CHEMISTRY LETTERS, pp. 883-884, 1978. Published by the Chemical Society of Japan

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

Kiyonori SHINODA
Toyama Technical College, Hongo, Toyama-shi 930-11

The co-pyrolysis of 1,2-dichloropropane (DCP) and methanol on activated alumina was carried out at 270°C. The reaction products contained a significant amount of oxygen-containing compounds as well as the ordinary pyrolysis compounds. The formation of acetone and acrolein increased as a function of the time factor.

It has been found that the pyrolysis of DCP gave the dehydrochlorination products consisting of four chloropropene (CP) isomers.[1)] The catalytic dehydrochlorination of DCP has been also studied by various investigators. It has been reported that the ratio of these CP isomers varied considerably according to the acid-base character of the catalysts.[2)3)] In the present study, the co-pyrolysis of DCP and methanol on activated alumina was carried out at 270°C with the fixed bed flow reactor described in the previous work.[4)] Activated alumina used as catalyst (KHA-34) was supplied by Sumitomo Chemical Co. and the particle diameter was in the range of 3 to 4 mm. The time factor (W/F:g·hr/g-mol) was varied by adjusting the feed rate of DCP (F:g-mol/hr), the weight of catalyst (W:g) being kept constant. DCP was mixed with methanol at the mole ratio 1.00:7.19. The reaction products were analyzed by gas chromatography (PEG 6000,50°C). These co-pyrolyzed products were composed of the oxygen-containing derivatives such as acetone and acrolein as well as chloropropenes. When the reaction products were treated with 2,4-dinitrophenyl hydrazine solution, these carbonyl compounds were converted into hydrazones. 2,4-Dinitrophenyl hydrazones of acetone and acrolein were separated with column chromatography and were confirmed by IR, NMR and MS techniques. The product distributions in the co-pyrolysis with the various time factors are shown in Table 1. Since hydrogen chloride was converted into methyl

Table 1 The effect of time factor (W/F) on the product composition

W/F	Product composition (mol %)					
(g·hr/g-mol)	2-CP	1-CP	3-CP	CH_3COCH_3	CH_2=CHCHO	DCP
131.6	0.71	11.49	0.41	1.39	0.50	85.50
198.0	1.27	15.64	0.47	2.52	0.63	79.47
303.0	1.95	17.96	0.57	4.00	0.86	74.66
392.2	3.48	23.52	0.61	6.44	1.27	64.68
800.0	9.10	24.41	1.31	25.23	3.70	36.23

chloride, the dehydrochlorination was more favorable than that of the ordinary catalytic cracking owing to the shift of the equilibrium composition. The formation of 2-chloropropene (2-CP) and acetone increased as a function of the time factor. Under similar reaction conditions, 2-CP was co-pyrolyzed with methanol into acetone and methyl chloride on activated alumina, whereas allyl methyl ether and acrolein were formed in the case of allyl chloride (3-CP). It has been known that solid basic catalyst was advantageous for the formation of 2-CP, while cis-1-chloropropene (1-CP) was favorably formed on acidic one.[2)3)] It is reasonably assumed that 2-CP reacts with methoxide anion[5)] formed on the basic sites of alumina and converts to the intermediate, $CH_3CCl(OMe)CH_3$ which may split into acetone and methyl chloride. The methoxide anion generated on the basic sites of alumina might play an important role, similarly to the co-pyrolysis of chloroethanes and methanol.[4)] This reaction is a nucleophilic addition of methoxide anion to the double bond of CP. On the other hand, a β-hydrogen of chloroethanes is abstracted by the nucleophilic attack of the same one, chlorine being removed at the same time. 2-CP and acetone are formed by the co-pyrolysis of DCP and methanol on activated alumina, in agreement with the previous data indicating that solid basic catalyst is favorable to the formation of 2-CP.

References

1) D. H. R. Barton and A. J. Head, Trans. Farad. Soc., 46, 114 (1950).

2) H. Tominaga, T. Nakamura, H. Arai and T. Kunugi, Kogyo Kagaku Zasshi, 74, 199 (1971).

3) N. Yamagata and S. Okazaki, Nippon Kagaku Kaishi, 1974, 636.

4) K. Shinoda, Bull. Chem. Soc. Jpn., 47, 2406 (1974).

5) J. R. Jain and C. N. Pallai, J. Catal., 9, 322 (1967).

(Received June 12, 1978)