

Effect of the synthetic zeolite modification on its physicochemical and catalytic properties in the preparation of the catalysts effectively removing sulphur dioxide from exhaust gases

Agnieszka Marcewicz-Kuba

*Maria Curie-Skłodowska University, Department of Environmental Chemistry, Faculty of Chemistry, Lublin, Poland
Corresponding author: e-mail: agnieszka.marcewicz-kuba@umcs.lublin.pl*

This work presents the research results of the influence of modification deSONOx type catalyst of the sulfur dioxide emissions in the process of the hard coal combustion. The addition of zeolite catalysts modified by transition metal ions: V, Mg, activated by zinc sorbent with or without graphite addition caused the deeper burning of coal grains. The addition of the deSOx catalysts to the coal resulted in lowered sulphur dioxide emission. The addition of unmodified zeolite to coal during combustion reduced sulphur dioxide emission at about 5%. The modification of the support by both V and Mg reduced the amount of sulphur dioxide significantly. The obtained results of SO₂ removal from exhaust gases were from 34.5% for Sip/Mg to 68.3% for Sip/V.

Keywords: catalyst, synthetic zeolite, desulphurisation, coal burning.

INTRODUCTION

The air quality is endangered by the human activity that is connected with the introducing of pollutants into atmosphere. Sulphur dioxide, carbon dioxide, nitrogen oxides, hydrocarbons and dust are main air contaminants. They participate in the chemical and photochemical reactions in the atmosphere generating toxic products: organic and inorganic oxides and acids, free radicals. The main attention is paid to sulfur oxides that pose danger to an environment, living organisms and human health consequently. Sulfur as oxides is one of the most important anthropogenic inorganic pollutants.

In 2013 the worldwide production of energetic coal was almost 6 billion tons and was increased by 60 million tons in contrary to previous year. The usage of energetic coal however increased at 193 million tons¹ meaning the emission of about 100 million tons of sulfur, mainly as sulphur dioxide². In contrary to other pollutants emission such as nitrogen oxides (that is dependent not only on the amount of N in the fuel but also on other factors such as furnace construction or burning technology) the generation of sulfur oxides is directly connected with the sulfur content in the fuel³. Desulfurization of exhaust gases is though the main aspect of environmental protection and key problem of coal based energetics⁴. The resignation from coal as source of fuel under present conditions is impossible. The selection of the proper purification method of exhaust gases is dependent both on technological and economic factors. There is a need for developing simple and cheap technologies that provide primarily effective and economically viable investment. The relevant legislation defining emission limits is established e.g. for fly ash, sulfur dioxide and nitrogen oxides in power and fossil fuel power plants.

In Polish power and fossil fuel power plants a Regulation of the Minister of Environment from 4th November of 2014 defining the emission standards for some installations, sources of fossil fuels and apparatus or co-burning of wastes is valid (DzU 1546. 2014). The permitted level of sulfur contamination is defined as that which enforces the need to find an effective way to reduce S emissions. Lots of new methods are devel-

oped to reduce the sulfur emissions from coal burning. The simplest way seems to be burning of coal with lower sulfur content^{5, 6}, but there is a lack of this type of coal and the desulfurization process is economically unjustified. Moreover, the combustion of coal with low sulfur content is insufficient to achieve the required SO₂ emission reduction from power boilers. Thus new ways to achieve the standards need to be developed. One of them is sulphur dioxide removal from exhaust gases⁶. Nowadays applied techniques of sulphur dioxide removal from stationary sources base mainly on the desulfurization using absorption⁷ and dry methods^{8–10}. However, almost all absorption methods require additional energy consumption, as well as additional hardware, significantly increasing the costs. In dry methods sorbent is directly blown into the combustion chamber or mixed with the fuel prior to delivery to the boiler.

The catalytic methods of sulphur dioxide to sulphur trioxide conversion using vanadium, magnesium or copper oxides based catalysts are known^{11–13}. Quite opposite paradigm of air desulphurization is to prevent formation of sulfur contaminants throughout the use of suitable binders of sulfur during the burning of coal grains. Such substances may be deSOx catalysts which added into coal reduce the emission of gases such as SO₂. The addition of these catalysts eliminates the formation of sulfur oxides and though their emission. The reduction of toxic emission is gained just during the combustion of coal.

The aim of the studies presented in this paper was the determination of the catalytic properties of deSONOx catalysts obtained using synthetic zeolite promoted by transition metal ions such as V and Mg activated additionally by zinc sorbent and graphite in the process of sulfur dioxide removal created during coal combustion.

METHODS AND MATERIAL

In deSONOx method, the emission of sulfur oxides is reduced during coal combustion process. This method can be considered an improved option of SO₂ emission reduction. Anyway, the method completely changes the approach to the reduction of SOx volumes, since the desulfurization of exhaust gasses occurs on the coal grain

subjected to combustion. deSOx materials used in this method are dry additives added to coal under burning. They bind sulfur compounds in furnace residuum. Due to such additives, the desulfurization process is shifted from the gaseous phase to the solid phase. Gaseous pollutants are not created because desulfurization occurs in the combustion process, which eliminates the use of a series of technological lines to remove new pollutants (sulphur dioxides, nitrogen dioxide). deSOx allows to separate desulfurization processes from the boiler type and efficiency. The efficiency of the processes depends only on coal types and conditions in which coal feed is burnt.

The first deSONOx type catalysts was based on MgO and ZnO^{14, 15}. In the next catalysts the matrix of MgO-ZnO was replaced by the synthetic aluminosilicates as the result of impregnation instead of precipitation techniques¹⁶. deSONOx type catalysts may be obtained using natural and synthetic aluminosilicates¹⁷. As it was described¹⁸⁻²¹ the application of zeolite as the support is very efficient. The supports are cheap and can be obtained from wastes. As the active component transition metal ions such as V or Mg may be applied. The addition of deSONOx catalysts to the burning coal does not allow to create the sulfur oxides and their emission. It eliminates also the technically complex desulfurization process as S in coal bounds with catalyst enriching in sulphates the solid residue after combustion (i.e. ash and slag).

Catalysts preparation

The base material in the present studies was synthetic zeolite Sipernat 820 A, (Degussa²²). It is white powder that can be applied for example as the paint additive reducing the pigment absorption. The zeolite properties are presented in Table 1. On a zeolite carrier an active material containing vanadium ions was laid, which was performed following the standard classical impregnation method (CIM) procedure described by Nazimek¹⁸. Zeolite carriers were subjected to drying at 388 K. Afterwards, the carriers were kept in contact with an NaOH and V₂O₅ solution in the first step – the samples was labeled Sip/V. On stage two after drying the carriers were kept in contact with Mg(NO₃)₂ – the samples was labeled as Sip/V-Mg. The obtained catalysts additionally were modified by zinc sorbent and graphite (samples were labeled as Sip/V-Mg-Zn, Sip/V-Mg-Zn/graphite). The scheme of the catalysts preparation is presented in Figure 1.

The synthetic zeolite Sipernat 820 A and zeolite with active phase morphology is presented in Figure 2 and 3. The scans were performed by a high resolution scanning electron microscope **Quanta 3D FEG (FEI)**.

The texture of the catalysts was determined from the studies of a static-volumetric low-volume sorption of argon, after having degassed the samples at 393 K (BET), and the content of metals in active phase (%) was determined by XRF (Analytical Laboratory of Fa-

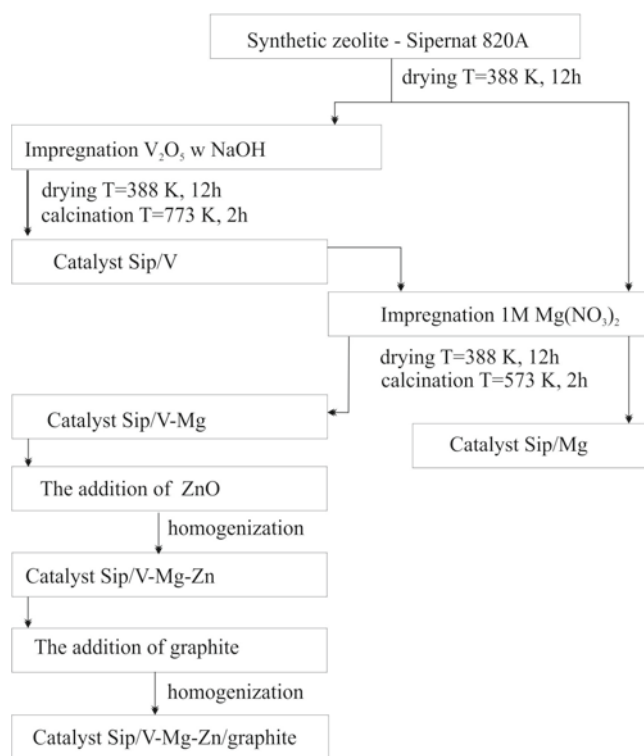


Figure 1. Scheme of catalysts preparation

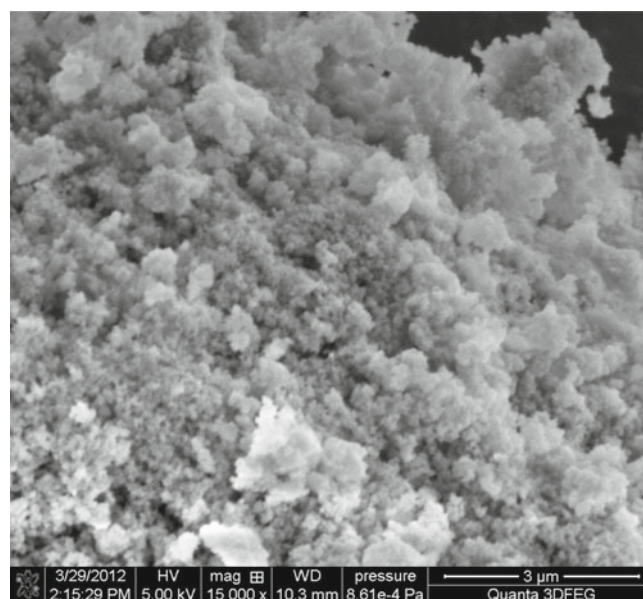


Figure 2. Synthetic zeolite SEM image

culty of Chemistry, UMCS). Bulk density of the obtained catalysts was determined by weighting method.

Apparatus

The process of desulfurization was conducted in the laboratory scale installation presented in Figure 4.

The main element of the installation was integral flow quartz reactor with a thermocouple mounted inside.

Table 1. The physical and chemical properties of zeolite Sipernat 820 A

Appearance	White powder	Norm
Mean agglomerates diameter	5 [μm]	ASTM C 690
Bulk density	300 [g/dm ³]	DIN ISO 787/XI
Specific surface area (BET)	90 [m ² /g]	DNI 66131
Humidity	<6%	DNI ISO 787/11
pH	10	DNI ISO 787/IX
Specific gravity	2,2 [g/cm ³]	DNI ISO 787/X

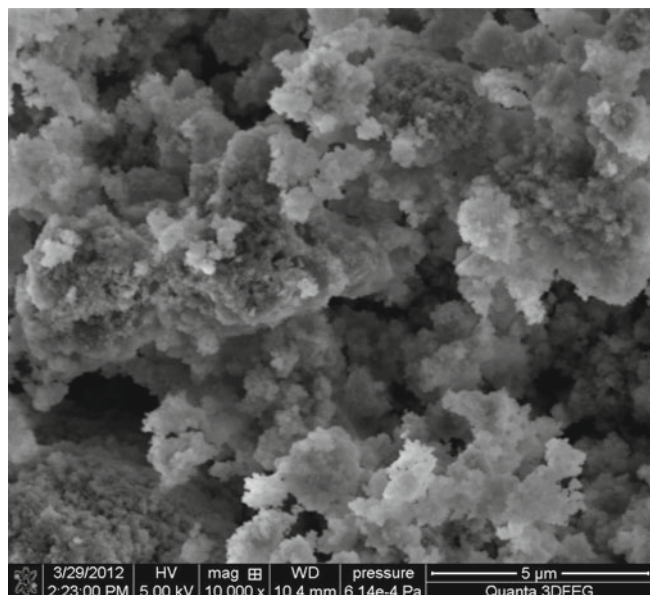


Figure 3. Synthetic zeolite coated with active phase SEM image

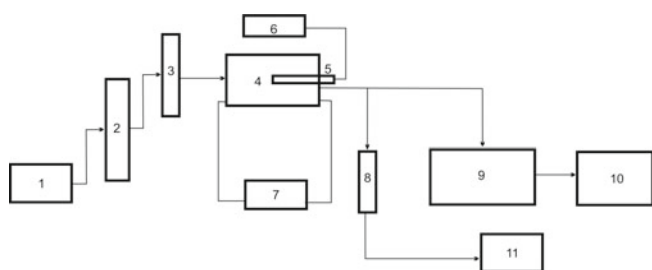


Figure 4. Scheme of apparatus used in the studies, where: 1. Compressor, 2. Manostat, 3. Flowmeter, 4. Flow quartz reactor, 5. Thermocouple 6. Temperature indicator 7. Autotransformer, 8. Tank air flow control, 9. Exhaust gas analyzer IMR 3000, 10. computer, 11. lift

Research methodology

In order to determine the effect of addition of modified zeolite upon reduction of sulphur dioxide emissions in the combustion of hard coal, performed was an experiment described in paper²⁰: samples of coal and coal with added zeolite were subjected a flow reactor in the air atmosphere at 1173 K. The weight ratio zeolite: coal was 1:200. Changes in sulfur dioxide contents in flue gasses caused by the additive were investigated by means of an exhaust gas analyzer IMR 3000. The experiment was conducted till the lack of carbon dioxide in the exhaust gases. The emissions levels of oxygen, carbon dioxide, carbon monoxide and sulphur dioxide were estimated. The data were collected in 1 s intervals and send "on line" to PC computer. The coal under investigation was from Ziemowit Coal Mine (Poland) (code Z). Characterization and physicochemical properties of coal used in these studies are presented in Table 2.

The combustion process was conducted at 1273 K with programmed temperature (Trol-8100) at the air flow 2 dm³/min (Brooks). There were combusted:

- coal,
- coal with the support,
- coal with the catalysts,
- coal with the catalysts and zinc sorbent and graphite.

The combustion residues from the burning of the samples were weighed to determine the degree of nonafterburning coal, which was calculated based on

Table 2. The technical analysis of studied hard coal from KWK "Ziemowit"

Calorific value, Q [kJ/kg]		19634
Sulfur content, S [%]		1.11
Humidity, W [%]		14.00
Ash, A [%]		20.06
Ash composition [%]	SiO ₂	54.02
	Al ₂ O ₃	29.80
	Fe ₂ O ₃	4.90
	CaO	1.53
	MgO	0.50–1.84
	Na ₂ O	0.50
	K ₂ O	3.30
	TiO ₂	1.20
P ₂ O ₅		0.30

the weight of the sample before and after the burning using the formula (1) where: m_w – mass of the sample before burning, m_p – sample weight after combustion, B – ballast (calculated on the basis of the carbon content of the ballast in A with the following formula: $B = 100 - A / 100$):

$$N_{\%} = 100 - (m_w - m_p / m_w \cdot B) \cdot 100\% \quad (1)$$

The scheme of the experiment was presented in Figure 5.

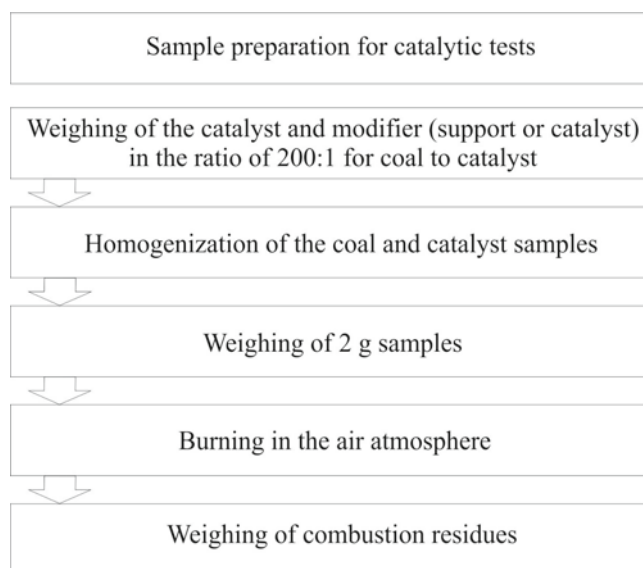


Figure 5. The scheme of combustion of the hard coal with the zeolite catalysts

RESULTS AND DISCUSSION

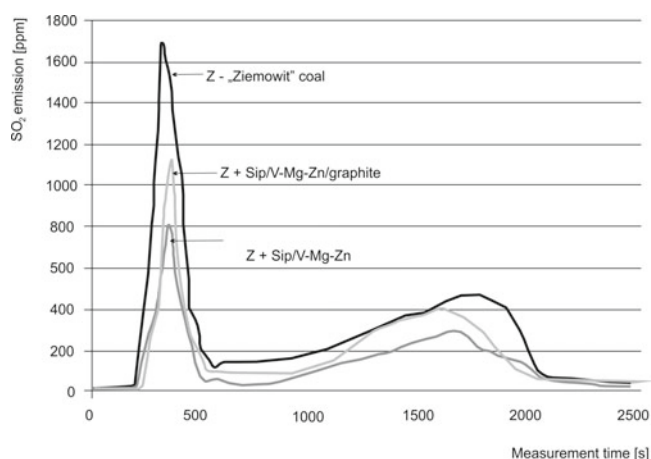
The results of the physicochemical characterization of the obtained catalysts were presented in Table 3.

The specific surface area of the support was estimated at 90 m²/g. After the introduction of the active component SSA was reduced from 73.4 m²/g for Sip/V-Mg-Zn with the graphite addition to 38.8 m²/g for catalysts activated by V ions. The content of the active material was from 0.6 wt.% for V to 1.2 wt.% for Mg. The content of zinc sorbent and graphite was 3 wt.%. The bulk density of the obtained catalysts was 0.27 to 0.33 g/cm³.

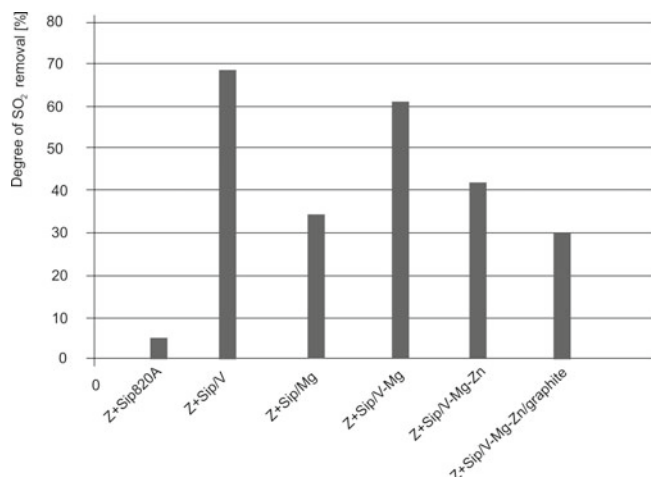
Table 3. The physical and chemical properties of studied catalysts

Catalyst/Support	Bulk density [g/cm ³]	Active phase [wt.%]			Surface area [m ² /g]
		V	Mg	Zn	
Sipernat 820A	2.20	–	–	–	90.0
Sip/V	0.27	0.6	–	–	38.8
Sip/Mg	0.27	–	1.2	–	41.3
Sip/V-Mg	0.30	0.5	0.6	–	40.2
Sip/V-Mg-Zn	0.31	0.5	0.6	3	48.0
Sip/V-Mg-Zn/grafit	0.33	0.5	0.6	3	73.4

For the determination of the catalytic activity of obtained deSONOx catalysts the process of coal combustion with catalysts was performed. The activity of the catalysts was determined on the content of sulphur dioxide in exhaust gases during coal combustion. The background level was estimated at the 100% emission of SO₂ from coal combustion. Coal was combusted at the ratio 200:1 with additives: support – Sipernat 820A and catalysts: Sip/V, Sip/Mg, Sip/V-Mg, Sip/V-Mg-Zn, Sip/V-Mg-Zn/graphite. The amount of sulfur dioxide was measured. The changes in the sulfur dioxide emission were presented in Figure 6.

**Figure 6.** The profile of SO₂ emission from combustion of hard coal WZ – Z and hard coal WZ with the catalysts Sip/V-Mg-Zn, Sip/V-Mg-Zn/graphite

The addition of the deSONOx catalysts to the coal resulted in lower sulphur dioxide emission. The sulphur dioxide emission profile suggests that the catalysts did not influence the mechanism of coal combustion that was confirmed earlier²¹. From the obtained data the degree of sulphur dioxide removal was estimated. The results are presented at Figure 7.

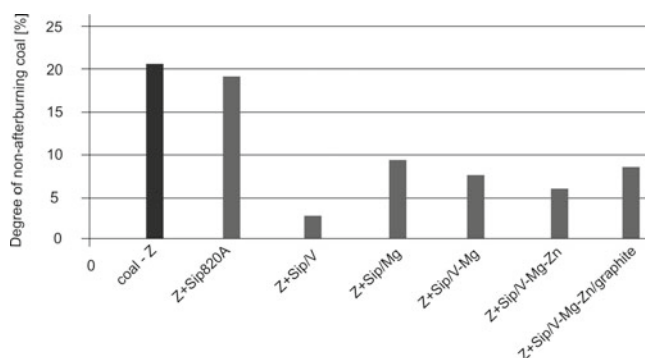
**Figure 7.** The effect of catalysts addition on the degree of sulfur dioxide removal from flue gases

The addition of unmodified zeolite to coal during combustion decreased SO₂ emission by 5%. The modification of the support by both V and Mg reduced the amount of sulphur dioxide significantly. The obtained results of sulphur dioxide removal from exhaust gases were from 34.5% for Sip/Mg to 68.3% for Sip/V. V is well known active phase in sulphur dioxide oxidation to sulphur trioxide, but its application is connected with the significant cost of catalysts and the enrichment of the ashes in V. Though the replacement of V by other transition metals such as Mg was studied. The total resigns from V as active phase caused reduced desulfurization at 50%, from 68 to 34%.

The promising results were obtained using partially replaced vanadium ions by magnesium ions. The addition of magnesium ions into obtained vanadium catalysts caused insignificant (to 62%) reduction in catalytic properties of deSONOx. The modification of V-Mg catalysts by zinc sorbent and graphite failed. The effectivity of the catalysts in the reduction of sulphur dioxide in exhaust gases was obtained in the following order:

Sip/V > Sip/V-Mg > Sip/V-Mg-Zn > Sip/Mg > Sip/V-Mg-Zn/graphite > Sip

The combustion residues were weighed to determine the amount of nonafterburning coal and the effect of catalytic addition on it. The degree of the nonafterburning coal is describing the size of a degree of burnt grain coal. The better burnt coal, the more heat can be obtained. The effect of catalysts on the degree of the unburnt coal was estimated. The results were presented in Figure 8.

**Figure 8.** Summary of degrees of the non-afterburning carbon from the coal mine “Ziemowit” and the coal with the addition of carrier and catalysts

The amount of nonafterburning coal is strictly connected with the ballast content in coal. The more ballast in coal, the higher degree of nonafterburning coal. The ballast content was estimated to be 20.06 %. The results indicate that coal was nonafterburned in 20.2%. The addition of the catalysts into coal improved the process of hard coal combustion significantly what was connected with deeper burning of coal grains. The best

results were obtained for V catalysts that enabled the reduction of nonafterburning coal from 20.2 to 2.2%; for the other catalysts the values were at 6–10%. The effectivity of the catalysts in the amount of nonafterburning coal was following:

Sip/V > Sip/V-Mg-Zn > Sip/V-Mg > Sip/V-Mg-Zn/graphite > Sip/Mg > Sip

The studies confirm the mechanism of deSONOX catalysts described in¹⁷. Macro kinetic spectrum of combustion process revealed the significant shift of isothermal zone of hard coal combustion into the depths of boiler (as burning coal is less cooled down by the endothermic reactions), that enabled better heat exchange and though higher boiler efficiency. The curve of the boiler efficiency to its power (Fig. 9) is more flat as the efficiency factor increased from 5 to 13.5% depending from boiler power and initial parameters; the plateau of the curve is shifted both in lower and higher boiler power regions.

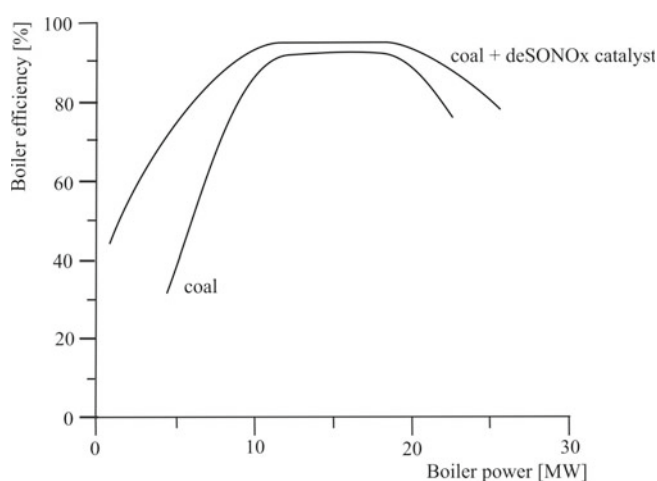


Figure 9. Boiler efficiency to power curve

The increase of performance coefficient is directly connected with the saved fuel as the nonafterburning coal was reduced.

CONCLUSIONS

The preparation of the zeolites catalysts is technically simple and cheap, and the obtained results are promising. Catalysts modified by V and Mg may be applied as deSONOX catalysts. The application of deSONOX catalysts changes completely the present paradigm of desulfurization as the process of desulfurization and denitrification was shifted from gaseous phase into solid phase at the level of burnt coal. This shift separates the desulfurization and denitrification processes from such factors as boiler type and its efficiency.

To sum it up:

- The addition of unmodified zeolite to coal during combustion reduced sulphur dioxide emission at about 5%.

- The introduction of vanadium ions on the zeolite carrier yielded the best catalytic results of an order of 68% for co-combustion of high level sulfur hard coal from 'Ziemowit' mine.

- The introduction of magnesium ions on the zeolite carrier yielded the catalytic results of an order of 35% for co-combustion of high level sulfur hard coal from 'Ziemowit' mine.

- The effectivity of the catalysts in the sulphur dioxide removal from exhaust gases during hard coal combustion was following:

Sip/V > Sip/V-Mg > Sip/V-Mg-Zn > Sip/Mg > Sip/V-Mg-Zn/graphite > Sip

- The addition of the catalysts into coal improved the process of hard coal combustion significantly what was connected with deeper burning of coal grains. The best results were obtained for V catalysts that enabled the reduction of nonafterburning coal from 20.2 to 2.2%; for the other catalysts the values were at 6–10%. The effectivity of the catalysts in the amount of nonafterburning coal was following:

Sip/V > Sip/V-Mg-Zn > Sip/V-Mg > Sip/V-Mg-Zn/graphite > Sip/Mg > Sip

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