SYNTHESIS AND TESTING CATALYSTS BASED ON FLY ASH FROM THERMAL POWER PLANTS AND NATURAL ZEOLITE FOR GAS EMISSIONS PURIFICATION AND CATALYTIC PROCESSING OF HEAVY OIL

T.V. Shakiyeva¹, L. R. Sassykova^{1,✉}, A.A. Khamlenko¹, A.R. Sassykova²,
A.A. Batyrbayeva¹, Zh. M. Zhaxibayeva³, M. A. Kozhaisakova⁴,
A. Muratova¹, B.T. Dossumova¹, T. S. Abildin¹ and M. Zhumagali¹

¹Al-Farabi Kazakh National University, Almaty-050040, Kazakhstan

²Almaty College of Economics and Law, Almaty-050004, Kazakhstan

³Abai Kazakh National Pedagogical University, Almaty-050000, Kazakhstan

⁴Almaty Technological University, Almaty, Kazakhstan

✉Corresponding Author: larissa.rav@mail.ru

ABSTRACT

In this study, hollow microspheres based on fly ash from the Ekibastuz coal field (Kazakhstan) and natural zeolite from the Taizhuzgen field (Kazakhstan) were used for the synthesis of catalysts. The catalysts were tested in the process of sulfur dioxide oxidation with different SO₂ content in the SO₂-Ar gas mixture at a flow vortex plant of the “Emulsifier” type with a capacity of 2 m³ / h. Technology for the oxidation of SO₂ with oxygen in an aqueous solution has been developed and the best technological parameters for the selective oxidation of SO₂ with the production of sulfuric acid as a product have been determined. The degree of SO₂ sorption is reached up to 95%. Also, the prepared catalysts were tested in the process of redox-catalytic cracking of fuel oil (with preliminary electromagnetic excitation of hydrocarbon molecules) to obtain light carbon fractions. The fuel oil of the Amangeldy Gas Processing Plant (AGPP, Kazakhstan) of the M-100 brand was studied as a feedstock. On the optimal catalyst in the products of oxidative cracking of fuel oil, the fraction of light gas oil makes up the main part. The resulting light gas oil contains a significant amount of alpha-olefins, which are scarce raw materials for the production of synthetic additives and oils.

Keywords: Fly Ash, Natural Zeolite, Water and Gas Purification, Highly Toxic Organic Compounds, Catalytic Cracking, Fuel Oil.

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INTRODUCTION

The problem of the utilization of ash and slag of the Thermal Power Plants (TPP) or CHP working on solid fuel is very urgent. Fly ash contains several components with valuable and unique technological properties: aluminosilicate hollow microspheres (AHM, which are the most original and perhaps the most valuable components of ash), magnetite microbeads, the unburnt carbonic particles, ferrosilicon and carbonate microspheres.¹⁻⁵ The value of AHM is determined by the fact that they can be ideal fillers. The main components of ash and slag are SiO₂ (up to 60%) and Al₂O₃ (up to 25%). The content of Fe₂O₃ is up to 15%, of CaO from 1.5 to 4.5%, of K₂O from 2.0 to 4.5 %. AHM is in great demand in many countries and ash dumps are technogenic deposits of valuable products.^{2,3,6,7} Features of the chemical and mineral-phase composition of cenospheres make it possible to synthesize microspheric fuel cracking catalysts based on them.

Thermal power plants, oil and gas processing plants are among the most important sources of atmospheric pollution: the atmosphere is polluted by emissions of sulfur and nitrogen oxides, carbon monoxide and its accompanying benzopyrene, and other harmful compounds, most of the emissions are toxic.⁸⁻¹² Gas treatment plants of CHP, as well as methods associated with structural changes of the unit, as a rule, are very expensive and not always economically justified. Therefore, it is very important to develop low-cost

methods for reducing emissions of pollutants using sorbents and catalysts based on local raw materials.^{11,12}

Traditional processes of catalytic cracking of heavy petroleum raw materials require continuous regeneration of expensive zeolite-containing catalysts and sophisticated equipment.¹³⁻¹⁵ Development of methods for the activation of heavy oil raw materials by such physical influences as ultrasound, magnetic treatment, microwave, infrared radiation, mechanochemistry, ultraviolet radiation can be an alternative or addition to traditional oil refining processes. One of the most promising methods for producing light hydrocarbon fractions is the implementation of catalytic cracking of heavy oil raw materials in the presence of air additives in the reaction medium, i. e. in an oxidizing medium.¹⁶⁻²³

In this work, the hollow microspheres based on fly ash from the Ekibastuz coal deposit (Kazakhstan), produced as a result of the operation of TPP-2 in Almaty (Kazakhstan) and natural Kazakhstan zeolite from Taizhuzgen field were selected and used for the preparation of catalysts. The research was carried out on the development of an effective way of purification of gas emissions from sulfur dioxide and also for oxidative catalytic cracking of fuel oil (with preliminary electromagnetic excitation of hydrocarbon molecules) to obtain light carbon fractions.

EXPERIMENTAL

Material and Methods

For this investigation, the catalysts were synthesized based on Kazakhstan's natural zeolite of the Taizhuzgen deposit and fractions of cenospheres resulting from the combustion of coal of Ekibastuz field (Kazakhstan) at the Almaty TPP-2 (Kazakhstan) with an aluminosilicate module $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$ and iron content of 3.03-3.67 wt. % in Fe_2O_3 . Coals of Ekibastuz coal basin (Kazakhstan) of medium metamorphism (R^0 0.8-1.3%), grade CC, high ash, very difficult to enrich, W^r 6.5%, V^{daf} 24-32, St^d 0.5-0.8%, Q_s^{daf} 33 MJ/kg, Q_i^r 14-19 MJ/kg.^{8-10,24,25} Ekibastuz coal is used in the hydroelectric power station of the Urals (Russia) and Kazakhstan. The scheme for producing mycospheres from the Ekibastuz coal ash is based on the use of dry magnetic separation methods, particle size classification and gravity separation using liquid separating media.

General Procedure

The kinetics of sodium sulfite oxidation by oxygen was studied under stationary conditions in a glass gradientless thermostated "duck"-type reactor, with a potentiometric device. The kinetic regime was ensured by intensive shaking of the reactor (300-400 oscillations per minute), the volume of the liquid phase was no more than 40 cm³, with a total volume of the reactor of 180 cm³. The reaction rate was determined by oxygen uptake. The process was carried out according to the previously developed methodology.^{3,5,15,18} The efficiency of the process was defined by the results of X-ray phase analysis and by visual control of the quality of the selected products using a microscope. A vibration magnetometer AMH-500 Hysteresisograph (Italy) was used for magnetic measurements.

It is known that the most suitable device that provides the intensity of gas-liquid mass exchange can be a device that performs gas-liquid mixing in a turbulent mode. Examples of such reactors are vortex apparatuses such as emulsifiers and Venturi tubes. The main element of the vortex apparatus of the emulsifier is a swirler, the gas passes at high speed through the slits between the guide vanes, acquires a rotational motion, splits the liquid entering the contact zone into small droplets at the exit of the slits, and engages them in a joint rotational-translational motion. Under the action of the centrifugal force that occurs during the rotation of the two-phase flow, liquid droplets move to the periphery and settle on the wall of the device, forming a rotating liquid ring.

In this research catalysts based on cenospheres and natural zeolite were tested in the process of sulfur dioxide oxidation at a pilot plant with different SO_2 content in the SO_2 -Ar gas mixture. A flow vortex installation of the "Emulsifier" type, with a capacity of 2 m³ / h was used. This installation provided an intensive gas-liquid mass exchange and allowed to remove the diffusion inhibition as a result of the dissolution of sulfur dioxide. The studies were carried out according to the following method: a certain volume of the catalytic solution was placed in the emulsifier and a gas mixture of SO_2 – Ag and air was passed through it simultaneously at a speed of 1 m³/h and a speed of 1 m³/h. Sulfur dioxide at the reactor inlet and after purification was quantified by iodometry and using hydrogen peroxide.

Also the catalytic cracking of M-100 grade fuel oil from Amangeldy Gas Processing Plant (AGPP, Kazakhstan) was studied. Distillations at atmospheric and reduced pressures were used to establish the fractional composition of fuel oil. The following operations are performed for starting and stationary operation of the fuel oil oxidative catalytic cracking reactor: purging of the reactor with an inert gas (CO_2 after the combustion furnace of gaseous products or nitrogen); heating of the reactor to a temperature of 470°C using an induction unit; stopping purging and blocking the supply of inert gas to the reactor; continuous supply to the central zone of the flow reactor through the inlet pipe of 0.2% catalyst suspension in fuel oil with a volume rate of 1.0 h^{-1} . The volume velocity is defined as the ratio of the volume of suspension introduced into the reactor within 1 hour to the volume of the entire reactor. Then are performed: a continuous supply of air to the central zone of the flow reactor through the inlet pipe with a volumetric speed of 0.15 h^{-1} simultaneously with the supply of a mixture of catalyst and fuel oil; continuous discharge from the flow reactor of tar mixed with spent catalyst into the receiving tank; the continuous output of gas. The vapor-like cracking products are directed from the flow reactor to the flow refrigerator-separator. Fractions of gasoline, light gas oil, vacuum gas oil and heavy residue ($T_{\text{boiling}} > 500^\circ\text{C}$) were taken. The content of each fraction (wt. %) was determined by the gravimetric method. The sulfur content of the liquid fuel and vacuum gas oil was determined by high-temperature oxidation of the samples followed by acid-base titration of the resulting sulfur dioxide. In the initial fuel oil, and gasoline and kerosene-gas oil fractions formed during cracking, the presence of oxygen and sulfur-containing compounds were determined by the infrared spectral method.

RESULTS AND DISCUSSION

NMR-analysis shows, that the proton spectrum of fuel oil from AGPP contains ^1H signals of paraffinic, naphthenic and aromatic compounds, which are the main components of the mixture (Fig.-1). Methyl proton signals from saturated hydrocarbons were detected as a broadened singlet at 0.90 ppm. A high-intensity signal with a chemical shift of 1.28 ppm indicates a significant content of protons of methylene groups of aliphatic cyclic and acyclic hydrocarbons. The highest-frequency signals ($\delta = 6.97\text{--}7.76\text{ ppm}$) indicate the presence of monoaromatic compounds and condensed aromatic rings in the fuel oil. Signals of methyl protons of saturated hydrocarbons are noted as a broadened singlet at 0.90 ppm. A small amount of CH_3 groups was noted in the α -position to the aromatic ring ($\delta = 2.30\text{--}2.63\text{ ppm}$). In the range of $2.70\text{--}4.50\text{ ppm}$ there is probably the resonance of protons of the CH_2 and CH groups in the α -position of aromatic compounds.²⁶⁻²⁸

Fig.-1: NMR Spectrum (^1H spectrum) of Fuel Oil from the AGPP

According to our research, the optimum sizes of active parts of the catalyst are in the range 45-55 nm. The specific surface of the catalyst found from the full isotherms of low-temperature adsorption of nitrogen by BET method makes 12.55 m²/g. The integral volume of pores is 0.57 ml/g. Fig.-2 shows SEM images of isolated aluminosilicate microspheres extracted from fly ash of Almaty TPP-2, working on the Ekibastuz coal.

Fig.-2: SEM Images of Aluminosilicate Microspheres extracted from Fly Ash of TPP-2 (Almaty), working on the Ekibastuz Coal

The typical chemical composition of isolated aluminosilicate microspheres is represented by different oxides: oxides of aluminum, silicon, iron, calcium, strontium, zirconium and titanium (wt. %): Al₂O₃ (26.3); SiO₂ (59.05); CaO (1.88); TiO₂ (1.16); Fe₂O₃ (5.45); Na₂O (1.82); S (1.1); P (0.51); SrO (0.043); ZrO (0.051). Thus, the composition of cenospheres is very valuable, which makes it possible to obtain catalysts or sorbents that are multifunctional and resistant to poisoning.

According to X-ray diffraction analysis, the Taizhuzgen zeolite contains the following components (concentration, % intensity): Fe (49.939/739.15); Ca (1.715/9.16); Sr (0.270/1.98); Mn (0.129/1.81); Al (21.955/0.31); Si (23.114/0.98); Ti (1.903/20.87) and K (0.976/1.96).

Purification of Gas Emissions from Sulphur Dioxide

The results of testing a modified catalyst based on fly ash on a flow-through vortex installation of the “Emulsifier” type, with a capacity of 2 m³ / h, are presented in Table-1. Tests have shown that the sulfur dioxide removal rate was 86-95%.

Table-1: Catalytic Purification of Gases from SO₂. The Ratio of the Aqueous Solution to the Catalyst is -1:1.

Solution Composition, mol / L		SO ₂ Content in the Gas Mixture, mg / m ³	
FeCl ₃	Fulvic Acid	Before Cleaning	After Cleaning
0.5·10 ⁻³	2.3·10 ⁻³	1,511	200
1.0·10 ⁻³	2.3·10 ⁻³	104	150
2.0·10 ⁻³	2.3·10 ⁻³	1,511	120
1·10 ⁻³	1.15·10 ⁻³	1,511	205
1·10 ⁻³	4.6·10 ⁻³	1,511	170
1·10 ⁻³	9.2·10 ⁻³	1,511	130
1·10 ⁻³	2.3·10 ⁻³	1,511	180
1·10 ⁻³	2.3·10 ⁻³	1,511	120
1·10 ⁻³	2.3·10 ⁻³	1,511	90

The effect of the partial pressure of sulfur dioxide on the oxidation of sulfur dioxide with oxygen in an aqueous solution in the range of P_{SO2} from 420 mg / m³ to 1,511 mg / m³ in a gas mixture SO₂ - ArO₂ was studied at P_{O2}= 21 vol. %. The test results are summarized in Table-2.

In the studied interval of P_{SO2}, the degree of conversion at the maximum load of the pilot plant was from 60 to 86%, increasing with an increase in the partial pressure of sulfur dioxide in the gas mixture. After the absorption of 4.7 m³ of gaseous sulfur dioxide (the concentration of SO₂ in the aqueous solution is 0.4 mol / L), the aqueous solution was separated from the catalyst and analyzed. Analysis showed the

presence of about 70% H_2SO_4 in the solution. Then a new portion of water is poured in and the gas purification from SO_2 is continued. The activity of the catalyst did not change after that. Thus, the use of the catalysts developed by us based on the fly ash cenospheres of CHPs for the purification of gases from sulfur dioxide with its simultaneous oxidation to sulfur trioxide makes it possible to significantly simplify the technological scheme of gas purification with the simultaneous production of sulfuric acid.

Table-2: Catalytic Oxidation of Sulfur Dioxide with Oxygen at Different Partial Pressures of Sulfur Dioxide.

Conditions: $T = 30^\circ\text{C}$, $= 5 \cdot 10^{-3} \text{ mol / L}$, Ash Sample - 0.1 g. Gas Mixture Feed Rate is $2 \text{ m}^3 / \text{h}$.

P_{SO_2} in the Gas Mixture, Vol. %	SO_2 Content in the Gas Mixture, mg / m^3		Degree of SO_2 Conversion, %
	Before Cleaning	After Cleaning	
1.21	1,511	200	86
1.03	1,286	186	85
0.85	1,061	181	82
0.65	811	180	77
0.42	524	175	66
0.34	424	168	60

Catalytic Cracking of Fuel Oil of the M-100 Brand from AGPP

The previous analysis shows that fuel oil of M-100 brand used for cracking is low-sulfur (Table-3).^{5,15}

Table-3. Fractional Composition and Sulfur Content in Fuel Oil from AGPP, Grade M-100

No	Fractional Composition	Content, wt. %	
		Hydrocarbon Fractions	Sulfur
1	initial fuel oil	100.0	0.7
2	gasoline	0.3	-
3	light gas oil	41.1	0.4
4	vacuum gas oil	18.4	1.3
5	heavy residue	39.3	0.7
6	losses	0.9	-

According to the IR spectral analysis of the fractions of the initial fuel oil, gasoline, light gas oil and heavy residue after the conversion of fuel oil from AGPP, their composition, together with alkanes of normal structure, includes a significant amount of olefin and aromatic hydrocarbons.

The presence of olefins is indicated by strong absorption bands at $3,080\text{-}3,050 \text{ cm}^{-1}$ in the spectra of gasoline and two fractions of light gas oil, as well as a band of medium intensity for a heavy residue. Aromatic hydrocarbons are also concentrated in light fractions, since the intensity of the absorption bands at $1,700$; $1,640$ and $1,600\text{-}1,580 \text{ cm}^{-1}$ decreases during the transition from gasoline to light gas oil ($185\text{-}340^\circ\text{C}$), and in the spectra for the $340\text{-}350^\circ \text{C}$ fraction and the heavy residue of the absorption bands at $3,150$; $1,700$ and $1,620 \text{ cm}^{-1}$ are absent. However, the bulk of all fractions is composed of aliphatic hydrocarbons with absorption bands characteristic of deformation vibrations of these molecules at $1,480\text{-}1,380 \text{ cm}^{-1}$ and $980\text{-}700 \text{ cm}^{-1}$.²⁹⁻³¹

Results of the X-ray phase analysis of the catalysts based on fly ash from TPP with the addition of the activated Taizhuzgen zeolite are presented in Table-4.

Table-4: X-ray Phase Analysis of Catalysts for Oxidative Cracking Fuel Oil (the numbering of minerals is given in decreasing order of their concentration in the analyzed samples)

Mineral Composition	Un-activated		Optimal	
	Before Calcination	After Calcination	Before Calcination	After Calcination
Chamosite $2[(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_5\text{Al}(\text{Si}_3\text{AlO}_{10})\cdot(\text{OH})_8]$	1	1	1	1
Hematite Fe_2O_3	2	2	2	2
Diaspore (boehmite) $\text{AlO}(\text{OH})$	3	4	3	5
Corundum Al_2O_3	4	3	4	3
The cell parameters of chamosite zeolite structure	absent	absent	absent	$A_0=12.8 \text{ \AA}$ $B_0=6.5 \text{ \AA}$ $C_0=3.1 \text{ \AA}$ $\beta=127.2$

On the optimal catalyst in the products of oxidative cracking of fuel oil, the fraction of light gas oil is the main part. Therefore, to elucidate the reaction mechanism, we set the task to determine the individual composition of the hydrocarbons included in this fraction. The results of gas chromatography-mass spectrometric analysis are presented in Table-5.

Table-5. Individual Hydrocarbon Composition of Light Gas Oil obtained as a Result of Oxidative Cracking of Fuel Oil M-100 from AGPP.

Cracking conditions: Catalyst based on fly ash from TPP-2 with the addition of Taizhuzgen zeolite activated by ion exchange (simultaneously with La^{3+} and NH_4^+ ions); $\omega_{\text{suspension}} = 1.0 \text{ h}^{-1}$, $\omega_{\text{air}} = 0.15 \text{ h}^{-1}$, 0.2 wt.% in starting material, $T = 470^\circ\text{C}$.

No	Hydrocarbons	Content, %	No	Hydrocarbons	Content, %
1	heptene-1, C_7H_{14}	1.92	25	hexadecane, $\text{C}_{16}\text{H}_{34}$	3.29
2	heptane, C_7H_{16}	2.82	26	2-methylhexadecane, $\text{C}_{17}\text{H}_{36}$	0.72
3	octene-1, C_8H_{16}	0.69	27	5-heptadecene, $\text{C}_{17}\text{H}_{34}$	0.77
4	octane, C_8H_{18}	1.30	28	heptadecane, $\text{C}_{17}\text{H}_{36}$	3.47
5	nonene-1, C_9H_{18}	0.67	29	2,6,10,14-tetramethyltetradecane, $\text{C}_{18}\text{H}_{38}$	1.43
6	nonane, C_9H_{20}	1.07	30	2,6,11-trimethylpentadecane, $\text{C}_{18}\text{H}_{38}$	0.70
7	decene-1, $\text{C}_{10}\text{H}_{20}$	0.83	31	2,6,10-trimethylpentadecane, $\text{C}_{18}\text{H}_{38}$	0.53
8	decane, $\text{C}_{10}\text{H}_{22}$	1.37	32	1-octadecene, $\text{C}_{18}\text{H}_{36}$	1.02
9	undecene, $\text{C}_{11}\text{H}_{22}$	1.01	33	octadecane, $\text{C}_{18}\text{H}_{38}$	3.96
10	undecane, $\text{C}_{11}\text{H}_{24}$	1.43	34	2-methyloctadecane, $\text{C}_{19}\text{H}_{40}$	2.42
11	pentylcyclohexane, $\text{C}_{11}\text{H}_{22}$	0.77	35	2,4-dimethylheptadecane, $\text{C}_{19}\text{H}_{40}$	1.60
12	dodecene-1, $\text{C}_{12}\text{H}_{24}$	1.26	36	nonadecane, $\text{C}_{19}\text{H}_{40}$	4.88
13	dodecane, $\text{C}_{12}\text{H}_{26}$	2.24	37	6-propylheptadecane, $\text{C}_{20}\text{H}_{42}$	1.82
14	1-butyl-2-pentylcyclopropane, $\text{C}_{12}\text{H}_{24}$	0.65	38	2-methylnonadecane, $\text{C}_{20}\text{H}_{42}$	1.15
15	2,6-dimethylundecane, $\text{C}_{13}\text{H}_{28}$	0.70	39	3-methylnonadecane, $\text{C}_{20}\text{H}_{42}$	0.93
16	tridecene-1, $\text{C}_{13}\text{H}_{26}$	1.25	40	eicosane, $\text{C}_{20}\text{H}_{42}$	6.55
17	tridecane, $\text{C}_{13}\text{H}_{28}$	2.70	41	3-methyleicosane, $\text{C}_{21}\text{H}_{44}$	1.76
18	3-tetradecene, $\text{C}_{14}\text{H}_{28}$	1.31	42	heneicosane, $\text{C}_{21}\text{H}_{44}$	6.63
19	tetradecane, $\text{C}_{14}\text{H}_{30}$	2.88	43	5-propylnonadecane, $\text{C}_{22}\text{H}_{46}$	2.82
20	3-methyltetradecane, $\text{C}_{15}\text{H}_{32}$	0.63	44	docosane, $\text{C}_{22}\text{H}_{46}$	5.05
21	2,6,1-trimethyldodecane, $\text{C}_{15}\text{H}_{32}$	0.51	45	3-butylnonadecane, $\text{C}_{23}\text{H}_{48}$	1.96
22	1-pentadecene, $\text{C}_{15}\text{H}_{30}$	1.09	46	tetracosane, $\text{C}_{24}\text{H}_{50}$	3.13
23	pentadecane, $\text{C}_{15}\text{H}_{32}$	3.36	47	pentacosane, $\text{C}_{25}\text{H}_{52}$	2.49
24	1-hexadecene, $\text{C}_{16}\text{H}_{32}$	0.99	48	heptacosane, $\text{C}_{27}\text{H}_{56}$	1.17

As can be seen from Table-5, the formation of C_7 - C_{12} hydrocarbons occurs exclusively due to the symmetric decomposition of C_{14} - C_{24} paraffin, since the products of this reaction are the corresponding α -olefins and n-alkanes. Thus, as a result of cracking reactions of the M-100 fuel oil from AGPP, the resulting light gas oil contains a significant amount of α -olefins (Table-5), which are a scarce raw material for the production of synthetic additives and oils. It is known from the literature that the best synthetic oils that ensure the operation of equipment in cold climatic conditions are obtained based on oligomers α -olefins C_8 - C_{12} .³¹⁻³⁴

CONCLUSION

In this work catalysts based on the hollow microspheres based on fly ash from the Ekibastuz coal deposit (Kazakhstan), obtained as a result of the operation of TPP-2 in Almaty were synthesized and tested in the process of purification of waste gases from sulfur dioxide. The degree of sorption of SO_2 is reached up to 95%. It was found that after the accumulation of the product in the solution - sulfuric acid at a concentration of 70%, it can be separated from the catalyst, add a fresh portion of water and continue gas purification. The activity of the catalyst did not change after that. The catalytic systems prepared from fly ash from TPP mixed with natural zeolite were used for oxidative catalytic cracking of fuel oil to obtain light carbon fractions. It was shown that microspheres of fly ash are highly effective sorbents of SO_2 and low-temperature catalysts of oxidation of Na_2SO_3 with oxygen in water solutions. As a result of the M-100 fuel oil cracking reactions, the final light gas oil contains a significant amount of α -olefins.

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