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Catalytic hydrochlorination of acetylene over a mixed zinc magnesium iron and bismuth chloride catalyst

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Каталитическое гидрохлорирование ацетилена на смешанном хлоридном катализаторе, содержащем цинк, магний, железо и висмут

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Abstract

Acetylene hydrochlorination provides a direct route to vinyl chloride monomer, but the replacement of volatile mercury catalysts remains a central process objective. This study examines a multicomponent chloride catalyst containing zinc, magnesium, iron, and bismuth chlorides and focuses on the effects of reactor temperature and acetylene gas hourly space velocity. The catalyst was evaluated in the 165 to 175 °C interval, with an acetylene gas hourly space velocity of 200 h^{-1}

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used as the reference throughput condition. Under these conditions, acetylene conversion reached 96.7 %, vinyl chloride yield was 91.1 %, and vinyl chloride selectivity reached 94.2 %. The result shows that the mixed chloride formulation can direct most converted acetylene toward vinyl chloride within a moderate temperature window. Reactor analysis indicates that 200 h^{-1} represents a practical compromise between contact time and throughput, while the narrow temperature interval limits both kinetic underperformance at the low end and thermally promoted side reactions or catalyst loss at the high end. The functions of the individual chlorides are discussed as mechanistic hypotheses rather than assigned active sites because phase and surface characterization were not available. The findings support further optimization based on acetylene conversion, space time yield, long duration stability, replicate measurements, and post reaction characterization.

Аннотация

Гидрохлорирование ацетилена представляет собой прямой способ получения мономера винилхлорида, однако замена летучих ртутных катализаторов по-прежнему остаётся одной из ключевых задач данного процесса. В настоящем исследовании изучен многокомпонентный хлоридный катализатор, содержащий хлориды цинка, магния, железа и висмута, с особым вниманием к влиянию температуры реактора и объёмной скорости подачи ацетилена. Испытания катализатора проводили в интервале температур 165–175 °C, при этом в качестве базового условия производительности использовали объёмную скорость подачи ацетилена 200 $ч^{-1}$. В указанных условиях конверсия ацетилена составляла 96,7 %, выход винилхлорида – 91,1 %, а селективность по винилхлориду – 94,2 %. Полученный результат показывает, что смешанный хлоридный состав катализатора позволяет направить основную часть прореагировавшего ацетилена на образование винилхлорида в умеренном температурном интервале. Анализ работы реактора свидетельствует о том, что объёмная скорость 200 $ч^{-1}$ представляет собой практический компромисс между временем контакта и производительностью. В то же время узкий температурный интервал позволяет ограничить как недостаточную скорость реакции при более низких температурах, так и термически стимулированные побочные реакции или потерю катализатора при более высоких температурах. Функции отдельных хлоридов рассматриваются в качестве механистических гипотез, а не как установленные активные центры, поскольку исследования фазового состава и характеристик поверхности не проводились. Полученные результаты подтверждают целесообразность дальнейшей оптимизации процесса на основе показателей конверсии ацетилена, объёмно-временного выхода продукта, длительной стабильности, повторных измерений и послереакционной характеризации катализатора.

Keywords: acetylene hydrochlorination, vinyl chloride monomer, mixed metal chlorides, gas hourly space velocity, temperature, selectivity.

Ключевые слова: гидрохлорирование ацетилена, мономер винилхлорида, смешанные хлориды металлов, объёмная скорость подачи газа, температура, селективность.

Introduction

Vinyl chloride monomer is the immediate precursor of polyvinyl chloride, and acetylene hydrochlorination remains an important production route in regions where acetylene is economically available. The overall reaction adds hydrogen chloride across the carbon–carbon triple bond of acetylene to form vinyl chloride. The reaction is strongly exothermic, so catalyst formulation and heat removal must be considered together. A catalyst that is chemically selective but produces local hot spots can still lose selectivity, deactivate, or release volatile components under practical fixed bed conditions.

$$C_2H_2 + HCl \rightarrow CH_2 = CHCl$$

Activated carbon supported mercuric chloride historically provided high activity for this reaction, but mercury loss and toxicity drove the search for mercury free catalysts. Early screening of supported metal chlorides established that catalyst identity strongly affects hydrochlorination activity [1]. Later work showed that cationic gold can be highly active and selective [2,3], while bismuth, copper, tin, ruthenium, palladium, and modified carbon systems have also been investigated. The most relevant lesson is that the oxidation state, dispersion, chloride environment, adsorption strength, and resistance to carbon deposition are interdependent. Performance therefore cannot be predicted from the identity of one metal salt alone.

Bismuth based catalysts are especially relevant to the present formulation. Phosphorus modified Bi/activated carbon produced 82 % acetylene conversion and 92 % vinyl chloride selectivity at 160 °C and 120 h^{-1}; characterization associated the active bismuth phase with BiOCl containing Bi (III) [4]. A Bi/carbon nanotube catalyst gave 91.7 % acetylene conversion and 97.3 % vinyl chloride selectivity at 160 °C and 120 h^{-1}, while loss of bismuth species and carbon deposition were identified as deactivation routes [5]. These results support the inclusion of $BiCl_3$ in mixed chloride formulations but also show why stabilizing and dispersing the bismuth component matters.

Materials and Methods

The $ZnCl_2$–$MgCl_2$–$FeCl_3$–$BiCl_3$ system combines several Lewis acidic chlorides in one formulation. $ZnCl_2$, $FeCl_3$, and $BiCl_3$ can create electrophilic environments capable of interacting with acetylene or chloride containing intermediates. $MgCl_2$ is less readily assigned as a primary hydrochlorination center and may instead influence salt distribution, acidity, and structural stability. These roles remain hypotheses until the fresh and used catalysts are examined by diffraction, spectroscopy, and adsorption measurements. The value of a multicomponent formulation lies in possible cooperation among adsorption, activation, and stabilization functions, but synergy must be demonstrated against single component and partial formulation controls.

Two operating variables directly determine how those surface functions are used. Temperature control’s intrinsic reaction rate, adsorption equilibria, desorption, and the rates of coke formation or active phase loss. Gas hourly space velocity controls the amount of acetylene fed per unit catalyst volume and therefore changes contact time and productivity. Higher space velocity usually

increases throughput but can reduce conversion when reactants leave the bed before reaction is complete. Lower space velocity increases contact time but may intensify secondary chemistry and reduces production per unit reactor volume.

This work evaluates the mixed chloride catalyst within a temperature interval of 165 to 175 °C and at an acetylene gas hourly space velocity of 200 h^{-1}. The principal reported result is a vinyl chloride selectivity of 94.2 %. The objective is to interpret this result within an IMRAD framework, define what it shows about the operating window, and identify the measurements required to convert a promising selectivity result into a complete catalyst performance assessment.

The catalyst formulation contained 5 wt% $ZnCl_2$, 3 wt% $MgCl_2$, 3 wt% $FeCl_3$, 1 wt% $BiCl_3$, and 88 wt% YuKS carrier is a granular activated carbon of the AG-3 grade (GOST 20464-75, manufacturer: JSC «Sorbent», Perm, Russia), with a specific surface area of 850–950 $m^2 \cdot g^{-1}$ (BET, N_2, 77 K), a total pore volume of 0.55–0.65 $cm^3 \cdot g^{-1}$, a micropore volume of 0.35–0.40 $cm^3 \cdot g^{-1}$, an ash content of ≤ 5 wt%, and a particle-size fraction of 1–2 mm. Accordingly, a nominal 100 g catalyst batch contained 5.0 g $ZnCl_2$, 3.0 g $MgCl_2$, 3.0 g $FeCl_3$, 1.0 g $BiCl_3$, and 88.0 g HZS; the total metal-chloride loading was 12 wt%.

Catalyst preparation

(1) The YuKS carrier was washed with distilled water (500 cm^3 per 100 g of carrier) to remove fines and water-soluble impurities, dried at 50 – 60 °C for 1 – 2 h, and sieved to a particle-size fraction of 1 – 2 mm.

(2) On a nominal 100 g catalyst basis, 5.0 g $ZnCl_2$, 3.0 g $MgCl_2$, 3.0 g $FeCl_3$, and 1.0 g $BiCl_3$ were separately dissolved in distilled water (25 cm^3 per salt) at 50 – 60 °C under stirring for 120 min. For BiCl3, a minimum volume of 0.1M HCl (10 cm^3) was added to prevent hydrolysis, and the resulting acidic solution was combined with the other chloride solutions before impregnation.

(4) A total of 88.0 g YuKS was added to the resulting sol, and the suspension was aged at 70 – 80 °C for 3 – 4 h.

(5) The obtained material was filtered or evaporated, dried at 250 – 300 °C for 10 – 12 h, and then heat-treated under a flow of dry nitrogen (99.99 vol%, 50 $cm^3 \cdot min^{-1}$) at 350 – 400 °C for 15 – 16 h.

Experimental setup and analytical accuracy

Hydrochlorination was carried out in a laboratory-scale fixed-bed reactor (laboratory fabrication ID: FB-1, manufactured at Navoi State University) made of type 316L stainless steel. The reactor had an internal diameter of 50 mm and a heated length of 450 mm, and was charged with 300 g of catalyst. Temperature was measured using three chromel–alumel (K-type) thermocouples (model TXA-K, manufactured by «Teplopribor», Moscow, Russia) connected to a PID controller (model REX-C100, RKC Instrument Inc., Japan) with an accuracy of ±1–2∘C.

The reactor effluent was analyzed using a gas chromatograph "Crystal 5000.2" (Chromatec, Yoshkar-Ola, Russia) equipped with a packed column 3m×3mm filled with Porapak Q (80/100 mesh) and a flame-ionization detector (FID). The uncertainty or repeatability of the chromatographic measurements was ±0.1–0.2%±0.1–0.2%, as established from 10 replicate

injections of a certified calibration gas mixture (supplier: "Monitoring", St. Petersburg, Russia; components: C_2H_2 99.5 vol%, $C_2H_3ClC_2$ 99.5 vol%, balance N_2; concentration range: 0.1–100 vol%).

The reaction was treated as a continuous gas phase process in a fixed catalyst bed. Hydrogen chloride and acetylene were contacted over the catalyst after the reactor reached the selected temperature. Catalyst charge, feed ratio, pressure, and analytical procedure were held constant while temperature was varied between 165 and 175 °C. The reference acetylene gas hourly space velocity was 200 h^{-1}. This definition separates reactor throughput from catalyst mass alone and allows results from beds of different sizes to be compared when the same volumetric basis is used.

$$GHSV = \frac{Q_{C2H2}}{V_{cat}}$$

In the equation, Q denotes the acetylene volumetric flow rate at the stated reference conditions and V_{cat} denotes the packed catalyst volume. A GHSV of 200 h^{-1} means that a gas volume equal to 200 catalyst bed volumes of acetylene is introduced each hour on the stated basis. The nominal space time is the reciprocal of GHSV, although the true gas residence time also depends on temperature, pressure, bed voidage, and the contribution of hydrogen chloride to total flow.

The reactor effluent was analyzed for unreacted acetylene, vinyl chloride, and detectable chlorinated or carbon-containing byproducts using the gas chromatograph specified above. Calibration was performed with the certified gas standard specified above (supplier: «Monitoring», St. Petersburg, Russia; components: C_2H_2, $C_2H_3ClC_2$, N_2; five calibration levels: 0.1, 1, 10, 50, and 99.5 vol%). Component response factors were obtained by [external/internal standard method], and each steady-state sample was analyzed [1-2] times. Acetylene conversion and vinyl chloride selectivity were calculated on a molar basis using the following expressions.

$$X_{C2H2} = \frac{F_{in} - F_{out}}{F_{in}} \times 100\%$$

$$S_{VCM} = \frac{F_{VCM}}{F_{in} - F_{out}} \times 100\%$$

F_{in} and F_{out} are the inlet and outlet molar flow rates of acetylene, and FVCM is the outlet molar flow rate of vinyl chloride. The formulas assume a one-to-one carbon molar relationship between reacted acetylene and vinyl chloride. For the quaternary ZMFB catalyst (Table 1, entry 7), acetylene conversion was 96.7 %, vinyl chloride selectivity was 94.2 %, and vinyl chloride yield was 91.1 %. The yield is internally consistent with 96.7 × 94.2 / 100 = 91.09 %. Space-time yield cannot be calculated until the actual molar feed rate and catalyst mass or packed-bed volume are reported.

Results and Discussion

Temperature was treated as a bounded process variable with an investigated interval of 165 to 175 °C. The reference space velocity was 200 h^{-1}. The reported measurements identify a performance point rather than a full response surface. Consequently, no regression, activation energy, confidence interval, or statistical optimum was calculated. A complete design should include replicated measurements at several temperatures and space velocities, randomized run order where practical, stabilization time before sampling, and a material balance closure criterion.

All testing of acetylene, hydrogen chloride, and vinyl chloride requires a closed and corrosion resistant system, exclusion of air, verified leak tightness, controlled vent treatment, and suitable gas detection. These controls are essential because acetylene is highly flammable, hydrogen chloride is corrosive, and vinyl chloride is toxic and carcinogenic. Safety controls do not alter the performance equations, but they determine whether the experiment can be conducted and reproduced responsibly.

Catalytic tests were conducted at 165 – 175 °C, a C_2H_2:HCl volumetric ratio of 1:1.5, and an acetylene gas hourly space velocity of 200 h^{-1}. The catalyst was prepared using the sol-gel procedure described above. The effect of catalyst composition on activity in acetylene hydrochlorination is summarized in Table 1.

As shown in Table 1, $ZnCl_2$ alone gave 63.5 % acetylene conversion, 43.0 % vinyl chloride yield, and 67.7 % selectivity. Relative to this baseline, both $AlCl_3$-containing ternary formulations increased vinyl chloride yield: $ZnCl_2 \cdot AlCl_3 \cdot NiCl_2$ gave 61.5 %, and $ZnCl_2 \cdot AlCl_3 \cdot CdCl_2$ gave 48.6 %. Within the two $AlCl_3$-containing formulations, replacing $NiCl_2$ with $CdCl_2$ reduced the yield by 12.9 percentage points (from 61.5 % to 48.6 %), although the $CdCl_2$-containing catalyst still exceeded the $ZnCl_2$-only yield by 5.6 percentage points.

Table 1. Effect of Catalyst Composition on Its Activity in the Catalytic Hydrochlorination of Acetylene (T = 165–175 °C; C_2H_2:HCl = 1:1.5; V = 200 h^{-1})

№	Catalyst composition	C_2H_2 conversion, %		Selectivity, %
		Overall	To vinyl chloride	
1	$ZnCl_2$	63,5	43,0	67,7
2	$ZnCl_2 \cdot MgCl_2$	72,0	50.1	69,6
3	$ZnCl_2 \cdot FeCl_3$	76,0	55.7	73,3
4	$ZnCl_2 \cdot BiCl_3$	68,5	47,8	69,8
5	$ZnCl_2 \cdot MgCl_2 \cdot FeCl_3$	52,3	31,6	60,0
6	$ZnCl_2 \cdot FeCl_3 \cdot BiCl_3$	77,8	56,0	72,0
7	**$ZnCl_2 \cdot MgCl_2 \cdot FeCl_3 \cdot BiCl_3$**	**96,7**	**91.1**	**94.2**
8	$ZnCl_2 \cdot AlCl_3 \cdot NiCl_2$	75,0	61,5	81,7
9	$ZnCl_2 \cdot AlCl_3 \cdot CdCl_2$	65,8	48,6	73,8

The binary $ZnCl_2$-based formulations gave vinyl chloride yields of 50.1 % with $MgCl_2$, 55.7 % with $FeCl_3$, and 47.8 % with $BiCl_3$; $FeCl_3$ therefore gave the highest yield among the three binary combinations. The ternary $ZnCl_2 \cdot MgCl_2 \cdot FeCl_3$ formulation gave a lower yield of 31.6 %,

whereas $ZnCl_2 \cdot FeCl_3 \cdot BiCl_3$ gave 56.0 %. These data show that the effect of adding a chloride depends on the complete catalyst composition and should not be interpreted as a uniform promotional effect.

A direct comparison of $ZnCl_2 \cdot MgCl_2 \cdot FeCl_3$ (Table 1, entry 5) with $ZnCl_2 \cdot MgCl_2 \cdot FeCl_3 \cdot BiCl_3$ (entry 7) shows the effect of adding $BiCl_3$ to the same base composition. Acetylene conversion increased from 52.3 % to 96.7 %, vinyl chloride yield from 31.6 % to 91.1 %, and selectivity from 60.0 % to 94.2 %. Thus, $BiCl_3$ had a positive effect in this specific composition pair, and the quaternary catalyst gave the best overall result in the screening series.

The 165 to 175 °C interval lies within the broader temperature range commonly used for gas phase acetylene hydrochlorination. Its practical advantage is that it is warm enough to support useful reaction rates while remaining below conditions at which local overheating becomes especially difficult to control. Because the reaction is exothermic, the measured furnace temperature is not necessarily the maximum catalyst temperature. Even a small axial hot spot can change selectivity and accelerate active phase loss. Temperature profiles along the bed should therefore accompany future activity measurements.

At the low end of the interval, incomplete acetylene activation or slow surface turnover can limit conversion. Increasing temperature generally improves the intrinsic rate and product desorption. At the same time, higher temperature can weaken adsorption of hydrogen chloride, change the chloride coordination of metal centers, and increase the rates of acetylene oligomerization and coke formation. Bismuth systems may also lose active species or change phase under reaction conditions [4,5]. The selected interval is therefore chemically plausible as a compromise, but the present data support an operating range rather than a mathematically determined optimum.

Space velocity changes the balance between utilization of each active site and production per reactor volume. At low GHSV, acetylene and hydrogen chloride remain in contact with the catalyst longer. Conversion may rise, but throughput falls and the product can remain on acidic surfaces long enough to undergo secondary reactions. At high GHSV, the opposite occurs: throughput rises, the gas phase is less exposed to secondary chemistry, and conversion can become limited by residence time or mass transfer. The 94.2 % selectivity measured at 200 h^{-1} indicates that secondary chemistry was controlled reasonably well at this reference condition.

The result should not be interpreted as proof that 200 h^{-1} maximizes vinyl chloride productivity. Productivity depends on the acetylene conversion multiplied by selectivity and molar feed rate. If conversion at 200 h^{-1} were low, high selectivity could coexist with a modest vinyl chloride yield. Conversely, a slightly lower selectivity at higher GHSV could still provide greater space time yield. A process relevant optimization should test at least three GHSV levels below and above 200 h^{-1} and report conversion, selectivity, yield, pressure drop, and carbon balance at steady state.

Conclusions

The $ZnCl_2$-$MgCl_2$-$FeCl_3$-$BiCl_3$ catalyst achieved 96.7 % acetylene conversion, 91.1 % vinyl chloride yield, and 94.2 % selectivity to vinyl chloride in the investigated temperature interval of 165 – 175 °C at an acetylene GHSV of 200 h^{-1}. The result identifies a practical operating window in

which the mixed chloride formulation directs most reacted acetylene to the desired monomer. Temperature and space velocity should be optimized together because temperature governs reaction and deactivation rates, whereas GHSV sets contact time and reactor throughput.

The data support the catalyst as a promising mercury free formulation, but they do not yet establish the most active composition or a unique optimum temperature. Acetylene conversion, vinyl chloride yield, space time yield, replicate uncertainty, byproduct distribution, and long-term stability are required for that conclusion. Controlled composition comparisons and surface characterization are also needed before specific catalytic functions are assigned to $ZnCl_2$, $MgCl_2$, $FeCl_3$, or $BiCl_3$.

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