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Catalytic processing of organochlorine wastes into valuable monomers

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The paper is devoted to experimental development of method for 1,1,2-trichlorethane (TCE) dehydrochlorination (DHC). The economic and environmental issues of organic chlorinated compounds processing are described. The basic principle and possible products of TCE processing are presented. The DHC of TCE, which is one of the chlorinated organic wastes produced in the ethylene dichloride process, to vinylidene chloride (VDC) was carried out over over CaO, MgO supported on SiO_2 and modified with CsCl catalysts. This process was carried out in a continuous flow fixed-bed reactor. The prepared catalysts were characterized by surface area and base properties before/after reaction. The methodology for determining properties of catalyst is described. Laboratory activity test apparatus was developed, and the schematic diagram is presented in the paper. The method of determination of TCE concentration of was calculated from its partial saturation vapor pressure at a given temperature is presented. Encouraging results were obtained on the catalyst containing 10 % CsCl/$CaO{\cdot}SiO_2$. The direction of the DHC reaction changed radically under described conditions: VDC was not formed at all and the major products were cis- and trans-1,2-dichloroethene. Interesting results were obtained with the catalytic system comprising 10 % (MgO-CsCl) (1:1) supported on SiO_2. DHC of 2 % TCE/Ar at 302 °C proceeds quantitatively over 20 h with selectivity for VDC of more than 80 %. These systems are suitable to study the factors providing the binding and removal of HCl from the reaction zone. A possible way to increase the selectivity for VDC is the creation of the conditions favoring the DHC of TCE into VDC by the radical mechanism, which was observed in experiments with 10 % CsCl/$CaSiO_3$. The directions for future researches are formulated and described.

Keywords: dehydrochlorination, 1,1,2-trichloroethane, vinylidene chloride, supported catalyst

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Introduction

Many types of chlorinated organics are important chemical raw materials. However, due to unreasonable wastewater discharge, these chlorinated compounds pose a serious threat to safety of the ecosystem and groundwater [1]. Therefore, how to use chlorinated hydrocarbons is an important topic. Gas-phase catalytic conversion of chlorinated organic wastes into useful hydrocarbons via dehydrochlorination is known as one of more promising methods. It has the advantages of economic efficiency and low environmental pollution and has attracted more attention from the academic and industrial circles. In addition to environmental advantages, this process has obvious economic merits because the resulting hydrocarbons can be recycled [2].

1,1,2-trichloroethane (TCE) is a typical chlorinated hydrocarbon that formed as a by-product in the production of 1,2-dichloroethane, which is the main intermediate in the synthesis of vinyl chloride (VC). It is contained in sufficient quantity in the distillation residues of the rectification of 1,2-dichloroethane. As a result of the distillation process of so-called "heavy fraction", it is possible to obtain about 10 kg of industrial grade 1,1,2-TCE / t VC [3]. In currently working factories of VC, it is utilized as a raw material in the chlorinolysis process or for combustion.

Therefore, it has been a long-term goal to develop the gas phase synthesis of 1,1-dichloroethene (1,1-DCE) from TCE in the presence of supported catalysts. Only catalytic processes for DHC of TCE can comply with the ecological requirements and provide the utilization of the major by-product - hydrogen chloride [2].

Dehydrochlorination of TCE results in four products (as shown in Fig. 1). Chlorineatoms within the molecules are shown with green color; carbon atoms – with dark grey and hydrogen atoms – with light grey:

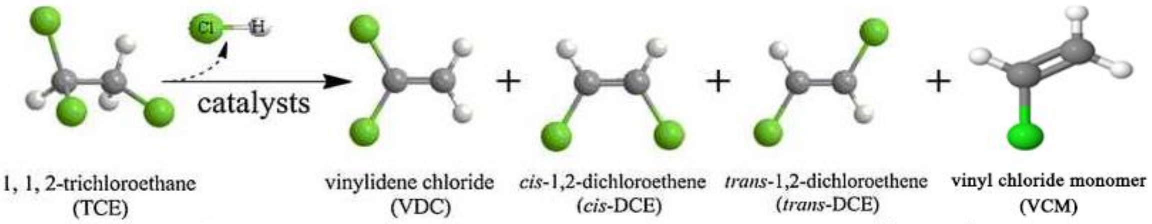

Fig. 1. Various products for dehydrochlorination of 1,1,2- trichloroethane.

Cis-DCE has been widely used as solvents for paint, resin, wax, rubber and acetate fibers. Vinylidene chloride (VDC) is the monomer of polyvinylidenechloride, that has been widely applied in food package due to its good performance in retarding food spoilage [3]. And VC is the monomer of polyvinylchloride that is one of the most widely used polymers.

In this study, the catalytic dehydrochlorination of 1,1,2-trichloroethane was carried out in a continuous flow fixed-bed reactor. The prepared catalyst was characterized by surface area and base properties before/after reaction.

Experimental part

Catalyst preparation

Calcium oxide was obtained by precipitation from a solution of $CaCl_2$ with KOH followed by washing out Cl^- ions and calcination at 650 °C for 2 h.

MgO/SiO_2 (20 wt.% MgO) was prepared by impregnation of SiO_2 with a solution of $Mg(OH)_2$ and calcination at 400 °C for 2 h to decompose $Mg(OH)_2$ to MgO.

CaO/SiO_2 was prepared by impregnation of SiO_2 with suitable amount of $CaCl_2$, treatment with aqueous KOH, washing, drying and calcination at 650°C for 2 h to decompose $Ca(OH)_2$ to CaO.

Calcium silicate, $CaSiO_3$ was prepared by heating SiO_2 of Grade KSS (S_{BET}= 520 m^2/g, pore diameter 70.8 Å) with 1 M solution of calcium chloride in ammonia buffer at 100 °C for 24 h. The product was dried at 120 °C for 3 h and calcined at 500 °C for 3 h. The sample obtained was analyzed to determine the content of calcium and silicon. Calcium was leached out with acid and determined by complexometric titration. Silicon was determined by the gravimetric method. Chemical composition is $1.08SiO_2{\cdot}0.48CaO{\cdot}0.47H_2O$.

MgO·CaO·CsCl. The 1:1 mixture of saturated solutions of $MgCl_2$ and $CaCl_2$ was treated with an aqueous solution of cesium oxide preliminarily prepared by calcination of Cs_2CO_3 at 650 °C. The suspension was evaporated and calcined at 600 °C for 3 h. This temperature is enough for magnesium and calcium hydroxides to be converted into the oxides [4].

Determination of catalystsurface area.

The sample is placed in the adsorber and flushed with the gas mixture for 0.5 h at 250 °C to remove moisture. The adsorber is heated with the electric furnace. After cooling the sample to room temperature under a flow of gas mixture(Ar-He),the katharometer current (100 mA) is conveyed. Once the baseline of the has been stabilized, the adsorber is immersed in liquid nitrogen.

During the adsorption of argon on a sample, we have a “reversed” peak. After a while the ADC fixes the normalization of the baseline which indicates that the adsorption is complete. The adsorptionduration depends on the surface area of a sample. After completion of the process, the adsorber is taken out of the Dewar vessel and defrosted. As aadsorber is warmed up to room temperature, argon is desorbed from the surface of the sample. It arrives, through the four-way cock, at the katharometer and the corresponding signal is recorded by ADC.

The surface area of the catalysts (S, m^2) was calculated from the volume of desorbed argon [5]:

$$S = F \times V_{Ar} = 4.73 \times V_{Ar} ,$$

whereV_{Ar} is the volume of desorbed argon (ml) and F=4.73 m^2/ml is the surface covered under normal conditions with 1 ml of argon adsorbed in a monolayer fashion. The area occupied by an argon atom on the surface was taken to be 17.6 A^2.

The $V_{Ar}$was determined by comparing peak areas of the desorbed argon (Q) and the sample of the gas with known volume V_{st} (Q_{st}) introduced through the dosing cock:

$$V_{Ar} = (Q_{St} \times V_{St}) / Q_{St} ,$$

Specific surface area (S_{sp}, m^2/g) was estimated as the ratio of the total surface area (S, m^2) to the weight (m,g) of the solid sample, i.e.[6],

$$S_{sp} = S / m ,$$

Estimation of catalyst base properties

The base properties are quantified after the measurement of specific surface area of sample. The surface basicity is determined from the data on adsorption of carbon dioxide.

The volume of adsorbed carbon dioxide (V_{ads}) is calculated as difference in volumes of the fed (V_{st}) and coming-out (V) gas.

Total number of B sites can be estimated as

$$B = (V_{ads} \times 6.023 \times 10^{23}) / (S \times 22400) = 2.7 \times 10^{19} \times V_{ads} / S \ (CO_2 molecules / m^2) ,$$

` where S is the total surface sample area.

Catalytic test

The catalytic cracking of TCE was carried out in the flow-type apparatus (Fig.2).

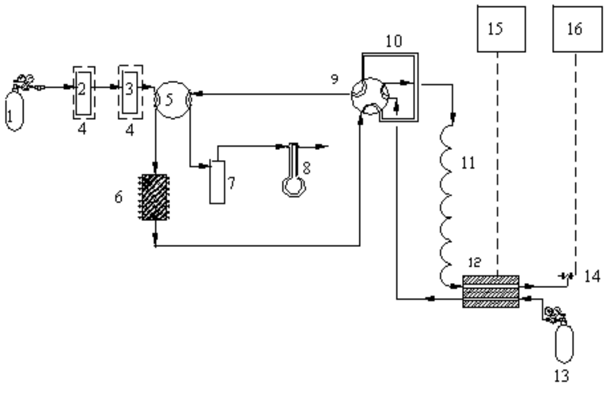

Fig. 2. Schematic diagram of laboratory activity test apparatus.

The reaction mixture was prepared by saturation of nitrogen (*1*) flow with TCE vapor in the saturator (*2*,*3*) at a given temperatureand fed, through the four-way cock (*5*), to the reactor (*6*) filled with a catalyst. The concentration of TCE in the feed gas can be controlled by changing temperature of the saturator (*4*). The reaction products were admitted to the six-way sampling cock (*5*). The outlets of the cock (9) are connected with the metal tube (*10*), the capacity of which determines the size of the sample.

With the cock (*9*) in the position indicated by solid lines, the products, having passed the way, fill the tube *(10)* and enter, through the cock (*5*), the receiver (*7*). At the same time, the carrier gas, helium, via the six-way cock *(9)* is admitted to the chromatographic column *(11)* and then it passes to the katharometer *(12)* and modified flame ionization detector (FID) (*14*) built in the chromatograph LKhW-72.

The capacity of the tube and its connectors is 0.906 ml at 150 °C. All the cocks and fittings are maintained at the indicated temperature to avoid condensation of the products.

Thus, with the cock (5) in the position indicated by solid lines, the effluents from the reactor are conducted to the analysis. In the alternative position (broken lines), the starting reaction mixture is analyzed. It is evident that the samples of the starting mixture and the reaction products to be analyzed are of the identical size and the relative error of the measurements is the same in all experiments.

The gas phase dehydrochlorination process of TCE was performed in a tubular fixed-bed stainless steel reactor (20 cm long and 4 mmi.d) at atmospheric pressure mounted in the thermostat. The temperature of the heated units was controlled accurate to within ± 0.3 °C.

In a typical procedure, the catalyst bed was charged with 0.5 g of catalyst, and then pretreated with Ar atmosphere at a flow rate of 30 cm^3/min at 200°C.The reactant flow (30 cm^3/min) was generated by flowing N_2 through a bubbler containing the liquid TCE. Once stabilized, the reactant flow was introduced to the catalyst bed consisting of catalysts. The compositions of the reaction effluent were analyzed by gas chromatograph with an FID detector and 3 m long, 3 mm diameter column filled with 3% OV-225 on Inerton-Super.

The 1,1,2-trichloroethane (Acros Organics) was of 99.9% purity. The identification of the reaction products and the calibration of the FID were performed with model mixtures of pure compounds (VC, VDC, *trans*- and *cis*-l,2-DCE).

The concentration of TCE was calculated from its partial saturation vapor pressure (P_i) at a given temperature (t) of saturator and pressure (P) in the condenser, i.e.,

$$C_v = 100 \times P_i / P\ (vol.\%)\ or\ C = C_v = 2240\ (mol/l)$$

whereC_v and C is TCE concentration in terms of vol.% and mol/l, respectively [6],

$$\lg P_i = 6.84164 - 1262.6/(t + 205)$$

The conversion of TCE, X (%), was estimated by the formula:

$$X = 100 \times (C^0_{TCE} - C_{TCE}) / C^0_{TCE},$$

where $C°_{TCE}$ and C_{TCE} are the concentrations of TCE before and after the reaction.

The selectivity for a particular product S_i *(%)* was calculated as

$$S_i = C_i \times 100 / (C^0_{TCE} - C_{TCE}),$$

where C_i is product concentration (mol/l).

In the cases where the material balance on carbon was obeyed accurate to within 20%, the selectivity for products was determined by the formula

$$S_i = C_i \times 100 / \sum C_{prod},$$

where $\sum C_{prod}$ is sum of product concentrations.

The balance on carbon δ (%) in TCE and the products was calculated by the formula

$$\delta = 100 - (C^0_{TCE} - C_{TCE} - \sum C_{prod}) \times 100 / C^0_{TCE}$$

Result and discussion

In our previous study [7] we investigated catalytic activity of II A group metal oxides (MgO, CaO, BaO etc.). In this work we investigated the activity of mixed oxides composed of SiO_2 and Group IIA metal oxides, i.e. $MgO \cdot SiO_2$ and $CaO \cdot SiO_2$ modified by CsCl.

The DHC of TCE over mixed oxide $CaO \cdot SiO_2$ modified with CsCl is characterized in Table 1.

Table 1**. Dehydrochlorination of TCE over catalysts CsCl/CaO·SiO$_2$ (Space velocity = 144h^{-1})**

Catalyst	τ, h	T°,C	TCE, vol.%	Conversion, %	Selectivity,%				**δ,%**
					VC	VDC	trans-DCE	cis-DCE	
1%CsCl/CaO·SiO$_2$	1	250	1.8	73.5	1.7	98.3	0.0	0.0	71.4
	2	250	1.8	41.0	8.6	85.2	6.1	0.0	75.9
	5.5	300	1.8	62.6	33.2	61.0	5.7	0.0	78.6
	6.5	300	1.8	62.4	11.3	60.2	5.0	23.5	69.9
	8.5	300	1.8	59.4	17.0	58.6	4.7	19.7	75.0
10%CsCl/ CaO·SiO$_2$	1	250	1.8	99.9	0.8	94.2	3.2	1.8	79.8
	2	250	1.8	99.9	0.9	92.0	5.0	2.1	95.5
	3	250	1.8	99.8	0.6	93.3	3.5	2.6	90.7
	5	365	1.8	99.9	13.9	67.3	9.9	8.9	75.8
	6	365	1.8	99.5	13.7	61.7	9.9	14.7	92.8
20%CsCl/CaO·SiO$_2$	1	320	14.8	99.8	0.3	70.0	7.8	8.4	90.0
	1.5	320	14.8	59.7	1.2	62.9	12.3	23.6	88.6
	2	320	14.8	60.1	1.7	59.8	13.0	25.5	87.6
	6	320	14.8	62.5	3.5	51.2	12.4	32.9	86.8
20%CsCl/CaSiO$_3$	1	330	9.5	59.5	17.4	32.6	10.0	40.1	84.2
	2	330	9.5	42.9	17.7	13.5	10.8	58.0	94.8
	2.5	330	9.5	38.0	17.1	10.2	10.6	62.0	100.0
	3	330	9.5	41.5	16.6	8.0	10.4	65.1	95.7
	3.5	372	9.5	95.0	18.9	6.2	14.2	58.9	79.1
10%CsCl/CaSiO$_3$ in the air	0.5	346	14.8	72.1	7.4	0	29.6	62.8	66.0
	1.5	346	14.8	89.3	0	0	30.5	69.4	70.0
	2.0	318	14.8	57.0	0	0	27.7	72.2	57.6
	2.5	318	14.8	77.5	0	0	27.3	72.6	68.5

δ (%) -balance on carbon,
τ - duration of the test, hour
TCE – trichloroethene
VC – vinyl chloride;
VDC – vinylidenechloride
DCE – dichloroethene

When 2 % TCE/N$_2$ was passed through 1% CsCl/CaO·SiO$_2$ at 300-350 °C, the catalyst provided 95-99% conversion and higher than 60% selectivity for VDC over 10 h. Only with fivefold increase in concentration of TCE in the feed gas the selectivity began to decrease. With 10 % TCE/N$_2$, the quantitative conversion of TCE over 10 % CsCl/CaO·SiO$_2$ was achieved at 365 °C, but VDC selectivity under these conditions decreased to 60%. The low decrease in the selectivity of the process conducted at higher temperature (365 °C) for 6 h should be considered as a positive result.

At 14.8 % concentration of TCE in N$_2$ the conversion was ~ 80 % at 346 °C and VDC selectivity was 48%.

Thedehydrochlorination over 10 % CsCl/CaO·SiO$_2$ conducted in the presence of air gave the unexpected result. The reaction direction waschanged radically under these conditions: VDC was not formed at all and the major products were *cis*- and *trans*-1,2-DCE. As oxygen is known to inhibit many homolytic reactions, we can suggest that VDC is formed over this catalyst by the radical mechanism [5]. Therefore, the use of radical initiators may increase the selectivity of this catalyst for VDC.

Interesting results were obtained with the catalytic system comprising 10 % (MgO-CsCl in a mass ratio of 1: 1) supported on SiO$_2$ (Table 2).

DHC of 2 % TCE/N$_2$ at 302 °C proceedsquantitatively over 20 h with selectivity for VDC of more than 80%. As TCE concentration is raised to 8.5%, the conversion and VDC selectivity gradually decrease and over first 5-10 h they remain almost constant, that is, ~ 30% and 57-60%, respectively.

Table 2. **Cracking of TCE over catalytic system 10%(MgO-CsCl)/SiO_2**

τ, h	T, °C	Space velocity, h^{-1}	TCE, vol.%	Conversion, %	Selectivity,%				δ, %
					VC	VDC	trans-DCE	cis-DCE	
1	200	120	2	30.2	0.0	96.3	0.9	2.8	96
5	200	120	2	13.6	3.2	86.5	5.1	5.1	94
7	254	120	2	63.1	1.2	89.5	3.9	5.4	86
8	302	120	2	100.0	3.4	84.9	5.5	6.3	100
1.6	200	133	3.4	16.7	0.1	87.2	6.6	6.2	92
2.2	246	133	3.5	57.0	0.0	95.2	2.4	2.4	64
3.4	246	133	3.5	38.1	1.4	81.8	8.4	8.4	80
4.0	300	133	3.5	97.6	3.5	75.0	9.3	12.2	47
5.5	300	114	3.3	97.4	0.0	75.1	10.6	14.3	48
6.2	300	114	3.2	90.7	0.0	74.3	10.7	14.9	52
8.3	300	114	3.3	80.3	0.0	73.1	11.5	15.5	58
0.4	300	121	7.9	99.8	0.3	74.5	10.4	14.9	52
1.5	300	121	7.5	86.8	2.2	71.2	10.9	15.7	62
2.4	300	121	7.6	79.6	3.2	69.1	11.0	16.7	60
3.0	300	121	7.7	71.8	3.3	65.9	12.0	18.8	64
4.1	300	121	7.5	56.4	4.1	64.7	11.6	19.6	71
7.8	300	132	8.0	30.6	3.4	57.5	14.5	24.6	85
8.5	300	132	7.8	29.7	3.4	56.8	14.3	25.6	87
10.0	300	132	7.9	31.8	1.8	56.5	13.2	28.5	83

δ (%) -balance on carbon,

τ - duration of the test, hour
TCE – trichloroethene
VC – vinyl chloride;
VDC – vinylidenechloride
DCE – dichloroethene

Table 3. **Determination of specific surface area and relative basicity of some metal oxides before and after dehydrochlorination (**S_{tot}, **-** total surface,m^2;S_{sp}- specific surface area, m^2/g)

Sample	Before/afterwork	*Weight, g*	V_{Ar}, adsorbed, ml	S_{tot}, m^2	S_{sp}, m^2/g	V_{CO2}, ml	B_{CO2}, mol/m$^{2}\cdot10^{19}$
20%CsCl/CaO·SiO_2	before	2.0084	1.40	6.6	3.3	0.58	0.24
	after	1.003	1.82	8.6	8.6	0.48	0.20
1%CsCl/CaO·SiO_2	before	0.7798	0.66	3.1	4.0	0.66	0.57
	after	0.9980	0.91	4.3	4.3	0.07	0.04
10%CsCl/MgO·SiO_2	before	0.9994	9.7	45.9	46.0	0.76	0.04
	after	1.0024	5.13	24.28	24.22	0.35	0.04
10%CsCl/CaO·SiO_2	before	0.5140	0.31	1.47	2.8	0.52	0.97
	after	0.5100	0.54	2.55	5.1	0.07	0.08
10%CsCl/$CaSiO_3$	before	0.4020	4.28	20.23	50.33	0.12	0.02
	after	0.4070	3.49	16.51	40.55	0.12	0.02

As it follows from table 3, the S_{sp} values for metal oxides loaded with 10% CsCl increases after the dehydrochlorination. It can be conjectured that the increase in S_{sp} of the strongly basic metal oxide after dehydrochlorinationis associated with phase transformations in the bulk of catalysts induced by chlorination reactions [8]. On the other hand, the low-basicity oxides are passivated evidently through chlorination of the extended surface area of MgO, neat or in systems with other oxides.

A great body of patent data on the use of Group IA metal chloride and, in particular, CsCl as the catalysts of dehydrochlorination displayed the problem of the effect the chlorides make on basicity of the catalytic systems composed of the metal chlorides and oxides.It can be supposed that Cl^- ions in CsCl/MgO act as additional proton-acceptor centers while cations Cs^+ play the role of L-acid sites on which the abstraction of Cl^- from TCE occurs [8, 9].

The current results clearly show the very different behaviors of the catalysts, which implies various reaction pathways on these catalysts, based on the analysis of literature data can be assumed thatdehydrochlorinationof $CHCl_2(\alpha)–CH_2Cl(\beta)$ the VDC is formed owing to abstraction of the more reactive α-proton for which purpose even weakly basic sites of surface. It can be assumed that strongly basic sites react with the less acidic β-protons as well and this may deteriorate a selectivity of thedehydrochlorination reaction. For this reason, it is difficult to predict the dependence of selectivity of the metal oxide catalysts for VDC on their basicity. Moreover, the basicity of oxides can influence their chemical interaction with hydrogen chloride evolving on dehydrochlorinationand, therefore, the contribution of the catalytic dehydrochlorinationto the overall process [10].

Conclusions

The exploration of the systems based on simple and double magnesium, calcium and silicon oxides is a prospective direction in the development of the selective catalyst for TCE dehydrochlorination. Two promising catalysts of this type have already been found, namely, 10% $(MgO\cdot CsCl)/SiO_2$ and 10% $CsCl/CaO\cdot SiO_2$.

As in both cases TCE conversion and VDC selectivity slowly decrease in time, it is necessary to find the means to stabilize these parameters. These systems are suitable to study the factors providing the binding and removal of HCl from the reaction zone. A possible way to increase the selectivity for VDC is the creation of the conditions favoring TCEdehydrochlorinationinto VDC by the radical mechanism, which was observed in experiments with 10% $CsCl/CaSiO_3$.

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Каталітична переробка хлорорганічних відходів у цінні мономери

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Дегідрохлорування 1,1,2-трихлоретану, який є одним із хлорвмісних органічних відходів, що утворюються в процесі перероблення дихлориду етилену, до хлориду вінілідену здійснювали за допомогою каталізаторів $MgO \cdot SiO_2$ та $CaO \cdot SiO_2$, модифікованих CsCl. Цей процесс проводили в проточному реакторі з нерухомим шаром каталізатора. Синтезовані каталізатори було охарактеризовано за площею поверхні та основними властивостями до/після реакції. Перспективні результати були одержані на каталізаторі 10 % MgO-CsCl, нанесеному на SiO_2. Дегідрохлорування 2 % 1,1,2-трихлоретану/N_2 при 302 °C відбувається кількісно протягом 20 год із селективністю щодо хлориду вінілідену понад 80 %. Ці системи придатні для вивчення факторів, що забезпечують зв'язування та виведення HCl із зони реакції.

Ключові слова: дегідрохлорування, 1,1,2-трихлоретан, вініліденхлорид, каталізатор