Direct Catalytic Reduction of SO$_2$ by CH$_4$ over Fe-Mn Catalysts Prepared by Granulation of Ferromanganese Nodules

N.V. Shikina[1*], S.R. Khairulin[1], S.A. Yashnik[1], T.N. Teryaeva[3], Z.R. Ismagilov[1,2,3]

[1]Boreskov Institute of Catalysis, pr. Akad. Lavrentieva, 5, Novosibirsk, 630090, Russia
[2]Institute of Coal Chemistry and Materials Science, Pr. Sovetskiy, 18, Kemerovo, 650000, Russia
[3]F.T. Gorbachev Kuzbass State Technical University, Kemerovo, 650000, Russia

Article info

Abstract

The chemical, textural, structural and strength properties of ferromanganese nodules and granulated Fe-Mn catalysts containing such nodules were studied. It was found that the granulated catalysts have a developed pore structure, which is close to that of the starting material, and surpass the starting material in strength parameters. The catalysts were tested in desulfurization by methane at a stoichiometric ratio SO$_2$/CH$_4$ = 2. The testing showed that Fe-Mn catalysts with the oxide or sulfide form of active components are active in desulfurization by methane and can selectively reduce SO$_2$ with a conversion above 80%.

1. Introduction

Sulfur dioxide, which is emitted to the atmosphere mostly as a component of flue gases from steam power plants, is a hazardous atmospheric pollutant producing a strong detrimental effect on the environment and human health [1-3]. Due to environmental problems and the necessity of balancing supply and demand in the power industry, great research efforts have been made worldwide to develop clean and efficient power-generating technologies.

The main ways of reducing SO$_2$ emission to the atmosphere are sorption methods [4-9], catalytic oxidation to sulfur trioxide leading to sulfuric acid [10-13], and selective catalytic reduction to elementary sulfur [13-15]. Each of desulfurization methods has its technological niche. The choice of a particular method is determined by various criteria, first of all by the efficiency of cleaning as well as technical and economic indices of the process (capital and current costs) affecting the prime cost of the end product (for steam power plants, the cost of generated thermal and electrical energy).

Most promising are the methods of catalytic reduction of sulfur dioxide to elementary sulfur with the use of various reductants (CO, H$_2$, CH$_4$, synthesis gas) because they enable the single-step conversion of sulfur dioxide to elementary sulfur. Desulfurization by methane or natural gas is the most appropriate process for cleaning of highly concentrated gas mixtures since natural gas is a readily available and inexpensive reductant.

The main reaction of SO$_2$ reduction by methane can be presented as

$$2SO_2 + CH_4 = 2[S] + CO_2 + 2H_2O \qquad (1)$$

where [S] denotes different states of sulfur (S$_1$, S$_2$, … S$_8$) in the gas phase. According to thermodynamic calculations, most probable is the existence of sulfur as diatomic molecule at a temperature above 600 °C [16].

Selective catalytic reduction of SO$_2$ by methane is performed on different type catalysts: aluminum oxide [17], sulfides of Mo and transition metals [18, 19], modified cerium oxide [13, 20, 21].

This work aims to estimate the possibility of using inexpensive and non-hazardous natural materials containing oxide or hydroxide compounds of transition metals as the catalysts for selective catalytic reduction of SO$_2$ by methane. In this connection, of great interest are the shelf ferromanganese nodules (FMNs), whose rich deposits have been found in the water areas of Russian seas. 50% of the ore component of such nodules is constituted by complex composites of Mn and Fe hydroxides and oxides [22]. However, the application of natural materials for cleaning of flue gases on industrial scale depends on the strength of such catalysts.

Our work is devoted to the development of granulated catalysts containing ferromanganese nodules and investigation of their physicochemical properties and activity in selective catalytic reduction of SO_2 by methane.

2. Experimental

2.1. Materials

SO_2 sorbents were prepared using the granulated and powdered material "Ore of ferromanganese nodules from the Gulf of Finland", Specs 0731-001-50855050-2005.

2.2. Catalyst preparation

The catalysts were prepared as cylinders by extrusion of a plastic pulp consisting of FMN powder with a binder. The starting components were mixed in a Z-shaped mixer and then formed using a pneumatic instrument through a spinneret 4 mm in diameter. Wet extrudates were cut to fragments, air-dried for a day, and calcined at 500 ºC for 4 h. Two types of the catalysts containing 80 wt.% of FMNs and 20 wt.% of a binder were prepared. In the case of Fe-Mn(Al) catalyst, aluminum hydroxide sol served as a binder, while for Fe-Mn(Ca-M) catalyst a wet Ca-montmorillonite paste was used. For preparation of the catalysts starting components were mixed subject to their moisture content: 17 wt.% in FMNs, 70 wt.% in aluminum hydroxide sol, 60 wt.% in Ca-M. The following geometry was employed: a diameter of 3.5 mm and a length of 5-10 mm. A photo of the catalysts is displayed in Fig. 1.

Fig. 1. A photo of the granulated samples of the catalyst containing FMNs: Fe-Mn(Al) on the left and Fe-MN(Ca-M) on the right.

3. Methods

3.1. Investigation of the chemical composition

Elemental composition of the samples was found by X-ray fluorescence spectroscopy on a VRA-30 analyzer with the Cr anode of X-ray tube. Measurements were made with granules of the test sample supplemented with boric acid or cellulose. The arithmetic mean of two parallel measurements with the admissible divergence less than 2% was taken as the result of analysis.

3.2. Investigation of the phase composition

Phase composition of the samples was revealed by the analysis of diffraction patterns obtained on an HZG-4 diffractometer with monochromatic Cu K_α source. The detected phases were identified using the JCPDS radiographic database.

3.3. Specific surface area and pore volume measurements

Pore structure of the samples was examined by the low-temperature nitrogen adsorption using an ASAP-2400 (Micromeritics, USA) instrument at the liquid nitrogen temperature, 77 K, after pretreatment of the samples at 150 ºC and a residual pressure below 0.001 mm Hg. A standard pretreatment by the BET and Barrett-Joyner-Halenda (BJH) methods was carried out.

3.4. Bulk density measurements

To estimate bulk density, a dried sample was placed in a 100 cm^3 measuring vessel and consolidated by shaking down. After that, weight of the sample in this volume was estimated. Bulk density (ρ), expressed in g/cm^3, was calculated by the formula: $\rho = m/V$, where m is the sample weight, g; and V is the sample volume, cm^3.

3.5. Mechanical strength measurements

Mechanical strength was measured using an MP-9C instrument under static conditions. The method is based on measuring the breaking force applied to the generatrix of each granule of the catalyst sample between two parallel planes. At least 30 granules of the sample were selected for testing.

3.6. Moisture capacity measurements

To measure moisture capacity with respect to water, a sample of mass m_0 was placed in a capped glass weighing bottle and poured with distilled water so that the water level was 1 cm above the granules. In 30 min, water was decanted from the granules. The granules were placed on a plastic sieve and blasted with compressed air to remove excess moisture. The sample impregnated with water (m_1) was weighed

and moisture capacity was calculated by the formula

$$V_{\Sigma} \text{ (water)} = (m_1 - m_0)/m_0$$

3.7. Estimation of total moisture content

Total moisture content was found by calcination of the starting sample with a mass m_0 at 800 °C. After calcination, the calcined sample (m_1) was weighed and total moisture content was calculated by the formula $\sum_{\text{moist}} = (m_0 - m_1)/m_0$

3.8. Estimation of activity in SO₂ reduction by methane

The experiments were carried out with the catalysts of size 0.5-1.0 mm. A 1 cm³ catalyst sample was mounted in a reactor. The reaction mixture containing SO_2 and CH_4 was fed to the reactor inlet. The required initial concentrations of reactants, flow rate and SO_2/CH_4 ratio were specified at room temperature of the reactor. According to the reaction equation (1), a stoichiometric ratio $SO_2/CH_4 = 2/1$ was chosen for the experiments.

Experiments for estimating the catalytic activity in SO_2 reduction by methane were performed under the following conditions: volume of the loaded catalyst sample – 1 cm³, weight hourly space velocity – 1200 h⁻¹, initial concentration of SO_2 – 67 vol.%, $SO_2/CH_4 = 2/1$, temperature range – 600-900 °C.

The concentrations of SO_2 and CH_4 were controlled by measuring the concentrations of substances by a gas chromatograph.

After establishing the required initial concentrations of reactants and flow rate, temperature of the reactor was raised to 600 °C and composition of the gas mixture at the reactor outlet was analyzed until stationary concentrations of the reaction products were obtained. After that, the reactor temperature was increased to 900 °C at a 50 °C step. Composition of the reaction products was analyzed at each temperature of the reactor until stationary concentrations were reached.

The concentrations of reactants and reaction products obtained in the experiments were used to calculate the SO_2 and CH_4 conversions, selectivity for the formation of elementary sulfur, hydrogen sulfide and COS as well as the yields of elementary sulfur, hydrogen sulfide and COS. The formation of CS_2 as the reaction product was not observed in the experiments; so, selectivity for elementary sulfur was calculated only from the concentrations of SO_2, H_2S and COS.

The balance on carbon was taken into account to find the value of coefficient k, which reflects changes in the gas mixture volume during the reaction:

$$k = \frac{C^o_{CH4}}{C_{CH4} + C_{CO2} + C_{COS}}$$

The coefficient k and concentrations of reaction products were used to obtain the volumetric velocities of reaction products at the reactor outlet:

$$V = \frac{k \cdot V_o \cdot C}{100}$$

The outlet velocities of S_2 and H_2O were calculated from material balance of the system on sulfur:

$$V^o_{SO2} = V_{SO2} + V_{H2S} + V_{COS} + 2V_{S2}$$

and on oxygen:

$$2V^o_{SO2} = 2V_{SO2} + 2V_{CO2} + V_{COS} + V_{H2O}.$$

Flow rates of individual components and the total flow rate were employed to estimate the concentrations of reaction products in the gas mixture at the reactor outlet.

The following expressions were used to calculate main parameters of the catalytic process:
a) conversion of SO_2

$$X_{SO2} = \frac{V^o_{SO2} - V_{SO2}}{V^o_{SO2}} \cdot 100\% \quad \text{where}$$

V^o_{SO2} – volumetric velocity of SO_2 at the reactor inlet, cm³/min

V_{SO2} – volumetric velocity of SO_2 at the reactor outlet, cm³/min

b) conversion of CH_4

$$X_{CH4} = \frac{V^o_{CH4} - V_{CH4}}{V^o_{CH4}} \cdot 100\% \quad \text{where}$$

V^o_{CH4} – volumetric velocity of CH_4 at the reactor inlet, cm³/min

V_{CH4} – volumetric velocity of CH_4 at the reactor outlet, cm³/min

c) selectivity for the formation of H_2S, %

$$S_{H2S} = \frac{V_{H2S}}{V^o_{SO2} - V_{SO2}} \cdot 100\% \quad \text{where}$$

V_{H2S} – volumetric velocity of H_2S at the reactor outlet, cm³/min

V^o_{SO2} – volumetric velocity of SO_2 at the reactor inlet, cm³/min

V_{SO2} – volumetric velocity of SO_2 at the reactor outlet, cm³/min

d) selectivity for the formation of COS

$$S_{COS} = \frac{V_{COS}}{V^o_{SO2} - V_{SO2}} \cdot 100\% \quad \text{where}$$

V_{COS} – volumetric velocity of COS at the reactor outlet, cm^3/min

V^o_{SO2} – volumetric velocity of SO_2 at the reactor inlet, cm^3/min

V_{SO2} – volumetric velocity of SO_2 at the reactor outlet, cm^3/min

e) selectivity for the formation of elementary sulfur

$$S_{S2} = \frac{V^o_{SO2} - V_{SO2} - V_{H2S} - V_{COS}}{V^o_{SO2} - V_{SO2}} \cdot 100\% \quad \text{where}$$

V^o_{SO2} – volumetric velocity of SO_2 at the reactor inlet, cm^3/min

V_{SO2} – volumetric velocity of SO_2 at the reactor outlet, cm^3/min

V_{H2S} – volumetric velocity of H_2S at the reactor outlet, cm^3/min

V_{COS} – volumetric velocity of COS at the reactor outlet, cm^3/min

f) the yield of elementary sulfur

$$Y_{S2} = \frac{X_{SO2} \cdot S_{S2}}{100} \quad \text{where}$$

X_{SO2} – conversion of SO_2, %

S_{S2} – selectivity for the formation of elementary sulfur, %

g) the yield of hydrogen sulfide

$$Y_{H2S} = \frac{X_{SO2} \cdot S_{H2S}}{100}$$

X_{SO2} – conversion of SO_2, %

S_{H2S} – selectivity for the formation of hydrogen sulfide, %

h) the yield of COS

$$Y_{COS} = \frac{X_{SO2} \cdot S_{COS}}{100}$$

V_{SO2} – conversion of SO_2, %

S_{COS} – selectivity for the formation of COS, %

The experimental data obtained were presented as the conversions of SO_2 and CH_4 and the yields of elementary sulfur, H_2S and COS versus temperature.

4. Results and Discussion

4.1. Properties of the catalysts

Table 1 shows the main physicochemical characteristics of a dry FMN powder: chemical, phase and fractional composition, specific surface area (S_{BET}), and total moisture content (Σ_{moist}); physicochemical properties of the catalysts: bulk density (ρ_{bulk}), specific surface area (S_{BET}), pore volume (V_{pore}), moisture capacity (V_Σ), pore diameter (D), mechanical strength (P), and phase composition are indicated in Table 2.

The pore structure parameters of the catalysts are most important for the process efficiency because they determine the dispersion of active components on the surface and allow access of reactants to the active sites. The use of aluminum hydroxide as a binder in the catalyst synthesis makes it possible to obtain the Fe-Mn(Al) sample that has a high specific surface area and a developed pore structure. Therewith, specific surface area and moisture capacity of the Fe-Mn(Al) sample are close to the values characterizing the starting FMN powder that was calcined at 500 ºC [23]; pore volume of this sample even surpasses the starting material (Figs. 2 and 3) due to the high developed pore structure of Al_2O_3 used as the binder of the catalyst. The Fe-Mn(Ca-M) catalyst, prepared with Ca-montmorillonite as a binder, has worse textural parameters than Fe-Mn(Al) but a higher mechanical strength.
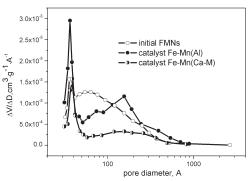

Fig. 2. The differential pore size distribution in the starting FMN powder and FMN catalysts.
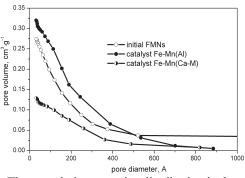

Fig. 3. The cumulative pore size distribution in the starting FMN powder and FMN catalysts.

Phase composition of the prepared catalysts is determined by chemical composition of the samples and calcination temperature. The both catalysts contain α-SiO$_2$, hematite and some unidentified crystalline phases, most likely oxides with a complex structure. Diffraction patterns of the samples differ due to the presence of different binders (Fig. 4). The Fe-Mn(Ca-M) sample contains the Ca-montmorillonite phase. Oxide compounds of aluminum were not found in the diffraction pattern of the Fe-Mn(Al) catalyst, which was prepared with aluminum hydroxide as a binder, due to superposition with the lines of other phases.
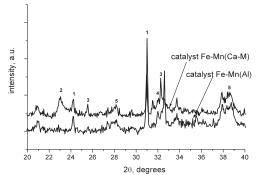

Fig. 4. The diffraction pattern of the catalysts containing FMNs. Phases: 1 – α-SiO$_2$; 2 – montmorillonite; 3 – F1; 4 – F2; 5 – Fe$_2$O$_3$.

Table 1
Characteristics of powdered ferromanganese nodules

Chemical composition, wt.%	Phase composition	Fractional composition	S$_{BET}$, m^2/g	P, kg/cm^2	Σ_{moist} 800 ºC, %
MnO – 24.19	X-ray amorphous phase	100 - 200 μm	162	6	17
Fe$_2$O$_3$ – 25.39		– 25 wt.%			
P$_2$O$_5$ – 3.22		< 100 μm			
Na$_2$O – 2.14		– 75 wt.%			
MgO – 1.79					
Al$_2$O$_3$ – 4.68					
SiO$_2$ – 16.72					
K$_2$O – 1.40					
CaO – 2.10					
TiO$_2$ – 0.07					

Table 2
Physicochemical properties of the FMNs and catalysts containing FMNs

Sample	ρ_{bulk}, g/cm^3	S$_{BET}$, m^2/g	V$_{pore}$, cm^3/g	V$_\Sigma$ (water), cm^3/g	D, Å	P, kg/cm^2	Phase composition
FMNs/500 ºC	0.5	78	0.27	0.66	140	55	α-SiO$_2$; highly dispersed hematite Fe$_2$O$_3$; unidentified phases
Fe-Mn(Al)/500 ºC	0.63	87	0.32	0.53	157	9.0	α-SiO$_2$; highly dispersed hematite Fe$_2$O$_3$; unidentified phases F1 with the maxima at 25.5 and 32.45º and F2 with a maximum at 31.95º
Fe-Mn(Ca-M)/500 ºC	0.77	37	0.13	0.23	132	30.0	α-SiO$_2$; highly dispersed hematite Fe$_2$O$_3$; Ca-montmorillonite; unidentified phases F1 with the maxima at 25.5 and 32.45º and F2 with a maximum at 31.95º

4.2. Reduction of SO$_2$ by methane

Testing was carried out with the catalysts calcined in air at 500 ºC and then treated in H$_2$S at 400 ºC for 2 h. To reveal the effect of preliminary sulfurization of the catalysts, the Fe-Mn(Al) sample was tested also in the oxide form.
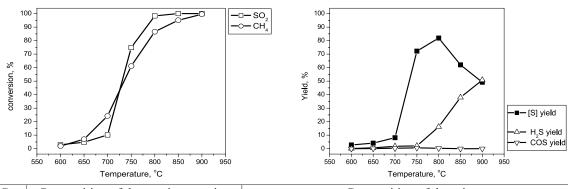
The catalytic characteristics of Fe-Mn(Al) samples in the oxide and sulfide form (the conversion of SO$_2$ and CH$_4$, the yield of main products of the reaction) and composition of the starting and final reaction mixtures are shown in Figs. 5 and 6. The catalytic properties of the sulfide form of Fe-Mn(Ca-M) sample are illustrated in Fig. 7.
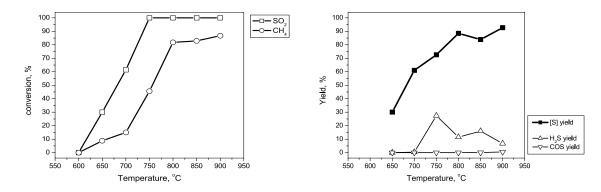

T, ºC	Composition of the starting reaction mixture, vol.%		Composition of the mixture at the reactor outlet, vol.%						
	SO$_2$	CH$_4$	SO$_2$	CH$_4$	CO$_2$	S$_2$	H$_2$S	COS	H$_2$O
600	65.90	34.10	36.55	21.56	9.83	12.09	0.04	0.10	19.83
650	65.90	34.10	19.24	16.81	14.11	18.94	3.46	0.89	26.55
700	65.90	34.10	0.11	1.96	25.59	21.17	10.76	0	40.11
750	65.90	34.10	0	0.94	27.48	16.61	21.70	0	33.27
800	65.90	34.10	0	0.34	28.08	15.42	24.09	0	32.07
850	65.90	34.10	0	0.11	28.73	13.68	28.39	0	29.08
900	65.90	34.10	0	0	29.16	12.53	31.30	0	27.02

Fig. 5. Activity of the oxide form of Fe-Mn(Al) catalyst in SO$_2$ reduction by methane.
GSHV – 1200 h^{-1}, SO$_2$/CH$_4$ = 2, volume of the sample – 1 cm^3

T, ºC	Composition of the starting reaction mixture, vol.%		Composition of the mixture at the reactor outlet, vol.%						
	SO$_2$	CH$_4$	SO$_2$	CH$_4$	CO$_2$	S$_2$	H$_2$S	COS	H$_2$O
600	68.47	31.53	66.37	30.86	0.61	0.95	0.06	0	1.16
650	68.47	31.53	63.50	28.61	2.07	1.36	0.39	0.07	3.89
700	68.47	31.53	55.37	21.50	6.70	2.51	1.06	0.18	12.69
750	66.92	33.08	14.69	11.20	17.33	21.09	1.21	0.34	34.14
800	66.92	33.08	0.96	3.72	23.94	23.04	9.07	0.16	39.12
850	66.92	33.08	0	1.39	26.94	17.79	21.74	0	32.14
900	66.92	33.08	0	0.15	28.53	14.26	29.49	0	27.57

Fig. 6. Catalytic properties of the sulfide form of Fe-Mn(Al) sample in SO$_2$ reduction by methane.
GSHV – 1200 h^{-1}, SO$_2$/CH$_4$ = 2, volume of the sample – 1 cm^3

Fig. 7. Catalytic properties of the sulfide form of Fe-Mn(Ca-M) sample in the reduction of SO_2 by methane. GSHV – 1200 h^{-1}, SO_2/CH_4 = 2, volume of the sample – 1 cm^3.

T, ºC	Composition of the starting reaction mixture, vol.%		Composition of the mixture at the reactor outlet, vol.%						
	SO_2	CH_4	SO_2	CH_4	CO_2	S_2	H_2S	COS	H_2O
600	66.90	33.10	66.97	33.03	0	0	0	0	0.
650	66.90	33.10	48.83	21.52	3.04	10.52	0	0	6.09
700	66.90	33.10	28.90	31.53	5.56	22.87	0.33	0	10.80
750	66.90	33.10	0	20.56	17.23	27.73	20.94	0	13.53
800	66.90	33.10	0	5.15	23.15	25.32	6.57	0.03	39.78
850	66.90	33.10	0	4.88	23.59	24.18	9.22	0.06	38.07
900	66.90	33.10	0	3.61	23.33	25.51	3.73	0.29	43.53

As seen from Figs. 5-6, sulfurization of the Fe-Mn(Al) catalyst shifted the conversion curves of SO_2 and CH_4 to the high-temperature region. Thus, a 100% conversion of SO_2 on the oxide sample was achieved at 700 ºC, and only at 850 ºC in the case of sulfurized sample. It should be noted that a substantial amount of H_2S in the reaction products was observed at high conversions on both the oxide and sulfurized Fe-Mn(Al) samples. The formation of H_2S occurs on the sulfurized sample at temperatures above 750 ºC, while on the oxide sample – at above 650 ºC, when SO_2 conversion exceeds 80%. As the reaction temperature increases, so does the yield of H_2S, which reaches 50% at 900 ºC on both samples. A decrease in selectivity for sulfur with increasing the reaction temperature can be related to the surface sulfurization of γ-Al_2O_3, which is used as a binder upon granulation of FMNs, as a result of its interaction with sulfur dioxide [24] and partial deactivation of the catalyst with respect to the target reaction or due to the promoting role of γ-Al_2O_3 in the reverse Claus reaction. A narrow temperature region associated with the optimal catalytic characteristics – a high conversion of SO_2 (80-100%) with more than 80% recovery of sulfur and a low content of H_2S in the reaction products – can be revealed for the catalysts. For the oxide sample, the optimal temperature of the reaction is 650–700 ºC, whereas for the sulfurized sample, 750–800 ºC.

The sulfurized Fe-Mn(Ca-M) sample showed good performance in the reduction of SO_2 by methane. On this sample, a 100% conversion of SO_2 is reached at 750 ºC. Therewith, the yield of the reaction by-product H_2S decreases with increasing the reaction temperature.

5. Conclusions

The granulated catalysts were synthesized using ferromanganese nodules with a high total content of Fe and Mn oxides. The catalysts have a developed pore structure and high mechanical strength.

The catalysts were tested and their performance in direct reduction of sulfur dioxide by methane was analyzed. It was found that selectivity of the catalysts for elementary sulfur depends on their chemical composition. A low selectivity of the alumina-containing Fe-Mn(Al) catalyst is related to sulfurization of its surface due to the interaction of alumina with sulfur dioxide. In addition, Al_2O_3 is highly active toward the reverse Claus reaction, thus decreasing the efficiency of the entire catalytic system. For this catalyst, a narrow temperature region can be specified where optimal catalytic characteristics are reached, in particular, a high conversion of SO_2 (80-100%) with more than 80% recovery of sulfur and a low content of H_2S in the reaction products. For the catalyst with the oxide form of active components, the

optimal reaction temperature is 650–700 ºC, while for the sulfurized sample, 750–800 ºC.

The Fe-Mn(Ca-M) catalyst containing Ca-montmorillonite is more selective than Fe-Mn(Al) and provides a 100% removal of SO_2 with the sulfur recovery not lower than 90%.

Acknowledgements

References

[1]. Z.R. Ismagilov, M.A. Kerzhentsev, Catal. Rev. Sci. & Eng. 32(1-2) (1990) 51–103.

[2]. Z.R. Ismagilov, M.A. Kerzhentsev, S.R. Khairulin, V.V. Kuznetsov, Chemistry for Sustainable Development 7(4) (1999) 375–396.

[3]. Z.R. Ismagilov, M.A. Kerzhentsev, S.R. Khairulin, Chemistry for Sustainable Development 7 (4) (1999) 443–449.

[4]. Z.R. Ismagilov, M.A. Kerzhentsev, Journal of Mendeleev Chemical Society XXXV (1):43 (1990).

[5]. F. Scala, R. Solimene, F. Montagnaro, Fluidized Bed Technologies for Near-Zero Emission Combustion and Gasification. P. 319 (2013).

[6]. L.E. Kallinikos, E.I. Farsari, D.N. Spartinos, N.G. Papayannakos, Fuel Process. Technol. 91(12) (2010) 1794–1802.

[7]. A. Gomez, N. Fueyo, A. Tomas, Comput. Chem. Eng. 31 (2007) 1419–1431.

[8]. T. Kameda, A. Kodama, T. Yoshioka, Chemosphere 93 (2013) 2889–2893.

[9]. B. Dou, W. Pan, Q. Jin, W. Wang, Y. Li, Energy Convers. Manag., 50 (2009) 2547–2553.

[10]. S. Koutsopoulos, S.B. Rasmussen, K.M. Eriksen, R. Fehrmann, Appl. Catal., A: Gen. 306 (2006) 142–148.

[11]. Y. Xiao, Q. Liu, Zh. Liu, Zh. Huang, Y. Guo, J. Yang, Appl. Catal., B: Environ. 82 (2008) 114–119.

[12]. M.J. King, W.G. Davenport, M.S. Moats, Wet sulfuric acid process fundamentals. Sulfuric Acid Manufacture (Second Edition). Analysis, Control and Optimization. P.295 (2013).

[13]. T. Zhu, A. Dreher, M. Flytzani-Stephanopoulos, Appl. Catal., B: Environ. 21 (1999) 103–120.

[14]. G.B. Han, N.K. Park, S.H. Yoon, T.J. Lee, K.J. Yoon, Appl. Catal., A: Gen. 337 (2008) 29–38.

[15]. G.B. Han, N.K. Park, S.H. Yoon, T.J. Lee, Chemosphere 72 (2008) 1744–1750.

[16]. V.E. Kaloidas, N.G. Papayannakos, Int. J. Hydrogen Energy 12 (1987) 403–409.

[17]. J. Sarlis, D. Berk, Ind. Eng. Chem. Res. 27 (1988) 1951–1954.

[18]. X. Zhang, D.O. Hayward, C. Lee, D.M.P. Mingos, Appl. Catal. B: Environ. 33 (2001) 137–148.

[19]. T.S. Wiltowski, K. Sangster, W.S. O'Brien, J. Chem. Tech. Biotech. 7 (1996) 204–212.

[20]. M. Flytzani-Stephanopoulos, T. Zhu, Yu. Li, Catal. Today 62 (2000) 145–158.

[21]. T. Zhu, L. Kundakovic, A. Dreher, M. Flytzani-Stephanopoulos, Catal. Today 50 (1999) 381–397.

[22]. A.M. Ivanova, A.N. Smirnov, V.S. Rogov, A.P. Motov, N.S. Nikolskaya, K.V. Palshin, Mineral Resources of Russia 6 (2006) 14–19.

[23]. N.V. Shikina, S.R. Khairulin, V.V. Kuznetsov, N.A. Rudina, Z.R. Ismagilov, Chemistry for Sustainable Development 23 (2015) 199–208.

[24]. M.Y. Smirnov, A.V. Kalinkin, A.V. Pashis, A.M. Sorokin, A.S. Noskov, K.C. Kharas, V.I. Bukhtiyarov, J. Phys. Chem. B. 23 (2005) 11712–11719.