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Co Catalysts Supported on Activated Clay for Selective Hydrogenation of Acetylene to Ethylene

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ABSTRACT

This work describes the simplest method of synthesis of a carbonized cobalt catalyst based on an available natural mineral, clay activated with nitric acid, which showed high selectivity and activity in hydrogenation of acetylene to ethylene. Metal catalysts with cobalt contents of 5 %-7 % in a bentonite clay carrier from the Tonkeris deposit were synthesised. The physicochemical properties were investigated by means of X-ray powder diffraction (XRD), scanning electron microscope (SEM), IR-Fourier spectrometer. Products were analysed using a Chrom-3700 gas chromatograph and gas chromatography–mass spectrometry (Agilent 7890A/5975C). The catalytic activities of the synthesised cobalt catalysts were investigated using an installation developed for the hydrogenation of acetylene to ethylene in a gaseous medium. Carbon nanofibers with diameters ranging from 57 to 400 nm were visible on cobalt catalyst samples. Selectivity of the modified cobalt-containing catalysts for hydrogenation ranged from 89.62 % to 97 %. Ethylene conversions of 93.58 % were achieved on 7 % Co/SiAl carbonized catalyst, at an optimum temperature of 140 °C. Side reactions are activated when the temperature rises above 180 °C, so the yield of ethylene is reduced.

Keywords: Acetylene, Hydrogenation, Catalysts, Carbonization, Cobalt, Acid treatment

1. Introduction

Selective hydrogenation of acetylene is an important industrial process for the mass production of polyethylene [1]. The presence of acetylene impurities in ethylene makes it impossible to use olefins in subsequent polymerisation processes. Acetylene poisons the catalysts used for ethylene polymerisation, so the acetylene content in the ethylene fraction of a polymerisation feed should be below 1 ppm [2-3]. The international oil refining industry is caused by more rigid ecological requirements imposed on oil refining processes and product. Therefore, one of the most important tasks in the preparation of raw materials for polymer production is the hydrogenation of dienes and acetylene without completely hydrogenating olefins that contain only one double bond with alkanes [4-5].

The most promising method for the purification of olefins from acetylenic impurities is their selective hydrogenation to olefins [6]. Thus, there is a high demand on the catalyst for the selective hydrogenation of acetylene to ethylene.

Various catalysts based on the platinum group metals Pt [1], Rh [4], Ru [7] and Pd [8] deposited on different carriers are used for the selective hydrogenation of acetylene in industry. Other catalysts used for this purpose are based on cobalt, copper or nickel on different supports. These catalysts have large surface areas with an abundance of active centres [2-4]. They also prevent sintering, and their reusability enables expensive metals to be conserved. Despite their high selectivity for hydrocarbon hydrogenation, the use of noble metal catalysts increases the cost of the process [9]. Cobalt-based catalysts with high activities are more practical for hydrogenation because they are relatively

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inexpensive compared with catalysts based on noble metals [10].

Information on the synthesis of carbon-based nanomaterials and their physicochemical properties is currently available. Because the activity of a catalyst depends substantially on the physicochemical properties of the support, the use of carbon-based materials as supports has led to the creation of a new generation of hydrogenation catalysts [11]. Catalyst supports (e.g., clay, Al_2O_3, SiO_2, TiO_2 and ZnO, [12-15]) favour the dispersion of the active phase in heterogeneous catalysis, thus increasing the amount of available active sites. In addition, the physico- chemical properties of the support could modify its electronic density.

The need of searching low-cost catalysts, which are competitive on an industrial scale, has prompted the development of inexpensive active phase and catalytic supports. With regard to the support, clay minerals are abundant, versatile and inexpensive natural materials that have been extensively studied in adsorption and catalysis fields. The characteristic of carrier efficiency in ordered aluminosilicates is mainly due to the presence of Si-O-Al bonds in acetylene hydrogenation reactions [13]. The size of the pores and the distribution of pore volumes along their radii ensure the availability and transport of reacting molecules. In this respect, the nature of clays with a catalytic property and a carrier containing an active mass play an essential role in the development of catalysts.

Bentonite clay has been used as a carrier for acetylene hydrogenation catalysts. Montmorillonite is the main rock-forming mineral in bentonite clays. The high specific surface area of montmorillonite is due to the fact that the surface area increases over the surface area between the sheets, called the interlayer region. For comparison, coarse sand has a specific surface area of about 0.01 m^2 / g, fine sand 0.1 m^2 / g, the active surface of montmorillonite is 700-800 m^2/g. Accordingly, the cation exchange capacity of montmorillonite is 80-150 mmol / 100 g (for comparison, the cation exchange capacity of kaolinite is 3-15 mmol / 100 g) [16]. Its structure comprises octahedral sheets consisting of aluminium coordinated with oxygen sandwiched between tetrahedral silicate layers. Partial isomorphic substitution of Al^{3+} with Mg^{2+}, Fe^{2+} or Fe^{3+} ions and substitution of Si^{4+} with Al^{3+} ions confera negative charge to the structure, which is compensated by exchangeable interlayer cations. It is necessary to treat bentonite clays with acid to prepare catalysts with large specific surface areas and high catalytic activities. During acid activation, the exchangeable cations are replaced by hydrogen ions. Structural cations are removed in the following sequence: $Mg^{2+} > Fe^{2+} > Fe^{3+} > Al^{3+}$. Clay minerals contain a significant quantity of Mg^{2+}, so their structures are rapidly destroyed by exposure to acids [17].

Novel metal-modified carbon materials are of interest as sorbents and catalyst supports. Metal-containing catalysts can be prepared by introducing metals into clay matrices and subjecting them to thermal treatment at high temperatures in an inert atmosphere [18]. Carbon nanomaterial supports can be introduced via carbonisation. Metal-containing catalysts on nanocarbon supports have high catalytic activities for hydrocarbon hydrogenation [19]. Pd catalysts supported by carbon-based materials were recently reported to show good selectivity and high activity.[20]. However, difficulties arise in the synthesis of Pd single-atom catalysts due to the absence of coordination centers, as a result of the aggregation of Pd nanoparticles formed. Synthesized Pd single atom catalysts on nitrogen doped catalysts on [21] were tested on hydrogenation of acetylene and reached 99% conversion of acetylene. The high prime cost of palladium, the high temperature requirements and a long time for catalyst synthesis complicate its application in industry.

In our work, we use the clay of the Tonkersk deposit as a carrier, which already simplifies the method of synthesizing the catalyst carrier and the relatively cheap metal-cobalt, which shows high activity and selectivity in the processes of acetylene hydrogenation. The aim of this work is the development of low-cost catalysts using cobalt as active phase, and natural bentonite, with high content in montmorillonite as supports by simple methods for the selective hydrogenation of acetylene to ethylene. The influence of the catalytic performance on the acetylene hydrogenation(in gas phase) of the cobalt content, carbonization temperature, as well as its structure and crystallite size, has been also evaluated. Low-cost cobalt catalysts with high catalytic activity and selectivity were synthesized by simple methods using natural raw materials.

2. Experimental

2.1. Synthesis of cobalt catalysts

Metal catalysts with cobalt contents of 5-7% in a bentonite clay carrier were synthesised for acetylene hydrogenation. Ground clay (CL) from the Tonkeris deposit was used for this investigation. The bentonite carrier was chemically activated with 10% nitric acid to remove the alkali and alkaline earth metals. 70% nitric acid (Purissimum, Sigma Aldrich) was used to induce acid activation in the clay. The catalysts were then prepared by impregnating the clay with aqueous cobalt

nitrate $(Co(NO_3)_2 \cdot 6H_2O)$ and $Al(NO_3)_3)$ JSC (Lenreaktiv, Russian Federation) solution. The formed extrudates were dried at room temperature. They were then carbonised at 550 °C for 30 min in a propane–butane medium.

2.2 Cobalt catalysts modified with aluminum oxide

Process of preparing the catalyst consists of successive impregnation of the oxide carrier with aqueous cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$ and $Al(NO_3)_3$ solution, followed by drying and high-temperature heat treatment in a propane-butane mixture. $Al(NO_3)_3$ solution is a source of alimunim(III) in catalysts. The final product was dark gray granules. According to the phase composition, the catalyst have carrier with a mass fraction of 88% (±1.0), there is a solid phase of aluminum oxide in the pores, a mass fraction of 10% (±0.5) and cobalt oxide, a mass fraction of 5.0% (±0.5).

2.3 Instrumentation

Scanning electron microscope (SEM) images of samples with a resolution of up to 0.14 nm were obtained using a JSM-7000F field-emission (FE) SEM (JEOL, Japan) at an accelerating voltage of 200 kV. The samples were first deposited on carbon supports affixed to copper grids. Monocrystalline gold was used as a reference. The SEM (installed at Istanbul Technical University (Istanbul, Turkey).) data were used to estimate the particle sizes of the supported metals and their particle size distributions. An X-ray powder diffraction (XRD) analysis was conducted with an X'Pert PRO Diffractometer (Philips Healthcare, Netherlands) operated at 40 kV and 35 mA utilising Cu K radiation. Chemical analysis were performed using an INCAx-sight energy-dispersive (EDS) detector (Oxford Instruments, UK) with a resolution of 130 eV. Chemical composition of catalyst was studied using IR-Fourier spectrometer (Simex FTIR-801, Russia).

2.4. Catalytic activity of catalysts

The catalytic activities of the synthesised cobalt catalysts were investigated using an installation developed for the hydrogenation of acetylene to ethylene in a gaseous medium, which is indicated in our previous works [7]. The catalysts were loaded into the reactor and treated under an argon stream at 100-120 °C for 80 min and then reduced under hydrogen for 60 min. Metred flows of acetylene and hydrogen were mixed in a ratio of 1:2 and 1:3 in the reactor-evaporator-mixer and then heated to the required temperature. The temperature in the reactor was monitored with a thermocouple. The compositions of the acetylene hydrogenation products were qualitatively and quantitatively analysed using an Agilent 7890A gas chromatograph (GC) equipped with a 5975C mass detector (Agilent, USA). Gas samples (4 mL) were injected in splitless mode in a 30 m × 0.25 mm DB-35MS capillary GC column (Agilent, USA) with a film thickness of 0.25 μm. The evaporation temperature was 80 °C, exposure time 10 min and ion monitoring was performed in the range of 10-550 *m/z*.

3. Results and Discussion

3.1.The synthesis and identification of catalysts

3.1.1 Chemical analysis of the catalyst

The chemical compositions of the pure clay, activated clay with 10% HNO_3 and 7% Co/clay without carbonization, 7% Co/clay carbonization at 450 °C are given in **Table 1**.

Treatment with 10 % nitric acid reduced the quantities of calcium and sodium in the clay by 64.71% and 58.3%, respectively. The Mg^{2+} content in the clay was reduced by 22.3%, which may indicate the beginning of structural cation removal. The quantity of K^+ in the clay remained unchanged. Potassium ions are found in feldspar, which is resistant to acids. The Al^{3+} and Si^{4+} contents were not reduced by chemical activation of the clay. Therefore, the structure of the clay mineral used as the catalyst carrier was largely preserved. As a result of clay activation, exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe^{3+}) are removed from the montmorillonite structure and replaced by lighter H^+ ions, the montmorillonite structure is transformed, which occurs during leaching of interlayer and octahedral cations, and the specific surface area increases. The authors of [17] also noted that the presence of impurities such as feldspar, calcite and other "accompanying" minerals complicates the complete removal of Ca^{2+}, K^+, Mg^{2+} ions from clay samples.

The chemical composition changed markedly after the clay carrier was impregnated with cobalt nitrate. Chemical analysis of the 7% Co/clay carbonization at 450 °C catalyst indicated the formation of carbon nanofibers. During the process of carbonization, catalytic active carbon fibers are formed on the catalyst surface, which improve the structure of the support and improve the catalytic performance for the selectivity of ethylene. Carbonisation increased the carbon content of the original sample by 65.8%. The presence of active carbon increases the dispersion of cobalt deposited on the clays. Thus, the elemental compositions of the nanofibers were determined using SEM-EDX and the results are shown in **Fig. 1**.

3.1.2 Morphology and structure characterizations of samples

Element	%
C	25.88
O	34.16
Na	0.56
Mg	0.74
Al	8.14
Si	16.47
K	2.56
Ca	2.91
Fe	2.03
Co	6.53
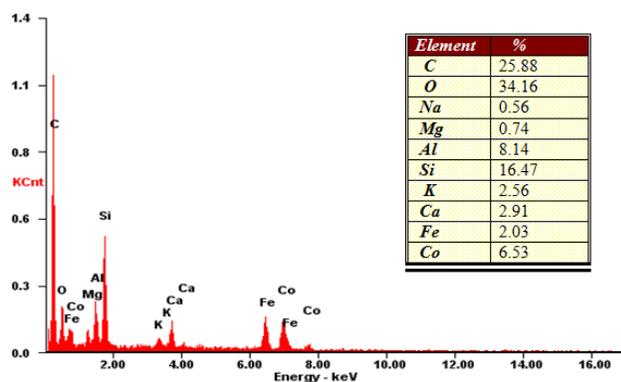
Fig. 1. EDAX spectrum of 7%Co/Clay catalysts, carbonised at 450 ℃

Morphological and structure characterization of samples are presented in **Fig. 2**. The images in **Fig. 2 a, b** show micrographs of pure bentonite clay and the clay carrier after chemical activation with 10% nitric acid. The pure clay sample in **Fig. 2a** contained agglomerates with particles' size ranging from 3.8 μm to 10.47 μm. The exchangeable cations were replaced by hydrogen ions during acid treatment with 10% nitric acid, and some of the structural Mg^{2+}, Fe^{2+} and Fe^{3+} cations were removed (**Table 1**). While exchangeable cations were removed, the primary ions in the montmorillonite structure were retained after activation of the clay.

Particles with varying diameters and irregularly sized channels are visible in the sample in **Fig. 2b**. This indicates the removal of exchangeable cations from the catalyst support structure, which decreased the concentrations of Na^+ and K^+ as shown in **Table 1**. Cobalt particles with different shapes and diameters of 13.01-13.61 μm are shown in **Fig. 2c**. At this magnification, fibres that formed in the catalyst structure after impregnation of the carrier with cobalt nitrate solution were visible. Carbon nanofibers with

diameters ranging from 57 to 400 nm are visible in the SEM image of the carbonised 7% Co/CL-10, carbonised at 450 ℃ in **Fig. 2d**.

According to SEM data, **Fig. 2e** shows micrographs of samples of synthesized catalysts. Particles of deposited cobalt were found in the form of agglomerates of warped particles in different shapes. Catalyst particles of 5% Co – 10% Al/ clay carbonization at 450 ℃ in size from 60 nm to 675 nm are shown in **Fig. 2e**. The addition of aluminum leads to the fact that the entire surface is covered with tightly packed structures, this reduced the specific surface area and mechanical strength (**Table 2**). As can be seen from **Table 2**, the specific surface area of 7% Co/clay carbonization at 450°C is significantly higher compared to other synthesized catalysts.

Fig. 3 shows the results of infrared (IR) spectra of 7% Co/clay carbonization at 450 ℃ catalyst. Analysis of the IR spectra of cobalt catalyst shows that the main bands belong to the valence bonds of silicon with oxygen and the hydroxyl group. Absorption bands appeared in the region of 797.75 cm^{-1}; 562.81 cm^{-1}; 479.22 cm^{-1} corresponding to bonds Al-O, Si-O. The presence of an OH-valence band with a maximum of 3447.31 cm^{-1} and a weaker band at 1631.59 cm^{-1} are attributed to interlayer water molecules.

XRD results of carrier, 5% Co/clay, 7% Co/clay carbonization at 450 ℃ and 5% Co – 10% Al/ clay carbonization at 450 ℃ are shown in **Fig. 4**. The diffraction pattern of the support indicates its high degree of crystallinity. The main reflections of the ceramic support refer to the trigonal-rhombohedral lattice of SiO_2 (α-quartz) and the hexagonal lattice of tridymite SiO_2, lattices of aluminosilicate, mullite.

Table 1. Chemical compositions of the clay and 7% Co catalyst.

Element	Pure clay	Clay activated with 10% HNO₃	7% Co catalyst on clay support	7% Co catalyst on clay support after carbonisation at 450°C
C	11.86	11.60	9.54	25.88
O	45.73	44.52	46.69	34.16
Na	1.20	0.50	0.68	0.58
Mg	2.20	1.71	2.06	0.74
Al	5.78	9.34	8.32	8.14
Si	14.12	22.15	16.72	16.47
K	2.57	2.62	2.48	2.56
Ca	11.76	4.15	2.67	2.91
Ti	1.13	0.63	0.74	-
Fe	3.65	2.78	2.57	2.03
Co	-	-	7.53	6.53
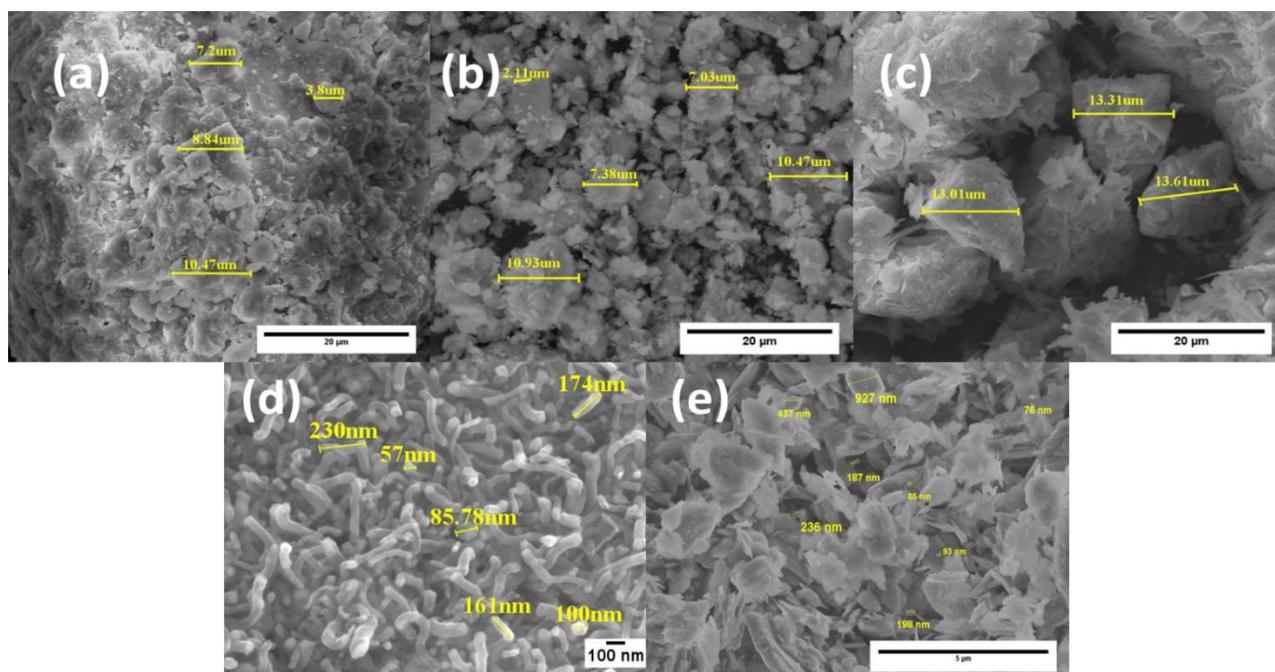
Fig. 2. SEM micrographs of a) pure clay; b) clay after chemical activation; c) 7% Co/clay catalyst; d) 7% Co/clay catalyst, carbonization at 450 °C; e) 5 % Co/clay catalyst, carbonization at 450 °C
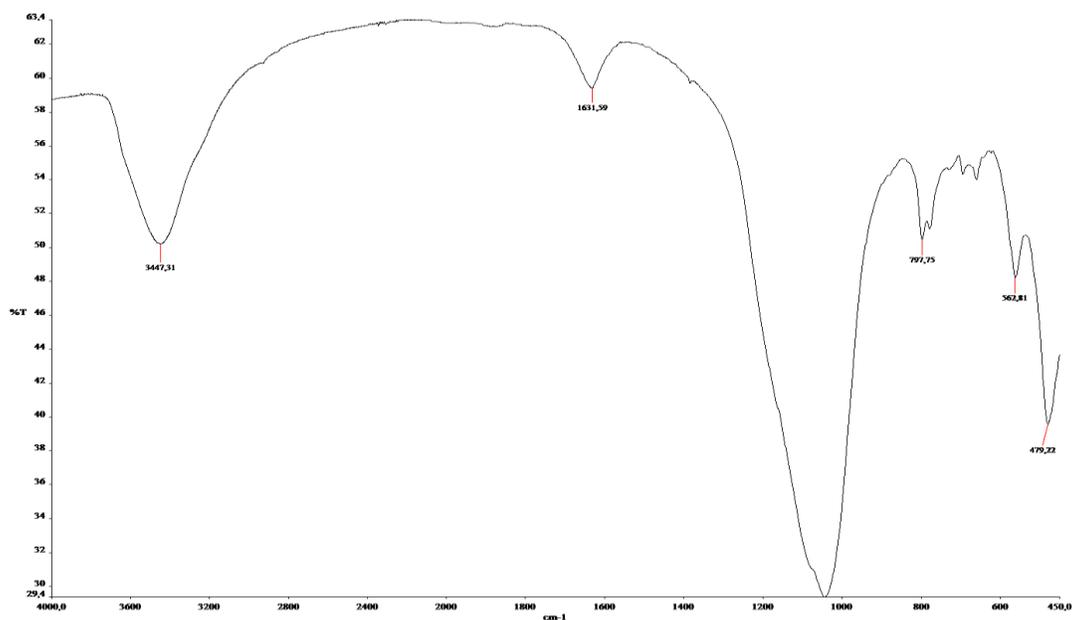
Fig. 3. Infrared (IR) spectra of 7% Co/ clay catalyst carbonization at 450°C

Peaks 36.3 and 42.5 indicate presence of Co_3O_4 in catalysts samples. A noticeable change in the structure of the catalyst and the presence of carbon are seen as a result of the carbonation process.

3.2.The study of catalytic performance of catalysts

3.2.1. Optimization of acetylene hydration reactions parameters

Synthesized cobalt containing catalysts were used for further research in the acetylene hydrogenation process: 7% Co/clay carbonization at 450 °C 5% Co – 10% Al/clay carbonization at 450°C.

1% Pd/Al_2O_3 was selected as the most active acetylene hydrogenation catalyst in the industry to compare the catalytic activity of the cobalt catalysts synthesized by us.
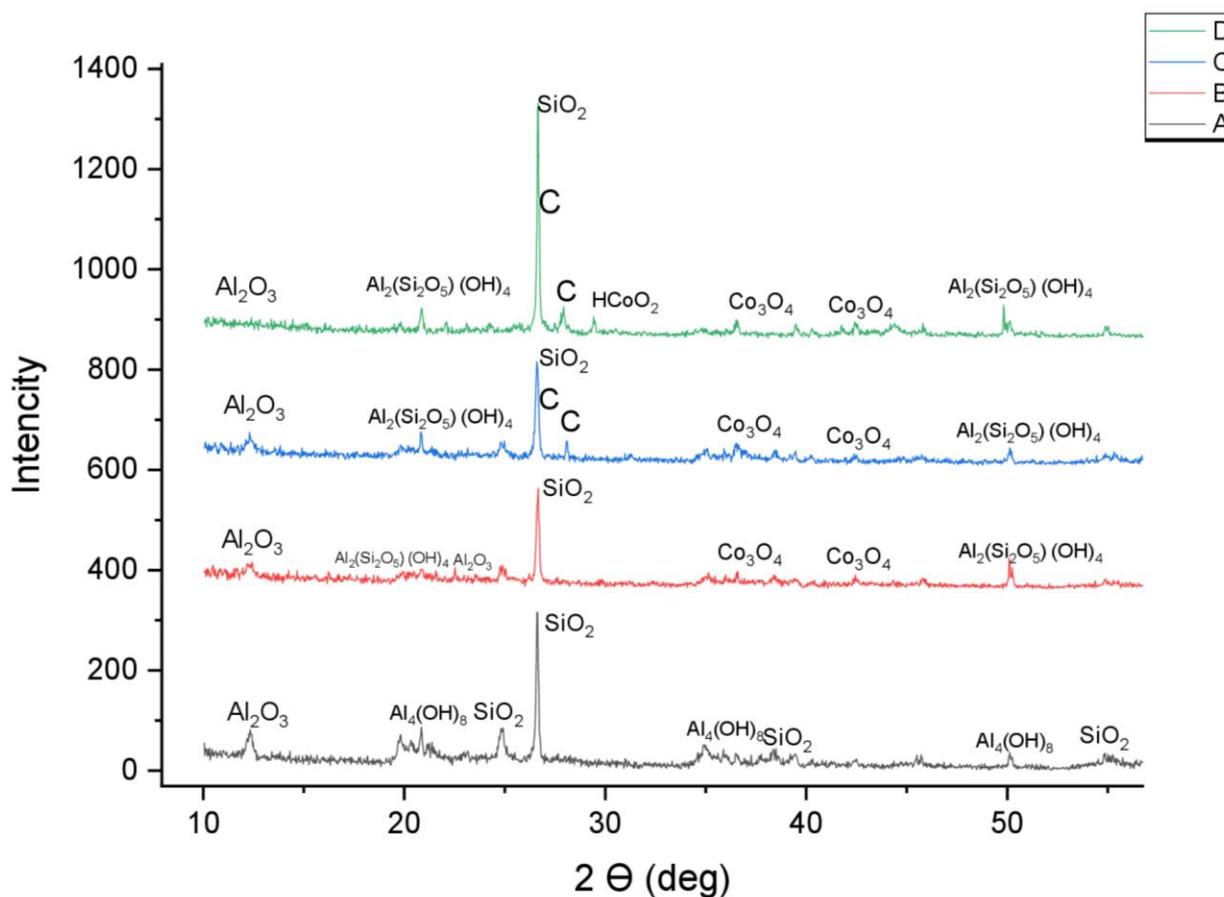
Fig. 4. X-ray diffraction pattern of the catalysts: a) pure clay; b) 5 % Co/clay; c) 7% Co/clay carbonization at 450°C; d) 5% Co – 10% Al/ clay carbonization at 450°C

Acetylene adsorbed on the Co surface transforms into associative chemisorbed (di-bonded) flat-lying acetylene (1), then into vinyl species (2), which are precursors of ethylene (**Fig. 5**). As a result of competitive chemisorption of the acetylene molecule onto cobalt, adsorbed hydrogen is again added to the obtained σ-alkenyl fragment (3), which leads to the formation of a π-olefin complex (4) and subsequent desorption of the ethylene molecule.

Effects of temperature on the selectivity of the catalysts and their conversion of acetylene are illustrated in **Fig. 6 a,b**, respectively.

The catalytic activity and selectivity of cobalt catalysts were compared with the palladium industry catalyst. The selectivity of the hydrogenation process reached 91.17% on catalyst of 5% Co – 10% Al/ clay carbonization at 450 °C that show the emergence of new active centers with increased reactivity when modifying the cobalt catalyst with aluminum. Increasing in the mass concentration of Co to 7% leads to increase in the selectivity of the acetylene hydrogenation process to 97%. 7% Co/clay carbonization at 450 °C results in selective hydrogenation of acetylene at 140 °C. The results of 7% Co/clay carbonization at 550°C catalysts had showed in our last work [22]. Reducing the temperature to 450 °C carbonization showed high results in the selectivity of acetylene hydrogenation. According to the analysis of SEM-EDX of the chemical composition of the catalyst, we can assume that the carbonization process proceeds at 450 °C quite well and has a positive effect on the catalytic activity of the catalyst.

Table 2. Phase composition and specific surface area of synthesized catalysts.

Carrier and catalysts	A_{BET}, m^2/g	Phase composition
Clay (SiAl)	114.62	SiO_2, $Al_2(Si_2O_5)(OH)_4$
Co/ SiAl	124.68	SiO_2, Co_3O_4, Al_2O_3
Co/ SiAl	150.54	SiO_2, Co_3O_4, Al_2O_3, $Na(AlSi_3O_8)$, $HCoO_2$
Co-Al/ SiAl	128.74	SiO_2, Co_3O_4, Al_2O_3, $Na(AlSi_3O_8)$, KSi_3AlO_8
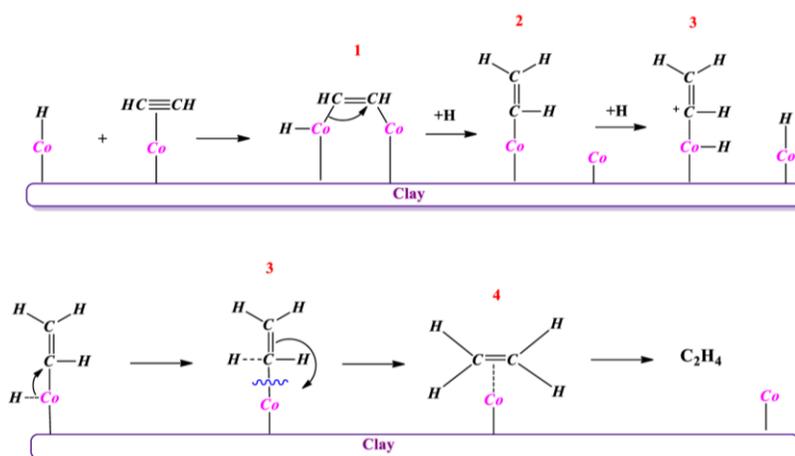
Fig. 5. Mechanism of Co catalyst performance
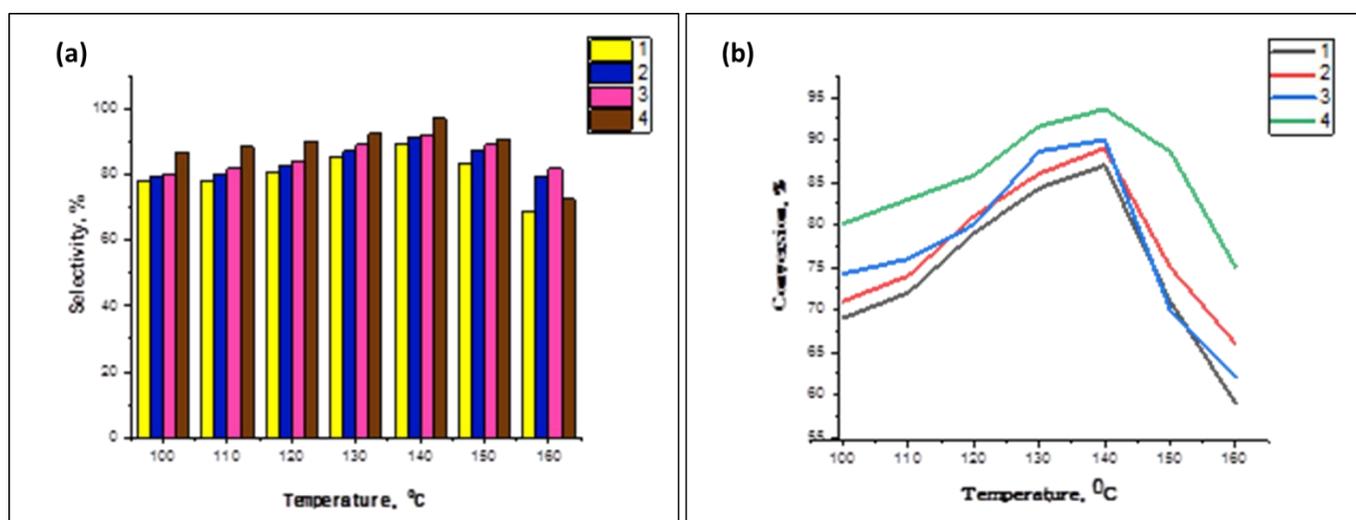
Fig. 6. Activities of the modified catalysts for acetylene hydrogenation. a) Effect of temperature on 7 % cobalt catalyst selectivity for ethylene during the hydrogenation of acetylene to ethylene. b) Effect of temperature on the conversion of acetylene to ethylene via hydrogenation. 1) 5 % Co/SiAl catalyst; 2) 5 % Co and 10 % Al/clay modified catalyst; 3) Pd / SiAl catalyst 4) 7 % Co/SiAl catalyst.

The highest yield of ethylene corresponds to the temperature range from 100 to 120 °C on a palladium catalyst. A further increase in temperature reduces the selectivity of ethylene formation. Ethane and butadiene were found in the reaction products. The most selective catalysts in the process of hydrogenation of acetylene are 7% Co/clay carbonization at 45 0°C   at the temperature 140 °C. Traces of oligomers appear when the temperature rises above 160 °C.

Subsequent increase temperature leads to a decrease in the yield of ethylene, whereas the selectivity decreases. As previously determined, the yield of ethylene increased on cobalt catalysts with increasing temperature to 140 °C. Because of increasing temperature, the selectivity of Co-based catalyst increased, and maximum selectivity appeared at 140 °C.

Acetylene conversions to ethylene of 93.58 % were achieved on 7% Co/clay carbonization at 450 °C at an optimum temperature of 140 °C. Side reactions are activated when the temperature rises above 180 °C, so the yield of ethylene is reduced. With an excess content of hydrogen, ethane and methane are formed, and traces of butadiene are found in a small amount.

4. Conclusions

In this work, changes in the morphological structures and chemical compositions of clay carrier and Co-based catalysts during preparation were studied. Chemical activation of the clay with 10% nitric acid decreased their calcium and sodium contents to 64.71% and 58.3%, respectively. Acid treatment removed 22.3% of the magnesium ions. The layered structure of the clay

mineral was preserved after activation, which was very important for subsequent modification of the surfaces of the obtained samples. Cobalt particles with different shapes and diameters ranging from 13.01 to 13.61 μm were visible in the SEM images of the 7%Co catalyst. At high magnification, fibres in the catalyst structure were observed following impregnation of the carrier with cobalt nitrate solution. Carbon nanofibres with diameters ranging from 57 to 400 nm were visible on cobalt catalyst samples following carbonisation in a propane-butane medium at 450 °C. The formation of carbon nanofibres was also indicated in the results of chemical analysis after carbonisation at 450 °C. The activity of the modified synthesised catalysts was studied during acetylene hydrogenation at temperatures from 100 °C to 180 °C. The increase of the hydrogenation temperature up to 140 °C increased the activity of the 7% Co/clay carbonization at 450 °C. Further increase in the temperature resulted in reduced catalytic selectivity and lower acetylene conversion to ethylene. The selectivity of the modified cobalt-containing catalysts for hydrogenation ranged from 89.62 % to 97 %. Acetylene conversions to ethylene of 93.58 % were achieved on 7% Co/clay carbonization at 450 °C, at an optimum temperature of 140 °C. The activity of the 7% Co/clay carbonization at 450 °C catalysts exceeded that of Pd catalysts.

Acknowledgements

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