

MODIFIED COBALT CATALYSTS FOR HYDROGENATION OF HYDROCARBONS

A.N. Aitugan^{1*}, S.K. Tanirbergenova², Ye. Tileuberdi^{1,2}, D. Tugelbayeva²

¹Al-Farabi Kazakh National University, 71 al-Farabi ave., Almaty, Kazakhstan

²Institute of Combustion Problems, 172 Bogenbay batyr st., Almaty, Kazakhstan

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ABSTRACT

This work is devoted to the study of the influence of aluminum oxide content on the activity of cobalt catalysts in the reaction of selective hydrogenation of acetylene to ethylene. Cobalt catalysts modified with aluminum oxide having size between 50 to 500 nm were synthesized. Chemical contents and structure of carrier were investigated. The catalytic activity of 5% Co/clay and 5% Co/SiAl catalysts at acetylene hydrogenation was studied in the temperature range 100-180 °C, with a ratio of 1:2 of acetylene and hydrogen. The ethylene yield is 87.8% in modifying the cobalt catalyst with aluminum oxide, whereas with the same process parameters, the ethylene yield is 72%. 5% Cobalt catalysts modified with 1.5% aluminum oxides are more active in hydrogenation acetylene process than 5% Co/clay 450 °C catalyst.

Keywords: hydrogenation, acetylene, ethylene, catalysts, cobalt.

Introduction

Industrial production of unsaturated hydrocarbons is usually based on cracking and/or dehydrogenation of oil alkanes, starting with light C₂-C₃ fractions and ending with heavy fractions, such as naphtha and gas oil [1, 2]. The target products are usually alkenes – ethylene and propylene. However, at the same time, extremely undesirable admixtures of acetylene and diene compounds are inevitably formed, which have an irreversible deactivating effect on the catalysts of many subsequent processes of processing the obtained olefins. For example, during the polymerization of ethylene, these impurities quickly poison the Ziegler – Natta catalysts and sharply reduce the quality of the resulting polymers. In this regard, the content of acetylene impurities in olefins of polymerization purity should not exceed 10 ppm [3-5]. The most promising method for purifying olefins from acetylene impurities is their selective hydrogenation into olefins

Currently, various applied catalysts are used in the industry as selective hydrogenation catalysts, which increase the surface of the active component, prevent sintering and save expensive material. Platinum group metals are used as active components of deposited catalysts for hydrogenation of multiple carbon-carbon bonds in industry: Pt, Rh, Ru, Pd deposited on different carriers, and copper, cobalt, and Nickel on carriers are also used. Despite the high selectivity of hydrogenation, the use of catalysts containing precious metals increases the cost of the process. Cheaper, for example, Nickel and copper systems perform this reaction at high temperatures and pressures, which significantly complicates the hardware design and safety of the process [6-7]. The most applicable is a cobalt-based hydrogenation catalyst, which has a high activity and relatively low cost compared to noble metal-based catalysts.

The selectivity of hydrogenation is even more important for the process of ethylene purification

*Ответственный автор
E-mail: aizat_9_3@mail.ru (A.N. Aitugan).

from acetylene. In this work, we used cobalt as the active component of the studied catalysts, which, like the platinum group metals, also has a high activity in hydrogenation reactions.

The possibility of using nanostructured carbon materials as carriers is of great interest. Among such materials, carbon nanotubes and nanofibers have remarkable physical and chemical properties, which allows them to be used as carriers in heterogeneous catalysis, including for hydrogenation reactions [8-11]. A number of studies have shown that a specific metal-carrier interaction has a significant effect on the behavior of metal-carbon catalysts in hydrogenation reactions [12-13].

The characteristic of carrier efficiency in ordered aluminosilicates is mainly due to the presence of Si-O-Al bonds in acetylene hydrogenation reactions. The size of the pores and the distribution of pore volumes along their radii ensures the availability and transport of reacting molecules. In this respect, the nature of clays with a catalytic property, as well as a carrier containing an active mass, plays an essential role in the development of catalysts.

This work is devoted to the study of the influence of aluminum oxide content on the activity of cobalt catalysts in the reaction of selective hydrogenation of acetylene to ethylene.

Experimental part

Clay from Tonkeris deposit was used as a carrier, the structure of which contained montmorillonite ($\text{Al}_2[\text{OH}]_2 \{\text{Si}_4\text{O}_{10}\} \cdot \text{mH}_2\text{O}$), a valuable clay mineral. The main feature of the mineral is the ability to adsorb various ions (mainly cations) and to ion exchange. The dominant (~60%) mineralogical form of montmorillonite [14] is typical of which is the aluminosilicate module $[\text{Al}]/[\text{Si}] \sim 1/3$, which corresponds to the composition of clay (Table 1).

In the natural form of clay, the acidic centers of the framework are occupied by mobile cations, primarily Na^+ and K^+ , whose exchange for

cations of heavy metals (forming poorly soluble aluminosilicates) actively proceeds in an acidic environment at $\text{pH} = 2-4$ with a sorption value of ~ 0.1 mmol/g. A solution of nitric acid was added to the crushed clay to a homogeneous state for acid activation of the carrier, followed by thorough washing with distilled water. Clay dough formed in the form of granules was dried and carburized at different temperatures. Cobalt was applied to clay by impregnation by water capacity from an aqueous solution of $\text{Co}(\text{NO}_3)_2$.

The metal content in the synthesized Co/clay catalysts is 5 %. Synthesized Co/clay and Co-Al/clay catalysts have been investigated by a number of physical methods.

The effect of the method of introducing the optimal concentration of aluminum oxide on the activity of cobalt catalysts is studied. To modify the cobalt catalysts, the finished carrier was impregnated separately with Al, after impregnation it was kept for 3 hours, after which it was impregnated with cobalt salts, the conditions for further processing were the same.

High-resolution scanning electron microscopy (SEM) was performed on a JEM 2010 instrument (JEOL, Japan) with a lattice resolution of 0.14 nm.

The catalytic activity of the synthesized catalysts was studied on a flow-type hydrogenation unit at atmospheric pressure and without in the temperature range 100-180 °C. The catalyst was pre-treated in an argon current at a temperature of 100-120 °C for 80 min., then restored in a hydrogen current for 60 min. The temperature in the reaction zone is measured by a thermocouple. When the set temperature was reached in the reactor, the flow of acetylene and hydrogen was dosed at different ratios. At the hydrogenation unit, acetylene and hydrogen are pre-mixed and heated to the desired temperature.

The hydrogenation unit consists of a reactor and gas rotameters. The catalytic activity of the synthesized catalysts was studied using a developed hydrogenation unit. The reaction products were analyzed using a gas chromatograph

Table 1
The content of components in the composition of the clay

Content	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	TiO_2
%, mass	55.16	15.52	6.51	5.33	2.73	1.0	0.83	0.81
The molar composition	9.18	1.52	1.16	0.48	0.67	0.11	0.13	0.10

«Chrome-3700» and gas chromatography with mass spectrometric detection (Agilent 7890A/5975C). Helium was used as the carrier gas. The analysis was performed in the following mode: sample volume (gas) 4 μ l in non-flow division mode, chromatographic capillary column DB-35MS (Agilent, USA) 30m x 0.25 mm, film thickness 0.25 microns, column thermostat temperature: 35 °C (10 min exposure), evaporator temperature: 80 °C, detection mode – ion monitoring in the range m/z 10-550.

Results and discussion

According to chemical analysis, clay consists of half of silica SiO₂ (Table 1), and according to the content of aluminum oxide, it belongs to semi-acidic materials. Alumina Al₂O₃ is found both in the composition of clay-forming minerals and in the free a-state. Clay contains about 30% montmorillonite, and the total proportion of clay minerals including chlorides is about 50%. Oxygen atoms can be bound to two silicon atoms by Si–O–Si bridging bonds, or to one by Si – o non-bridging bonds.

The elemental analysis of the carrier is shown in Fig. 1.

The structural features of the catalyst carrier – clay from Tonkeris deposit-were studied using a scanning electron microscope. According to Fig. 2, montmorillonite crystals less than 1 microns in size have the appearance of thin leaves with irregular outlines.

Micrographs of SEM of cobalt catalysts modified with aluminum are shown in Fig. 3. Cobalt particles of different shapes with a diameter of 10-100 microns are observed in Fig. 3 (a). There are disordered channels inside which cobalt particles are present as can be seen from figure (3a). According to electron microscopy data, the Co-Al/clay sample contains particles of different sizes and located in the intervals between large aggregates. Figure (3b) shows images of a cobalt catalyst modified with aluminum by separate impregnation. According to SEM data, in samples of cobalt catalysts modified with aluminum, cobalt particles are uniformly deposited on the surface of the catalyst (3b). Sample 2 consists of agglomerates with cobalt particles ranging in size from 50 to 500 nm. The average content of evenly distributed cobalt particles in the sample is 4.5%, and trace amounts of aluminum were detected.

The catalytic activity of 5% Co/clay and 5% Co/SiAl catalysts at acetylene hydrogenation was studied in the temperature range 100-180 °C, with a ratio of 1:2 of acetylene and hydrogen.

Optimal modes were determined on cobalt catalysts for acetylene hydrogenation processes. The results are shown in figures 4. As can be seen from figure 4, when modifying the cobalt catalyst with aluminum oxide, the ethylene yield is 87.8%, whereas with the same process parameters, the ethylene yield is 72%. 5% Cobalt catalysts modified with 1,5% aluminum oxides are more active in hydrogenation acetylene process than 5% Co/clay 450 °C catalyst.

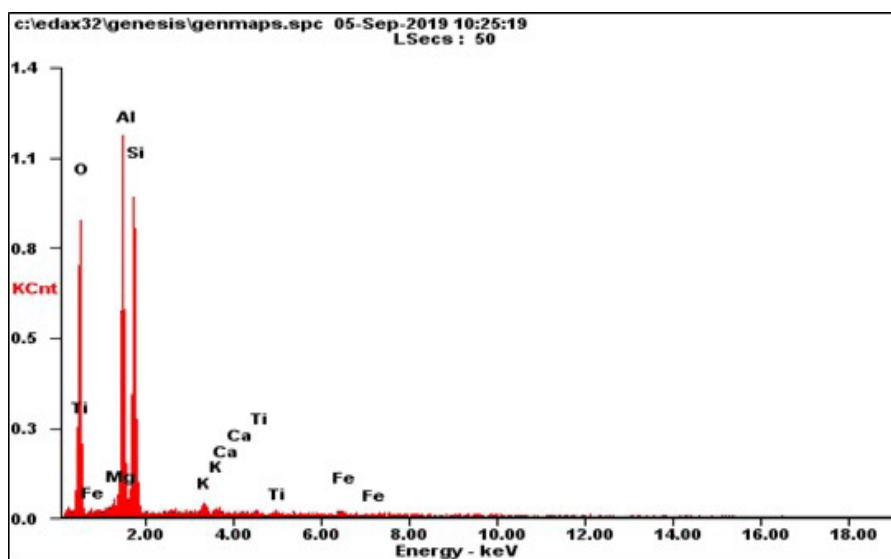


Fig.1. Elemental analysis of clay

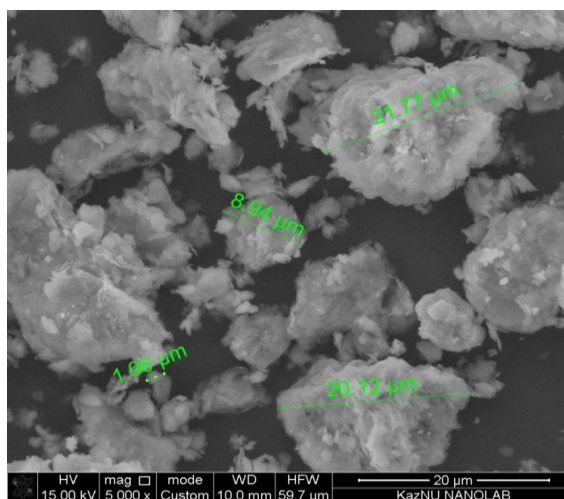


Fig. 2. Electron microscopic image of pure clay.

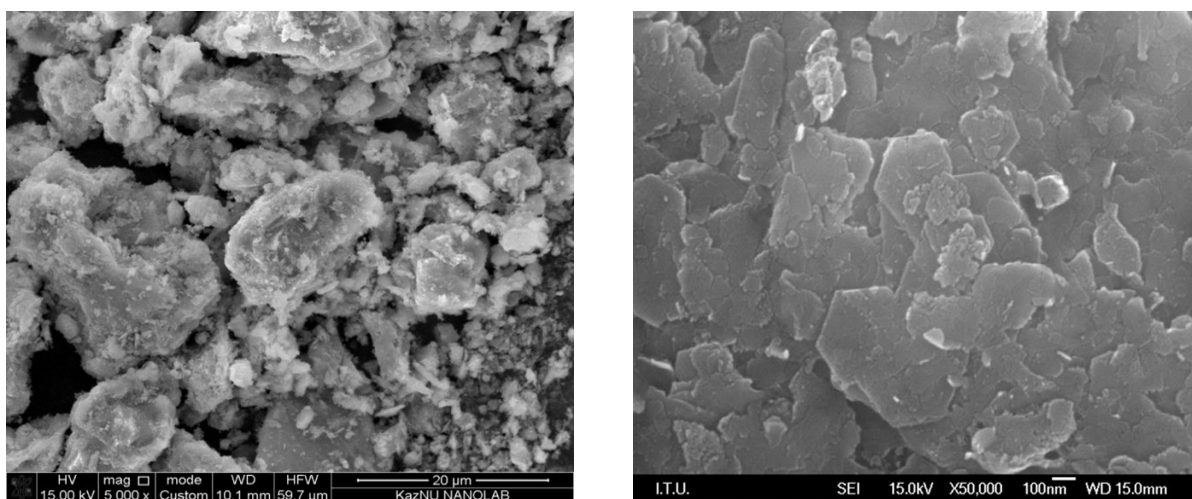


Fig. 3. Electron microscopic image of pure clay.

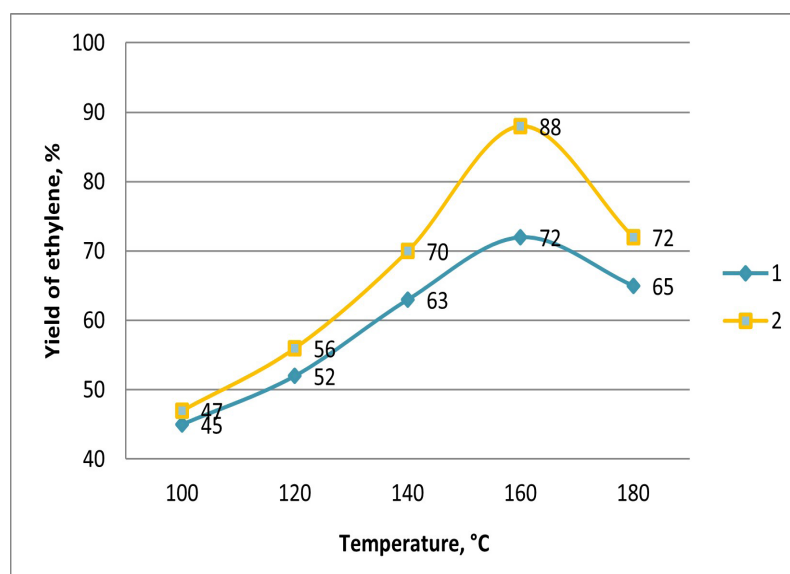


Fig. 4. The influence of modifying additives on the yield of ethylene at different temperatures: 1 - 5% Co-1,5% Al/clay 450 °C catalyst, 2 - 5% Co/clay 450 °C catalyst.

Conclusion

Modified cobalt catalysts with aluminum oxide were synthesized. Chemical contents and structure of carrier were investigated. Clay consists of half of silica SiO_2 , and according to the content of aluminum oxide, it belongs to semi-acidic materials. The structural features of the catalyst carrier – clay from the Tonkeris deposit -were studied using a scanning electron microscope. Montmorillonite crystals less than 1 micron in size have the appearance of thin leaves with irregular outlines. According to electron microscopy data, the Co-Al/clay sample contains particles of different sizes and located in the intervals between large aggregates. Cobalt particles have size from 50 to 500 nm. The catalytic activity of 5% Co/clay and 5% Co/SiAl catalysts at acetylene hydrogenation process was studied in the temperature range 100-180 °C, with a ratio of 1:2. The ethylene yield is 87,8% in modifying the cobalt catalyst with aluminum oxide, whereas with the same process parameters, the ethylene yield is 72%. 5% Cobalt catalysts modified with 1,5% aluminum oxides are more active in hydrogenation acetylene process than 5% Co/clay catalyst.

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Модифицированные кобальтовые катализаторы для гидрирования углеводородов

А.Н. Айтуған¹, С.К. Танирбергенова²,
Е. Тілеуберді^{1,2}, Д. Тугельбаева²

¹Казахский национальный университет им. аль-Фараби, Алматы, Казахстан

²Институт проблем горения, Алматы, Казахстан

АННОТАЦИЯ

Данная работа посвящена изучению влияния содержания оксида алюминия на активность кобальтовых катализаторов в реакции селективного гидрирования ацетилена до этилена. Кобальтовые катализаторы, модифицированные оксидом алюминия размером от 50 до 500 нм были синтезированы. Химический состав и структура носителя были исследованы. Каталитическая активность катализаторов 5% Co/глина и 5% Co/SiAl изучали в процессе гидрирования ацетилена в интервале температур 100-180 °С при соотношении 1: 2 ацетилена и водорода соответственно. При модификации кобальтового катализатора оксидом алюминия выход этилена составляет 87,8%, тогда как при тех же параметрах процесса выход этилена составляет 72%. 5% Co/SiAl Кобальтовые катализаторы более активны в процессе гидрирования ацетилена, чем катализатор 5% Co/глина.

Ключевые слова: гидрирования, ацетилен, этилен, катализаторы, кобальт.

Көмірсутекті гидрлеуге арналған модифицирленген катализаторлар

А.Н. Айтуған¹, С.К. Танирбергенова²,
Е. Тілеуберді^{1,2}, Д. Тугельбаева²

¹Аль-Фараби атындағы Қазақ Ұлттық университеті, Алматы, Қазақстан

²Жану проблемалары институты, Алматы, Қазақстан

АННОТАЦИЯ

Бұл жұмыс ацетиленді этиленге селективті гидрлеу реакциясында алюминий оксиді мөлшерінің кобальт катализаторларының белсенділігіне әсерін зерттеуге арналған. Алюминий оксидімен модифицирленген, өлшемі 50-500 нм болатын кобальт катализаторлары синтезделді. Тасымалдаушының химиялық құрамы мен құрылымы зерттелді. 5% Co/саз және 5% Co/SiAl катализаторларының каталитикалық белсенділігі ацетилен гидрлеу үрдісінде 100-180 °С температура диапазонында 1: 2 ацетилен мен сутектің қатынасында зерттелді. Кобальт катализаторын алюминий оксидімен модификациялау кезінде этиленнің шығуы 87,8 % құрайды, ал сол процесс параметрлерінде этиленнің шығуы 72% құрайды. 5% Co/SiAl катализаторлары 5% Co/саз катализаторына қарағанда ацетиленді гидрлеу процесінде белсенді.

Түйінді сөздер: гидрлеу, ацетилен, этилен, катализаторлар, кобальт.