

High-octane gasoline production processes using catalysts containing platinum

Abstract. *The catalytic reforming process is designed to increase the detonation resistance of gasolines and to obtain individual aromatic hydrocarbons, mainly benzene, toluene, xylenes - petrochemical feedstocks. It is important to obtain a cheap hydrogen-containing gas in the process for use in other hydrocatalytic processes. The importance of catalytic reforming processes in oil refining increased significantly in the 1990s. due to the need to produce unleaded high-octane gasoline.*

Keywords: *catalytic reforming, high-octane gasoline, hydroforming, platforming, platinum-rhenium catalysts, nitrogen compounds, sulfur compounds, paraffins, naphthenes, aromatics, hydrogenation reactions, dehydrogenation.*

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Introduction

Catalytic reforming is a process of converting low-octane gasolines in order to increase their octane number or obtain aromatic hydrocarbons for chemical processing.

To obtain high-octane gasoline, a fraction of 80-180° C is used as a raw material. As a result of catalytic reforming, gasoline with an octane rating of 80-85 is obtained. To obtain aromatic hydrocarbons, narrow fractions are used: 60-85° C - for benzene; 85-110° C - toluene; 110-140° C - xylenes.

The processes of catalytic reforming are subdivided [1, 280 p; 2, 24 p]:

- for processes with catalysts based on metal oxides. These are hydroforming processes. Hydroforming catalysts are oxides of molybdenum, chromium, cobalt. Temperature 480-540° C, hydrogen pressure 1-2 MPa; currently not used;

- processes using catalysts containing platinum. These are platforming processes. Platforming catalysts consist of platinum (usually 0.3-0.6 wt.%) supported on γ -alumina, which is activated by HCl or HF in order to increase its acidic activity (Cl or F content of 0.5-1%). In addition to aluminum oxide, amorphous aluminosilicates and zeolites are used as carriers. The temperature of platforming processes is 470-540° C, the hydrogen pressure is 2.5-5 MPa.

Recently, more efficient platinum-rhenium catalysts have become widespread, with the use of which it is possible to reduce the hydrogen pressure to 1-1.5 MPa, and to increase the yield and quality of gasoline. Rhenium prevents recrystallization (enlargement of particles) of platinum on the surface of the support, due to which a high number of platinum active centers is retained for a long time.

Materials and methods

Hydroforming was one of the earliest catalytic reforming processes. At present, it has lost its significance due to the low activity of oxide catalysts in comparison with platinum ones and gave way to platforming. Platforming catalysts (especially platinum-rhenium) work continuously for a long time without reactivation (1-2 years). This is due to the fact that in the presence of platinum under hydrogen pressure, unsaturated hydrocarbons are hydrogenated, which prevents their compaction and the formation of "coke", which reduces the activity of the catalyst. The catalyst is reactivated by passing air diluted with flue gases (oxygen content up to 2%) through it at 300-450° C and 1-2 MPa. Reactivation is also carried out by treatment with hydrogen. The total life of the catalyst is several years. Nitrogen and

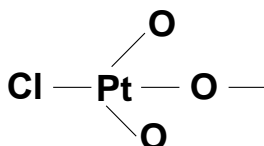
sulfur compounds, as well as impurities in raw materials of arsenic and lead, have a significant effect on the duration of platforming catalysts [3, P. 49-53].

Nitrogen compounds inhibit the activity of acid sites. Sulfur compounds cause reversible poisoning of platinum (activity is restored after reactivation), and arsenic and lead poison it irreversibly. Therefore, the platforming raw material should contain no more than 0.002 wt. % sulfur, 0.5×10^{-4} wt. % nitrogen and must be completely free of arsenic and lead. This is achieved by hydrotreating the feedstock in a hydrotreating reactor containing an aluminum-cobalt-molybdenum catalyst or an aluminum-nickel-molybdenum catalyst.

Results and discussions

The main reactions occurring during platforming

Platforming catalysts are bifunctional, since they contain two types of active sites: acidic active sites of the support (hereinafter we will conventionally denote H⁺) and metal active sites (platinum atoms). It was also shown that platinum cations are located on the surface of alumina-plateyzer [4, 14063 p]:

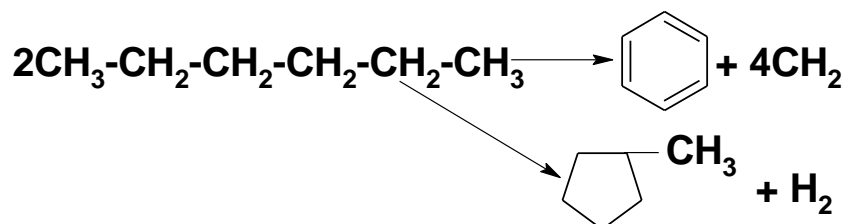


In the process of platforming at these active sites, hydrocarbons of the petroleum fraction undergo deep transformations. This is evidenced by the data on the group composition of raw materials (straight-run gasoline) and the product of its transformation during platforming (Table 1). From table. 1 it can be seen that in the process of platforming, mainly the transformation of alkanes and naphthenes occurs, as a result of which the content of aromatic hydrocarbons and isoalkanes increases, which, accordingly, leads to an increase in the octane number of the platformate [5, 144 p].

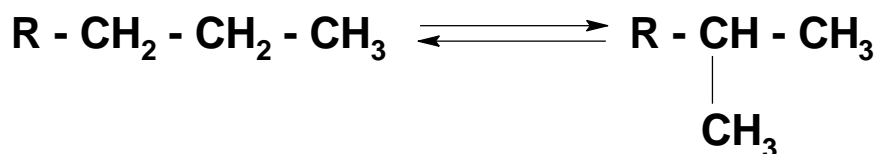
Table 1

Composition of raw materials and platforming products

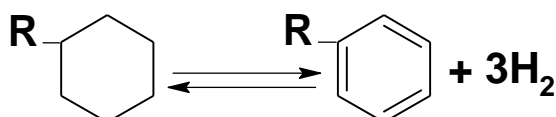
Hydrocarbons	Contents, mass. %	
	inrawmaterials	inplatformingproduct
Aromatic	10	50
Naphthenic	40	4
Isoparaffins	15	28
n-alkanes	35	18



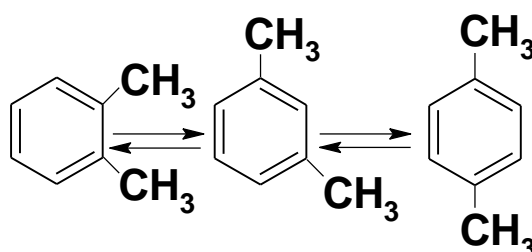
Isomerization takes place at acid sites (possibly on platinum ions), and hydrogenolysis at platinum sites [6, 23 p]:



Naphthenes. Six-membered naphthenes undergo dehydrogenation at platinum centers with the formation of aromatic hydrocarbons [7, 22 p]:



Aromatic hydrocarbons are isomerized at the acid sites of the carrier:



Reforming feedstock requirements

Straight-run gasoline fractions are used as raw materials for the catalytic reforming of gasolines, less often - gasolines of secondary processes [8, P. 10-13]. The composition of the raw material largely determines the yield and quality of the resulting product and has a significant effect on the efficiency of the catalyst [9, P.378-383]. The temperature limits for the selection of fractions (fractional composition) are selected depending on the purpose of the installation. The initial and final boiling points of the fraction (n.a. and c.c.) are the main characteristics. The low boiling point of the fraction (for example, 70 ° C) can lead to an increased content in straight-run gasoline of such light components as C₅, which practically do not contribute to an increase in the octane number, and C₆, the cyclization of paraffins of which with the formation of aromatic compounds proceeds with great difficulty. compared with C₇ or heavier paraffins. As the feedstock becomes heavier in the range of 62 - 105° C, the formation of aromatic hydrocarbons increases and the octane number of the product rises. Fractions with a boiling point of up to 85° C during the reforming process hardly undergo changes and therefore do not affect the quality of the resulting gasoline [10, 252 p].

The maximum possible end-boiling point of the oil fraction is largely determined by the requirements for the boiling point of stable catalyzate, the main reforming product. The difference between the boiling point temperatures of gasoline and raw materials should be 17-25° C, depending on the expected octane number. The boiling point of stable catalyzate is related to the boiling point of 90% of the gasoline fraction, since a higher value will promote increased formation of coke and polycyclic compounds. To determine the quality of the feedstock, you need to know the hydrocarbon composition of the feedstock - the quantitative content of paraffins, naphthenes and aromatics in the feedstock [11, 233 p]. Raw materials with an increased content of naphthenic hydrocarbons are of the greatest value for the process, since this condition contributes to an increase in the product yield and an increase in the concentration of hydrogen in the circulating gas.

The content in the feedstock of an excessive amount of olefins and diolefins is undesirable, since this leads to increased consumption of hydrogen and coke accumulation. Diolefins should be completely removed from the feed, and the olefin content should not exceed 0.1 wt%. It is also undesirable for the presence of impurities in the feed, the content of which adversely affects the

operation of the catalyst. The sulfur content leads to the poisoning of the metal function of the catalyst, and nitrogen-containing compounds negatively affect its acid function. The same can be said about the impurities of metal compounds, the content of which must be maintained at a very low level, since they are irreversibly adsorbed on the catalyst, which inevitably leads to a decrease in its activity. The presence in the raw material of the above impurities, which are poisons for alumina-platinum reforming catalysts, necessitates preliminary hydrotreating, and already pre-purified and prepared raw materials are supplied to the reforming unit [8, P. 10-13; 12, P. 185-190].

Conclusion

Depending on the technological design of the process, catalytic reforming is carried out at a temperature of 480-550 ° C and a pressure of 0.35-3.0 MPa [7, 22 p]. Temperature is an important parameter that has a significant effect on the rate of ongoing reactions, which is reflected in the yield of target products. The catalytic reforming process is highly endothermic (with heat absorption), therefore, its implementation requires several reactors (3 or 4) with intermediate heating of raw materials in furnaces. In the first reactor, the naphthenes dehydrogenation reaction proceeds at the highest rate. In the latter reactor, endothermic dehydrocyclization reactions and exothermic paraffin hydrocracking reactions take place. The temperature difference across the reactors depends on the group composition of the feedstock, the selectivity of the catalyst and decreases as the catalyst depletes and the hydrocracking reaction develops. In this connection, in the first reactor, the largest, and in the last reactor, the smallest temperature difference between the inlet and outlet of the reactor is observed. A decrease in the temperature difference in the reactors occurs by reducing the contact time of the feedstock with the catalyst, that is, by reducing the volume of the catalyst in the reactors. Therefore, the first and last reactors differ in the loaded volumes of the catalyst. The former has the smallest volume compared to the latter, which contains the largest amount of the loaded catalyst. To reduce the role of hydrocracking reactions in the first reactors, an increasing temperature regime is maintained in the reactor cascade. In practice, there are installations with different options for changing the temperature across the reactors: "ascending", "descending", "straight". Ultimately, the temperature profile for reactors is determined at the design stage of a specific installation [10, 252 p].

These elements affect the kinetics of the hydrogenation and dehydrogenation reactions and regulate the effective size of Pt clusters, which contributes to better selectivity, stability, and activity of the catalyst [12, P. 185-190; 13, P. 90-95].

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Құрамында платина бар катализаторларды пайдалана отырып, жоғары октанды бензиндерді алу процестері

Аңдатпа. Каталитикалық риформинг процесі бензиндердің детонацияға төзімділігін арттыруға және жеке хоши істі көмір сутектерді, негізінен бензол, толуол, ксилолдар-мұнай-химия шикізатын алуға арналған. Басқа гидрокаталитикалық процестерде қолдану үшін процесте арзан сутегі бар газды алу маңызды. Мұнай өңдеуде каталитикалық риформинг процестерінің маңызы 1990 жылдары айтарлықтай өсті. қорғасынсыз жоғары октанды бензин шығару қажеттілігіне байланысты.

Түйін сөздер: каталитикалық риформинг, жоғары октанды бензин, гидроформинг, платформалау, платина-рений катализаторлары, азот қосылыстары, күкірт қосылыстары, парафиндер, нафтендер, ароматты заттар, гидрлеу реакциялары, дегидрлеу.

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Процессы производства высокооктановых бензинов с использованием платиносодержащих катализаторов

Аннотация. Процесс каталитического риформинга предназначен для повышения детонационной стойкости бензинов и получения индивидуальных ароматических углеводородов, преимущественно бензола, толуола, ксилолов - нефтехимического сырья. В процессе важно получить дешевый водородсодержащий газ для использования в других гидрокаталитических процессах. Значение процессов каталитического риформинга в нефтепереработке значительно возросло в 1990-х годах в связи с необходимостью производства неэтилированного

высокооктанового бензина.

Ключевые слова: каталитический риформинг, высокооктановые бензины, гидроформинг, платформинг, платино-рениевые катализаторы, соединения азота, соединения серы, парафины, нафтены, ароматика, реакции гидрирования, дегидрирование.

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