INTERNATIONAL JOURNAL ON HUMAN COMPUTING STUDIES

ıttps://journals.researchparks.org/index.php/IJHCS e-ISSN: 2615-8159 | p-ISSN: 2615-1898

Volume: 03 Issue: 10 |Dec 2021

The Effect of Catalytic Activity of Catalyst (Carrier) Nature in the Synthesis of Vinyl Acetate

Fayzullayev Normurot

Doctor of Technical Sciences, Professor, Samarkand State University, Samarkand, Uzbekistan

Buronov Firdavsiy

Assistant, Karshi Engineering Economics Institute, Karshi, Uzbekistan

----------***----------

Annotation: The article examines the effect of γ-Al2O3, high-silicon zeolite (HSZ), bentonite, expanded clay, the nature of bentonites, their porous structure, methods of preparation and modes on the activity of the catalyst consisting of palladium, copper and potassium acetate for the vapour phase synthesis of ethylene-vinyl acetate. IR spectra of the synthesized samples were recorded in the reflection mode in the range 400–4000 cm–1 using a Nexus Nicolet Fourier transform IR spectrometer (Thermo Scientific). Thermal studies (TG/DTG-DTA) were carried out on an STA-1500H thermal balance. The specific surface area was determined by low-temperature argon adsorption on a Crystallux-4000M gas chromatograph. The size and radius of the pores were determined using mercury porometry directly on the amount of mercury compressed in them in a mercury porometric device that allows the measurement of the size of the pores. Vinyl acetate synthesis in a pilot device on a catalyst containing 0,4%Pd+4%Cu+7%CH3COOK/HSZ for 2000 hours at a temperature of 165 ℃, a pressure of 0.1 MPa, a vapour-gas mixture at a volumetric rate of 2000 h-1 and the amount of oxygen in the mixture with ethylene Performed when 7 vol.%. During 2000 hours of operation, the catalyst activity was 95-97% selectivity at 370-350 g of vinyl acetate/l. cat. hours.

Keywords: ethylene, acetic acid, acetoxylation, vinyl acetate, carrier, selectivity.

INTRODUCTION

Vinyl acetate (VA) is one of the most important monomers in the plastics industry and serves as the main raw material for the synthesis of polymers of complex vinyl esters of carbonic acids. Polyvinyl acetate is a complex ester of polyvinyl alcohol, as well as derivatives of polyvinyl alcohol and polyvinyl alcohol - polyvinyl acetals, in particular polyvinyl butyral, polyvinyl formal and others [1].

In the former Soviet Union, Stavrolen LLC (Russia) is intended for the production of ethylene and vinyl acetate on the basis of Nevinnomysskiy Nitrogen (Russia) and SSME Nitrogen Association (Ukraine) - acetylene. The production capacity of vinyl acetate at Stavrolen LLC is 50,000. t/year. The synthesis of vinyl acetate is carried out in the gas phase in the immobile layer of a heterogeneous catalyst, the spherical particles of aluminosilicate containing finely dispersed palladium, copper and potassium acetate act as a catalyst. The activity of the catalyst is 270-300 g of vinyl acetate/*l* cat. h, the selectivity for the formation of vinyl acetate on ethylene is 89-91%. The service life of the catalyst is at least 1 year.

Acetylene-based vinyl acetate production unit capacity is 20-25 thousand tons per year. In this process, zinc acetate absorbed into activated carbon acts as a catalyst [3-7]. The activity of the catalyst is 50-60 g VA/l cat. h, service life - no more than 4 months. Today, the annual growth of the global market for vinyl acetate production averages 5% per year, and the expected growth rates in Asian countries are expected primarily in China [8].

Synthesis of vinyl acetate from ethylene is carried out at a pressure of 0.8 MPa and a slow rise in temperature from 145 to 200 °C to maintain the specified activity of the catalyst throughout the year; the volumetric velocity of the gas mixture is 2000 h-

https://journals.researchparks.org/index.php/IJHCS e-ISSN: 2615-8159 | p-ISSN: 2615-1898
Volume: 03 Issue: 10 |Dec 2021

[1], the proportion of oxygen in relation to ethylene to dry gas is 7.0% by volume, which is limited by the explosive limit of the mixture of ethylene with oxygen. It should be noted that the synthesis of vinyl acetate is carried out by incomplete conversion of the primary reagents - ethylene, acetic acid, and oxygen (~ 8; 18 and 45%, respectively). After proper purification, the initial components that did not react are returned to the vinyl acetate synthesis reactor node. Therefore, the problems remain relevant on the basis of research, including palladium and its compounds, aimed at accelerating the synthesis of vinyl acetate from ethylene and finding new catalytic systems [9].

In addition to the search for more active catalysts based on the optimization of the chemical composition of the catalyst and the methods of its preparation, the study of the nature and effectiveness of the inorganic carrier as an important component of the catalyst is of great interest. Relatively inexpensive and common inorganic materials are activated carbon, pumice, alumina, asbestos, silicon carbide, zeolites, aluminosilicate gel, silica gel [10-18] and other materials resistant to acetic acid as catalyst holders in the synthesis of vinyl acetate. Despite the large selection of materials available, most of the published work, based on experimental data, states that alumina and silica gel-based carriers are preferred [19-28].

In this article, we studied the effect of γ-Al_2O_3, high-silicon zeolite (HSZ), Claydite, nature of bentonites, porous structure, methods and modes of their preparation on the activity of the catalyst consisting of palladium, copper and potassium acetate for the synthesis of ethylene-vinyl acetate in the vapour phase.

EXPERIMENTAL PART

The content of Pd and Cu in the catalytic composition was determined by the X-ray spectral fluorescence method on a VR A-30 analyser with an X-ray tube Cr anode. The texture properties of the coatings (specific surface area and pore volume) were studied by low-temperature nitrogen adsorption on an ASAP 2400 Micro metrics setup at 77 K. The morphological properties of the coatings were studied by scanning electron microscopy (SEM) using a JSM 6460LV microscope (JEOL, Japan) and transmission electron microscopy (TEM) using a JEM-2010 microscope (JEOL, Japan). The local elemental composition of the catalyst surface was studied by energy dispersive X-ray analysis using an EDA X (EDA X Co) energy dispersive X-ray spectrometer. The activity of the catalysts in the ethylene acetoxylation reaction was measured in a flow-through reactor at a space velocity of 1000 h^{-1}.

The synthesis of a colloidal solution of palladium nanoparticles was carried out according to the procedures [8-12]. Weighed portions of polyvinylpyrrolidone and sodium hydroxide were dissolved in ethylene glycol with constant vigorous stirring and heating under reflux. The resulting reaction mixture was heated to 120 °C and aqueous solutions of $PdCl_2$ and $CuCl_2$ were slowly added dropwise.

The resulting solution was kept at 120 °C for 60 min and cooled to room temperature. The resulting colloid containing palladium nanoparticles stabilized by polyvinylpyrrolidone was precipitated with acetone with stirring, followed by redispersion of the precipitated precipitate in ethyl alcohol.

Catalysts supported with palladium nanoparticles on a high-silica (HSZ) support were prepared as follows. The required volume of colloidal solution was added to the high-silica supports pre-dried at 200 °C, based on the content of 0.4% Pd and 4% Cu in the finished catalyst, and dried, stirring occasionally, at 75-80 °C, preventing the solution from boiling, with further drying at 160 °C for 4 h. The deposition of palladium and copper nanoparticles on HSZ was carried out as follows. The carrier was preliminarily crushed, a 0.25-0.5 mm fraction was selected, and calcined at 650 °C in a muffle furnace. The cooled HSZ was mixed with an appropriate amount of palladium colloid to obtain 0,4%Pd+4%Cu+7%CH_3COOK/HSZ and evaporated at 85 °C with periodic stirring until the catalyst was completely dry. The resulting mass was dried at 130 °C for 4 h. Samples for obtaining TEM

INTERNATIONAL JOURNAL ON HUMAN COMPUTING STUDIES
https://journals.researchparks.org/index.php/IJHCS e-ISSN: 2615-8159 | p-ISSN: 2615-1898
Volume: 03 Issue: 10 |Dec 2021

(Transmission electron microscopy) images were prepared by applying a drop of a colloidal solution of nanoparticles in ethanol onto a copper grid covered with a thin carbon film. A sample of 600-800 particles was used to construct particle size distribution diagrams.

Samples of 0,4%Pd+4%Cu+7%CH_3COOK/HSZ were ground in an agate mortar to a powdery state and dispersed in ethanol, after which TEM images were obtained in a similar manner. The content and concentration of acid sites were determined by the Boehm method. A weighed portion of the sample was kept in a 0.05 N NaOH solution for a day, after which the sample was filtered and a given volume of hydrochloric acid was added to the filtrate. The resulting sample was titrated potentiometrically with 0.05N sodium hydroxide solution.

According to the TEM data (Figure 1), the initial sample (calcined at 630 °C) contains palladium in the form of $PdCl_2$ chloride nanoparticles with a size of 2-4 nm. Thermal ageing of the sample at 1000 °C leads to significant particle agglomeration. The size of the formed agglomerates, according to TEM data, is 150-200 nm.

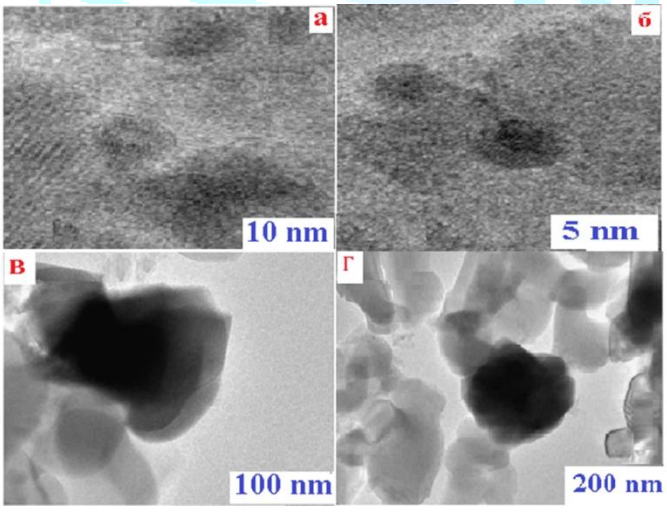

Figure 1. TEM micrographs of the catalyst 0,4%Pd+4%Cu+7%CH_3COOK/HSZ calcined at 630 °C (a, b) and 1000 °C (c, d).

A sample of 0,4%Pd+4%Cu+7%CH_3COOK/HSZ containing palladium was examined by the XRF method (X-ray fluorescence analysis). Figure 2 shows the diffractograms for this sample as well as for the carrier. It can be seen that, as a result of calcination, the formation of the HSZ crystal structure occurs, which corresponds to the appearance of the corresponding reflections in the diffractogram. The diffractogram for the palladium-containing catalyst also clearly shows an enlarged region in the region of 33°, related to the dispersed phase of $PdCl_2$. It should be noted that for other samples with lower metal content, similar changes in the diffractograms of relatively pure support were not observed.

CONCLUSION

The study of catalysts for the gas-phase synthesis of vinyl acetate by oxidative acetylation of ethylene showed that the nature of the carrier and the porous structure have a significant effect on the parameters of the catalytic process of vinyl acetate synthesis.

The nature of the change in the amount of vinyl acetate (n_0) generated over time indicates a decrease in the activity of the catalysts over time, but the time dependence of n for the catalyst in the HSZ-1 carrier is almost linear, indicating stable catalyst performance.

To confirm this conclusion, an experimental test of the stability of 1 dm3 of catalyst performance per reactor on an HSZ-1 carrier containing 0,4%Pd+4%Cu+7%CH_3COOK/HSZ was performed on a vinyl acetate synthesis pilot device. The test was performed by ingestion of potassium acetate with a vapour-gas mixture at a temperature of 165 °Ç a pressure of 0.1 MPa for 2000 h, a volumetric velocity of 2000 h^{-1} and a volume of oxygen with ethylene in the mixture at 7 vol.%. During 2000 hours of operation, the catalyst activity is 370-350 g of vinyl acetate / l.cat. hours at 95-97% selectivity.

A catalyst batch of 100 l of similar composition was then produced under industrial conditions and loaded into 20 (5 *l* each) tubes (tubes) of the industrial reactor. The catalyst was operated at a temperature of 145–165 °Cfor about 6 months and, after removal, was tested in a pilot device: its activity was 380–360 g of vinyl acetate/l.cat.hours at

https://journals.researchparks.org/index.php/IJHCS e-ISSN: 2615-8159 | p-ISSN: 2615-1898
Volume: 03 Issue: 10 |Dec 2021

97–95% selectivity, which is 22-27% higher than the values obtained in the industrial catalyst (270-300 g of vinyl acetate/l.cat.hours at 89-91% selectivity of vinyl acetate formation on ethylene).

REFERENCES

1. Rozenberg M.E. Vinyl acetate-based polymers. Leningrad. Himija, 1983. (in Russian).
2. Plate N.A, Slivinky E.V Foundations of monomer's chemistry and technology. Moscow. MAIK "NAUKA". 2002. 696 p.(in Russian).
3. M.N.Ibodullayeva N.S.Sarimsakova, N.I. Fayzullaev, N.X.Musulmonov, S.T. Atamirzayeva. Kinetics and Mechanism of Reaction for Producing Ethyl Acetate from Acetic Acid. International Journal of Control and Automation. 2020; 13:373-382
4. Voskanjan P.S. Influence of natural substances on the catalytic activity of palladium catalyst synthesis of vinyl acetate gas-phase acetylation by ethylene.. Kataliz v promyshlennosti. 2014 Nov 20(4):33-41. (in Russian).
5. Файзуллаев, Н. И., Буронов, Ф. Э., Мусулмонов, Н. Х., Кодиров, О. Ш., & Тошбоев, Ф. Н. (2021). Влияние количества активных компонентов катализатора на выход продукта при синтезе винилацетата из этилена и уксусной кислоты. *Bulletin of Science and Practice*, *7*(4), 301-311.
6. Файзуллаев, Н., & Буронов, Ф. (2021). ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКОЙ АКТИВНОСТИ КАТАЛИЗАТОРА В СИНТЕЗЕ ВИНИЛАТЦЕТАТА ИЗ ЭТИЛЕНА ПРИ РАЗЛИЧНЫХ НОСИТЕЛЬЯХ. *Збірник наукових праць ЛОГОΣ*. DOI 10.36074/logos-30.04.2021.v1.44
7. Firdavsiy, B. (2021). Influence of the Nature of the Retainer (Carrier) on the Catalytic Activity of the Catalyst in the Gas-Phase Synthesis of Vinyl Acetate from Ethylene. *Turkish Journal of Computer and Mathematics Education (TURCOMAT)*, *12*(10), 2262-2270.
8. Buronov, F.E., &Fayzullayev, N.I., Optimization of vinyl acetate production process. International scientific journal GRAIL OF SCIENCE
№ 4 May 2021 (Vienna, Austria). (pp 187-191). ISSN: 2710–3056 DOI 10.36074/grail-of-science.07.05.2021.035
9. Macleod N, Keel JM, Lambert RM. The effects of ageing a bimetallic catalyst under industrial conditions: a study of fresh and used Pd-Au-K/silica vinyl acetate synthesis catalysts. Applied Catalysis A: General. 2004 Apr 15;261(1):37-46. https://doi.org/10.1016/j.apcata.2003.10.032
10. Chen M, Kumar D, Yi CW, Goodman DW. The promotional effect of gold in catalysis by palladium-gold. Science. 2005 Oct 14;310(5746):291-3. https://doi.org/10.1126/science.1115800
11. Han YF, Kumar D, Goodman DW. Particle size effects in vinyl acetate synthesis over Pd/SiO2. Journal of catalysis. 2005 Mar 10;230(2):353-8. https://doi.org/10.1016/j.jcat.2004.12.018
12. Han YF, Wang JH, Kumar D, Yan Z, Goodman DW. A kinetic study of vinyl acetate synthesis over Pd-based catalysts: kinetics of vinyl acetate synthesis over Pd–Au/SiO2 and Pd/SiO2 catalysts. Journal of catalysis. 2005 Jun 10;232(2):467-75. https://doi.org/10.1016/j.jcat.2005.04.001