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Д.В. Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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HETEROGENEO-CATALYTIC SYNTHESIS OF VINYL CHLORIDE AND CHLOROPRENE FROM ACETYLENE

Abstract. For the catalytic hydro chlorination of acetylene in the vapor phase based on local raw materials for the Zola-gel technology, we selected an active and high-performance catalyst $(ZnCl_2)_x$*$(FeCl_3)y$*$(CuCl_2)_z$ and also under the influence of various factors (partial pressure, temperature, ratio of reagent properties, contact time, catalyst concentration) the yield and reaction rate were studied with the participation of the selected catalyst. Based on the results obtained, a kinetic equation was proposed that satisfies the reaction, its adequacy is estimated, and a scheme of the reaction mechanism and the basis on the kinetic model are proposed. Because of studying the influence of the mass transfer coefficient on the process productivity and the influence of other factors, the technological parameters of the catalytic flocculants of vinyl chloride and the chloroprene extraction reactor of acetylene were calculated and the main indicators of the compatibility of technological capabilities of environmental and economic factors were substantiated. The successful development of the production of VC from ethylene was associated with the search for a cheaper hydrocarbon feed than acetylene. Analysis of the structure of the cost price of VC obtained by various methods shows that the acetylene method gives the highest cost, with acetylene accounting for about 90%. However, the world hydrocarbon price environment is constantly changing. In the future, it is possible to increase prices for oil and gas raw materials, the convergence of prices for acetylene and ethylene, and the latter may lose its main advantage in this regard.

Keywords: vinyl chloride, synthesis, acetylene, polyvinyl chloride, catalyst.

Introduction. It is shown for example; that the cost of VC is approximately the same if the cost of acetylene is higher than ethylene, even by 40%. A known method of producing VC by gas-phase hydro chlorination of acetylene at 80–200 ^{0}C in the presence of a fluidized catalyst bed - mercuric chloride on activated carbon and isolation of the target product by distillation. This method is characterized by insufficiently high productivity of the used catalyst. Vinyl chloride (VC) and chloroprene are a valuable monomer for the production of polyvinyl chloride - artificial rubber and others. Polyvinyl chloride (PVC) is one of the most versatile thermoplastics with a wider range of applications than all other plastics. Not surprisingly, it is used everywhere and has a positive attitude towards it. Indeed, PVC is a universal, stable, hygienic, safe and cost-effective material that has significant advantages over other materials. Over 90% of vinyl chloride is consumed in the production of polyvinyl chloride. PVC is used for molding and molding of hard products - window and doorframes, water pipes, technical and construction products. From plasticized PVC (flexible PVC) linoleum is made, insulation for wires. Apply PVC for the manufacture of artificial leather, shoes, chemical dishes [1]. Vinyl chloride is currently mainly produced in several ways [2].

Methods for producing vinyl chloride. Synthesis of VC by alkaline dehydrochlorination of one, 2-dichloroethane. In industry, two methods for dehydrochlorination with alkali are used to obtain VC from DCE: in the liquid phase: $CH_2Cl - CH_2Cl + NaOH \rightarrow CH_2 = CHCl + NaCl + H_2O$; in the gas phase: $CH_2Cl - CH_2Cl \rightarrow CH_2 = CHCl + HCl$.

Liquid phase dehydrochlorination is carried out in vertical batch or continuous cylindrical reactors equipped with a jacket and a propeller stirrer. Methyl or ethyl alcohol and 42% alkali are charged to the reactor, and then DCE is gradually added.

Due to the presence of alcohol, which dissolves both DCE and alkali, the process takes place in a homogeneous liquid medium. Temperature 85–90 ^{0}C at a pressure of 2 atmospheres. The duration of the process is 5–6 hours. The disadvantage of this method is the frequency. The consumption of alkali and alcohol is also great. For 1 kg of VC, 0.82 tons of solid alkali and 0.12 kg of alcohol (100%) are needed. Therefore, a continuous process of alkaline dehydrogenation of DCE has been developed - by mixing DCE with 6% sodium hydroxide solution, at T = 140 ^{0}C and a pressure of 10–12 atmospheres. Contact duration 2-3 minutes. The yield of BX is 90–92%.

Getting VC through the stage of formation of DCE. The synthesis of chemical compounds of their ethylene and chlorine is carried out in two stages: chlorination of ethylene; the removal of hydrogen chloride.

Ethylene chlorination is usually carried out in the liquid phase. As a feedstock, both concentrated ethylene and ethylene diluted with inert gases are used. The reaction proceeds according to the scheme:

$$CH_2 = CH_2 + Cl_2 \rightarrow CH_2Cl - CH_2Cl.$$

The reaction is carried out in a DCE solution at a temperature of 25–50 ^{0}C and a pressure of 1 to 20 atmospheres in the presence of chlorides. The yield of DCE reaches 95% with an ethylene conversion of 98%.

The removal of hydrogen chloride can be carried out in various ways. In one method, dichloroethane is treated with alcohol alkali or an aqueous alkali solution:

$$CH_2Cl - CH_2Cl \rightarrow CH_2 = CH_2Cl + HCl$$

However, due to the consumption of large quantities of auxiliary substances, this method is very disadvantageous and is currently almost never used in industry. Thermal decomposition of dichloromethane is widely used in industry:

$$CH_2Cl - CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

Pyrolysis is carried out at a temperature of about 500 ^{0}C above pumice or kaolin. The reactor consists of two pipes inserted into each other (with a diameter of 100 and 70 mm). The VC yield is up to 95%, and the degree of DCE conversion is maintained at a level not exceeding 50%. Specific capital costs for the production of VC by this method are relatively small. The advantage of the method is the availability and low cost of raw materials. The main disadvantage of this method is the need for the disposal of large quantities of hydrogen chloride [3].

The combined process of obtaining VC from a concentrated mixture of acetylene and ethylene. The process consists in obtaining one, 2-dichloroethane from ethylene, followed by its thermal dehydrochlorination at 400–450 ^{0}C in VC; Hydrogen chloride released in this process is sent to acetylene hydrochlorination. The process is described in the following diagram:

$$CH \equiv CH + HCl \rightarrow CH_2 = CHCl$$
$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2 - CH_2Cl$$
$$ClCH_2 - CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

The combined method for producing VC turned out to be 30 and 14% more economical than alkaline dehydrochlorination of 1, 2-dichloroethane and acetylene hydrochlorination, respectively, since 50% of acetylene is replaced with less expensive ethylene; At the same time, hydrogen chloride is skillfully used.

The mixture is sent for hydro chlorination, which is carried out at 180 ^{0}C; the degree of acetylene conversion is close to 100%. After extraction of the BX from the gas, the gas enters into the chlorination of the ethylene contained in it. The ratio between chlorine and ethylene provides a 2–3% excess of ethylene versus stoichiometric; the one, 2-dichloroethane formed after cooling and purification is transferred to dehydrochlorination, the degree of conversion of 1, 2-dichloroethane per passage is about 70%.

This method is economically disadvantageous, as half of the ethylene is replaced by acetylene that is more expensive.

Obtaining VC by catalytic chlorination of ethane. The Lummus Co announced the technology it developed for producing VC in a single reactor, which simultaneously carries out the stages of chlorination, oxidative chlorination and dehydrochlorination (the so-called “transcat process”).

The yield of vinyl chloride is 98% for chlorine and 80% for ethane. Thanks to the use of cheaper ethane, the cost of VC is reduced by 25%. The method is applicable to other combined processes.

In addition to the above, there are two more ways of synthesizing VC: oxidative chlorination of ethylene with ammonium chloride and oxidation of ethyl over chromium oxide precipitated on alumina.

Chlorine-balanced process for producing VC from ethylene. This process is a combination of three reactions: direct additive chlorination of ethylene in one, 2-dichloroethane, thermal dehydrochlorination of one, 2-dichloroethane in VC and oxidative chlorination of ethylene in VC using hydrogen chloride formed during dehydrochlorination:

$$2H_2C = CH_2 \rightarrow 2\ ClCH_2 - CH_2Cl$$

$$ClCH_2 - CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

$$CH_2 = CH_2 + 2HCl + 0{,}5O_2 \rightarrow CH_2 = CHCl + H_2O$$

$$3CH_2 = CH_2 + 2Cl_2 + 0{,}5O_2 \rightarrow 3CH_2 = CHCl + H_2O$$

As a result, VC is obtained from ethylene, chlorine, and oxygen, chlorine is completely consumed, and hydrogen chloride is not formed.

The ox chlorination step is carried out in a fluidized bed reactor at a pressure of 0.3-0.5 MPa at 210-250 ^{0}C. Ethylene, recycle gas and hydrogen chloride are mixed in a mixer, to which technical oxygen is added.

The pyrolysis of DCE in VC and HCl is carried out in a tube furnace under a pressure of 1.5-2.0 MPa and 500 ^{0}C. The resulting vinyl chloride contains 99.9% of the basic substance and is quite suitable for subsequent polymerization. Currently, this method is one of the most economical to obtain VC [4].

Getting VC from acetylene. The liquid-phase method for producing VC from acetylene and hydrogen chloride consists in passing the latter through a catalyst. The process is carried out at a temperature of 50-95 ^{0}C in the bubble-type reactors. The concentration of HCI in water should be at least 5%. Acetylene conversion per passage is 40-50% on copper catalysts and 75-90% on mercury.

Of great interest is conducting studies on the hydro chlorination of acetylene in the liquid phase in the presence of a homogeneous or suspension sublimate catalyst. The main difficulty in the implementation of the process is the choice of structural materials for a strapped reactor; for pumps, valves, etc.

The main advantage of the liquid-phase process [5] is the relative ease of solving the problem of heat removal, and, consequently, the enlargement of the reaction apparatus. The disadvantages of the process include the lower conversion of acetylene and the selectivity of the process, as well as the greater complexity of the hardware design of the reaction unit and the technological scheme [6, 7].

In order to eliminate this drawback, it is proposed that the catalyst used in the process be further promoted with lanthanum chloride. The performance of the catalyst is increased by 15-20%. The content of active substance (mixture of mercuric chloride and lanthanum chloride or their compounds) in the catalyst is 12.9 wt. percentage. The temperature of the process is 220 ^{0}C. Thus, the obtained data can be the basis for the development of a fundamentally new technological scheme for the production of VC from acetylene [8].

Hydrochlorination of acetylene in the gas phase. The successful development and implementation of this process in the industry was facilitated by the simplicity of technological design and high rates. The process is carried out in a stationary catalyst bed. The reactor is a shell-and-tube apparatus, in which the refrigerant circulates in the annular space, the catalyst is loaded into the tube space [9-14]. The temperature of the process is 120-220 ^{0}C. The catalyst is mercury dichloride (mercuric chloride) deposited on activated carbon. The sublimate catalyst (average mercuric chloride content 10-12%) is characterized by high activity and selectivity, the degree of acetylene conversion is about 99%, and the selectivity according to VC is 98-99%. As a rule, hydrochlorination is carried out in a mode with 5-10% excess hydrogen chloride. The unit capacity of the reactor is 2-10 thousand tons per year. Due to the rapid development of the production of VC based on ethylene according to a balanced scheme, the process of hydrochlorination of acetylene has now lost the position of the leading industrial method and exists only as a chemical stage of combined schemes.

First subjected to hydrochlorination without separation, and then ethylene is chlorinated to dichloroethane, after dehydrochlorination of which the resulting VC is returned to hydrochlorination.

The successful development of the production of VC from ethylene was associated with the search for a cheaper hydrocarbon feed than acetylene. Analysis of the structure of the cost price of VC obtained by various methods shows that the acetylene method gives the highest cost, with acetylene accounting for about 90%. However, the world prices for hydrocarbons are constantly changing. In the future, it is possible to increase prices for oil and gas raw materials, the convergence of prices for acetylene and ethylene, and the latter may lose its main advantage in this regard. It is shown for example; that the cost of VC is approximately the same if the cost of acetylene is higher than ethylene, even by 40%.

All of the above convincingly shows that the problem of creating new production of VC from acetylene at the modern technical and economic level, as well as the improvement and intensification of existing ones, is relevant [15]. The production of VC from acetylene in our country has a low technological level. One of the most mastered methods is the combined method described above. The Japanese company «Kureha» developed this technology [16-17].

VC at the stage of hydrochlorination of acetylene is formed by the interaction of acetylene contained in the cracking gas of naphtha and hydrogen chloride, obtained at the cracking stage of DCE in the presence of a catalyst - mercuric chloride supported on activated carbon, by the reaction:

$$CH \equiv CH + HCl \rightarrow CH2 = CHCl + 25.5\ kcal / g \cdot mol$$

Further development of the industrial method of producing VC from acetylene can go along the path of creating aggregates of large unit capacity (60-120 thousand tons per year). However, the increase in the productivity of acetylene hydrochlorination reactors in a stationary catalyst bed is limited primarily by the heat removal rate. A study of the kinetics of this reaction showed that under industrial conditions, the specific activity of the catalyst is 10-15% of the kinetically possible. An increase in the load on the catalyst without effective heat removal leads to overheating of the catalyst, sublimation of mercury chloride and its entrainment and, ultimately, a significant reduction in the life of the catalyst. Therefore, the implementation of the acetylene hydrochlorination reaction in a stationary unit of high unit power will require significant complication of the hardware design of the reactor unit. Therefore, further improvement of the catalyst is necessary [18].

For effective heat removal, dilution of the catalyst with inert materials is also used, and dilution is carried out only in the first catalyst layer. This reduces local overheating and prevents rapid degassing of the catalyst [19].

A.L. Macho and B.K. Turin dealt with the issue of increasing catalyst productivity. The process of obtaining VC from acetylene is carried out on a catalyst, which is a mechanical mixture of activated carbon without any impregnation and coal impregnated with a 10% mercuric chloride solution, in a ratio of 1: 3. It is proposed to conduct the process first on a mixture of activated carbon without impregnation and coal, impregnated with a 10% solution of mercuric chloride, and then on the catalyst, consisting of coal, impregnated with a 10% solution of mercuric chloride and 8% solution of ammonium vanadium. The reaction gas mixture is fed from the bottom up. A moving layer of heat carrier (water) of isothermal cooling removes heat from the reaction zones. The performance of the method increases by 1.5 times [20].

The traditional method of manufacturing the catalyst is to impregnate the carrier with an aqueous solution of mercuric chloride followed by drying.

The method of manufacturing such a catalyst developed at TU NPO Sintez (Moscow) consists in the fact that mercuric chloride is applied to the carrier by sublimation of dry salt, followed by absorption on the surface of activated carbon. This method is called STO - dry heat treatment. According to the developers, the SRT method makes it possible to obtain a better catalyst, since the mercuric chloride is deposited in fact with a monomolecular layer, that is, the probability of cluster formation is reduced. Such a catalyst is characterized by a longer service life and, possibly, increased activity. According to the staff of NPO Sintez, the application of the STO method can extend the life of the catalyst by 1.5–2 times. In addition, the stage of preparation of an aqueous solution of mercuric chloride and, as a consequence, the removal of mercury containing wastewater is excluded. [Nineteen].

Thus, all of the above makes this method quite promising in technical and economic terms, which explains the continuation of work to improve it.

Currently, the annual global productivity of vinyl chloride is 42 million tons of which 98% is spent on polyvinyl chloride. The largest vinyl chloride companies are Oxy-Vinyl, Dow Chemical, Mitsubishi Chemical, Georgia Gult, which produce vinyl chloride by catalytic hydrochlorination of acetylene. The disadvantages of their methods are: they use a toxic substance ($HgCl_2$), unstable catalysts, a low degree of catalyst activity (0.5-1 year), and also due to the volatility of mercuric chloride, the low-temperature process (150-180 ^{0}C) is another disadvantage of this method lies in the fact that the catalyst carrier is activated carbon, which corresponds to its low mechanical strength [21-23].

The most convenient way to obtain vinyl chloride in the Republic of Uzbekistan is the preparation of a cheap, active, selective and high-performance catalyst based on domestic raw materials for the catalytic hydrochlorination of acetylene.

In general, the reaction of catalytic hydro chlorination of acetylene is as follows:

$$\mathrm{HC{=}CH + HCl \rightarrow CH2 = CHCl}, \ \Delta H = -112.4 \ \mathrm{kJ / mol}.$$

The process of acetylene hydrochlorination is in addition to reversible. At low temperatures, the equilibrium mixes to the right, at 200 ^{0}C Кр = $8{\cdot}10^4$, and at 300 ^{0}C Кр = $7{\cdot}10^2$. Therefore, when acetylene reacts with hydrogen chloride, vinyl chloride is formed from the beginning, and then 1.1-dichloroethane:

$$\mathrm{CH \equiv CH \xrightarrow{HCl} CH_2 = CHCl \xrightarrow{HCl} CH_3 - CHCl_2}$$

Therefore, to obtain vinyl chloride by the first reaction, the HgCl2 and CuCl salts that accelerate the indicated reaction are a selective catalyst. When acetylene is hydrochlorinated, the following adverse reactions are possible:

$$\mathrm{CH_2 = CHCl + HCl \rightarrow CH_3 - CHCl_2}$$

$$\mathrm{2CH \equiv CH \rightarrow CH_2 = CH - C \equiv CH}$$

$$\mathrm{CH_2 = CH - C \equiv CH + HCl \rightarrow CH_2 = CHCl - CH = CH_2}$$

Conclusion. Therefore, the hydrochlorination of acetylene and its homologues is carried out in the presence of selective catalysts that accelerate only the first stage of addition. For this purpose, salts of divalent mercury and monovalent copper are effective.

Of divalent mercury salts, mercuric chloride $HgCl_2$ is used. In addition to the main reaction, it greatly accelerates the hydration of acetylene with the formation of acetaldehyde. For this reason, and because of the deactivation of mercuric chloride in hydrochloric acid solutions, it is used in gas-phase process at 150-200 ^{0}C, using possibly drier reagents. In this case, acetaldehyde (due to a small admixture of moisture) and 1.1-dichloro-ethane are incidentally formed, but the yield of the latter does not exceed 1%. Vinyl chloride is currently mainly prepared in two ways: by hydrochlorination of acetylene with hydrogen chloride at 190-220 ^{0}C in the presence of a mercuric chloride supported on activated carbon and by dehydrochlorination of 1,2-dichloroethane. Chloroprene is mainly obtained by hydrochlorination of vinylacetylene in the presence of mercury and copper (at 50-60 ^{0}C in the presence of copper chloride) catalysts. The joint catalytic synthesis of vinyl chloride and chloroprene by hydrochlorination of acetylene is an urgent task of synthetic organic chemistry. In order to simultaneously produce vinyl chloride and chloroprene, we studied the gas-phase coupled.

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ВИНИЛ-ХОРИДИ ЖӘНЕ ХЛОРОПРЕНДЕР ГЕТЕРОГЕНДІ-КАТАЛИТИКАЛЫҚ СИНТЕЗІ

Аннотация. «Зол-гель» технологиясына арнап жергілікті шикізатқа негізделген бу фазасында ацетиленнің каталитикалық гидрохлорлану реакциясына белсенді және өнімділігі жоғары катали-заторды (ZnCl2) x * (FeCl3) y * (CuCl) z таңдап алдық, сонымен қатар түрлі факторлар әсерінен (ішінара қысым, температура, реактивтік қасиеттер қатынасы, байланыс уақыты, катализатор концентрациясы және т.б.) таңдалған катализатордың қатысуы негізінде шығым және реакция жылдамдығы зерттелді. Алынған нәтижелерге сүйене отырып, реакцияны қанағаттандыратын кинетикалық теңдеу ұсынылды, оның адекваттығы бағаланады және реакция механизмінің сұлбасы және кинетикалық модель негізі ұсынылады.

Масса ауысу (тасымалдау) коэффициентінің процесс өнімділігіне және басқа факторларға әсерін зерттеу нәтижесінде винилхлоридтің каталитикалық флокулянты және ацетиленнің хло-рофрен алу реакторының технологиялық параметрлері есептелді және экологиялық, экономикалық факторлардың технологиялық мүмкіндігі үйлесімділігінің негізгі көрсеткіштері негізделді. Зерттеу нәтижесінде винилхлорид пен хлоропренді біріктіріп қабылдаудың технологиялық сызбасы жасалды, үдерістің материалдық балансы есептелді.

Сондай-ақ, винилхлорид пен хлоропреннің бірлескен өндірісі, ацетиленнің сұйық фазадағы гидрохлорация үдерісі зерттелді. Ацетиленнің жоғары селективтілігі мен конверсиясымен винил-хлорид пен хлоропрен өндірісін қамтамасыз ететін үдеріс параметрлері анықталды. Ацетилен гидрохлорлаудың кейбір кинетикалық заңдылықтары да зерттелді. Сондықтан ацетилен мен оның гомологтарын гидрохлоризациялау тек қосудың алғашқы кезеңін жеделдететін селективті катали-заторлардың қатысуы негізінде жүзеге асырылады. Бұл үшін бөлінетін сынап пен моновалентті мыс тұзы тиімді.

Бөлінетін сынап тұзынан $HgCl_2$ сынап хлориді қолданылады. Негізгі реакциядан басқа ацетилдегид пайда болуы арқылы ацетилен гидратациясын едәуір жылдамдатады. Сондықтан тұз қышқылы ерітіндісінде сынап хлоридін залалсыздандыруға байланысты құрғақ реагенттерді пайдаланып, 150–200 ^{0}C температурадағы газ фазасында қолданылады. Бұл жағдайда ацетальдегид (ылғалды қоспаның аздығына байланысты) және 1,1-дихлороэтан кездейсоқ қалыптасады, бірақ соңғысының шығымы 1%-дан аспайды. Винилхлорид қазіргі кезде негізінен екі жолмен: активтендірілген көмірге қолдау көрсететін сынап хлоридінің қатысуы негізінде ацетиленді сутегі хлоридімен 190–220 ^{0}C-та гидрохлорлау және 1,2-дихлорэтанды дегидрохлорлау арқылы дайындалады. Хлорофрен негізінен сынап пен мыстың қатысуы арқылы (мыс хлоридінің қатысуы 50–60 ^{0}C) катализатор қосу негізінде винилацетилен гидрохлорлайды.

Қазіргі уақытта винилхлоридтің жыл сайынғы әлемдік өнімділігі 42 млн. тоннаны құрайды, оның 98% поливинилхлоридке жұмсалады. Винилхлоридтің ірі компаниялары – ацетиленнің каталитикалық гидрохлорациясы арқылы винилхлорид шығаратын Oxy-Vinyl, Dow Chemical, Mitsubishi Chemical, Georgia Gult. Әдістерінің кемшілігі: улы затты ($HgCl_2$), тұрақсыз катализаторды, катализатордың төмен деңгейлі белсенділігін (0,5–1 жас) пайдаланады, сонымен қатар сынап хлоридінің құбылмалылығына байланысты үдеріс төмен температурада жүреді (150–180 °C), аталған әдістің тағы бір кемшілігі мынадай: активтендірілген көміртегі оның әлсіз механикалық беріктігіне сәйкес келетін катализатор тасымалдаушысы қызметін атқарады.

Винилхлорид алудың ыңғайлы әдісі – ацетиленнің каталитикалық гидрохлорациясы үшін отандық шикізат негізінде арзан, белсенді, селективті және жоғары өнімді катализатор дайындау.

Түйін сөздер: винилхлорид, синтез, ацетилен, поливинилхлорид, катализатор

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ГЕТЕРОГЕННО-КАТАЛИТИЧЕСКИЙ СИНТЕЗ ВИНИЛХЛОРИДА И ХЛОРОПРЕНА ИЗ АЦЕТИЛЕНА

Аннотация. Для реакции каталитического гидрохлорирования ацетилена в паровой фазе на основе местного сырья для «Зол–гель» технологии, нами был выбран активный и высокопроизводительный катализатор $(ZnCl_2)_x*(FeCl_3)_y*(CuCl)_z$ а также под влиянием различных факторов (парциальное давление, температура, соотношение свойств реагентов, время контакта, концентрации катализатора и.др) были исследованы выход и скорость реакции с участием выбранного катализатора. На основании полученных результатов было предложено кинетическое уравнение, удовлетворяющее реакции, оценена его адекватность и предложена схема механизма реакции, основания на кинетической модели.

В результате исследования влияния коэффициента массопередачи (транспортирования) на производительность процесса и влияния других факторов были рассчитаны технологические параметры каталитического флокулянта винилхлорида и хлоропренового экстракционного реактора ацетилена и обоснованы основные показатели совместности технологических возможностей экологических и экономических факторов.

В результате проведенных исследований создана технологическая схема совместного поступления винилхлорида и хлоропрена, а также рассчитан материальный баланс процесса.

Также изучен процесс совместного получения винилхлорида и хлоропрен, гидрохлорированием ацетилена в жидкой фазе. Найдены параметры процесса, обеспечивающие получение винилхлорида и хлоропрена с высокой селективностью и конверсией ацетилена. Изучены некоторые кинетические закономерности процесса гидрохлорирования ацетилена.

Поэтому гидрохлорирование ацетилена и его гомологов проводят в присутствии селективных катализаторов, ускоряющих только первую стадию присоединения. Для этой цели эффективными являются соли двухвалентной ртути и одновалентной меди.

Из солей двухвалентной ртути применяют сулему $HgCl_2$. Кроме основной реакции, она сильно ускоряет и гидратацию ацетилена с образованием ацетальдегида. По этой причине, а также из-за дезактивирования сулемы в солянокислых растворах ее используют в газофазном процессе при 150–200 ^{0}C, применяя возможно более сухие реагенты. При этом побочно образуются ацетальдегид (за счет небольшой примеси влаги) и 1,1-дихлорэтан, но выход последнего не превышает 1 %. Хлористый винил в настоящее время в основном получают двумя способами: гидрохлорированием ацетилена хлористым водородом при 190–220 ^{0}C в присутствии сулемы, нанесенного на активированный уголь и дегидрохлорированием 1,2-дихлорэтана. Хлоропрен в основном получается гидрохлорированием винилацетилена в присутствии ртутных и медных (при 50-60 ^{0}C в присутствии полухлористой меди) катализаторов.

В настоящее время ежегодная мировая производительность винилхлорида составляет 42 млн тонн, из них 98% расходуется на получение поливинилхлорида. Самые большие компании по производству винилхлорида – фирма Oxy-Vinyl, Dow Chemical, Mitsubishi Chemical, Georgia Gult, которые при каталитическом гидрохлорирования ацетилена получают винилхлород. Недостатками их методов являются: применяют ядовитое вещество ($HgCl_2$), нестабильные катализаторы, низкая степень роботы катализатора (0,5–1 год), а также из-за летучести сулемы процесс-низкотемпературный (150–180 ^{0}C) ещё одним из недостатком данного метода заключается в том, что носителем катализатора служит активированный уголь, что соответствует его низкой механической прочности.

Самым удобным способом получения винилхлорида являются приготовление дешевого, активного, селективного и высокопроизводительного катализатора на основе отечественного сырья для каталитического гидрохлорирования ацетилена.

Ключевые слова: винилхлорид, синтез, ацетилен, поливинилхлорид, катализатор.

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