

Application of recycled natural aluminasilicate doped with vanadium for the decontamination of the air

¹Agnieszka Marcewicz-Kuba, ²Danuta Olszewska

¹Maria Curie-Skłodowska University, Faculty of Chemistry, Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland, e-mail: amarcewi@hermes.umcs.lublin.pl

²AGH University of Science and Technology, Faculty of Fuel and Energy, al. A. Mickiewicza 30, 30-059 Cracow, Poland

This paper reports studies on the influence of vanadium concentration on the catalytic activity of DESONOX catalysts (in DESOX reaction) based on modified montmorillonite from Jelsovy Potok. The investigation of the influence on the physicochemical properties of the catalysts on their behaviour has also been studied.

Keywords: DESONOX catalysts, SO₂ removal, montmorillonite, vanadium.

Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

Combustion of hard coal causes emission of gaseous chemicals (SO₂, NO_x), airborne particles and fly ashes into the atmosphere¹. Sulphur dioxide is one of the chemicals emitted during the process of hard coal combustion. The desulphurization of solid fuels is one of the main ways of decreasing the environmental impact of their combustion product. The catalytic process of SO₂ removal from combustion gases takes place on the grain plane of hard coal. The method proposed for the removal of SO₂ from combustion gases is quite different from the classical wet desulphurization methods². This solution eliminates the technically complicated wet desulphurization of exhausts: sulphur within the hard coal reacts with catalyst compounds, what enriches the ashes with sulphates^{3–4}. The technical research⁵ has shown that DESONOX type catalyst causes the lowering of both sulphur dioxide and nitrogen oxide emissions from the exhaust coming from the combustion of the solid fuels.

The main aim of the paper is to study the influence of vanadium on the catalytic activity of DESONOX catalyst (in DESOX reaction) based on modified montmorillonite. The research results of the influence of catalysts' physicochemical properties on their activity are also studied. The authors compared the catalyst effectively removing SO₂ from the combustion gases by catalyst with vanadium introduced by support at different time periods.

EXPERIMENTAL

Catalysts

The starting natural material was the montmorillonite from Jelsovy Potok from Slovakia. The composition of this material (wt. %) as given by the X-ray fluorescence method XRF is: N₂O – 2.48, MgO – 3.23, Al₂O₃ – 18.90, SiO₂ – 58.69, P₂O₅ – 0.05, K₂O – 0.36, CaO – 0.07, TiO₂ – 0.20, MnO – 0.08 and Fe₂O₃ – 3.54⁶. The CaCO₃ and Fe₂O₃ were removed from the starting material by Jackson's method⁷. The 1% suspension of montmorillonite which was contacted with 1 M NaCl, gives rise to the Na⁺-montmorillonite form. The support was calcined for 5 h at the temperature of 723 K. The investigated DESONOX catalysts were obtained by the double impregnation method

with the EDTA and the Na₄V₄O₇ solutions. After each impregnation the support was dried in air and calcined. The scheme of catalysts preparation on different supports is presented in Figure 1.

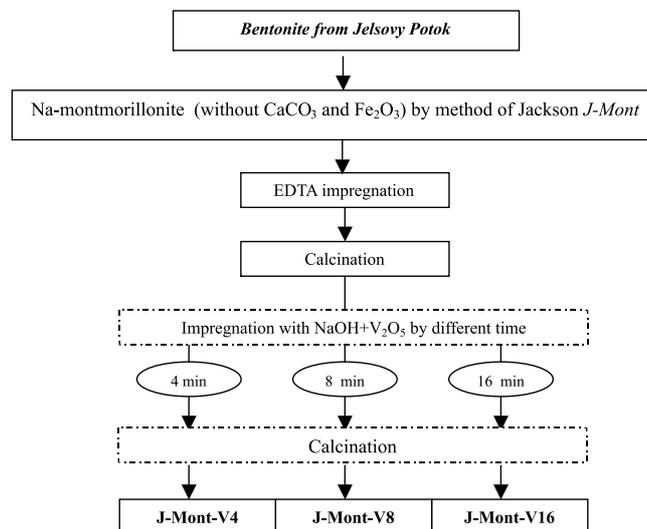


Figure 1. The scheme of catalysts preparation

Methods

The total surface areas of the examined catalysts were determined using the BET method by argon adsorption at boiling temperature of liquid nitrogen, in a volumetric apparatus ensuring a vacuum of at least 10⁻⁵ mm Hg⁸. The concentrations of vanadium in the examined catalysts were determined by the XRF method⁵.

In order to study of catalysts the following experiment was carried out, coal combustion with catalysts. In this method hard coal from Silesian mine „Julian” from Poland was burnt with or without the catalysts using a flow reactor.

The concentration of sulphur dioxide in combustion gases was measured with the use of the VARIO PLUS exhaust analyzer. The proximate and ultimate analyses of hard coal are presented in Table 1. The mass ratio of the DESONOX catalyst added to the investigated samples of the hard coal was 1:500. Hard coal (without any addition) and hard coal with the catalyst addition were burnt in an

Table 1. Proximate and ultimate analyses of hard coal. W^a – moisture content, A^a – ash content, V^{daf} – volatile matter content, C^a – coal content, H^a – hydrogen content, N^a – nitrogen content, S^a_{total} – total sulphur content

Sample	Proximate analysis (%)			Ultimate analysis (%)			
	W ^a	A ^a	V ^{daf}	C ^a	H ^a	N ^a	S ^a _{total}
WJ	5.0	5.9	37.5	71.3	4.23	1.24	0.564
Heating value Q _s ^a : 29026 kJ/kg, Calorific value Q _i ^a : 27852 kJ/kg							

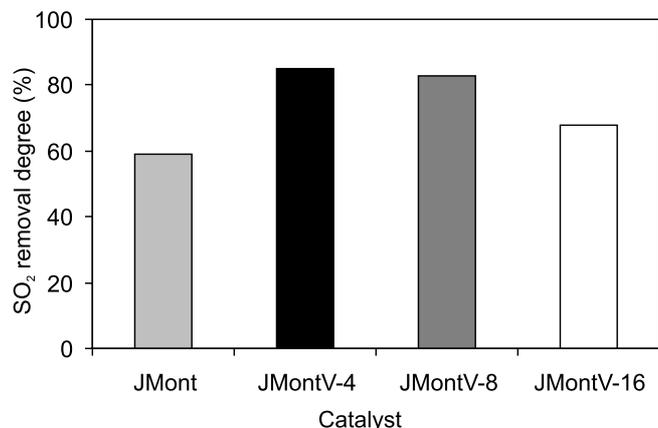
atmosphere of air at 1123K for 4 hours and using an electric furnace.

Sulphur concentration into the samples of coal ashes, which included DESONOX catalysts, was determined by the XRF method. The hard coal uncombustionable degree was calculated on the basis of the sample weight before and after burning.

Results and discussion

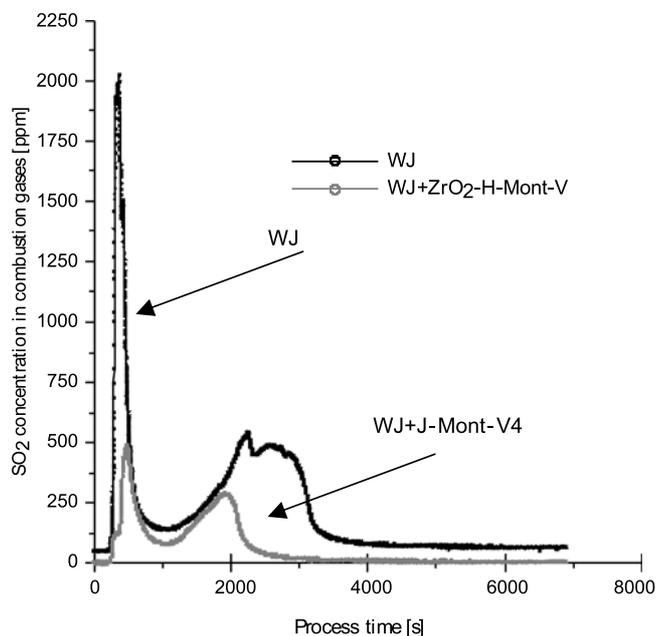
Specific surface areas of the obtained supports based on montmorillonite are respectively: J-Mont – 45 m²/g. After vanadium ions impregnation and calcination at the temperature of 723 K, this parameter decreased, arranging the samples as follows: J-Mont-V4 (7 m²/g) < J-Mont-V8 (9 m²/g) < J-Mont-V16 (21 m²/g). Vanadium concentrations in the studied samples were about 2.3%. The bulk densities δ of the catalysts are ca 1.1 g/cm³.

The presented results of the DESONOX type catalysts show that impregnation of the montmorillonite with the use of vanadium, influences favorably the desulphurization process resulting in the reduction of sulphur dioxide emission in the exhaust gases.

**Figure 2.** SO₂ removal degree [%] in the combustion process for the studied catalysts

From Fig. 2 of the presented SO₂ removal degree, it may be seen that sulphur dioxide concentration in exhaust gases after hard coal with catalyst combustion is less than in the absence of the catalyst. Combusting hard coal with the support of the SO₂ only, the removal degree is 35%, however, with catalyst it is as follows: J-Mont-V16 (68%) < J-Mont-V8 (83%) < J-Mont-V4 (85%). From the compared catalytic activities (SO₂ removal degree) and the specific surface areas it may be seen that the catalyst with the smallest area has the bigger activity. Fig. 3 presents an example of SO₂ concentration in combustion gases and the combustion time for the sample of hard coal WJ and hard coal WJ with the J-Mont-V4 catalyst.

The degree of non-afterburning in the samples with a catalyst equals about 14% for all the burned samples. No direct dependence between the degree of non-afterburning of the investigated coal and the size of the total surface

**Figure 3.** The relationship between SO₂ concentration in combustion gases and the combustion time for the sample of hard coal WJ and hard coal WJ with the J-Mont-V4 catalyst

area of the catalysts has been observed. The used catalytic system with the catalysts based on the modified montmorillonite would make the introduction of technological changes in the process of the coal combustion possible, and would enhance the resignation from expensive, conventional methods of combustion gases purification, which include SO₂.

Conclusion

According to the above-mentioned results of sulphur removal degree of the DESONOX type catalysts based on the modified montmorillonites, the following conclusions can be drawn:

- the addition of the DESONOX catalyst (coal to the catalyst mass ratio 500:1) containing vanadium results in the retention of SO₂ in ashes within the range from 68% to 85%,
- for the catalysts with montmorillonite supports the degree of sulphur removal formed a sequence: J-Mont < J-Mont-V16 < J-Mont-V8 < J-Mont-V4,
- the degree of non-afterburning in samples with catalyst equals about 14% for all the burned samples.
- no direct dependence between the degree of nonafterburning of the investigated coal and the size of the total surface area of catalysts has been observed.

LITERATURE CITED

- (1) Verhovnik V.: Research of function showing the dependence between FVK, FEV₁ and the body height and mass being exposed to small concentrations of SO₂ and smoke. Man and his Ecosystem, Proceeding of the 8th World

Clean Air Congress **1989**, Ed. by Brassier L. J., Mulder W. C., Elsevier, Amsterdam-Oxford-New York-Tokyo **1989**.

(2) Kucowski J., Laudyn D., Przekwas M.: *Energetyka a Ochrona Środowiska*, WNT, Warszawa **1994**.

(3) Marcewicz-Kuba A., Nazimek D.: Influence of the Vanadium and Zinc Contents in DESONOX Catalysts on the Course of the DESOX Reaction, *Ads. Sci. & Technol.*, 16, 803, **1998**.

(4) Marcewicz-Kuba A., Nazimek D.: Influence of Added Zeolite and Vanadium on the Physico-chemical Properties of DESONOX Catalysts, *Pol. J. of Envir. Stud.*, 6, 29, **2000**.

(5) Marcewicz-Kuba A., Nazimek D.: Influence of added molybdenum on the activity of DESONOX catalysts, *Ads. Sci. & Technol.* 6, 549, **2002**.

(6) Grzybek T., Klinik J., Olszewska D., Papp H., Smarzewski J.: The Influence of Montmorillonite Treatment on Structure, Sorption Properties and Catalytic Behaviour: Part I. Zirconia Pillared Clays Modified with Manganese as DENOX Catalysts. *Polish J. Chem.* 75, 857, **2001**.

(7) Jackson M. L.: *Soil chemical analysis*, Prentice Hill, Englewood Cliffs, N.Y., (**1958**).

(8) Ościk J.: *Adsorpcja*, PWN, Warszawa **1983**.