ANNOTATION

to the dissertation for the degree of Doctor of Philosophy (PhD)
by educational program
"6D074000-Nanomaterials and nanotechnologies".
Aitugan Aizat Nagmetollakyzy, on the topics
«Nanostructured catalysts for the hydrogenation of hydrocarbons

General characteristics of the work:

The dissertation is devoted to the preparation of nanostructured cobalt catalysts deposited on various natural supports using the carbonization process to increase their activity, with the aim of applying them in the selective hydrogenation of acetylene toethylene, and an experimental study of the physicochemical properties of catalysts to determine theiractivity and selectivity in the hydrogenation of hydrocarbons.

The relevance of the work:

The processes of thermal and catalytic cracking of propane and butane, as well as pyrolysis of oil fractions, are used to produce gaseous unsaturated hydrocarbons. Pyrogases contain alkanes, alkenes, and alkynes (including acetylene hydrocarbons). The most valuable of these are ethylene and propylene, which are used for the production of polymer materials. High degree of purity of raw materials is required (the acetylene content should not exceed 5 ppm) for the production of polyethylene and polypropylene, since the presence of alkynes in polymers can lead to the termination of the polymer chain and decrease in its molecular weight.

Using of hydrocarbon resources is not sufficiently developed in our country, and the introduction of raw hydrocarbons in the technological process can increase the market value of its products by about 2 times. Therefore, the development of new catalysts and processes for the synthesis of olefins from hydrocarbons that make up components of natural and associated petroleum gas and gas condensate is of scientific and applied importance for the development of the economy of Kazakhstan. The solution of this problem is possible through the production of catalysts with selective catalytic properties and different structures of micro-and nanosized particles.

Catalytic hydrogenation is used to purify the ethane-ethylene fraction from acetylene impurities гидрирование. Highly active catalysts based on y-oxides of aluminum and activated carbon (MA-15, PU-2, KHPU-1, G-58E) are widely used for this process. Their main disadvantages are low mechanical strength, high cost and side reactions of ethylene and acetylene oligomerization that occur due to the formation of "green oil".

The development of nanostructured metal catalysts based on domestic raw materials which have high selectivity, high mechanical strength and low cost, with characteristics comparable to industrial catalysts, is one of the urgent tasks of our time. It was found that the efficiency of nanocatalysts increases several times,

when preparing catalysts in the form of particles from 1 to 100 nm in size. This is due not only to an increase in the specific surface area of the catalyst consisting of nanoparticles, but also to the possibility of optimizing their morphology and structure during synthesis using nanotechnological methods. An important task in the study of catalytic hydrogenation is to increase the conversion of hydrocarbons and the selectivity of catalysts.

Purpose of the work

The purpose of this dissertation is to create highly active, highly selective nanostructured carbonized catalysts from domestic raw materials for the catalytic hydrogenation of acetylene hydrocarbons, and to investigate the impact of these catalysts' physicochemical properties on the process.

Objectives of the dissertation:

- Selection of an effective support for nanostructured metal catalysts based on the morphology and physicochemical properties of the support. Establishment of effective methods of media activation.
- Determination of the active metal and its optimal concentration during catalyst development. Determination of optimal conditions for the carbonization process.
- Synthesis of carbonized nanostructured cobalt catalysts, determination of the relationship between morphological characteristics and activity of carbonized nanostructured cobalt catalysts.
- Determination of optimal technological parameters in the reaction of selective hydrogenation of acetylene to ethylene and investigation of the activity and selectivity of developed nanostructured catalysts based on their morphology and physicochemical properties.

The main provisions submitted for defense:

- Chemical activation of clay with 10% HNO3 solution for 1 hour makes it possible to obtain a catalyst with a high catalytic activity (40%). In this case, the exchange cations $Ca2^{+}$, Na^{+}, and Mg^{2+} decrease by 92.3%, 93.02%, and 46.61%, respectively, which leads to the formation of new active sites due to the formation of H^{+} and Al^{3+} cations and an increase in catalytic properties.
- It was found that the yield of ethylene reaches 71%, when using a 5% Co / clay catalyst. This is due to the presence of the aluminosilicate phase, cobalt oxide, and cobalt particles in the catalyst structure with size 2-4.9 μm. The yield of ethylene reaches 89.62%, when 5%Co/ Clay catalyst is carbonized at 450 ° C temperature, which is explained by the formation of nanosized cobalt particles with size 337-596 nm.
- Increasing cobalt content from 5% to 7% in the clay supported catalyst increasing yield of the target product to 97%. This is due to the presence of multilayer catalytically active carbon nanofibers with a diameter of 11-24 nm, which contribute to an increase in the dispersion of cobalt and the formation of

cobalt particles with a size of 57-230 nm.

- High conversion of acetylene (95%) is achieved with the following effective parameters: reaction pressure-20 atm., temperature-140 ℃, raw material ratio C_2H_2 -1:1. It was found that the synthesized 7% cobalt/clay nanostructured catalysts work continuously for 28 hours, which indicates high activity and high efficiency. The high specific surface area of nanostructured cobalt contributes to its thermal stability.

Object of research: Nanostructured catalyst, clay, zeolite, aluminum oxide, cobalt.

Subject of the study: Selective hydrogenation of acetylene to ethylene

Research methods: The dissertation work utilized various instruments such as the JEOL JSM-7000F Field Emission Scanning Electron Microscope (SEM), Oxford Instruments X-Max 80T Energy Dispersive Spectrometer (EDS), JEOL 2100 High Resolution Transmission Electron Microscope (TEM), Selected Area Electron Diffraction (SAED), X-ray diffraction method X'Pert PRO diffractometer (XRD), Shimadzu 8300 Fourier spectrometer (IR), thermographic analysis (TGA 101, Labmen Instrument Technology Limited, China), X-ray fluorescence method Horiba Scientific (Japan), and BET-adsorption method. Qualitative analysis of reaction products was carried out in a gas chromatograph. The results are based on data obtained by reliable and accurate methods.

The scientific novelty of the research:

A new method for the preparation of a catalyst for the selective hydrogenation of acetylene to ethylene has been developed using clay support from the Tonkeris deposit, Shortandy district of the Akmola region, which was chemically activated with 10% HNO_3 solution for 1 hour.

For the first time, a highly active catalyst for the selective hydrogenation of acetylene to ethylene has been obtained, containing nanostructured carbon fibers with diameters of 11-24 nm and nanoparticles ranging from 57-230 nm, formed during the carbonization of the catalyst at 450°C. This catalyst allows for the effective hydrogenation of acetylene to ethylene.

It has been established that the increase in the catalytic activity of the cobalt nanostructured catalyst is dependent on the size of the nanoparticles in its structure. Additionally, it was shown that the variation in metal concentration has a positive effect on the specific surface area, contributing to improved catalyst activity.

Optimal conditions for the selective hydrogenation of acetylene have been determined, leading to the production of pure ethylene suitable for polyethylene production.

Field of application: catalysis, organic synthesis, nanotechnology.

The theoretical and practical significance of the work:

The results of the dissertation work contribute to the creation of an analog system that allows to explore the world science in the field of nanotechnology. A technology has been developed for the synthesis of a carbonized nanostructured catalyst using domestic clay as a carrier, which makes it possible to purify ethylene

from an acetylene mixture — the main raw material for the production of polyethylene.

Using the developed technique, the obtained catalysts can be widely used in a number of laboratory and industrial hydrogenation and hydrogenation processes requiring the use of highly selective catalysts.

The reliability and validity of the results primarily correspond to the observational data. The reliability and validity of the results of the dissertation work are confirmed by the presence of publications in international journals with a high impact factor, as well as in publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan, and in the materials of international scientific conferences.

The personal contribution of the author in obtaining the results of the dissertation. The author participated in all stages of the research of the dissertation work: in carrying out quantitative calculations and choosing research methods. The discussion of calculations and results was conducted jointly with scientific supervisors.

Approbation of the dissertation work.

The results of the dissertation work were presented at the following conferences and seminars:

1. Aitugan A.N., Naurzbaeva G.M // Synthesis of nanostructured catalysts for improving the quality of motor fuels // IV Conference of students and young scientists "Chemical physics and nanomaterials", 2019

2. Aitugan A.N., Kudaibergenova S., Tileuberdi E.// The impact of carrier as part of catalysts to catalytic selectivity in benzene hydrogenation // International scientific Conference of students and young scientists "Farabi alemi", 2019

3. Aitugan A.N., Tanirbergenova S.K., Mansurov Z.A // The selective hydrogenation of benzene to cyclohexane by the domestic nanostructured rhodium catalyst // VI International Scientific and Practical Conference «Global science and innovations 2019: Central Asia», 251-253, 2019

4. Aitugan A.N., Tanirbergenova S.K., Mansurov Z.A, Tileuberdi E. // Selective hydrogenation of acetylene to ethylene on cobalt catalysts // XI International Scientific Symposium "Combustion and Plasma Chemistry", 2019

5. Aitugan A.N., Tugelbayeva D. // New generation catalysts with high activity for hydrogenation of hydrocarbons // «Conference of students and young scientists "Chemical physics and nanomaterials", 2020

6. Aitugan A.N., Tugelbayeva D. // New generation catalysts with high activity for hydrogenation of hydrocarbons // International Kazakh-Russian symposium "Chemical Physics and Nanomaterials", December, 2020.

7. Aitugan A.N., S. K. Tanirbergenova, D. A. Tugelbayeva, G. M. Moldazhanova, Z. Azizov, Z. A. Mansurov. // Catalytic effect of cobalt catalysts in the reaction of hydrogenation of ethylene-containing acetylene to ethylene // AIP Conference Proceedings 2380, 020002, 2021

Publications: The results of the dissertation work were published in 13 publications, of which 2 articles are included in the Scopus database, 3 publications are published in publications recommended by the KKSON of the Republic of Kazakhstan, and 7 articles are in international scientific collections, symposiums and foreign conferences. 1 patent for utility model published.

Connection with scientific research and government programs:

1. AP05135250-OT-20 - "Development of nanocarbon catalysts for the catalytic hydrogenation of acetylene", 2018 – 2020 y

The scope and structure of the work:

The dissertation is presented on 118 pages and consists of 84 illustrations and 5 tables. The work includes an introduction, a review of the literature, a description of the objects and methods of research, the results and their discussion, a conclusion and a list of references containing 167 titles.