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CATALYTIC CONVERSION OF PROPYLENE CHLORID DERIVATES TO PROPINE AND PROPADIENE

Abstract: The process of conversion of propylene chloride derivatives - waste glycerol production - into valuable monomers - propine and propadiene on an industrial catalyst based on magnesium oxide has been studied. It was found that the highest conversion of feedstock to target products is observed from dichloropropane at minimum contact time. The considered dependencies allow assuming, that propylene and monochloropropenes are formed by independent routes, while propine and propadiene – are mainly from monochloropropenes. Under experimental conditions, surface condensation varies from 8.0 to 39 %, and other side transformations of feedstock (into ethylene and acetylene) in the interval of 400-500°C practically do not change. As an alternative, the diagram of catalytic transformation of 1, 2-dichloropropane is supposed.

Key words: propylene chloride derivatives, waste, propine, propadiene, industrial catalyst.

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Introduction

The extremely high reactivity of allene and allylene opens up wide opportunities for their use in the synthesis of many industrially important products (polymeric and cellulose-paper materials, toxic chemicals, medicines, rocket fuel, etc.) Numerous attempts to get propine and propadiene by pyrolysis of propylene and allyl chloride [1, p 65; 2, p.45] at high temperatures (800-1200°C) have failed because of the formation of significant amounts of by-products of reactions. Pyrolysis and cracking of low molecular weight hydrocarbons at high temperatures of the order 800-1200°C, accompanied by significant of resinification [3, p.24; 4, p.30; 5, p.24; 6, p.31; 7, p.21] are of limited interest, therefore, the search for new, more efficient methods of producing propadiene based on cost-effective raw materials and a catalyst is relevant. The present study is dedicated to the regularities of the process of dehydrochlorination of chlorine derivatives of propylene to obtain propine and propadiene, which are of practical importance for the recycling of waste glycerol production in order to obtain valuable monomers.

Glycerol production is associated with the formation of wastes, in which chloropropanes (2chloropropane, 1, 2-dichloropropane, 1, 2, 3trichloropropane) and allyl chloride constitute a significant Processing proportion. these chlorohydrocarbons into propine and propadiene seems tempting not only from the environmental side. It can help to increase the capacity of this multitonnage plant since the waste problem is profitably solved by creating a closed oxychlorinationdehydrochlorination cycle and using the dehydrochlorination product-propadiene-to convert it into glycerol.

The possibility of catalytic conversion of propylene dichloro derivatives into propine and



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propadiene has been studied by the author earlier [8, p. 270; 9, p. 453; 10, p.46].

Experimental part

Experiments were performed on a flow-through unit in the temperature range of 300-500°, with a contact time of 0.7-7 s at atmospheric pressure. As a catalyst, an industrial oxide catalyst was used.

The reaction products were analyzed chromatographically and IR spectroscopically. The chromatographic analysis was performed on a LChM-2M, the stationary phase was ceolite and vaseline oil on TZK, the condensate analysis was performed on ChL-69 (stationary phase was PEG-1540 on chromaton), the carrier gas was hydrogen.

Results and discussions

To reveal comparative reactivity of propylene chlorine derivatives in dehydrochlorination reaction 2-Chloropropane (2-CP), 1,2-Dichloropropane (1,2-DCP), 1,2,3-Trichloropropane (1,2,3-TCP) and allyl chloride (CA) extracted from waste glycerol production were used. Dehydrochlorination was carried out at 400°C on an industrial catalyst based on magnesium oxide (table 1).

According to the data obtained the reactivity of propylene chlorine derivatives expressed by the average formation rate (mol/l·h) of propine and propadiene decreases in the series:

1,2-DCP (0.31) > 1,2,3-TCP (0.22)≥ AC (0.13) >> 2-CP (trace)

Raw materials	The average speed of formation, [mol/l ·hr.]					Conversion
	$\Sigma C_3 H_4$	C_2H_4	C_2H_2	C_3H_6	$\Sigma C_3 H_5 C_1$	of raw materials %
1,2-DCP	0.33	1.87	0.16	8.5	15.6	53.5
1,2,3-TCP	0.23	2.08	-	4.16	0.53	38.7
Allyl Chloride	0.14	1.26	1.68	17.61	0.74	45.2
2-CHP	traces	traces	-	108.02	-	84.7

Table 1. Comparative reactivity of propylene chloride derivatives

Experimental conditions: t = 400 °C, contact time 0.8 s, $V_{cat.} = 5$ cm³.

The comparatively higher yield of allene and allylene in the case of 1,2-DCP compared to allyl chloride is apparently due to the initiating effect of the resulting chlorine on the further dehydrogenation of intermediate structures. Probably, in the case of allyl chloride, due to the relatively low concentration of chlorine on the surface, hydrogenation of intermediate forms prevails, which leads to a relatively higher yield of propylene. At significantly higher chlorine content in the hydrocarbon molecule, for example, 1,2,3trichloropropane, the formation of propylene is significantly reduced:

2CP > AC > 1,2-DCP > 1,2,3-TCP

Table 2 shows the formation patterns of 1,2-DCP dehydrochlorination products at different contact times and temperatures. It can be seen that when the contact time is increased up to 7 s, there is a tendency to a decrease in the average formation rates of all reaction products: monochloropropenes, acetylene, propylene, ethylene, allene, and allylene, which is associated with the course of side reactions of surface condensation.

The conversion of 1,2-dichloropropane to propine and propadiene can occur in two ways: through monochloropropenes and propylene, i.e. as a result of hydrogen chloride and chlorine stripping, including the intermediate stage of allyl structure formation.

Items of reactions	The average rate of formation, [mol/l.hr]								
reactions		Temper	rature, ⁰ C		Contact time, sec.				
	350	400	450	500	0,5	2,5	4,5	6,5	
acetylene	0,8	0,2	0,2	0,2	1,6	1,4	1,3	1,2	
ethylene	1,3	0,6	0,8	0,9	2,4	2,1	1,4	1,3	
propine	0,5	1,1	2,4	3,8	17,6	12,8	10,2	5,3	
propylene	0,8	2,2	2,8	3,5	9,1	6,4	5,1	2,6	
chloropropenes	2,4	2,3	2,2	2,1	15,9	8,3	4,2	3,1	

Table 2. Effect of temperature and contact time on the average rate of formation of target products.



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The dependences of formation rates of monochloropropenes, propylene and propinepropadiene on the temperature at contact time of 0.8 s are different. Thus, in the case of propylene and propine-propadiene the increase in temperature is accompanied by a monotonic increase in their formation rates, and monochloropropenes - by a decrease, and the order of decrease in the reaction rate in this case sharply differs from the rate of formation of propylene.

Results and discussions

Therefore, the results of this research, suggest that the considered dependences suggest that propylene and monochloropropenes are formed by independent routes, while propine and propadiene are formed mainly from monochloropropenes. Under experimental conditions, the surface condensation ranges from 8.0 to 39%, and other side transformations of feedstock (into ethylene and acetylene) in the range of 400-500°C are virtually unchanged.

As an alternative, the following scheme of catalytic transformation of 1,2-dichloropropane can

be suggested. The obtained data suggest that the ratio of the rates of the intermediate hydrogenation stages (1-2b), degradation (III), and allyl radical dehydrogenation (1-2a) has a determining influence on the shift of the cracking reaction of the studied chlorohydrocarbons toward propine and propadiene or side products. The obtained data suggest that the ratio of the rates of the intermediate hydrogenation stages (1-2b), degradation (III), and allyl radical dehydrogenation (1-2a) has a determining influence on the shift of the cracking reaction of the studied chlorohydrocarbons toward propine and propadiene or side products.

It should be emphasized that the synthesis of propine and propadiene from dichloropropane and trichloropropane - glycerol production waste - is favorable not only in terms of reducing the consumption of valuable monomers - propylene, isobutylene and allyl chloride in pyrolysis processes, but also because in case of these chlorohydrocarbons it is possible to simultaneously use the catalytic action of both oxide and chlorine at the moment of its formation in the intermediate stages on the surface.





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