PREPARATION OF CATALYSTS FOR METHANE OXYCHLORINATION AND PRELIMINARY TESTING OF CATALYSTS.

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Abstract. In the work, catalysts for methane oxychlorination were prepared and the process of preliminary testing of the prepared catalysts was carried out. Thermal analysis of the catalysts was carried out by Q-1500D derivatography, the porous structure was determined by nitrogen adsorption using the NOVA 1200e device, the surface area of the catalyst was calculated by the BET method, and the average mesopore volume was calculated by the BJH method. The composition of the catalyst samples was studied by X-ray phase analysis (XPA) using a DRON-4 diffractometer under monochromatic CuKα radiation. The peaks were measured on a 100-point scale by height. The interplanar distance in the crystal lattice was calculated using the Wolf-Bragg formula. Qualitative and quantitative analysis of the reaction products was determined using LHM-80 and “Crystal 4000” chromatographs. **The purpose of the work** is to prepare catalysts for methane oxychlorination and conduct preliminary testing of the prepared catalysts.

Keywords: Monochloromethane, oxychlorination, methane, ethylene, propylene, pyrolysis, catalyst, porosity, oxygen, nitrogen, hydrogen chloride.

Аннотация. В работе были приготовлены катализаторы для оксихлорирования метана и проведены предварительные испытания приготовленных катализаторов. Термический анализ катализаторов проводился методом дериватографии Q-1500D, пористая структура определялась методом адсорбции азота на приборе NOVA 1200e, площадь поверхности катализатора рассчитывалась методом БЭТ, а средний объем мезопор – методом BJH. Состав образцов катализаторов исследовался методом рентгенофазового анализа (РФА) на дифрактометре ДРОН-4 в монохроматическом CuKα-излучении. Пики измерялись по высоте в 100-балльной шкале. Межплоскостное расстояние в кристаллической решетке рассчитывалось по формуле Вольфа-Брэгга. Качественный и количественный анализ продуктов реакции проводили на хроматографах ЛХМ-80 и «Кристалл 4000». **Цель работы** – приготовление катализаторов оксихлорирования метана и проведение их предварительных испытаний.

ISSN 3030-3907

Ключевые слова: монохлорметан, оксихлорирование, метан, этилен, пропилен, пиролиз, катализатор, пористость, кислород, азот, хлористый водород.

Anotatsiya. Ishda metan oksixlorlash uchun katalizatorlar tayyorlandi va tayyorlangan katalizatorlarni dastlabki sinovdan o'tkazish jarayoni amalga oshirildi. Katalizatorlarning termik tahlili Q-1500D derivatografiyasi yordamida amalga oshirildi, g'ovakli tuzilishi NOVA 1200e qurilmasi yordamida azot adsorbsiyasi orqali aniqlandi, katalizatorning sirt maydoni BET usuli bilan hisoblandi va o'rtacha mezopora hajmi BJH usuli bilan hisoblandi. Katalizator namunalarining tarkibi monoxromatik CuKα nurlanishi ostida DRON-4 difraktometri yordamida rentgen fazasi tahlili (XPA) orqali o'rganildi. Cho'qqilar balandlik bo'yicha 100 balli shkala bo'yicha o'lchandi. Kristall panjaradagi tekisliklararo masofa Wolf-Bragg formulasi yordamida hisoblandi. Reaksiya mahsulotlarining sifat va miqdoriy tahlili LHM-80 va “Crystal 4000” xromatograflari yordamida aniqlandi. **Ishning maqsadi-**metan oksixlorlash uchun katalizatorlarni tayyorlash va tayyorlangan katalizatorlarni dastlabki sinovdan o'tkazishdir.

Kalit so'zlar: Monoxlorometan, oksixlorlash, metan, etilen, propilen, piroliz, katalizator, g'ovaklik, kislorod, azot, vodorod xlorid.

Introduction.

The method of obtaining alkenes by catalytic pyrolysis of methyl chloride is based on the chemical processing of methane (natural gas). In this process, first, methane is oxychlorinated to obtain methyl chloride, and then, in the second stage, methyl chloride is catalytically pyrolyzed to obtain lower alkenes[1-5].

Among the alternative methods mentioned in the literature, the most promising method is the conversion of methane (natural gas) to ethylene via the intermediate product methyl chloride[6]. Currently, high-silica zeolites have high catalytic activity in the catalytic pyrolysis of methyl chloride to obtain C2-C4 alkenes [7-11].

Many studies have shown [12-16] that when high-silica zeolites are modified with metals such as Co, Fe, Mn, and Mg, the catalyst lifetime increases, which is explained by the fact that these metals reduce the degree of coking of the catalyst.

The activity promoter for the lanthanum-copper-based catalysts for the oxychlorolysis of methane with hydrogen chloride in the presence of air oxygen to obtain monochloromethane and di- and trichloromethane derivatives is lithium or potassium, which increases the stability of the catalyst[17-21].

EXPERIMENTAL PART

Method of preparing a mesoporous catalyst with high catalytic activity. In the work, UCC obtained from kaolin in the Pakhtachi district of the Samarkand

ISSN 3030-3907

region of the Republic of Uzbekistan was used as a porous carrier. A mesoporous catalyst with high catalytic activity was prepared as follows: 100 g of UCC was soaked in a 30% solution of CuCl2, KCl, ZnCl2, MnCl2 for 12 hours. Then, the mesoporous catalyst with high catalytic activity was isolated from the solution and dried in a nitrogen stream at 350-400°C for 3 hours and brought to a state of granules with a size of 5-7 mm.

The experiments were carried out in a flow reactor under differential reactor conditions in a laboratory setup. The experiments were carried out in a flow reactor made of chromium-nickel alloy with an internal diameter of 20 mm. The catalyst was placed in a 10 mm high part of the reactor. The rest of the reactor was filled with porcelain pieces. The height of the catalyst layer was ~ 2 mm. For qualitative and quantitative analysis of the products of the methane oxychlorination reaction, LHM-80 (thermal conductivity detector) and "Kristall 4000" (with a flame ionization detector) chromatographs were used. Thermal analysis of the obtained catalysts was carried out on a Q-1500D derivatography. The pore structure of the samples was studied using the low-temperature nitrogen adsorption method using the NOVA 1200 e device. The specific surface area of the samples was calculated using the BET method, and the average mesopore volume was calculated using the BJH method.

EXPERIMENTAL RESULTS AND DISCUSSION

As a result of the conducted studies, the following optimal conditions were determined for the catalytic oxychlorination reaction of methane with hydrogen chloride in the vapor phase in the presence of oxygen: a mesoporous catalyst composition with high catalytic activity, $(CuCl_2)_x \cdot (KCl)_y \cdot (ZnCl_2)_z \cdot (MnCl_2)_k$, the size of the mesoporous catalyst fractions with high catalytic activity is 0.7÷1.2 mm, P = 0.1 MPa, gas flow rate is 17.2 l/h, contact time is 0.1 sec, and linear flow velocity is 10.2 cm/sec.

The total gas flow rate in the reactor was kept constant by varying the nitrogen flow rate. This condition ensures that the reaction proceeds in the kinetic domain. The effect of by-products (methylene chloride, chloroform, carbon (IV) chloride, and products of the complete oxidation reaction of methane) was not taken into account, since under kinetic conditions the selectivity of the process to monochloromethane is more than 95%.

Based on the results obtained, the contact time for monochloromethane (Fig. 1),

ISSN 3030-3907

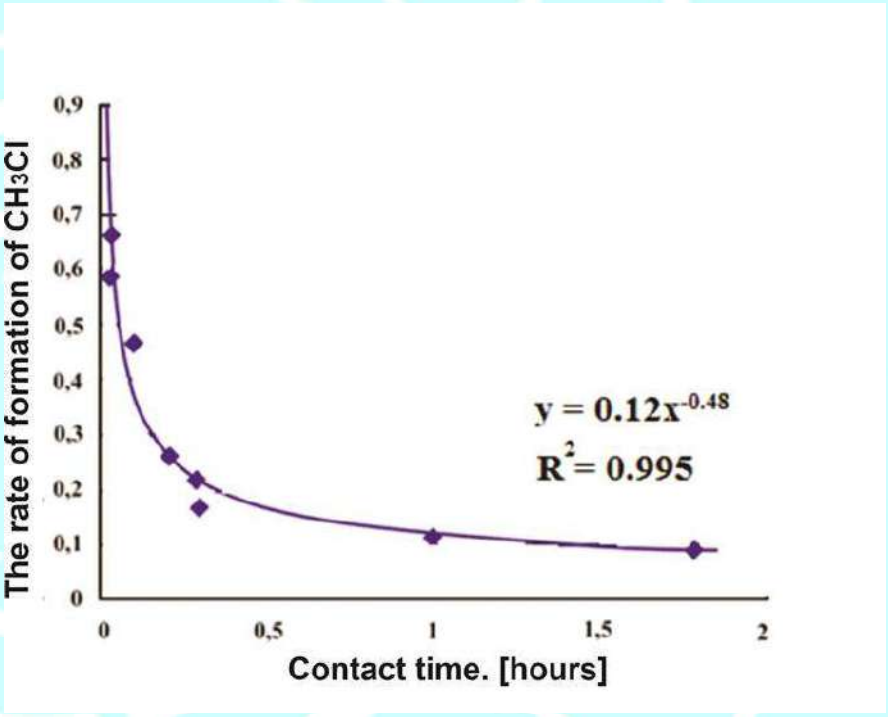


Fig. 1. Dependence of CH_3Cl formation on contact time.

polychloromethanes (Fig. 2)

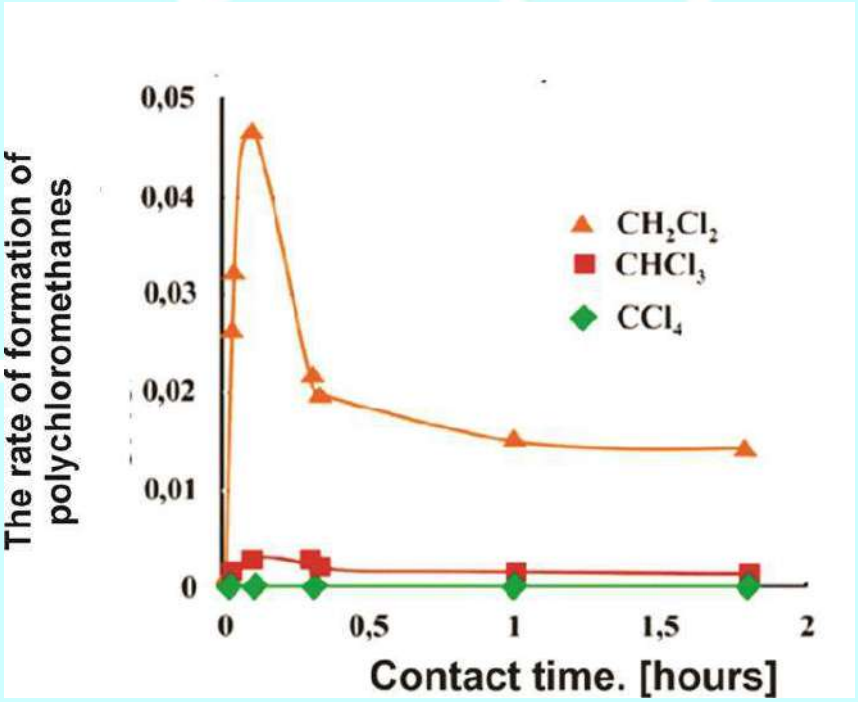


Fig. 2. Dependence of contact time on the formation of polychloromethanes.

and combustion products (Fig. 3)

ISSN 3030-3907

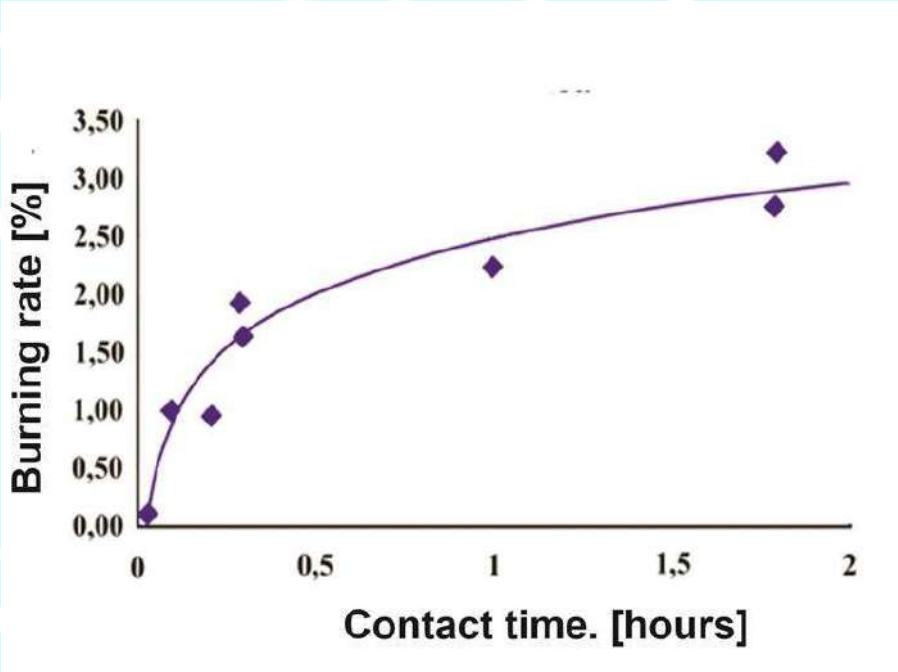


Fig. 3. Dependence of the combustion rate on the time constant

graphs of dependence on formations were made.

CONCLUSION

A catalyst with high activity, selectivity, and stability for methane oxychlorination was prepared by dissolving 30% $CuCl_2$, KCl, $ZnCl_2$, and $MnCl_2$ in a 30% solution of $CuCl_2$, KCl, $ZnCl_2$, and $MnCl_2$. The catalyst was subjected to preliminary tests and the conversion of monochloromethane, product selectivity, and combustion product formation were studied at a contact time of 2 seconds.

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ISSN 3030-3907