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Article

Development and Testing of Modified Alumina Catalysts for Hydrotreating Petroleum Gasoline Fraction

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Abstract: The oil produced in the oil fields of the Republic of Kazakhstan contains a high percentage of sulfur. Synthesis and improvement of the properties of catalytic systems for the production of fuels with high octane number and low sulfur content is currently an urgent task for Kazakhstan. In this study, catalytic systems with a new composition based on zeolites with the addition of rare-earth metals (E) and phosphorus (P) have been prepared and tested in the process of the catalytic hydrotreating of straight-run gasoline and gasoline of catalytic cracking. In case of $NiO-MoO_3$-E-P-HZSM-HY-Al_2O_3 catalyst, the octane rating of the gasoline after hydro-processing was increased to 88-90, which is much higher than for other catalysts. The octane number of straight-run gasoline up to 400°C is a maximum of 90 (Research Method) and 83.7 (Motor Method). At the same time, the sulfur content in the resulting gasoline decreases from 0.0088% to 0.0011%. In the case of catalytic cracking gasoline, the sulfur content is reduced from 0.0134% to 0.0012%. The smallest residual sulfur content in the final product, 0.0005% is revealed in case of catalyst $CoO-WO_3$-E-P-HZSM-HY-Al_2O_3, and it is 2-4 times lower than for catalysts $CoO-MoO_3$-E-P-HZSM-HY-Al_2O_3 and $NiO-MoO_3$-E-P-HZSM-HY-Al_2O_3. These amounts of sulfur residue in raw materials is lower than that required by the Euro-5 Standard. The surface of the prepared catalysts was 211.0-274.0 m^2/g, diameter of pores $d \approx 1.5$-2.5 nm and $d \approx 7.0$ nm. The total pore volume of the catalysts was not higher than 0.28-0.41 ml/g. The catalysts developed in this study can be used for hydrotreating raw materials and producing high-octane gasoline with a low sulfur content, corresponding in its characteristics to the Euro-5 Standard.

Keywords: alumina; catalysis; gasoline fraction of oil; hydrotreating; rare earth element; zeolite

1. Introduction

In the modern world, the demand for motor fuels, which must meet international quality standards, is growing more and more every year. In this case, there is a tendency to reduce the reserves of crude oil and the need to process heavy fractions of oil [1-8]. The processing of the raw materials, which contain heavy oil residues, natural bitumen, shale oil, and highly viscous heavy oil, is becoming increasingly important. However, it becomes more difficult to process such heavy hydrocarbons on traditional catalysts. In the oil refining industry, deep hydrotreating and hydroisomerization of oil fractions are increasingly used to produce high-quality motor fuels [9-16]. Oil produced in the oil fields of the Republic of Kazakhstan is characterized by a high content of sulfur. According to the Ministry of Energy of the Republic of Kazakhstan, the sulfur content in domestic oil is in the range of 0.35%-1.69%. Therefore, refineries need to radically change the technology of catalytic processing in order to reduce the sulfur content in the resulting fuel and synthesized petroleum products to meet the European Standards. The development and application of new active catalytic systems for producing fuel with a high octane number and low sulfur content is an urgent task.

When choosing the most efficient technology, great importance is attached to the hydrocarbon composition and the physicochemical characteristics of the raw materials. In the world, various modifications of the processes (thermal, thermal catalytic and hydrogenation technologies) for processing heavy fractions of oil and high-sulfur fuel oils have been developed [17-24].

According to the international standards, significant restriction of content of sulfur, benzene, aromatic and olefin hydrocarbons in motor fuels is required. For carrying out deep hydrotreating of various fractions of oil it is necessary to use new effective catalysts and technologies [25-29]. Worldwide active search and development of new catalysts of deep hydrotreating of oil fractions is conducted and the production technology of motor fuels is improved. In this case more attention is paid to development of the catalyst of hydrotreating for a certain type of oil products [30-39].

The aim of the work was to elaborate the new composition of catalysts based on alumina modified with additives of rare earth metals, phosphorus, zeolite ZSM-5, and to determine their efficiency in the process of the catalytic hydrotreating of straight-run gasoline and catalytic cracking gasoline.

2. Materials and Methods

In this study, catalytic systems with a new composition based on zeolites with the addition of rare-earth metals (E), phosphorus (P) have been prepared: $CoO-MoO_3$-E-P-HZSM-HY-Al_2O_3, $CoO-WO_3$-E-P-Al_2O_3-ZSM, $NiO-MoO_3$-E-P-HZSM-HY-Al_2O_3, where “E” is a rare-earth element (Table 1, Figure 1). A mixture of aluminum hydroxide with zeolites HZSM-5 and HY, water-soluble salts of nickel, cobalt, molybdenum, tungsten, rare-earth element (E), phosphoric acid were used for catalysts preparation.

Table 1. Catalytic systems used in the research, where “MZC” is a “Metallic Zeolite Catalyst”, “E” is a rare-earth metal.

Catalyst sample	Catalyst composition
MZC-1	$CoO-MoO_3$-E-P-ZSM-Al_2O_3
MZC -2	$CoO-MoO_3$-E-P-HZSM-HY-Al_2O_3
MZC -3	$NiO-MoO_3$-E-P-HZSM-HY-Al_2O_3
MZC-4	$NiO-MoO_3$-E-P-ZSM-Al_2O_3
MZC -5	$CoO-MoO_3$-E-P-ZSM-Al_2O_3

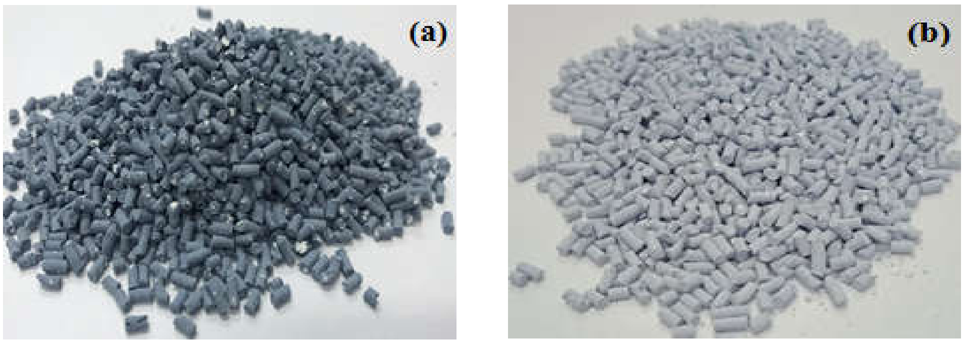

Figure 1. Appearance of freshly prepared granules of catalyst samples: a) MZC-1; b) MZC-4.

Procedure of preparation includes stages of impregnation. When heated, the liquid catalyst solidifies. Using a special device, the catalyst was pulled out, lengthened, and poured onto filter paper. The catalyst was left to cure. Then, the modified catalysts were separated into small pieces. Next, the catalyst samples were heated in a laboratory oven at 350°C for 5 hours. After that, the catalyst samples were heated in a muffle furnace at 500°C for 5 hours. The process for preparing the described catalyst is typical for a similar type of catalyst, which makes it possible to prepare sufficiently large batches of modified zeolite-containing catalysts and propose the for the industrial application.

The percentage composition of the catalysts studied was as: NiO (3%) - MoO_3 (12%) - E (rare earth element - Ce_2O_3 (1%) - P (P_2O_5) - (3%) - HZSM-HY-Al_2O_3, CoO (3%) - MoO_3 (12%) - E (rare earth element Ce_2O_3 (1%) - P-HZSM-HY-Al_2O_3 and CoO (3%) - WO_3 (12%) - E (rare earth element Ce_2O_3 (1%) - P (P_2O_5) - (3%) - Al_2O_3-ZSM.

The effectiveness of the developed catalysts was studied in the process of the catalytic hydrotreating of straight-run gasoline and catalytic cracking gasoline. For the study, a gasoline fraction containing 0.037% sulfur, paraffins 33.4%, olefins 3.7%, aromatic hydrocarbons 5.6%, isoalkanes 26.3%, naphthenic hydrocarbons 31.0% was used. The starting gasoline had an octane rating of 77.7 according to the research method and 53.8 according to the motor method.

The reaction process has been carried out at the common flow installation with a fixed bed (Figure 2) at temperatures of 320-400 ºC, volume rate of 2.0 h^{-1} and pressure 4.0 MPa by the method developed earlier in the laboratory and described in refs. [28, 31-34]. The reactor is made of a metal tube, the lower part is equipped with glass nozzles, which are filled with a layer of stationary catalyst at the required height and placed on top of another porcelain nozzle. The upper layer of the nozzle provides evaporation of the feedstock supplied to the reactor. A thermocouple for temperature control is installed in the middle of the reactor. The reactor type is continuous, i.e. one cycle of the entire process was carried out continuously.

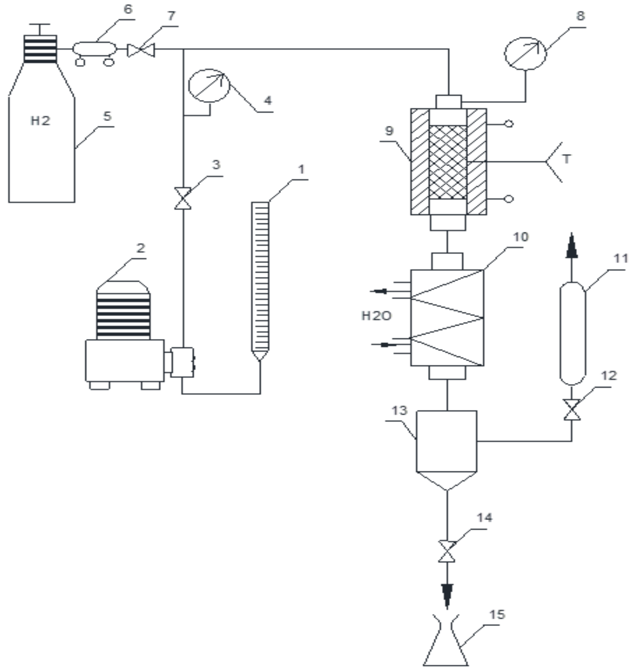

Figure 2. Diagram of a laboratory gasoline hydrotreating unit: 1-burette, 2 – pump; 3, 7, 12, 14-valves; 4, 8-pressure gauges; 5-hydrogen cylinder; 6-reducer; 9-reactor; 10-refrigerator 11-rotameter; 13-separator; 15-flask.

To place the catalyst in the reactor, the reactor was first removed. A filter was first installed inside the reactor, then quartz, then the catalyst and quartz were placed. To activate the catalyst, it was first heated to P=0.7 MPa at 150°C. Then it was heated at P=2.0 MPa at 200°C for 2 hours. After that, it was heated at P=2.5 MPa at 250° C for 2 hours. Then it is heated at P=3.0 MPa at 300°C for 2 hours. Finally, it was heated at P=3.5 MPa at 350°C for 1 hour. After the catalyst was activated, the unit was started up at full capacity. The hydrogen cylinder was opened to P=4.0 MPa using a reducer. Then the automatic shutter was opened and the thermostat turned on, the temperature rose to 320°C. Then gasoline was poured into the flask, pumped directly. At the end of the experiment, the pump is turned off, the hydrogen cylinder is closed, and the product is poured into the container.

The final products of the process have been cooled in the receiver by means of a capacitor placed in a special immersion refrigerator. Gas liquid chromatography (GLC method) using "Chrom-5" and the column with alumina of "Supelco" were applied for analysis. The analysis of the liquid products was defined by "Agilent 6890" (capillary column 60m×0.250mm). For determination of the hydrocarbon composition of the reaction products chromatographs "Chromatec-Crystal" (Russia) was applied. The sulfur content in the starting material and products was defined using SPECTROSCAN Instrument. The physico-chemical characteristics of the catalysts were studied using BET methods, TEM microscopy, and TPD of ammonia [28, 31-34, 40-42].

IR spectra were recorded using a Nicolet IR200 IR-Fourier spectrometer in the range of 500-4000 cm^{-1}. The samples were preliminarily ground into a homogeneous powder.

3. Results

The effect of temperature on the change in the composition of straight-run gasoline and catalytic cracking gasoline as a result of hydroprocessing of raw materials has been studied. Under conditions of enlarged laboratory studies of hydrotreating of straight-run gasoline on the MZC-5 catalyst it was found that the content of isoalkanes increases from 26.7 to 36.2% for straight-run gasoline and from 25.4 to 42.3% for catalytic cracking gasoline compared to original gasoline. The amount of paraffins decreases with increasing temperature, but this trend is not typical for catalytic cracking gasoline. In contrast, with increasing temperature, the percentage of paraffins increases in the composition of catalytic cracking gasoline.

With an increase in temperature by 320-400 °C, the content of aromatic hydrocarbons increases from 8.3% to 21.1% for straight-run gasoline, from 30.1% to 34.4% for catalytic cracking gasoline, the yield of naphthenic hydrocarbons decreases from 31.5 % to 24.4% for catalytic cracking gasoline, from 7.0% to 8.3% for straight-run gasoline. The yield of the liquid phase with an increase in temperature from 320 to 400°C decreases in straight-run gasoline from 82.0 to 36.4%, in catalytic cracking gasoline from 97.6 to 88%. The octane number of straight-run gasoline up to 400°C is a maximum of 90 (research method) and 83.7 (motor method). At the same time, the sulfur content in the resulting gasoline decreases from 0.0088% to 0.0011%. In the case of catalytic cracking gasoline, the sulfur content is reduced from 0.0134% to 0.0012%.

In case of $NiO-MoO_3-E-P-HZSM-HY-Al_2O_3$ catalyst, the octane rating of the gasoline after hydro-processing was increased to 88-90, which is much higher than for other catalysts. The smallest residual sulfur content in the final product, 0.0005% is revealed in case of catalyst $CoO-WO_3-E-P-HZSM-HY-Al_2O_3$, and it is 2-4 times lower than for catalysts $CoO-MoO_3-E-P-HZSM-HY-Al_2O_3$ and $NiO-MoO_3-E-P-HZSM-HY-Al_2O_3$. These amounts of sulfur residue in raw materials is lower than that required by the Euro-5 Standard.

It is noted that the amount of sulfur found in the final sample decreases with increasing temperature. In general, this tendency was observed for all catalyst samples. With an increase in temperature, the sulfur content decreased, the octane number increased, that is, the quality of the gasoline fraction increased. In this case, the most impressive results from the considered temperature range were found at 400 °C.

According to the dependencies shown in Figure 3 and Figure 4, changes in the sulfur content in two different gasoline samples, i.e. in straight-run gasoline and catalytic cracking gasoline, caused by an increase in temperature in the hydrotreating reaction, decrease, and the octane number increases. In the hydrotreating of straight-run gasoline, the MZC-5 catalyst sample exhibits the activity of the catalyst in terms of sulfur content, and the MZC-1 sample is especially active in catalytically cracked gasoline. If we consider the growth of the octane number, then the most active catalyst samples for gasoline are MZC-5, for catalytic cracking gasoline - MZC-4.

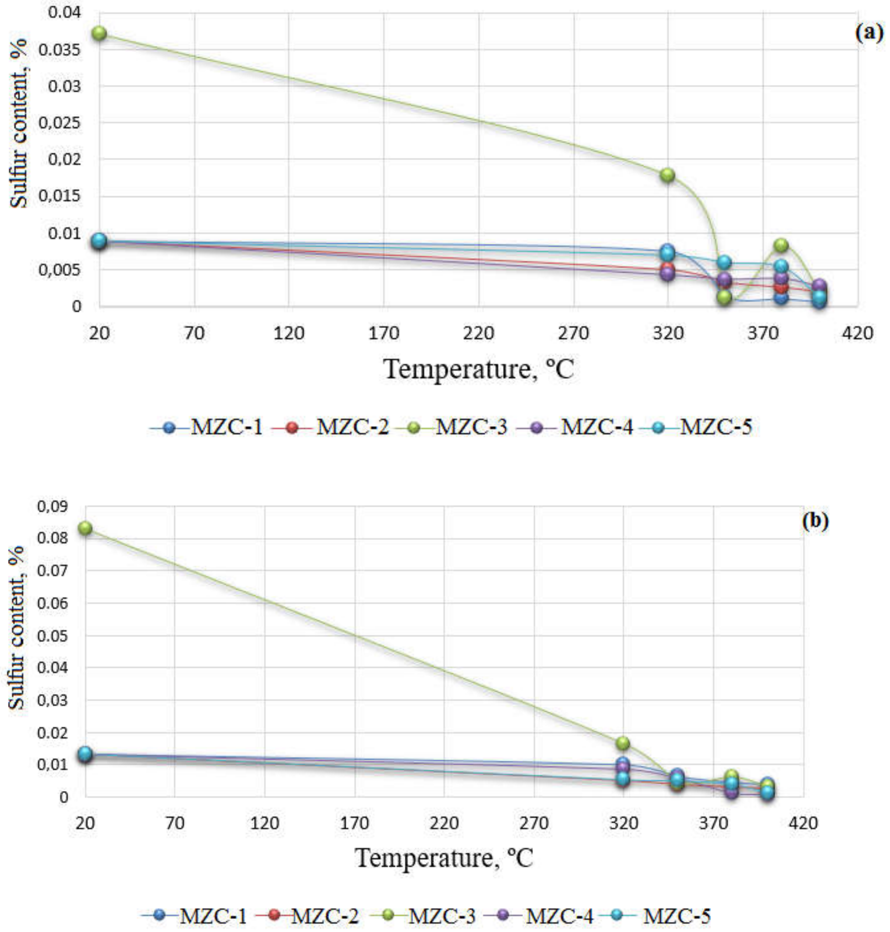

Figure 3. The effect of temperature on the sulfur content in the final sample after hydrotreating of raw materials: a) straight-run gasoline; b) catalytic cracking gasoline.

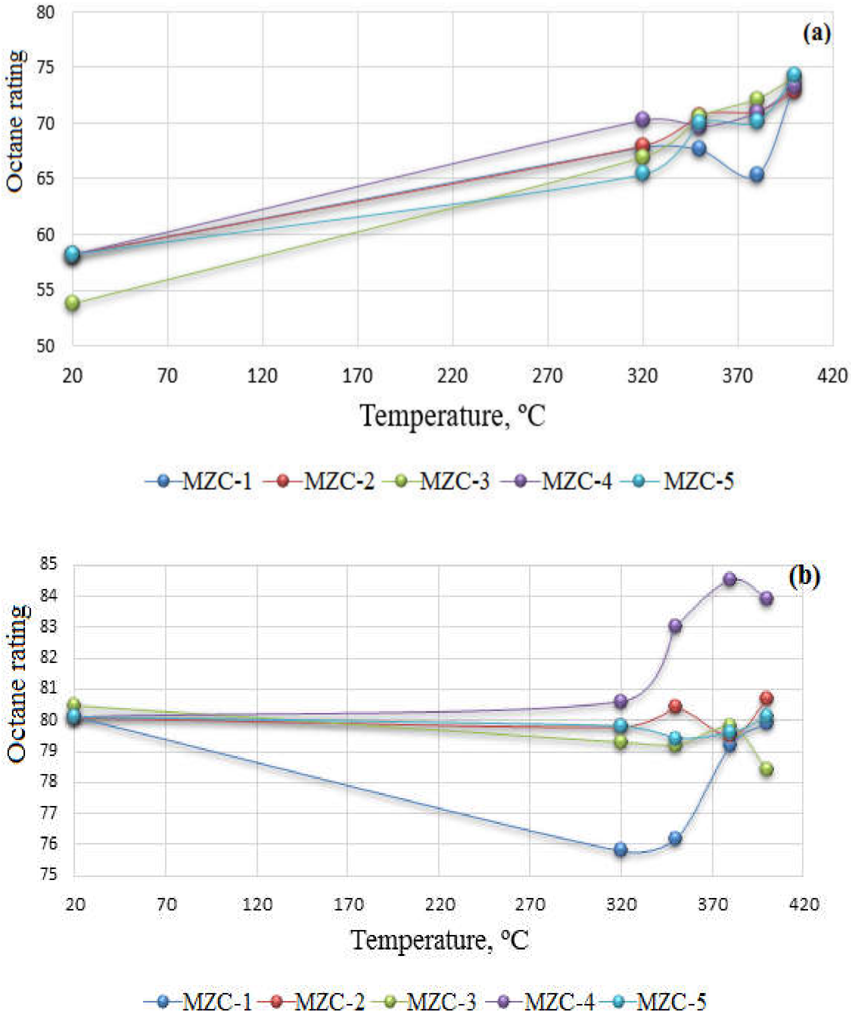

Figure 4. The effect of temperature on the octane rating in the final sample after hydrotreating of raw materials: a) straight-run gasoline; b) catalytic cracking gasoline.

The acid-base characteristics of the catalysts were determined using temperature-programmed desorption of ammonia (Table 2, Figure 5). Ammonia is adsorbed on the catalyst surface in two forms.

Table 2. Results of temperature-programmed desorption of ammonia on test catalysts.

Catalyst	Peak maximum temperature,		Amount of desorbed ammonia, 10^{-4}, mol $NH_{3\ desorption}$ / g catalyst		ΣNH_3 desorbed 10^{-4} mol $NH_{3\ desorption}$ / g catalyst
MZC-1	175	220	10.2	9.48	19.8
MZC-2	150	250	1.88	8.57	10.45
MZC-3	—	215	—	31.3	31.3
MZC-4	140	205	traces	9.26	9.26
MZC-5	150	230	2.33	8.05	10.38

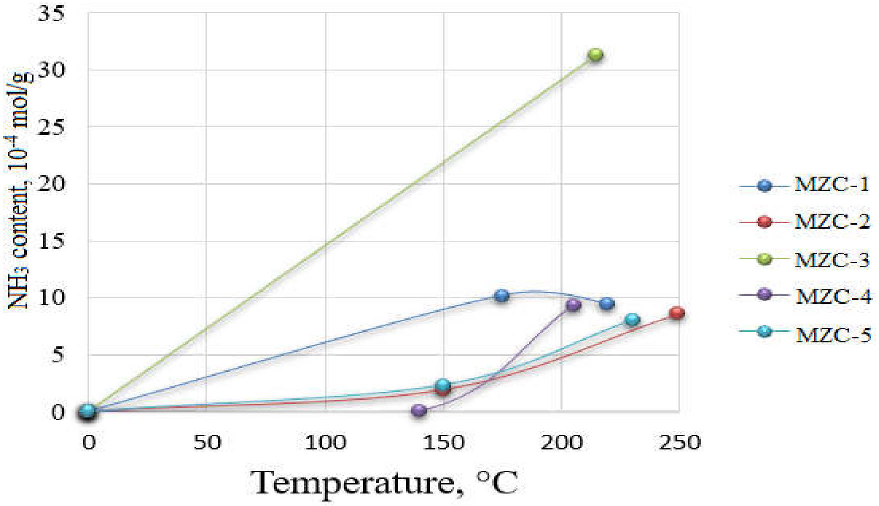

Figure 5. Desorption of ammonia on the catalyst surface.

Acid sites predominate on the surface of the MZC-2 catalyst $T_{desorbtion}$ = 250 °C, their content in the catalyst is 8.57×10^{-4} mol / g. The temperature of desorption of ammonia from the surface of the MZC-5 and MZC-1 catalysts ranges from 220 to 230°C, the content of substances in the catalyst is 8.05×10^{-4} mol / g and 9.48×10^{-4} mol / g. In addition, the amount of desorbed ammonia in various forms is close to the catalyst MZC-1 and is 10.2 and 9.48 mol NH_3 des / g, respectively. The maximum amount of desorbed ammonia in MZC-3 is 31.3×10^{-4} mol / g. In catalysts MZC-2 and MZC-5, the number of strongly weakly bound acid sites falling to 150°C is small and amounts to 1.88 and 2.33×10^{-4} mol / g, respectively. The total amount of ammonia obtained from the surface of catalysts MZC-2 and MZC-5 is the same: 10.45 and 10.38×10^{-4} mol / g of catalyst.

The mechanical strength of the catalyst granules was also determined. Depending on the composition, the different mechanical strengths of the MZC-1, MZC-2, MZC-4 and MZC-5 catalysts are in the range of 26.1-65.4 kg / mm.

The data of the TEM and XPA studies (Figure 6) show that the catalysts proposed in the work are highly dispersed, and the metals of the active phase are mainly in an oxidized state. There are associated clusters on the surface, and their characteristics, such as dispersion, structure, are determined by the nature of the catalyst components [11, 20, 38].

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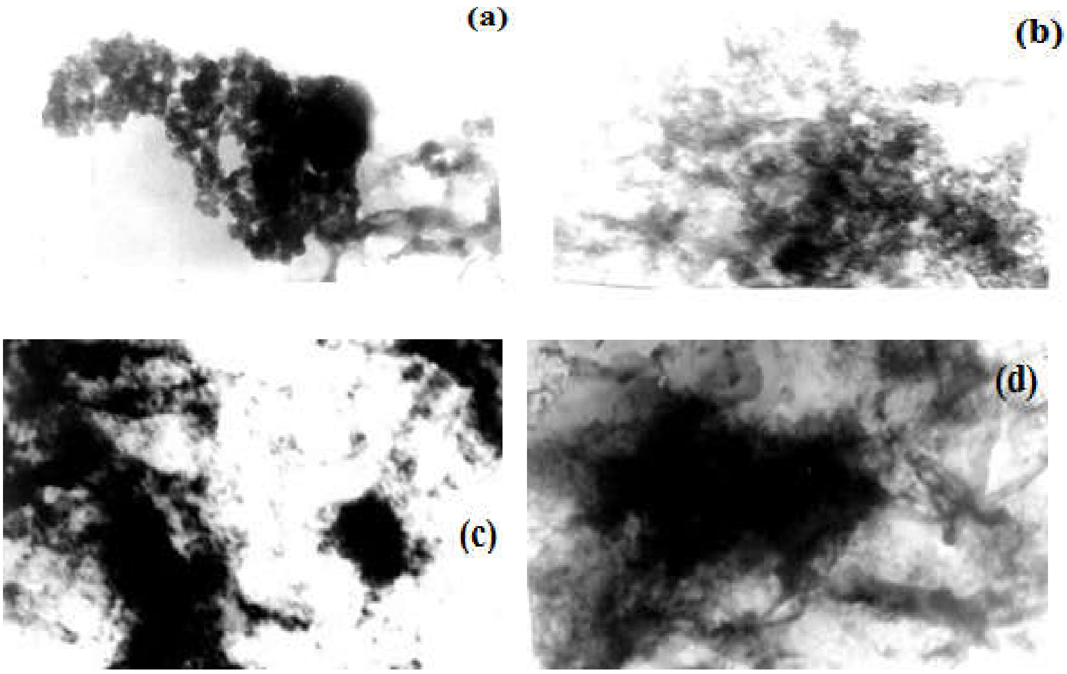

Figure 6. TEM images of catalysts (at 80,000 magnification): MZC -2 (a, b); MZC -3 (c, d).

According to the results of IR spectroscopy (Figure 7), all samples are characterized by the presence of peaks at 1050 and 780 cm-1, which are responsible for the stretching and bending of the Si–O–Si bond (asymmetric and symmetric stretching vibration of Si–O–Si), respectively, 1215 cm^{-1} is the peak corresponding to the bond Si–O–H [43-47]. The absorption band at 550–560 cm^{-1}, which is characteristic of zeolites, is associated with vibrations of the internal bonds of the SiO_4 and AlO_4 tetrahedra. The IR spectrum of MZC-5 (Figure 7, c) includes a weak absorption band at 620 cm^{-1}, which is characteristic of cristobalite [8, 35, 38]. An unidentified small peak at 1620 cm^{-1} is also visible. The peak at 2350 cm^{-1} is carbon dioxide, which is present in the air.

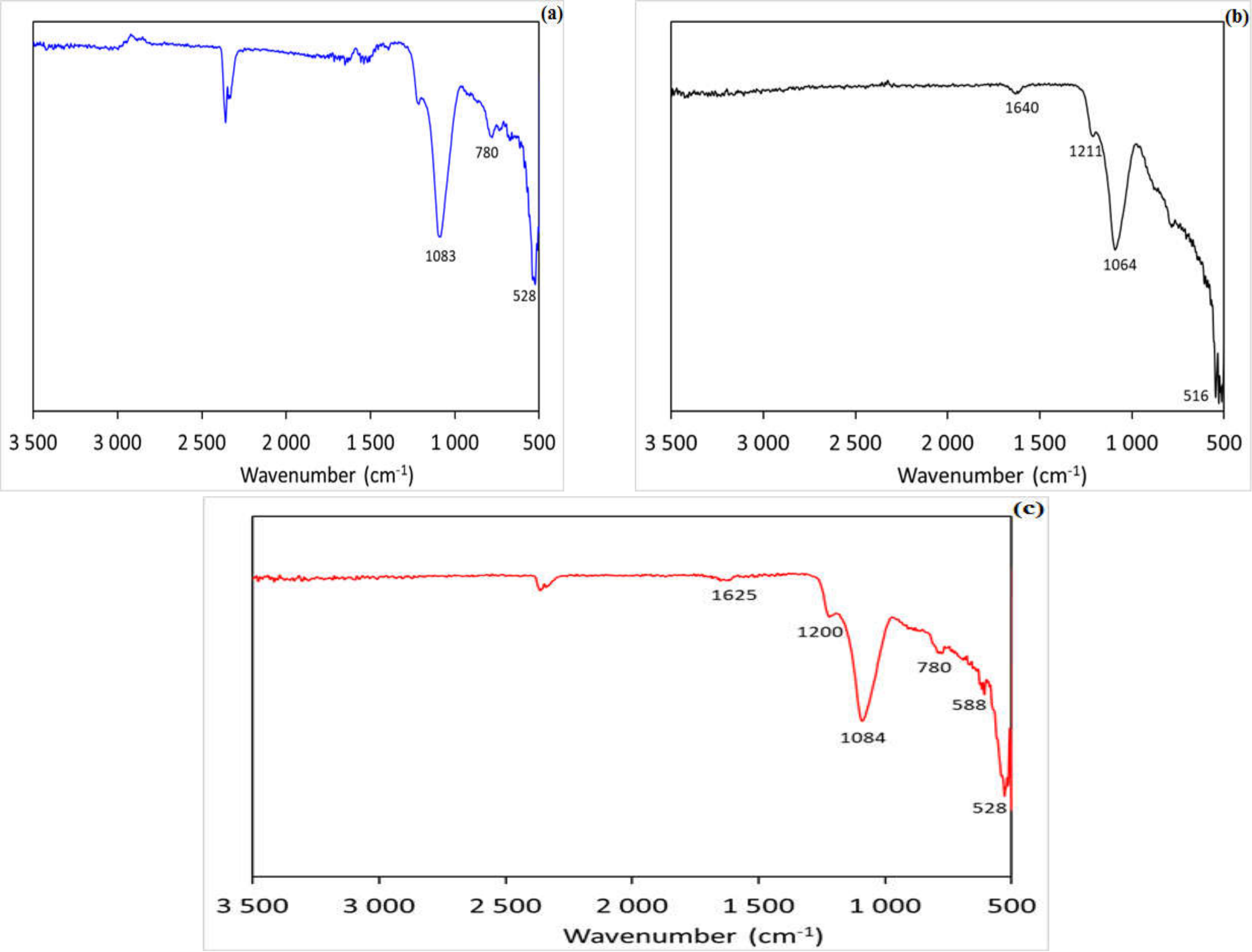

Figure 7. IR spectra: a) MZC-1, b) MZC-2, c) MZC-5.

4. Conclusions

The aim of the work was to elaborate the new composition of catalysts based on alumina modified with additives of rare earth metals, phosphorus, zeolites, and to determine their efficiency in the process of the catalytic hydrotreating of straight-run gasoline and catalytic cracking gasoline. The amount of sulfur found in the final sample decreases with increasing temperature. In fact, this tendency was observed for all catalyst samples. With an increase in temperature, the sulfur content decreased, the octane number increased, that is, the quality of the gasoline fraction increased and the best results were found at 400°C. Catalysts are characterized by the simultaneous presence of acidic, metallic and mixed centers. Using the catalysts developed in the study, it is possible to obtain high-octane low-sulfur gasoline conforming to the Euro-5 standard.

Author Contributions: Conceptualization, B.T., L.S. and A.O.; methodology, B.T.; software, G. S. and L. S.; validation, B.T., A.A. and S.S.; formal analysis, G. S. and L.S.; investigation, G. S., A.O. and M.T.; resources, B.T. and A.A; data curation, B.T., A.O., M.T. and S.S.; writing—original draft preparation, B.T., L.S., A.O. and G. S.; writing—review and editing, B.T. and L.S.; visualization, M.T.; supervision, B.T. and S.S.; project administration, B.T.; funding acquisition, B.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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