Eurasian Chemico-Technological Journal 21 (2019) 341–346

https://doi.org/10.18321/ectj891

Physical and Chemical Characteristics of Cobalt Catalysts in the Process of Hydrogenating Acetylene

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Article info

Received:
18 June 2019

Received in revised form:
22 August 2019

Accepted:
19 October 2019

Abstract

This paper describes the results of studies of the physicochemical characteristics of cobalt catalysts and methods for modifying them with alumina. The elemental composition, the peculiarities of formation of the structural and phase composition of cobalt catalysts are studied. The influence of the carbonization process of cobalt catalysts at a temperature of 550 °C on the specific surface is determined. The increase in the specific surface in cobalt catalysts was studied to proceed uniformly, as the formation of large grains and accumulations of active components was not observed. According to the results of X-ray diffraction (XRD) analysis, the formation of aluminosilicate phases, cobalt oxide, and cobalt are detected. The surface of cobalt samples was investigated by scanning electron microscope (SEM). Electron microscopy revealed crystallites of cobalt particles with sizes of 300–400 nm. It is shown that in the course of modification with alumina, in cobalt catalysts active centers are formed that enhance their catalytic properties during the reaction of hydrogenation of acetylene to ethylene. It is found that cobalt catalysts exhibit catalytic activity in the acetylene hydrogenation reaction. On cobalt catalysts at a temperature of 160 °C at a conversion of 82%, the yield of ethylene is 64.1%.

1. Introduction

Currently, in the petrochemical industry, various applied catalysts for selective hydrogenation of hydrocarbons with a larger surface area of the active component are used. As the active components of the supported catalysts in the process of hydrogenation of acetylene compounds, metals of platinum group are used: Pt, Rb, Ru, Pd deposited on carbon, alumina, silica and other supports. In addition to the metals of the platinum group, copper, cobalt, and nickel deposited on various supports are used [1–2]. Palladium catalysts are highly active, but their selectivity is limited, they are rapidly deactivated during the reaction with the formation of paraffin and olefin hydrocarbons [3]. The applied value of these catalysts has increased particularly with the rise in platinum prices.

The properties of the supported catalysts are determined not only by the composition and nature but also by the texture features of the support and the particle size of the active component. The strategic choice is the choice of media and the method of preparation of the catalyst. Bentonite clays do not have a large number of acid sites, but due to their resistance to high temperatures and ease of surface modification, the catalytic properties can be enhanced [4]. According to the authors, by controlling the size and electronic state of the supported active components, it is possible to obtain catalysts with improved characteristics for hydrocarbon hydrogenation processes.

In the reactions of hydrogenation of acetylene, a large role is played by the size of the surface, which determines its adsorption and catalytic properties. The size and distribution of pore volumes over radii ensure the availability and transportation of reacting molecules. In this regard, the nature of clays with catalytic properties plays a significant role in the development of catalysts. Therefore, aluminosilicates and natural clay minerals in the petrochemical industry for the production of catalysts are used as sorbents and carriers.

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Clays have a small cation exchange ability, which grows linearly with a decrease in particle size. Acid activation and calcination at high temperatures lead to the formation of acid centers, contributing to an increase in catalytic activity. Clays modified by various metals, calcined at temperatures of 550 °C and higher have catalytic activity in hydrocarbon hydrogenation reactions [5–6].

The aim of this work is to study the influence of the structure of cobalt catalysts modified with alumina and to study their physicochemical characteristics.

2. Experimental

As modifying additives, solutions of aluminum and cobalt nitrates were used. Before aluminum is modified, the catalyst support is activated by nitric acid, where the process of removing alkali and alkaline earth metals from the clay composition is ongoing. After acid processing of clay, a phased modification is carried out with constant stirring with aluminum and cobalt salts. An important parameter of the carbonization of cobalt samples in a propane-butane medium is a temperature of up to 550 °C, which predetermines the process of thermal decomposition of salts and transformation of the catalyst structure. The carbonization process causes interaction between $A1_2O_3$ and SiO_2 necessary to obtain an active catalyst for hydrogenation. After application of the active components on the carrier, samples of cobalt catalysts, are formed by the extruder and dried, then the samples are carbonized in a propane-butane medium at temperatures of 480–550 °C [7].

The peculiarities of formation of the phase composition, morphology, and the ability to restore in the medium of propane-butane were investigated.

The specific surface area of the samples and the carrier was measured using low-temperature nitrogen adsorption. The volume and pore size distribution were measured by the Brunauer-Emmett-Teller (BET) method.

Research on a scanning electron microscope JEOL JSM-6390 LA with an energy dispersive X-ray detector JED 2300 was carried out by employees of the Federal Research Center Boreskov Institute of Catalysis SB RAS (Novosibirsk, Russia).

Analysis methodology: cobalt catalyst powder was applied onto the surface of carbon tape pasted onto an aluminum stage. To determine the homogeneity of Co distribution in the granules, we studied the granule surface and the cut surface.

Microphotographs of the surface were obtained in the registration mode of backscattered electrons (contrast depending on the atomic number of the element) and characteristic X-ray radiation (mapping of chemical elements). Registration was carried out under a low vacuum (residual pressure of 100 Pa) to remove a charge from the surface of the samples.

The elemental composition of the surface of the samples was determined using a JED 2300 energy dispersive X-ray detector (resolution 133 eV). The percentage of each element in the analyte was calculated using the obtained X-ray spectra using Analysis Station software version 3.62.07 (JEOL Engineering, Germany).

The catalytic activity of the synthesized catalysts was investigated using the developed acetylene hydrogenation unit (Fig. 1). The installation includes a reactor, gas rotameters, a gas flow meter IRG, a gas mixer (evaporator) and a heater, a separator and a temperature controller. After loading into the reactor, the catalysts are dried in an argon stream at a temperature of 100–120 °C for 80 min, then they are reduced with hydrogen for 60 min. The temperature in the reaction zone is measured by a thermocouple. Upon reaching the set temperature in the reactor, the flow of raw materials was dosed at different ratios using the gas flow regulator IRG-3. After the IRG-3, the gas enters the mixer (evaporator) and is heated at a temperature of up to 200 °C. When the gas stream passes through the mixer-evaporator, a gas mixture uniform in a composition is formed. The effluent from the evaporator is fed to the inlet of the reactor. From the outlet of the reactor, the vapor-gas mixture flow is directed to the separator and fed to the chromatographic analyzer for analysis. The reaction products were analyzed using a Chrom-3700 gas chromatography and Gas Chromatography with mass spectrometric detection (Agilent 7890A/5975C).

Helium was used as carrier gas. The analysis was performed in the following mode: sample volume (gas) 4 μl in non-dividing mode, capillary chromatographic column DB-35MS (Agilent, USA) 30 m × 0.25 mm, film thickness 0.25 μm, column thermostat temperature: 35 °C (exposure 10 min), evaporator temperature: 80 °C, detection mode – ion monitoring in the range m/z 10–550.

3. Results and discussions

All developed cobalt catalysts were investigated by a number of physicochemical methods of

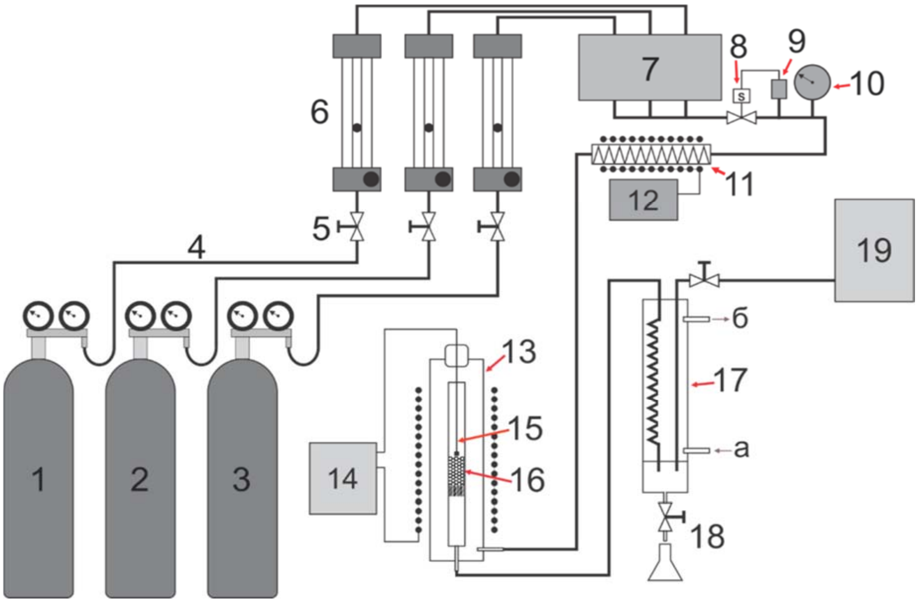


Fig. 1. Scheme of a pilot catalytic installation for hydrogenation of acetylene: 1, 2, 3 – gas cylinders; 4 – gas pipelines; 5 – needle valve; 6 – gas flow meters; 7 – gas flow meter IRG 3; 8 – solenoid valve; 9 – gas pressure safety device; 10 – gas manometer; 11 – gas mixer (evaporator) and heater; 12 – thermostat; 13 – reactor; 14 – thermo controller; 15 – thermocouple; 16 – catalyst; 17 – separator (a, b – cooling water); 18 – drain valve and condensate collector; 19 – chromatograph.

analysis. Table 1 shows the physicochemical characteristics of the synthesized catalysts. As can be seen in Table 1, the specific surface of the support (SiAl) is 24.62 m^2/g and cobalt catalyst (Co/SiAl-(5) is 78.68 m^2/g. For different modifier ratios (5%, 7% and 10%), the specific surface area of cobalt catalysts is 150.54, 128.74 and 114.58 m^2/g. Modification of cobalt samples with 5% alumina contributes to an increase in the specific surface area and pore volume of the catalysts, but an increase in the content of modifiers to 10% on the surface of the support leads to a decrease in the specific surface area of the. Among the samples studied, Co/SiAl-(5-5) carbonized at a temperature of 550 °C has the highest specific surface area of 150.54 m^2/g.

As can be seen in Table, the main phase in the samples, depending on the modification, is quartz, alumina, Co_3O_4, Na $(AlSi_3O_8)$, KSi_3AlO_8. When modified with alumina, orthoclase and albite are formed. These changes occur due to the formation of alumina and silica. These data clearly show that upon modification, new active centers with increased reactivity arise. Reduced Co, aluminum and orthoclase, albite, and muscovite were discovered. Carbon is not defined since the main line of graphite is very close to the main line of quartz, strong in intensity. If carbon is present as an amorphous component, then the halo from the amorphous phase is not visible (Fig. 2).

Figure 2 shows X-ray diffraction patterns of cobalt catalyst and clay samples. It was determined that upon modification with alumina, there takes place a redistribution of the intensities of the peaks corresponding to different planes. During the carbonization process, silicon and aluminum oxides form phases, including albites and glaucosites.

But in general, the structure of samples upon modification does not undergo radical changes. Ethane predominates in samples with a content of more than 10% alumina in the hydrogenation reactions of acetylene.

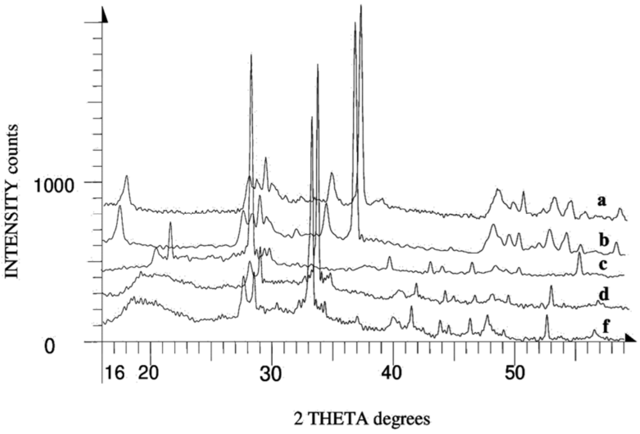


Fig. 2. X-ray diffraction pattern of cobalt catalysts and clay: a – clay; b – clay activated by nitric acid; c – Co-Al/SiAl-(5-5); d – Co-Al/SiAl-(5-7); f – Co-Al/SiAl-(5-10).

Table
Physico-chemical characteristics of cobalt catalysts

Catalysts	A_{BET} m^2/g	$V_{mesopore}$, cm^3/g	Phase composition of samples according to XRD	$K_{C_2H_2}$	Ethylene yield
Clay (SiAl) not modified	24.62	0.009	SiO_2, $Al_2(Si_2O_5)(OH)_4$	15.75	3.2
Co/SiAl (H_2O, carbon.) (5)	78.68	0.011	SiO_2, Co_3O_4, Al_2O_3	40.45	23.1
Co-Al/SiAl-(5-5)	150.54	0.064	SiO_2, Co_3O_4, Co, Al_2O_3, $Na(AlSi_3O_8)$, KSi_3AlO_8, $C_{12}H_{10}N_2$, $HCoO_2$	82.02	64.1
Co-Al/SiA-(5-7)	128.74	0.050	SiO_2, Co, Al_2O_3, $Na(AlSi_3O_8)$, KSi_3AlO_8	80.23	50.3
Co-Al/SiAl-(5-10)	114.58	0.047	SiO_2, Co, CoO, Al_2O_3, $Na(AlSi_3O_8)$, KSi_3AlO_8	86.05	46.8

A positive effect is observed when the clay is modified with 7% alumina, which under certain conditions forms macro and mesopores. This is consistent with the published data and explains catalytic selectivity [8–9]. The data of elemental analysis of cobalt catalyst samples show that after modification with alumina, the ratio of the silicate module is equal to 3 and the content of alkali and alkaline-earth metals is minimal.

Table 1 compares the test results of the catalytic properties of cobalt catalysts depending on the composition of the catalysts at a constant temperature of 160 °C. As can be seen in Table 1, catalyst Co-Al/SiAl-(5-5) allows you to selectively carry out the process of hydrogenation of acetylene. On a Co-Al/SiAl-(5-5) catalyst sample, at a conversion of 82.02%, the ethylene yield is 64.1%. Ethane predominates in the samples of catalysts Co-Al/SiAl-(5-7), Co-Al/SiAl-(5-10) in the reaction products of hydrogenation of acetylene. Side reactions of hydro-oligomerization proceed on Co-Al/SiAl-sample (5-10); traces of butane and butene were detected.

According to the results of the thermal analysis of catalyst samples, the dehydration process in an inert atmosphere is carried out at temperatures above 50 °C. As can be seen in Fig. 3, in the decomposition temperature range 50–250 °C, at 120, 150 and 180 °C there is a gradual decrease in the mass of the sample, which may be associated with the loss of water contained in the sample. At a temperature of 250 °C, a decrease in mass occurs (–4.55%) (Fig. 3).

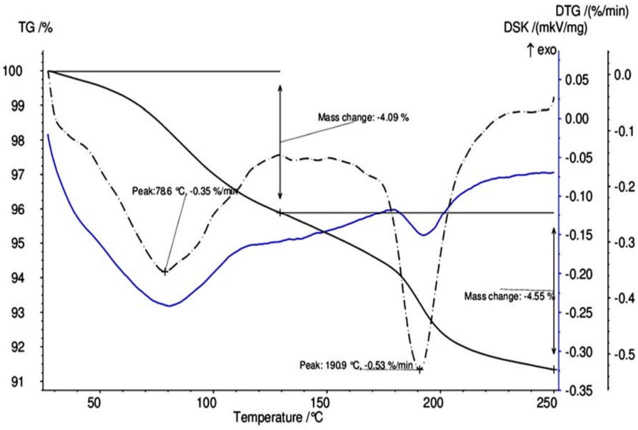
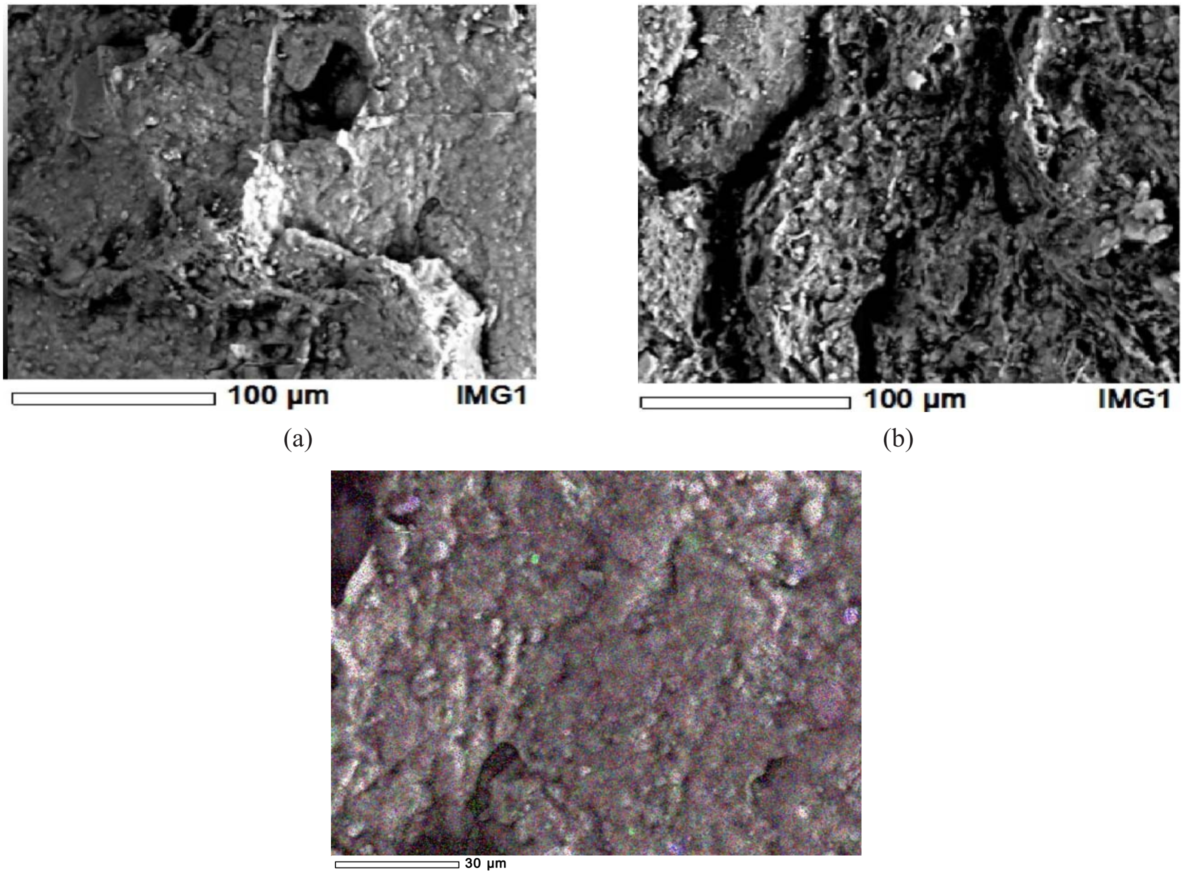


Fig. 3. Thermogram of cobalt catalysts.

This is due to the fact that there takes place the destruction of aluminosilicate structures. The bilayer clay lattice consists of alternating layers of octahedral $A1_2O_3$ and tetrahedral SiO_2 with a geometric arrangement similar to the arrangement of layers in montmorillonite, although the alternation of these layers is different. It is assumed that in kaolin, the $A1_2O_3$ layer is bonded to the corresponding SiO_2 layer and is held in this position by hydrogen atoms bonded to another SiO_2 layer. From this, it can be seen that such a system has a flat hexagonal structure. In halloysite – endellite clays, the water located between the layers weakens the indicated bonds between $A1_2O_3$ and SiO_2. Dehydration leads to the opening and compaction of the layers, forming a kaolin-like structure [9–11].

Figure 4 shows SEM photographs of cobalt Co-Al/SiAl-(5-5) catalysts. According to SEM, in the synthesized samples of catalysts modified with alumina and cobalt, cobalt particles are uniformly deposited on the surface of the catalyst (Fig. 4a). Scanning electron microscopy data showed a uniform distribution of the deposited cobalt particles over the surface of the carrier (Fig. 4a). The structure of the samples has channels of different sizes, small and large pores. (Fig. 4b).



(a) (b)

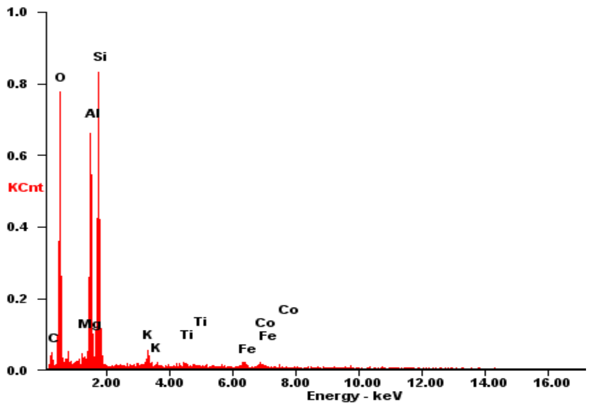
(c)

Fig. 4. Microphotography of cobalt catalysts: (a) – surface of cobalt catalyst (Co-Al/SiAl-(5-5)); (b) – microphotography cobalt catalyst section (Co-Al/SiAl-(5-5)); (c) – Co-Al /SiAl-(5-7) surface.

Figure 4b,c shows the results of SEM in the granule section. As can be seen, in Fig. 4b inside there are disordered channels of different sizes. According to electron microscopy, the Co-Al/Si-Al-sample (5-5) contains particles of different sizes, and with a magnification of 1000 times, many scaly particles located in the gaps between large aggregates are seen [12]. In Fig. 4c, cobalt particles are observed in the range of 300–400 nm, which leads to compaction of the interlayer structures.

Figure 5 shows the results of the elemental and spectral analysis of a cobalt-containing catalyst Co-Al/SiAl-(5-5).

Figure 6 shows the results on the dependence of selectivity on temperature. As is seen in Fig. 6, the most optimal cobalt catalyst is Co-Al/SiAl-(5-5). Ethane, methane, butene, and butane predominate in the reaction products on the Co-Al/SiAl-(5-7) and Co-Al/SiAl-(5-10) catalyst.



Element	***Wt%***	***At%***
C	11.30	19.11
O	36.36	46.18
Mg	0.72	0.60
Al	16.00	12.05
Si	24.35	17.62
K	2.33	1.21
Ti	1.06	0.45
Fe	3.35	1.22
Co	4.54	1.56
Matrix	Correction	ZAF

Fig. 5. Elemental and spectral analysis of cobalt-containing catalyst Co-Al/SiAl-(5-5).

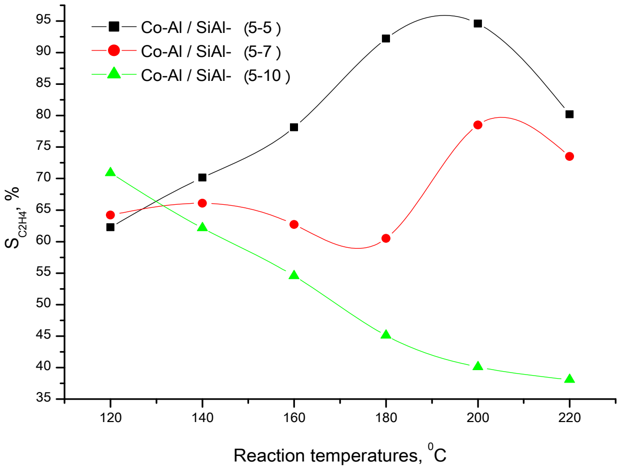


Fig. 6. Influence of temperature on ethylene selectivity during acetylene hydrogenation to ethylene.

Samples of cobalt catalysts were developed under identical conditions. When modifying cobalt catalyst supports with different alumina contents, it was determined that modification has a promoting effect on the catalytic properties in the reaction of hydrogenation of acetylene to ethylene. Thus, modification of a cobalt catalyst with 5–5% alumina increases the ethylene yield selectivity.

4. Conclusions

The effect of the composition of cobalt catalysts on the catalytic properties in the reaction of hydrogenation of acetylene to ethylene was studied. Large crystallites of cobalt particles with sizes of 300–400 nm are revealed electron microscopy. According to the XRD results, the formation of aluminosilicate phases, cobalt oxide and cobalt in the structure of cobalt catalysts are shown. Increasing content of up to 10% aluminum oxide leads to increasing in catalytic activity and further increase leads to decreasing selectivity on the yield of ethylene. The catalytic ethylene selectivity of modified cobalt catalysts in the acetylene hydrogenation reaction is 92–95%.

Acknowledgments

The work was carried out according to project No. AP05135250 by the support of the Ministry of Education and Science of the Republic of Kazakhstan.

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