6.8$) m mol/g	Remark
cat-A	0.35	0.08	b)
cat-B	0.37	0.08	c)
cat-C	0.34	0.22	d)
cat-D	0.28	0.45	e)

a) These reagents were calcined in nitrogen stream at 350°C.
b) The Kanto Kagaku Co.
c) The Wako Chemicals Co.
d) The Sumitomo Chemical Industry Co.
e) The Kishida Kagaku Co.

The acidity and basicity of the catalyst were determined by the titration methods[5)]. The product distributions at various reaction temperatures are shown in Table 2.

Trans/cis ratio increased as a function of the reaction temperature. However, the selectivities for VDC formation were approximately constant at a high level.

Table 2. The effect of the reaction temperature on the product composition

Reaction temperature (°C)	Conversion of TCE (%)	Product composition CH_2:CCl_2	trans-CHCl:CHCl	cis-CHCl:CHCl
220	17.9	71.9	14.6	13.5
240	33.2	70.7	18.7	10.6
270	40.6	70.1	20.9	9.0
295	55.7	69.6	22.2	8.2
320	86.4	69.0	23.0	8.0

Catalyst : cat-A
Time factor : 58 g of catalyst/g-mol of TCE/hr
Mole ratio : 2.0 CH_3OH/TCE

The selectivities for the elimination reaction of hydrogen chloride from TCE in the presence of methanol on activated alumina are shown in Fig. 1.

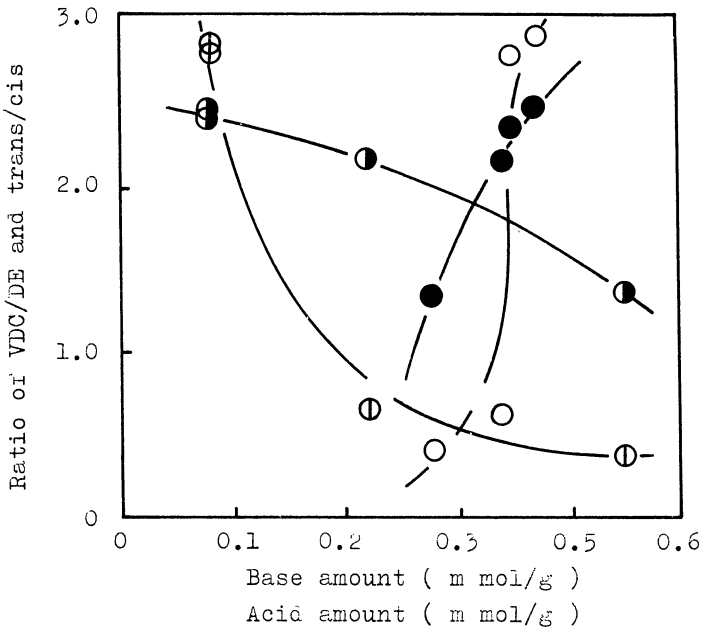

Fig. 1. The effect of the acid-base character of alumina catalysts on the dehydrochlorination of TCE at 300°C.

● VDC/DE ratio vs. base amount
○ Trans/cis ratio vs. base amount
◑ VDC/DE ratio vs. acid amount
◐ Trans/cis ratio vs. acid amount

A higher ratio of VDC/DE had a higher ratio of trans/cis. This accords with the results of the elimination from TCE on solid catalysts[2),6)]. As the base amount of the catalyst increased, VDC/DE ratio was found to increase. VDC/DE ratio varied considerably according to the acid-base character of the catalysts. The durability of these catalysts was sufficient to continue the moderate reaction for periods up to 10 hours.

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(Received May 14, 1973)