

Hydrogenation Processing of Carbon-Containing Wastes in a Mixture with Oil Shale from the Kenderlyk Deposit

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Abstract—New composite catalysts based on ferroalloy industry wastes and natural zeolite from the Taizhuzgen deposit (Republic of Kazakhstan) were studied as applied to the joint thermochemical processing of carbon-containing wastes (worn tires and plastic crumbs) and oil shale from the Kenderlyk deposit. The surface and structural properties of the composite catalysts were studied by IR spectroscopy, electron microscopy, X-ray spectrum analysis, and X-ray diffraction analysis. The relationship of the nature of the active centers of catalysts with the composition and yield of fuel distillates was found with the use of IR spectroscopy and chromatography–mass spectrometry analysis.

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The thermochemical processing of carbon-containing wastes together with oil shale makes it possible to obtain liquid fuel products, combustible gas, and carbon black [1–3]. As a rule, the use of natural shale as additives to carbon-containing source materials based on industrial rubber wastes and waste plastics facilitates the appearance of a synergetic effect caused by the more intense degradation of organic matter with the predominant formation of liquid products.

Osipov with coauthors [4, 5] found that an increase in the conversion and yield of oils was observed on the joint processing of a mixture of coal and polymer wastes. Data on the effective thermochemical processing of heavy petroleum residues in the presence of activating additives were published [6–8]; it was proposed to use oil shales, sapropelites, liptobiolites, and boghead coals as these additives, which contain ≥ 7 wt % hydrogen on an organic matter basis. It was shown that the joint processing of petroleum residues and sapropelites is possible because the organic components of the latter are very close to heavy oils and natural bitumens in terms of component and group compositions.

Kairbekov et al. [9] studied the effect of the additives of Kenderlyk shale, which contained about 10% hydrogen and to 77% carbon, on the hydrogenation of carbon-containing wastes and assumed that this shale can be used as an additional source of hydrocarbons and a hydrogenating agent in the process of thermal dissolution.

The organic matter of shale (OMS) can be more readily converted into liquid and gaseous products in

thermocatalytic destruction processes because the hydrogen content of oil shale is higher than that of coal [9–11]. The cleavage of particular bonds in the molecules of hydrocarbons can be controlled by the selective action of a catalyst on functional groups, and hence the processes can be performed selectively. Therefore, a search for new effective catalysts based on natural zeolites and readily available polymetallic ferroalloy industry wastes is of great scientific and practical interest.

Here, we report the results of studies of the catalytic activity of composite catalysts based on ferroalloy industry wastes and natural zeolite from the Taizhuzgen deposit (Republic of Kazakhstan) in the joint thermochemical processing of carbon-containing wastes (worn tires and plastic crumbs) and oil shale from the Kenderlyk deposit.

Table 1. Textural characteristics of the catalyst samples

| Catalyst | Specific surface area (BET), m ² /g | Total pore volume (BJH, desorb.), cm ³ /g | Average pore diameter (BJH, desorb.), Å |
|----------|------------------------------------------------|------------------------------------------------------|-----------------------------------------|
| Zeolite | 7.2 | 0.02 | 104.1 |
| FIW* | 108.6 | 0.16 | 86.6 |

* Ferroalloy industry wastes.

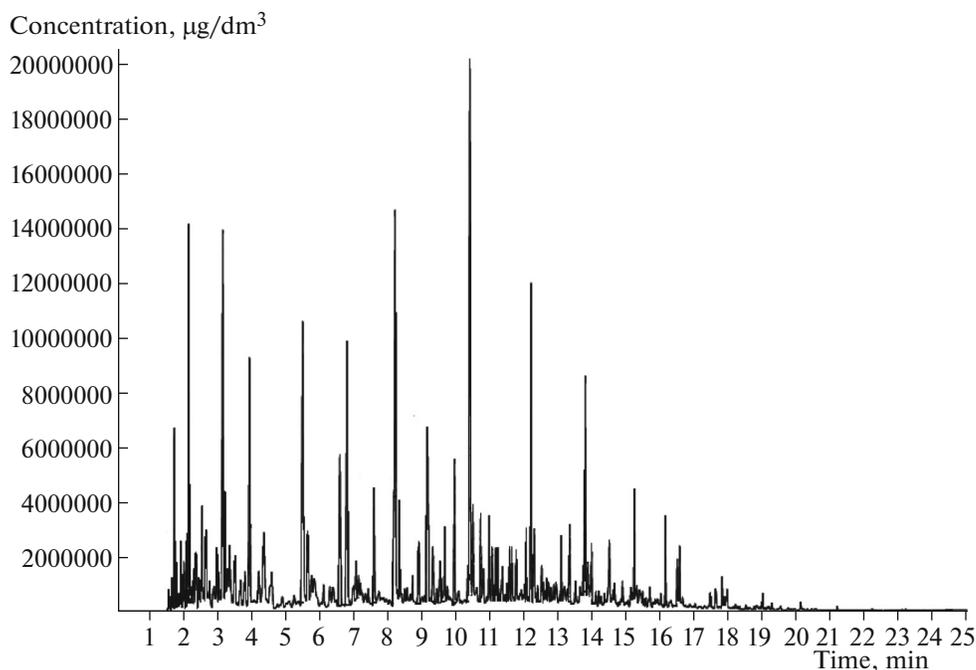


Fig. 1. Chromatography–mass-spectrometric analysis of a gasoline fraction with bp to 180°C.

EXPERIMENTAL

The source materials (worn tires and waste plastics) were ground to a particle size of 3–6 mm, and shale was crushed to a particle size of 0.25 mm. The shale contained the following elements (wt %): C^{daf} , 74.1–77.3; H^{daf} , 7.3–9.9; N^{daf} , 1.9–2.1; S_t^d , 0.6–1.3; and O^{daf} , 10.4–16.8. The H : C atomic ratio was 1.18–1.53.

The process was performed in a batch system under an argon pressure of 5–6.5 MPa at a temperature 450°C with continuous stirring. The distillation residue (with a boiling point of 360–500°C) of petroleum from the Kumkol oil field (Republic of Kazakhstan) was used as a paste-forming agent, which was characterized by a high paraffin hydrocarbon content, a high solidification point, and a low sulfur content. The asphaltene–tar paraffin deposits of this petroleum residue contained 6–10% paraffins, 10–16% tars, 52–55% asphaltenes, and 20–28% oils and mechanical impurities. The melting point of these deposits varied in a range of 82–85°C.

The wide range of pressure changes in the system was caused by the release of hydrogen from both the petroleum residue and the oil shale, the organic matter of which contained from 7 to 10 wt % hydrogen.

Zeolite from the Taizhuzgen deposit (Republic of Kazakhstan), which was activated by acid treatment and calcination, and polymetallic ferroalloy industry wastes (Aksu) were used as catalysts; they were taken in different zeolite to ferroalloy industry waste ratios, namely, 80 : 20, 60 : 40, 40 : 60, and 20 : 80.

The following three crystalline phases were identified in the structure of the zeolite by X-ray diffractometry on an ARL X'TRA instrument: quartz, heulandite [$Ca(Ca_{3.6} K_{0.8} Al_{8.8} Si_{27.4} O_{72} \cdot 26.1H_2O)$], and clinoptilolite [$Ca(K, Na_2 Ca_2(Si_{29} Al_7) O_{72} \cdot 24H_2O)$].

The shale concentration was 3–5 wt % on a carbon-containing material basis.

A mixture of plastic, rubber, oil shale, and paste former with catalyst additives, which was preheated to 70–80°C, was loaded in a reactor and blown with argon; the pressure and temperature were specified. The process was performed under optimum conditions (450°C; reaction time, 15 min), which were determined previously in the hydrogenation processing of scrap rubber and waste plastics in the presence of activated zeolite, ferroalloy industry wastes, and ferroalloy industry wastes–zeolite [12–14].

The zeolite was prepared by preliminary crushing and sifting the particles through sieves with a size to 0.25 mm. The ion exchange of the zeolite was performed with a 0.1 M solution of HCl in a round-bottom flask with stirring in a boiling water bath for 6 h. After the acid treatment, the zeolite was separated by filtration, washed with distilled water to remove chloride ions using a reaction with silver nitrate, and dried in air at 100°C to constant weight. Then, it was thermally treated in a flow of air in a temperature range of 100–500°C for 3.5 h. The catalyst was ground to a particle size of 0.25 mm.

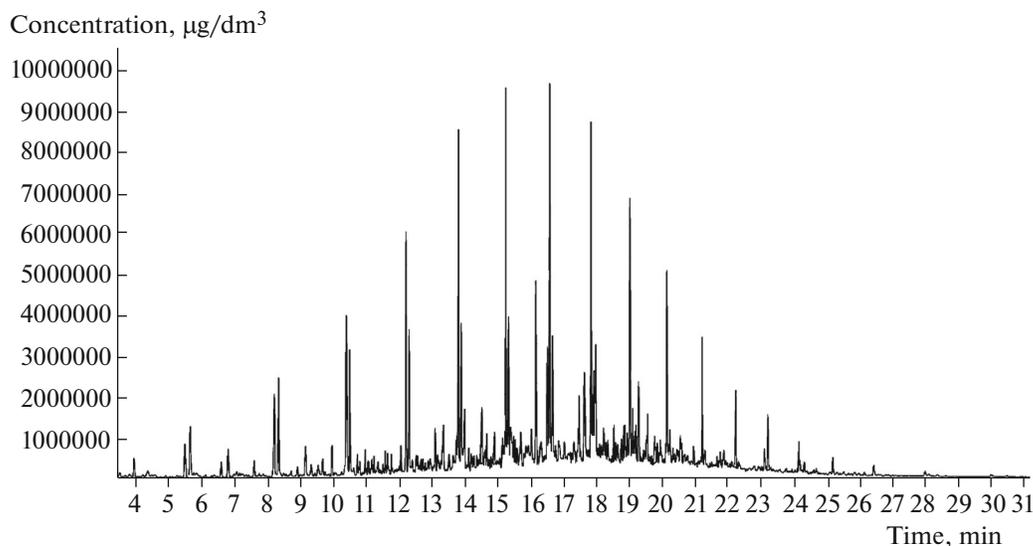


Fig. 2. Chromatography–mass-spectrometric analysis of a diesel fraction with bp 180–250°C.

The catalyst based on ferroalloy industry wastes was prepared by preliminary crushing to a particle size of 0.25–0.30 mm and sifted through a sieve.

Gas chromatography with mass-spectrometric detection (Agilent 6890N/5973N) was carried out under the following conditions: the injected (liquid) sample volume was 0.2 µL with a split ratio of 500 : 1; an HP-INNOWax chromatographic capillary column (Agilent) of 30 m × 0.25 mm with a film thickness of 0.25 µm; injector temperature, 240°C; column oven temperature, 500°C (exposure of 5 min), the final temperature of 240°C (exposure of 10 min). The total analysis time was 34 min. The scanning of ions was performed in an m/z range from 10 to 350.

The IR spectra of the samples were recorded on a Shimadzu 8300 Fourier transform spectrometer with a resolution of 4 cm^{-1} and the number of accumulated spectra of 200. The spectra were represented after treatment with the use of the ORIGIN program package.

The acidic properties of catalysts were determined by the IR spectroscopy of adsorbed CO based on the numbers of bands corresponding to the Lewis and Bronsted adsorption sites. The concentration of Lewis sites was measured from the integrated intensity of the bands of adsorbed CO:

$$N[\mu\text{mol/g}] = A/A_0,$$

where A is the integrated intensity of the band of adsorbed CO; A_0 is the integral absorption coefficient.

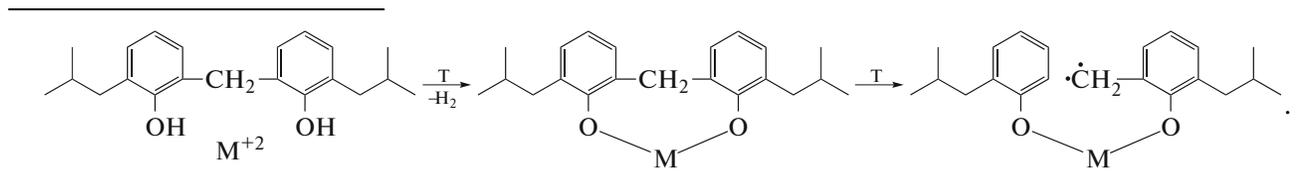
The specific surface areas of the samples of catalysts were determined on an ASAP 2400 Micrometrics surface area analyzer (the United States) by the BET method based on the low-temperature adsorption of nitrogen.

The samples of distillate fractions were studied by IR spectroscopy on a VERTEX 70 fully digital Fourier transform IR spectrometer from BRUKER at frequencies of 7500–400 cm^{-1} .

X-ray diffraction analysis was carried out on an ARL X'TRA X-ray diffractometer. The detected reflections were compared with reference data.

RESULTS AND DISCUSSION

It is well known that reactions with the breaking of specific bonds can be controlled by the selective introduction of a metal catalyst into the functional groups of shale matter. For example, the temperature of the breaking of an aliphatic bond, which connects two aromatic fragments, can be decreased due to the replacement of the protons of two adjacent phenol groups by a divalent metal cation according to the reaction scheme



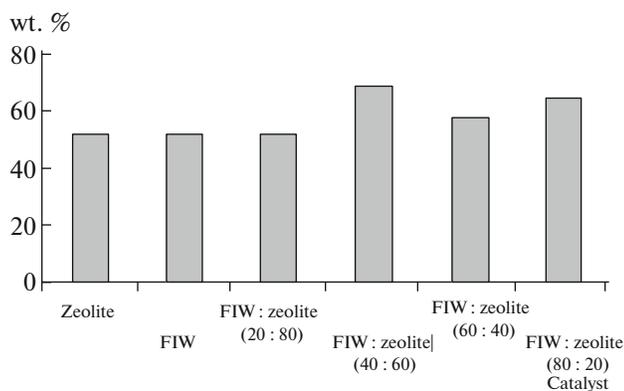


Fig. 3. Yields of liquid products on different catalysts.

Acid catalysts are the best catalysts for the hydrogenolysis of solid fossil fuels. They should prevent the secondary polymerization of the resulting low-molecular-weight molecular fragments and be resistant to sulfur poisoning and capable of binding nitrogen and sulfur from products; they should also be inert to the mineral matter of shale and metals that occur in ash [15]. Therefore, in this work, we studied the surface and structural properties of the initial and prepared composite catalysts with the use of IR spectroscopy, electron microscopy, spectrum analysis, and X-ray diffraction analysis.

Acid sites in a sample of activated zeolite from the Taizhuzgen deposit were determined by IR spectroscopy on a Shimadzu FTIR 8300 instrument. Based on the shift of a line due to CO vibrations, it was estab-

lished that Lewis and strong Bronsted acid sites were absent from the zeolite structure; however, weak Bronsted sites (close to aluminum oxides and silica gel in terms of acidity), which are somewhat stronger in the sample of ferroalloy industry wastes, were present. The absence of strong centers may be caused by the presence of alkaline or alkaline earth elements on the surface of the samples.

The compositional analysis of the activated zeolite from the Taizhuzgen deposit in the course of acid treatment showed that the concentrations of metals such as Fe and Mn in its structure are, apparently, very small.

The experimental data allowed us to hypothesize the potential activity of zeolite in the catalytic process of the cleavage of carbon-containing source materials with the predominant formation of a liquid product enriched in short-chain hydrocarbons from the paraffin, naphthene, and arene series.

The qualitative and quantitative composition of the initial and composite catalysts was determined by X-ray fluorescence analysis. The analysis data are consistent with the data obtained by energy-dispersive spectroscopy.

The X-ray diffraction analysis of catalyst samples carried out on an ARL X'TRA X-ray diffractometer showed the presence of iron and silicon oxides and, probably, calcium and aluminum compounds in the samples of ferroalloy industry wastes. With the use of diffuse reflectance electron spectroscopy (DRS) on a UV-2501 PC Shimadzu spectrophotometer with an ISR-240A diffuse reflectance attachment, the occurrence of Fe(II) cations in an octahedral coordination and the presence of a matrix like Al-Si in the sample of ferroalloy industry wastes was found. This allowed us to assume that the metal constituents of the catalyst occur in a highly dispersed state; it is likely that, for this reason, different catalytic centers responsible for the activity and selectivity of the catalyst were formed.

The morphology of the catalyst samples was studied on a JEOL JSM 6460LV scanning electron microscope. The chemical composition of the catalyst samples was determined by energy-dispersive spectroscopy with the use of an INCA microscope setup (an analog of X-ray fluorescence analysis). It was established that inhomogeneous structures in terms of the degree of dispersion, which had an evenly uniform laminar surface, were visible in the zeolite activated by acid treatment with a magnification factor of 3000.

At the same time, with a magnification factor of 3000, the structure of the ferroalloy industry waste catalyst was friable with a large specific surface area, and predominantly amorphous rounded particles were observed in it.

Table 1 summarizes data on the study of the surfaces of the zeolite activated by acid treatment and ferroalloy industry wastes by the BET method.

Table 2. Chemical composition of a gasoline fraction with bp to 180°C

| Hydrocarbon | Concentration, wt % |
|-------------------------------------------|---------------------|
| <i>n</i> -C ₆ H ₁₄ | 1.64 |
| <i>n</i> -C ₇ H ₁₆ | 3.84 |
| <i>n</i> -C ₈ H ₁₈ | 5.53 |
| Toluene | 3.79 |
| <i>n</i> -C ₉ H ₂₀ | 5.30 |
| Methylbenzene | 4.05 |
| <i>m</i> -Xylene | 5.07 |
| Ethylbenzene | 2.50 |
| Benzene | 1.72 |
| <i>n</i> -C ₁₀ H ₂₂ | 7.17 |
| 1,2-Methylethylbenzene | 3.87 |
| Cymene (4-isopropyltoluene) | 10.00 |
| <i>n</i> -Dodecane | 3.66 |
| <i>n</i> -Tetradecane | 1.07 |
| Naphthalene | 0.89 |
| Pentadecane | 0.60 |

Table 3. Chemical composition of a fraction with bp 180–250°C

| Hydrocarbon | Concentration, wt % |
|----------------------------------------------|---------------------|
| <i>cyclo</i> -C ₈ H ₁₆ | 2.61 |
| <i>n</i> -Dodecane | 7.83 |
| Dodecyl | 5.09 |
| Tridecane | 10.83 |
| Tridecedene | 5.43 |
| Tetradecane | 11.71 |
| Hexadecedene | 5.82 |
| Naphthalene | 6.14 |
| <i>n</i> -Pentadecane | 11.69 |
| Hexadecane (cetane) | 9.97 |
| Dimethylnaphthalene | 5.52 |
| Heptadecane | 8.54 |
| Trimethylnaphthalene | 3.41 |
| Heptadecane | 8.54 |
| Octadecane | 6.64 |
| Nanodecane | 4.19 |

The hydrogenation processing of scrap rubber and waste plastics in the presence of oil shale was conducted at 450°C and the following reaction mixture composition: petroleum residue, 15 g; rubber and plastics, 15 g; shale, from 3 to 5 wt %; and catalyst, .67 g. The process was performed for 15 min.

Figures 1 and 2 show the chromatographic analysis data of the liquid products that boiled away to 180°C and within a range of 180–250°C, respectively. Figure 3 shows the characteristics of the liquid fractions obtained upon the processing of carbon-containing waste materials on the test catalysts in the presence of shale additives.

Tables 2 and 3 summarize the chemical composition of products. It was established that the catalyst based on ferroalloy industry wastes and zeolite in a ratio of 40 : 60 was optimal in terms of the total yield of

liquid hydrogenation products; this catalyst was characterized by a higher yield of fractions with bp to 180 and 180–250°C. It was found that an optimum concentration of oil shale is 3 wt %, at which the total yield of the obtained liquid products was 70.28 wt % (Table 4).

The IR-spectrometric analysis of the hydrogenation products showed the presence of absorption bands characteristic of alkanes, cyclanes, and arenes in the spectra. The spectra of liquid products that boiled away to 180°C and at 180–250°C exhibited intense absorption bands at 2956, 2925, and 2871 cm⁻¹, which indicate the presence of the CH₃ group, and absorption bands at 1377 and 1460 cm⁻¹, which are characteristic of the CH₂ group. A great number of peaks in a range of 620–811 cm⁻¹ is indicative of the presence of a bond between carbon and sulfur, which is characteristic of compounds such as mercaptans and thiols. The presence of absorption bands at 1459 and 1602 cm⁻¹ suggests the presence of aromatic hydrocarbons. Vibrations at 1641 cm⁻¹ correspond to unsaturated compounds. Bands at 699 cm⁻¹ indicate deformation vibrations in a monosubstituted aromatic ring.

Absorption bands in a range of 620–1030 cm⁻¹ were present in the spectra of liquid hydrogenation products; this fact indicated the presence of different functional groups.

Based on the results of the experiments, we calculated a material balance for the thermochemical processing of scrap rubber, waste plastics, and oil shale at 450°C and 5 MPa (Table 5).

CONCLUSIONS

We used natural heulandite–clinoptilolite zeolite from the Taizhuzgen deposit (Republic of Kazakhstan) activated by acid treatment and calcination and ferroalloy industry wastes as catalysts for the thermochemical processing of scrap rubber and waste plastics in the presence of oil shale additives at a low pressure of argon (to 5 MPa).

Based on the study of the surface and structural properties of the composite catalysts performed with the use of currently available physicochemical meth-

Table 4. Characteristics of the liquid fractions of the processing ($P = 5$ MPa) of carbon-containing materials

| Catalyst | Gas volume (V), mL | Yield of distillate fractions, wt % | | | | Yield of sludge, wt % | Σ LF with consideration for losses, wt % |
|------------------------|------------------------|-------------------------------------|-----------|-----------|-------------|-----------------------|-------------------------------------------------|
| | | до 180°C | 180–250°C | 250–320°C | Σ DF | | |
| Zeolite | 3850 | 15.03 | 2.32 | 22.27 | 39.62 | 24.25 | 52.22 |
| FIW | 4700 | 18.47 | 2.64 | 22.28 | 43.39 | 15.97 | 52.99 |
| FIW : zeolite, 20 : 80 | 4490 | 8.18 | 8.25 | 26.77 | 43.20 | 23.11 | 53.35 |
| FIW : zeolite, 40 : 60 | 4400 | 18.15 | 17.74 | 22.59 | 56.48 | 23.80 | 70.28 |
| FIW : zeolite, 60 : 40 | 3600 | 13.99 | 13.31 | 20.02 | 47.32 | 21.84 | 59.72 |
| FIW : zeolite, 80 : 20 | 3800 | 14.87 | 18.78 | 20.77 | 54.42 | 20.08 | 66.02 |

Table 5. Material balance of the thermochemical processing of carbon-containing wastes

| Item | Concentration, wt % |
|-------------------------------------------------|---------------------|
| Income | |
| 1. Petroleum residue | 47.51 |
| 2. Plastics | 23.76 |
| 3. Rubber | 23.76 |
| 4. Shale | 2.85 |
| 5. Catalyst | 2.12 |
| Total | 100.0 |
| Expenditure | |
| 1. Liquid products (C ₅ and higher): | 70.28 |
| to 180°C | 18.15 |
| 180–250°C | 17.74 |
| 250–320°C | 22.59 |
| loss (in the course of distillation) | 11.8 |
| 2. Sludge (solid residue) | 17.6 |
| 3. Gas | 5.92 |
| 4. Losses + H ₂ O | 6.2 |
| Total | 100.0 |

ods of analysis, we found that the structure and composition of the catalysts exerted a considerable effect on both the total yield of the resulting distillate fractions and their hydrocarbon compositions; this was likely due to the nature of the active acid sites formed.

REFERENCES

- Kairbekov, Zh.K., Karabalin, U.S., Yakupova, E.N., et al., *Vestn. Kaz. Nats. Univ., Ser. Khim.*, 2011, vol. 61, no. 1, p. 531.
- Strizhakova, Yu.A. and Usova, T.V., *Khim. Tverd. Topl.* (Moscow), 2008, no. 4, p. 7.
- Maloletnev, A.S., Kairbekov, Zh.K., Yemelyanova, V.S., et al., *Vestn. Kaz. Nats. Univ., Ser. Khim.*, 2012, vol. 68, no. 4, p. 22.
- Osipov, A.M., Popov, A.F., Shendrik, T.G., et al., <http://www.ecologylife.ru/utilizatsiya-2001/nekotoryie-problemyi-sovmestnogo-ozhizheniya-uglya-i-othodov-plastmass.html>.
- Osipov, A.M., Popov, A.F., Grishchuk, S.V., et al., *Ekotekhnol. Resursoberezh.*, 2004, no. 4, p. 26.
- Gorlov, E.G., Kotov, A.S., and Gorlova, S.E., *Khim. Tverd. Topl.* (Moscow), 2009, no. 1, p. 31.
- Kotov, A.S. and Gorlov, E.G., *Khim. Tverd. Topl.* (Moscow), 2009, no. 3, p. 30.
- Suvorov, Yu.P., *Khim. Tverd. Topl.* (Moscow), 2006, no. 6, p. 57.
- Kairbekov, Zh.K., Emel'yanova, V.S., Myltykbaeva, Zh.K., et al., *Fundament. Issled.*, 2012, no. 9, p. 924.
- Kairbekov, Zh.K., Maloletnev, A.S., Emel'yanova, V.S., et al., Abstracts of Papers, *IV mezhdunar. nauchno-tekhn. konf.* (IV Int. Sci.-Techn. Conf.), 2013, p. 52.
- Aubakirov, E.A., Tashmuhambetova, Zh.H., and Kairbekov, Zh.K., et al., *Mater. XII mezhdunar. konf. "Resursovosproizvodyashchie, malootkhodnye i prirodookhrannye tekhnologii osvoeniya nedr"* (Proc. XII Int. Conf. "Resource-Generating, Low-Waste, and Nature-Conservative Technologies for the Exploitation of Mineral Resources"), 2013, vol. 1, p. 554.
- Kairbekov, Zh.K., Aubakirov, E.A., Tashmukhambetova, Zh.Kh., et al., Abstracts of Papers, *X mezhdunar. nauchno-prakt. konf. "Ashirovskie chteniya"* (Ashirov Reading: X Int. Sci.-Pract. Conf.), Samara: Izd. SGTU, 2014, vol. 1, p. 119.
- Aubakirov, E.A., Tashmukhambetova, Zh.H., Burkhanbekov, K.E., et al., *Appl. Mech. Mater. Trans. Tech. Publ. Switzerland*, 2014, vol. 618, p. 136.
- Kairbekov, Zh.K., Maloletnev, A.S., Emel'yanova, V.S., et al., *Mater. mezhdunar. nauchno-prakt. konf. "Tekhnologiya kompleksnoi pererabotki uglevodородного syr'ya"* (Proc. Int. Sci.-Pract. Conf. "Technology for the Complex Processing of Crude Hydrocarbons), Almaty: Izd. KazNU, 2014, p. 30.
- Kairbekov, Z.K., Yemelyanova, V.S., and Myltykbaeva, Z.K., *Eur. J. Nat. History*, 2012, no. 5, p. 17.

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