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Effect of Rhenium on the Physicochemical Properties of MFI-type Zeolite and the Dynamics of its Deactivation in the Course of Upgrading the Straight-Run Gasoline Fraction of Oil

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Abstract

Rhenium containing catalysts are prepared on the basis of high-silica zeolite of pentasil family with a silicate modulus 40. Modification of the zeolite with rhenium introduced using various methods results in the changes in its structural characteristics: a decrease in specific surface area, pore volume and diameter. The most noticeable decrease in these parameters is observed when impregnation and ion exchange are used. The use of rhenium-containing zeolite catalysts for upgrading the straight-run gasoline fraction of oil allows increasing the yield of liquid products – high-octane gasolines characterised by a low content of aromatic hydrocarbons and a high octane number. A decrease in the aromatizing activity of Re-containing catalysts contributes not only to improvements in the environmental characteristics of resulting gasolines but also into an increase in the time of the stable operation of catalysts. Due to an increase in the rate of hydrogenation, the introduction of rhenium significantly reduces the amount of coke deposits formed on the catalysts under study during the process. According to the rate of formation of coke deposits, Re/MFI catalysts prepared using different methods are ranked as follows: ion exchange < ultrafine powder < impregnation < mixing with salt < MFI. Carbon densification products formed on rhenium-containing catalysts are less condensed and more homogeneous than coke obtained on unmodified zeolites. According to the degree of decrease in catalytic activity or aromatizing ability during the same time of operation, the catalysts under study may be ranked as follows: MFI > Re/MFI (ion exchange) > Re/MFI (ultrafine powder) > Re/MFI (impregnation) > Re/MFI (mixing with salt).

Keywords: MFI-type zeolite, rhenium, modification, coke

INTRODUCTION

Catalysts containing a metal applied on different supports (aluminium or silicon oxides, zeolites, etc) are of great industrial significance. Making an active surface, it is important to use a modifying agent that does not undergo recrystallization during catalysis. From this point of view, rhenium is of interest because it is characterized by the high melting point (3186 °C) and density (21.02 g/cm^3). The high solubility of rhenium salts in water allows catalyst modification by means of impregnation (IM) and ion exchange (IE). As an active dehydrogenating agent, rhenium accelerates the reactions of proton detachment and transfer in hydrocarbon molecules, so it is used in oil processing: hydrogenation of the fractions of commercial mixtures of synthetic fatty acids and propylene hydroformylation, metathesis of olefins, *n*-alkane cracking and reforming, a large-scale process [1–5]. The application of platinum-rhenium catalysts in the industry allowed an increase in the productivity of reforming installations, a decrease in expenses by replacing the major part of platinum with rhenium, an increase in the yield of gasoline and the operation lifetime of catalytic systems; special attention is paid to the problems connected with an increase in stability [6, 7].

One of the major obstacles on the way to the broad application of the catalysts based on high-silica zeolites in industrially significant processes is their relatively low stability. To decrease coke content and the degree of its condensation, the authors of [8] considered modification of zeolite surface by means of structurally selective IE. For this purpose, polyvalent cations are chosen that are able to form a solvate shell in an aqueous solution, thus preventing cation penetration into zeolite crystals. Changes in the specific activity of the centres of coke formation promote a substantial increase in the stability of zeolite catalyst operation.

It was demonstrated by us previously [9] that the application of various methods of rhenium introduction into high-silica zeolite causes an increase in the yield of target products – high-octane gasoline characterized by a decreased content of aromatic hydrocarbons and the high octane number. A decrease in the amount of aromatic hydrocarbons in the resulting gasoline, along with improvement of the ecological parameters of gasoline, should promote an increase in the time of stable operation of the catalyst.

The goal of the present work was to study the effect of the method of modification with rhenium on the physicochemical properties of MFI type zeolite and the dynamics of its deactivation during processing the straight-run gasoline fraction of oil.

EXPERIMENTAL

The MFI zeolite with silicate module 40 was modified by means of IE, IM (the “wet” method) and dry mixing with ammonium perrhenate (NH4ReO4) (DM), as well as with the ultrafine powder (UFP) of rhenium (the “dry” method). Rhenium content in the catalysts was 0.5 mass %, the average size of rhenium UFP was ~770 nm. Dry mechanical mixing of zeolite with the salt or with rhenium UFP was carried out in a KM-1 vibromill in the air for 2 h. Catalysts modified by means of IE and IM were dried at 100 °C for 5 h till the constant mass. Then these samples and the sample obtained by dry mixing with rhenium salt (DM) were annealed at 550 °C for 4 h. Zeolite modified with rhenium UFP was not annealed to conserve the properties of UFP. The resulting powdered mixtures were pressed in tablets, ground, and the fraction of 0.5–1.0 mm was taken for tests.

The specific surface area (S) of the catalysts was determined using Brunauer–Emmett–Teller method (BET) from the data on low-temperature (–196 °C) nitrogen adsorption recorded with the help of an automatic gas adsorption analyzer Sorbtometer M (KATAKON CC, Russia). To purify the sample surface before measurements, so-called sample training was carried out, which included heating at 260 °C for 100 min in a steady flow of a helium-nitrogen mixture of the required composition. Nitrogen desorption was performed at 40 °C. The volume and size of pores in the samples were calculated with the help of Barett–Joyner–Halenda (BJH) model from the data of adsorption and desorption isotherms at a relative pressure of $P/P_0 = 0.99$.

The catalytic activity and stability of initial zeolite and rhenium-containing catalysts obtained on its basis were studied in the course of upgrading the straight-run gasoline fraction ($T_{\text{s.b.}} = 155$ °C) of oil (mass %): cycloalkanes C_5–C_{10} (37 %), isoalkanes C_4–C_{10} (30 %), *n*-alkanes C_3–C_{14} (25 %), aromatic hydrocarbons C_6–C_{12} (8 %); octane number determined using a research procedure was 70 points.

The process was carried out for 30 h at atmospheric pressure, at a temperature of 380 °C, with the flow rate of raw material supply 2 h^{-1} in a flow installation with the immobilized catalyst bed. The volume of the catalyst loaded into the reactor was 4 cm^3, and the size of its granules was 0.5–1.0 mm. The concentration of aromatic hydrocarbons in the resulting gasoline was used as a measure of the catalytic activity of the samples.

Analysis of the composition of initial raw material and the products of its transformation was carried out by means of gas-liquid chromatography using a Khromatek-Kristall 5000.2 chromatograph (GK Novye Tekhnologii, Russia). To determine the composition of the liquid phase, we used a capillary column BP-1 PONA (100 m × 0.25 mm × 0.5 μm), while the gas phase was analyzed using a capillary GS-Gas-Pro column (60 m × 0.32 mm) and a prepacked column Carbosieve S-II (4 m × 2 mm, 60/80 mesh). The octane numbers of initial raw material and the products obtained in the catalytic process were determined through calculation relying on the chromatographic data.

Investigation of the nature of coke deposits formed on the surface of the catalysts under study during the transformation of the straight-run gasoline fraction of oil was carried out by means of thermal analysis with the help of a Q-1500 D derivatograph of Paulik-Paulik-Erdey system (MOM, Hungary). Measurement results were processed using Tanaliz software providing control and measurement of temperature (*T*) and sample heating rate (*W*), changes of sample mass (TG), thermal effects (DTA). Heating rate was 10 °C/min, the mass of the sample under investigation was 400 mg, measurements were carried out in the air. Aluminium oxide (α-Al_2O_3) was used as a reference sample.

RESULTS AND DISCUSSION

Changes in the texture characteristics of the MFI zeolite modified with rhenium using different methods are shown in Table 1. Initial zeolite has the largest specific surface area and pore (including the volume of meso- and micropores). Zeolite modification with rhenium leads in all cases to a decrease in these parameters. Specific surface area decreases to the lowest extent after the addition of rhenium UFP, which occupy mainly the surface of zeolite and block the access of adsorbate molecules to sample surface, which is evidenced by a decrease in the average pore diameter from 2.00 to 1.68 nm, but promote an increase in the volume of mesopores. Dry mixing of the zeolite with NH_4ReO_4 also leads to a decrease in specific surface area. However, it decreases to the most substantial extent after modification using the wet procedures – IM and IE, though pore diameter and volume remain almost unchanged.

The composition of the gaseous products of the transformation of straight-run gasoline fraction of oil, obtained after 1, 15 and 30 h of operation of initial and rhenium-containing zeolites are shown in Table 2. For all catalysts, *n*-alkanes prevail in the formed gases, while isoalkane content is substantially lower, and alkenes are present in insignificant amounts. With an increase in the time of catalyst operation, the yield of *n*-alkanes increases with a simultaneous decrease in the content of isoalkanes and alkenes as a result of deactivation of their active centres. It may be stressed that the amount of light isoalkanes formed on rhenium-containing catalysts is much larger in comparison with the initial sample.

The catalysates obtained on all samples are identical in qualitative composition but differ from each other in the content of specific hydrocarbons (Table 3). Similarly to the case of the gaseous products of reactions, the concentration of *n*-alkanes in gasoline increases with an increase in the time of catalyst operation, while the concentrations of other hydrocarbons decrease. The observed regularities are connected with the partial loss of the catalytic activity by the catalysts as a result of coalification of their surface. However, a decrease in catalytic activity proceeds non-uniformly. For example, after operation for 1 h, the highest aromatizing activity is exhibited by the zeolite modified with Re UFP (arene content 34.0 mass %), the lowest activity is exhibited by the sample prepared by means of IM (22.2 mass %). After 15 h, the maximal amount of aromatic hydrocarbons is still formed on the Re/MFI (UFP) sample: 22.1 mass %, while the minimum amount is formed on initial MFI (13.1 mass %). After reaction for 30 h, this dependence is still conserved. The octane numbers of the resulting gasoline samples decrease with an increase in the time of catalyst operation. So, if the catalytic activity is measured as the fraction of aromatic hydrocarbons in reaction products, it decreased for the samples: MFI – 2.6 times; Re/MFI (IE) – 1.9 times; Re/MFI (UFP) – 1.8 times; Re/MFI (IM) – 1.6 times; Re/MFI (DM) – 1.4 times.

The data of thermal analysis (DTA and TG) of initial MFI and rhenium-containing catalysts af-

TABLE 1

Texture characteristics of zeolite catalysts

Catalyst	S_{BET}, m^2/g	S_{mezo}, m^2/g	S_{micro}, m^2/g	V_{total}, cm^3/g	V_{mezo}, cm^3/g	V_{micro}, cm^3/g	*D*, нм
MFI	443	158	285	0.19	0.06	0.13	2.00
Re/MFI (UFP)	416	137	279	0.17	0.10	0.07	1.68
Re/MFI (DM)	364	112	252	0.17	0.05	0.12	1.87
Re/MFI (IM)	346	121	225	0.17	0.06	0.11	1.98
Re/MFI (IE)	334	95	239	0.17	0.05	0.12	2.00

Note. S_{BET} is the specific surface area of the catalyst, measured according to the BET procedure; S_{meso}, S_{micro} is specific surface area of meso- and micropores; V_{total} is the total specific pore volume; V_{meso}, V_{micro} is specific volume of meso- and micropores; D is average pore diameter.

TABLE 2

Composition of gaseous products of the transformation of straight-run gasoline fraction of oil on zeolite catalysts, %

Catalyst	Products	Process duration, h		
		1	15	30
MFI	*n*-Alkanes C_1–C_5	71.4	73.9	75.1
	Isoalkanes C_4–C_5	25.9	24.2	23.3
	Alkenes C_2–C_4	2.7	1.9	1.6
Re/MFI (UFP)	*n*-Alkanes C_1–C_5	70.4	73.8	75.5
	Isoalkanes C_4–C_5	27.2	24.7	23.2
	Alkenes C_2–C_4	2.4	1.5	1.3
Re/MFI (DM)	*n*-Alkanes C_1–C_5	69.8	71.8	72.5
	Isoalkanes C_4–C_5	27.1	26.5	25.9
	Alkenes C_2–C_4	3.1	1.7	1.6
Re/MFI (IE)	*n*-Alkanes C_1–C_5	68.8	70.5	71.9
	Isoalkanes C_4–C_5	28.2	27.6	26.6
	Alkenes C_2–C_4	3.0	1.9	1.5
Re/MFI (IM)	*n*-Alkanes C_1–C_5	66.7	68.9	70.5
	Isoalkanes C_4–C_5	30.2	29.1	28.2
	Alkenes C_2–C_4	3.1	2.0	1.3

TABLE 3

Composition of the liquid products of transformation of the straight-run gasoline fraction of oil on zeolite catalysts, %

Catalyst	Products	Process duration, h		
		1	15	30
MFI	*n*-Alkanes C_3–C_{12}	6.4	29.1	33.5
	Isoalkanes C_4–C_{10}	33.0	28.5	28.1
	Arenes C_6–C_{12}	28.0	13.1	10.6
	Cycloalkanes C_5–C_{10}	28.6	26.5	25.7
	Alkenes C_4–C_{10}	4.0	2.8	2.1
	Octane number	92	76	72
Re/MFI (UFP)	*n*-Alkanes C_3–C_{12}	10.1	28.5	31.9
	Isoalkanes C_4–C_{10}	35.0	29.1	28.9
	Arenes C_6–C_{12}	34.0	22.1	19.0
	Cycloalkanes C_5–C_{10}	18.1	18.0	17.9
	Alkenes C_4–C_{10}	2.8	2.3	2.3
	Octane number	94	82	80
Re/MFI (DM)	*n*-Alkanes C_3–C_{12}	11.8	23.9	28.4
	Isoalkanes C_4–C_{10}	34.2	29.1	28.7
	Arenes C_6–C_{12}	26.0	20.9	18.1
	Cycloalkanes C_5–C_{10}	24.4	23.2	22.6
	Alkenes C_4–C_{10}	3.6	2.9	2.2
	Octane number	89	81	78
Re/MFI (IE)	*n*-Alkanes C_3–C_{12}	9.9	22.7	29.7
	Isoalkanes C_4–C_{10}	34.9	30.4	29.3
	Arenes C_6–C_{12}	25.3	18.4	13.2
	Cycloalkanes C_5–C_{10}	26.5	25.8	25.4
	Alkenes C_4–C_{10}	3.4	2.7	2.4
	Octane number	91	80	73
Re/MFI (IM)	*n*-Alkanes C_3–C_{12}	13.4	28.5	32.8
	Isoalkanes C_4–C_{10}	36.9	28.5	28.0
	Arenes C_6–C_{12}	22.2	17.1	14.1
	Cycloalkanes C_5–C_{10}	23.9	23.7	22.7
	Alkenes C_4–C_{10}	3.6	2.2	2.1
	Octane number	90	79	75

ter the operation in upgrading straight-run gasoline for 30 h are presented in Fig. 1. DTA curves for all samples look alike, while DTG curves for initial MFI and for Re/MFI (IM) sample at low temperatures (in the region of water desorption) differ from three other curves. The removal of adsorbed and weakly bound water is responsible for endothermal effects in the region of 117–194 °C and the corresponding maxima on DTG curves. The changes of mass with respect to the mass of the portion of coked catalyst samples are also shown in the derivatograms. The value related to the mass of "pure" catalyst (remaining after coke burning out) was used for a quantitative comparison of the results. The values recalculated in this manner are presented in Table 4.

A minimal amount of water was present on MFI sample, and among the modified samples – on Re/MFI (IM). For other rhenium-containing catalysts, the amount of released water was larger, and the maximum water removal was shifted to higher temperatures. Broad clearly pronounced low- and high-temperature shoulders on DTG and DTA curves of the samples under study point to nonuniformity of coke formed from them and to the presence of several forms of it. Exothermal effects observed above 340 °C and peaks on DTG curves correspond to the removal of coke deposits. At a temperature of 340 °C, coke deposits that are present on initial zeolite and on Re/MFI (IM) and Re/MFI (UFP) samples start to burn out. Zeolite catalysts obtained by means of DM and IE have higher temperatures of the start of coke removal (354 and 360 °C, respectively), which provides evidence of the formation of more condensed carbon deposits on them. The temperature of the termination of carbon product burning out for all catalysts under study (except non-modified MFI zeolite) is 660 °C. According to the temperature maxima of coke burning out, the catalysts may be ranged in the following sequence: Re/MFI (IE) < MFI (without modification) < Re/MFI (DM) ≈ Re/MFI (IM) < Re/MFI (UFP).

According to the data of thermal analysis, the total mass of coke deposits for initial zeolite after operation for 30 h in the process of the transformation of straight-run gasoline fraction of oil is

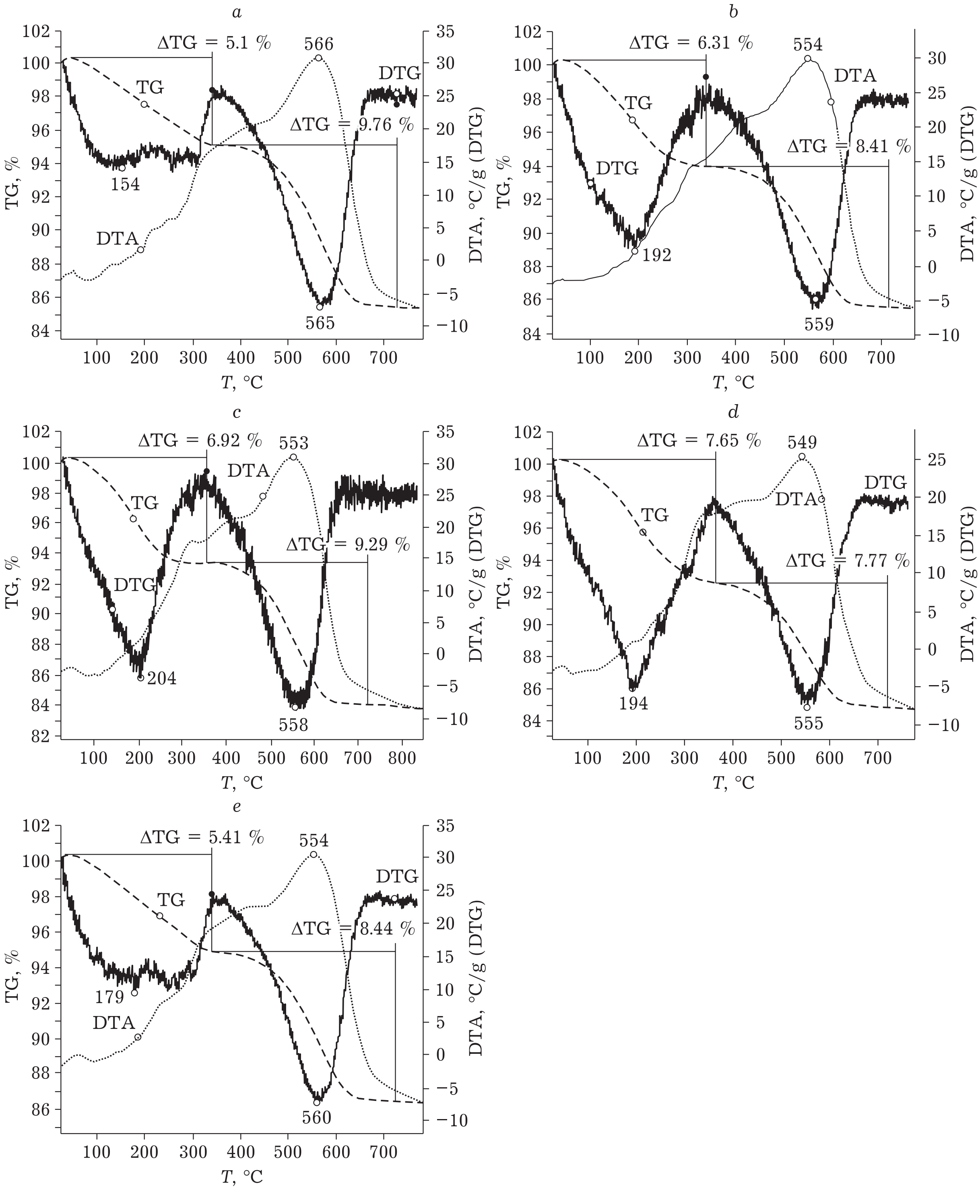

Fig. 1. Data of thermal analysis for the catalysts: MFI (*a*), Re/MFI (UFP) (*b*), Re/MFI (DM) (*c*), Re/MFI (IE) (*d*), Re/MFI (IM) (*e*), after the operation in the transformation of the straight-run gasoline fraction of oil for 30 h.

9.76 %. This is the highest coke content; smaller amounts of coke are formed on rhenium-containing catalysts. Depending on the method of zeolite modification, the amount of coke increases in the sequence: Re/MFI (IE) < Re/MFI (UFP) < Re/MFI (IM) < Re/MFI (DM) < MFI (without modification). So, independently of the method of rhenium introduction into zeolite, a substantial de-

TABLE 4

Data of thermal analysis for the catalysts after operation in the transformation of the straight-run gasoline fraction of oil for 30 h

Catalyst	Mass change, %		Temperature of coke burning, °C		
	Water	Coke	Start	Maximum	Termination
MFI	−5.10 (117 °C)	−9.76	340	574	666
Re/MFI (UFP)	−6.31 (192 °C)	−8.41	340	566	660
Re/MFI (DM)	−6.92 (194 °C)	−9.29	354	563	660
Re/MFI (IE)	−7.65 (194 °C)	−7.77	360	558	660
Re/MFI (IM)	−5.41 (117 °C)	−8.44	340	563	660

Note. Mass changes with respect to the mass of pure catalysts (after coke burning up to 900–1000 °C). The corresponding temperatures of the maxima of peaks on DTG curves, the removal of adsorbed water are indicated in parentheses.

crease in the formation of coke deposits on catalysts occurs, which is connected with an increase in the rate of hydrogenation. It should be noted that not only the least amount of coke is formed on rhenium-modified zeolite Re/MFI (IE) but also the products of densification get burnt out within a narrower temperature range.

CONCLUSION

The introduction of rhenium into MFI zeolite using different procedures causes a decrease in specific surface area, pore volume and diameter. The most noticeable changes in these parameters are observed when the ‘wet’ methods of modification are used: impregnation and ion exchange.

A decrease in the aromatizing activity of rhenium-containing samples promotes a decrease in coking due to an increase in the rate of hydrogenation and, as a consequence, an increase in the time of the stable catalyst performance. Depending on modification method, the amount of coke present in the catalysts increases as a sequence: Re/MFI (ion exchange) < Re/MFI (ultrafine powder) < Re/MFI (impregnation) < Re/MFI (mixing with a salt) < MFI (without modification). Carbon products of compaction formed on rhenium-containing catalysts are less condensed and more uniform in comparison with coke present on non-modified zeolite. With respect to the degree of a decrease in catalytic activity or aromatizing capacity during the same operation time, the catalysts under investigation may be ranged as a sequence: MFI (without modification) > Re/MFI (ion exchange) > Re/MFI (ultrafine powder) > Re/MFI (impregnation) > Re/MFI (mixing with a salt).

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