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CATALYSTS OF THE HYDROCARBONS CONVERSION FOR LONG-CHAIN α -OLEFINS OBTAINMENT

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Abstract: A literature review on the catalysts, used in the hydrocarbons conversion to produce α -olefins, is given in the article. The catalysts derived from natural raw materials are considered as the most accessible ones. Methods of decationization and modification of clinoptillolite, the main component of natural zeolites of Russia and Kazakhstan, are described. Montmorillonite clay is used as a carrier. The most attention in the cracking catalysts review was drawn in the direction of the paraffin cracking with obtainment of long-chain α -olefins. The production of long-chain α -olefins by the oligomerization of ethylene and propylene, where Bronsted and Lewis acids are used as catalysts, is shown along with cracking. In addition to natural and synthetic zeolites, heteropoly acid (HPA) is also used in the catalysts production.

Keywords: cracking, paraffin, heteropolyacid, natural zeolite, aluminum oxide

ҰЗЫНТІЗБЕКТІ α - ОЛЕФИНДЕРДІ АЛУ ҮШІН КӨМІРСУТЕКТЕРДІ КОНВЕРСИЯЛАУҒА АРНАЛҒАН КАТАЛИЗАТОРЛАР

Аңдатпа: α -олефинді алу үшін көмірсутектерді конверсиялау катализаторы бойынша әдеби шолу келтірілген. Табиғи шикізаттан алған катализаторлар ең қолжетімдісі болып табылады. Ресей және Қазақстанның табиғи цеолиттерінің негізгі компоненті клиноптилолит болып есептеледі, оны дайындау және модификациялау әдістері келтірілген. Тасымалдағыш ретінде монтморрилонитті басықты алады. Крекинг катализаторларына шолу жасағанда ұзынтізбекті α -олефинді алу үшін парафиндерді крекинглеу бағытына қарай жасалынды. Крекингпен бірге Бренстед және Льюис қышқылы катализаторлар ретінде пайдаланылатын этилен мен пропиленді олигомеризациялау арқылы ұзын тізбекті α -олефиндерді алу ұсынылған. Катализаторларды алу үшін табиғи және синтетикалық цеолиттермен қатар гетерополиқышқылдар да (ГПК) қолданылады.

Түйінді сөздер: крекинг, парафин, гетерополиқышқыл, табиғи цеолит, алюминий оксиді

КАТАЛИЗАТОРЫ КОНВЕРСИИ УГЛЕВОДОРОДОВ ДЛЯ ПОЛУЧЕНИЯ ДЛИННОЦЕПНЫХ α - ОЛЕФИНОВ

Аннотация: Приведен обзор литературы по катализаторам конверсии углеводородов для получения α -олефинов. Самыми доступными являются катализаторы, полученные из природного сырья. Основным компонентом природных цеолитов России и Казахстана являются клиноптилолит, приведены методы его декационирования и модифицирования. В качестве носителей используется монтморрилонитовая глина. При обзоре катализаторов крекинга сделан в сторону крекинга парафинов с получением длинноцепных α -олефинов. Наряду с крекингом показано получение длинноцепных α -олефинов олигомеризацией этилена и пропилена, где в качестве катализаторов используется кислоты Бренстеда и Льюиса. Наряду с природными и синтетическими цеолитами для получения катализаторов используется гетерополикислота (ГПК).

Ключевые слова: крекинг, парафин, гетерополикислота, природный цеолит, оксид алюминия

The rapid development of the chemical industry in the second half of the 20th century led to the fact that catalysis and catalysts, which penetrated practically all industrial processes, became the main levers of development [1]. Petrochemical syntheses have become highly dependent on the nature of the hydrocarbon feedstock — oil and gas. The main problem of the processing of natural hydrocarbon raw materials was the problem of conversion of relatively inert alkanes, which were compounds of oil and gas, into reactive olefins. From olefins, you can get almost any compound of organic chemistry.

The importance of olefins caused the fact that the product with the trade name “ α -olefins” appeared in international market. Moreover, the monographs on higher olefins [2], analysis of petrochemical syntheses based on it and methods from the production of various hydrocarbons were published. Long chain α -olefins can be obtained by several methods. These are oligomerization of the simplest olefins, like ethylene and propylene, and the dehydration of the corresponding monohydric alcohols. The most available raw materials for their synthesis were paraffins, which are formed in large quantities during the production of winter types of diesel fuel during the dewaxing process. Long chain α -olefins are the feedstock for the production of lubricating oils, surfactants, flotation agents and many other consumer goods. The development of deep processing of hydrocarbons [3,4] prompted the disclosure of the action mechanism of the catalysts for saturated hydrocarbons cracking. The process comes down to the separation of hydrogen from the limiting hydrocarbon molecule by strong acidic centers (which are synthetic zeolites (solid acids)) on the catalyst surface. The presence of the D.Sokolsky Scientific School in Almaty [5] and appreciation of the role of the catalyst allowed representatives of the school to create catalysts for the cracking of paraffins in the synthesis of long-chain α -olefins [6], to make a significant contribution to the theory of heterogeneous catalysis [7], and to develop catalysts of light alkane conversions [8–9]. The development of low-cost methods for producing long-chain α -olefins is one of the priorities in the processing of technical paraffin and “slack wax”.

In the current work we have tried to analyze the methods of long-chain α -olefins obtainment by the paraffins cracking.

The reference data analysis has shown that the paraffins cracking problems can be conditionally divided into several groups by the used catalyst types. The authors [11–34] used the catalysts based on the natural and synthetic zeolites and various clays. The works [35–46] are devoted to the cracking of paraffins on different catalysts. The works of the authors [47–61] study obtainment of the olefins of different structure, [62–77] used the catalysts based on the synthetic heteropolyacids (HPA), [78,79] have tried to carry out the paraffins cracking process on the superacids.

Large deposits of natural zeolite, consisting mostly of clinoptilolite, have been discovered and are being developed in the Almaty region near the Shankanai settlement. The chemical structure of Shankanai natural zeolite in percentage is: SiO_2 – 57–65; Al_2O_3 – 8,4–8,5; TiO_2 – 0.07–0.7; Fe_2O_3 – 6,0–10,2; MnO – 0,067–0,199; MgO – 2,5–3,4; CaO – 3,5–4,6; Na_2O – 2–2,1; K_2O – 5–2,3; P_2O_5 – 0,012–0,173; H_2O – 4,09; the surface area does not exceed 9,5 m^2/g [6].

According to [24], the empirical formula of the natural clinoptilolite of the Amur Region is $(\text{Na},\text{K})_4\text{Ca}[\text{Al}_6\text{Si}_{30}\text{O}_7]\cdot 24\text{H}_2\text{O}$, the Si/Al ratio is > 4 (~82% of the tetrahedra are occupied by silicon, which makes it heat-resistant in air up to 1000 K, and also resistant to aggressive substances and ionizing radiation). The two-dimensional system of clinoptilolite intracrystalline channels is oriented parallel to the axes with window sizes of 0.4x0.56 nm and 0.44x0.72 nm respectively. The free volume of its intracrystalline space is 34%. The density of the mineral varies within 2,11 – 2.20 g/cm^3 . The specific surface area reaches ~ 105 cm^2/g . Water filling the intracrystalline space of a clinoptilolite has the ability to be reversibly removed many times over a wide range of temperatures (from room temperature to ~ 900 K) without destroying its structure. Shankanai zeolite has no similar characteristics described in the references.

Research on the use of natural zeolites in various areas of the national economy are carried out in Kazakhstan during the last decades. We

were interested in obtaining catalysts, sorbents and carriers from natural clinoptilolite. Using the patterns of modifying natural minerals in [10] in our studies [6], we have observed that decantation of the Shankanai zeolite from alkali and alkaline earth metal ions goes well in dilute hydrochloric acid solutions. With an increase in the concentration of hydrochloric acid above (1:1), the crystalline framework of the zeolite is destroyed and the clinoptilolite is transformed into an amorphous aluminosilicate. The composition of natural zeolite contains oxides of three valent iron from 6.0 to 10.2%, depending on the depth of the formation.

Analysis of the reference data on the use of clinoptilolite shows that the main problem with modifying is the removal of iron compounds from the surface and pores of natural clinoptilolite. The authors of [12] removed ferric compounds by treatment with nitric acid at 70°C. The adsorption capacity of iron chloride on clinoptilolite pretreated with HNO_3 was two times greater than that of potassium chloride and cesium chloride. Removal of chloride salts is not difficult, since they dissolve well in water and acid. The problem is much more difficult if the iron on the surface or pores of the zeolite is in the form of Fe_2O_3 or Fe_3O_4 . There is information in [13] that natural clinoptilolite is used as a carrier for a catalyst for the hydrogenation of citral (2.42% Pd/c clinoptilolite), kinetic parameters are determined and it is shown that the used catalyst allows to increase the selectivity of hydrogenation of citral to citronellal to 90%. The catalyst restores the original activity after regeneration and can be reused.

In the works [14-19] the information about the properties of natural zeolites is given. So in the work [14] it is indicated that there is a high yield of grapes in the vicinity of the deposits of natural clinoptilolite in Georgia. This information is consistent with the observations of residents of the Shankanai village of the Almaty region. Thus on Mount Maitobe, under which there are deposits of natural clinoptilolite, there is an increased growth of medicinal herbs and fattening of livestock, which are famous for their positive properties. The authors of [14] explain

this phenomenon by the increased adsorption and ion-exchange properties of natural clinoptilolite. The authors [15-16] studied macro and mesopores in natural zeolites, including clinoptilolite, which by their characteristics are close to those on montmorillonite [18] and can be used as sorbents for purifying drinking water from heavy metal ions. The authors of [19] studied the kinetics of ion exchange of zinc and lead on a modified clinoptilolite, determined the diffusion coefficients of Zn^{2+} and Pb^{2+} ions depending on their concentration in the solution and the time of onset of ion exchange before its equilibrium. It was established [19] that the diffusion coefficient does not depend on the initial concentration and decreases with time until equilibrium in the system.

A number of works [20-34] provide information on the study of natural minerals, among which are natural clinoptilolites, montmorillonites and other minerals that can be used as catalysts, carriers, or sorbents.

The authors of [23] note that the latter crystallize on the surface when clinoptilolite is combined with NiO , ZnO , and Cu_2O nanoparticles. The particle size varies from 2 to 5 nm, which exceeds the pore size of the clinoptilolite channel (approximately 0.4 nm), therefore the crystallization of the oxide phases takes place on the surface of the clinoptilolite microcrystals. Clinoptilolite dehydrates at 550 °C when heated in air with nickel, zinc and copper oxides planted on it, whereas it decomposes into amorphous aluminosilicate if manganese oxides are present on the surface.

In [21], a heteropolyanion-polyaniline ($\text{Na}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ PVMo/PANI) nanocomposite was used for polymerization. The carrier, designated PANI, had the structure of natural montmorillonite. The authors [30] studied tuffs (B) from Western Turkey, containing large amounts of clinoptilolite to produce sorbents of sulfur dioxide. Using the methods of diffraction of slow electrons (XRD) and FT-IR, it was shown that the natural sample consists of clinoptilolite (80 - 85%) with a small amount of quartz (7-8%), feldspar (5-6%) and mica-illite (4-5%). Adsorption capacity towards SO_2 depends on the type of cat-

ion that is surrounded by solid acid and the treated samples are arranged into the following row: Na-B > K-B > Mg-B > natural-B > Ca-B. Summarizing their results, the authors of [30] come to the conclusion that tuffs rich in clinoptilolite can be considered as potentially good sorbents for the removal of SO_2 . In the study of natural clinoptilolite mined in the Sonora mine, Mexico, the chemical composition and its dependence on the pretreatment of natural zeolite was established using the XRD and XPS methods, as well as FT-IR [30]. The state of iron compounds in natural samples is shown by the EPR and EDS methods (disperse spectroscopy), but the compositions of natural clinoptilolite are absent in the work.

The authors of [28] report the chemical composition of natural zeolites and tuffs containing clinoptilolite of the Kholinskoe, Shivurguyskoe, Chugueskoe and Honguruu deposits (Russia), determined by the X-ray fluorescence method. The content of iron compounds is a maximum of 2.23% in the Sivurguyskoye field, in the others it fluctuates around 1%. The maximum content of clinoptilolite is 90% in Honguruu, and in other fields it ranges from 51.0 to 68.0%. Samples of these zeolites after heat treatment at 120–150°C were subjected to mechanical treatment (crushing) for 3 hours. The ratio of Si/Al varies between 2.29 (Shabazit) - 5.57 (Honguruu), the specific surface varies from 20.14 to 30.45 m^2/g , the pore volume varies from 0.084 to 0.101 cm^3/g , depending on the dose of mechanical processing. The crushed samples of natural clinoptilolite were tested for the adsorption of strontium and copper ions from solutions and their high adsorption capacity was shown [28]. Mechanical activation leads to the increase in specific surface area, which leads to the increase in the adsorption capacity of both clinoptilolite and chabazite.

According to the authors of [20, 33] clinoptilolite is the most common natural zeolite, whose crystalline three-dimensional framework consists of aluminum oxide-silicon tetrahedra $(\text{Si}, \text{Al})\text{O}_4$ and is penetrated in several directions by large channels connected to each other and to the surface of the crystal through narrow openings (entrance windows). The unit cell composition is $(\text{Na}, \text{K})_4\text{Ca} [\text{Al}_6\text{Si}_{30}\text{O}_{72}] \cdot 24\text{H}_2\text{O}$. Large

reserves of them were found in Transbaikalia and the Far East. In [33], samples of zeolites from the Vanginsky field, consisting mainly of clinoptilolite, were studied, and their adsorption properties towards benzopyrene were determined. Modification of a natural zeolite with various cations leads to the improvement in adsorption processes [33], the greatest effect is achieved when modifying with silver cations. Over time, the rate of adsorption of 3,4-benzopyrene molecules decreases significantly, which is apparently due to the achievement of adsorption saturation.

The results of studies of natural zeolite of Transbaikalia and the Far East are summarized in the thesis [24], where it was stated that modifying clinoptilolite with alkali metal ions Li^+ , Na^+ and K^+ is determined by their physicochemical properties, ionic radius and hydration pattern, and its efficiency decreases in $\text{K} > \text{Na} > \text{Li}$ row. Further conclusions are made on the basis of the results of the data on the electrical conductivity of natural clinoptilolite. The exchange of ferric ions in clinoptilolite is realized by two mechanisms: fast - external diffusion and slow - intra diffusion. The rate of the ion-exchange capacity of the Fe^{3+} form, realized by the external diffusion mechanism, is 40–80%, and 20–60% by the intradiffusion mechanism. The equilibrium time in the exchange of Fe^{3+} decreases with the size of the zeolite granules. The calculated values of the kinetic parameters of Fe^{3+} ion exchange in both modified and unmodified clinoptilolite samples depend on the temperature and size of the zeolite granules. Almost complete regeneration after metabolic processes occurs in a 1 M solution of sodium chloride within 24 hours. The ion-exchange properties of the clinoptilolite samples studied allow us to recommend this zeolite as a highly efficient ion exchange for the deironing of natural waters.

The authors of [31] give results on the use of clinoptilolite zeolites as a binder component in the preparation of building materials. In the work [32], X-ray fluorescence analysis was used to study ion exchange in clinoptilolite in order to improve it. The authors of [34] give results on the treatment of natural zeolite by ion exchange, mineral acid, temperature, and water vapor.

Summarizing the cited literature in [11–34], we can conclude that researchers are looking for ways to use cheap natural zeolite. Moreover, the bulk of natural zeolite with a predominant content of clinoptilolite, which, when modified, can be a good sorbent, a component of building ma-

terials, is located in Russia. There are few data on the systematic study of natural zeolites in Kazakhstan, while many dissertations and review articles are devoted to Transbaikal and Far Eastern zeolites.

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