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Reduction of polycyclic aromatic hydrocarbons and nitrogen monooxide in combustion engine exhaust gases by clinoptilolite

Introduction

The contribution of exhaust gases from combustion engines to environmental pollution amounts to 60% of the total contamination. Recently there has been an increased interest in utilization of zeolites for partial reduction of NO_x, CO and hydrocarbons in combustion engine exhaust gases. The catalysts used for detoxication of combustion engine exhaust gases are less effective during periods of relatively low temperatures, such as the initial cold-start period of engine operation. Some global research teams focused their efforts on the use of zeolites as sorbents and catalysts of noxious gases. The electrical field can be changed by modyfying the size of zeolite pores, and as a consequence, also the molecular sieve and selective sorption properties (Zeng et al. 2004; Reháková et al. 2003; Čeliščev et al. 1987). The properties and potential applications of the modified zeolitic forms depend on the method of sorption and the interaction of the host components from the zeolitic channels

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and cavities. The incorporation of certain elements to the structure of zeolite improves its catalytic properties (Monticceli et al. 1999; Wiliams et al. 1995; Miller et al. 1993; Mizuno et al. 2000; Jacobs 1991).

The experiments investigated the ability of natural zeolite – clinoptilolite to reduce the level of hydrocarbons and nitrogen oxide in the exhaust gases of combustion engines. For the experiments, zeolite – clinoptilolite with the following properties was used:

- Mineralogical composition
  - Clinoptilolite – 84%,
  - Illite – 4%,
  - Cristobalite – 8%,
  - Quartz traces,
  - Fieldspar – 4%,
  - Carbonate minerále – <0,5%;
- Chemical composition
  - SiO_2 – 65,0–71,3%,
  - Fe_2O_3 – 0,7–1,9%,
  - Al_2O_3 – 11,5–13,1%,
  - MgO – 0,6–1,2%,
  - CaO – 2,7–5,2%,
  - Na_2O – 0,2–1,3%,
  - K_2O – 2,2–3,4%,
  - TiO_2 – 0,1–0,3%,
  - Si/Al – 4,8–5,4%.
- Partial exchange capacity NH_4^+ 0,7 $mol \cdot kg^{-1}$;
- Total exchange capacity NH_4^+ 1,2–1,5 $mol \cdot kg^{-1}$;

The influence of zeolite chemical treatment was studied. The chemical treatment included the incorporation of metal elements. Our analysis focused on components of exhaust gases containing polycyclic aromatic hydrocarbons with carcinogenic and mutagenic properties, for example benzo[a]pyrene and naphtalene.

The polycyclic aromatic hydrocarbons were analysed in the extract of both thermally-activated natural zeolite and chemically-modified zeolite subjected to amonnium chloride, cobalt chloride and copper sulfate treatment. The zeolite samples used were exposed to exhaust gases produced by the combustion engine of a SKODA *Favorit* model automobile with a 1300 cm^3 motor and without a catalytic converter. The experimentation used 95-octane petrol.

Nitrogen monooxide concentration was measured simultaneously using a filter-sorption apparatus.

1. Materials and methods

1.1. Chemicals and materials

The experiments investigated the influence of chemical treatment on zeolite sorption properties and on its catalytic activity. Samples of zeolite in its natural form, and chemicaly modified, of grain size 5–8 mm, were used.

The contaminates samples were analysed by three independent methods – gas chromatography, high-efficiency liquid-chromatography and three-dimensional fluorescence analysis.

For identification of the polyaromatics, a 16-standard mixture of the most important polycyclic aromatic hydrocarbons was used in accordance with the American Environmental Protection Agency (EPA).

The standard solution of polycyclic aromatic hydrocarbons (PAHs) (200 $\mu g \cdot ml^{-1}$ in methanol or methylene chloride) containing naphtalene, acenaphtylene, acenaphtene, fluorene, phenantrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indenopyrene as well as standard solutions containing individual polyaromatics were purchased from Supelco (Bellefonte, USA).

All other reagents and chemicals were either HPLC or analytical grade. Acetonitrile, methanol and 2-propanol were obtained from Merck (Darmstadt, Germany). Ammonium chloride, cobalt chloride and copper sulphate were purchased from Lachema (Brno, Czech Republic). Solid-phase cartridges of C18 Strata were obtained from Phenomenex (Phenomenex, USA).

1.2. Zeolite treatment

The adsorption characteristics of zeolites are dependent upon the detailed chemical/ /structural makeup of the adsorbent. The Si/Al ratio and the cation type are influential in adsorption. The thermal treatment and the level of dehydration may also affect the final properties of the adsorbent (Ackley 1991). The clinoptilolite has a two-dimensional system of channels. The incoming openings proportions are 0,4 × 0,55 nm (Barrer 1987). In the experiments, the clinoptilolite was used in a natural form, thermally activated at 270°C and chemically modified. The experiments used zeolite which was 84% clinoptilolite. [By literature (Patent Cooperation Treaty 1997; Japanese Patent Office 1993) to the sturcture of the zeolite can to be incorporate metal cations by water solution of this cations effect (the meaning of this sentence is unclear)]. The clinoptilolite with a grain size of 5–8 mm from Nižný Hrabovec (Slovakia) was modified to an ammonium form by the ion-exchange process using an ammonium chloride water solution with a concentration of 1 $mol \cdot dm^{-3}$. The clinoptilolite was treated with ammonium chloride to obtain an NH_4^+ type of ion-exchanged zeolite. To obtain the NH_4^+ type, 700 g of the natural zeolite-clinoptilolite sample was washed for 24 hours with an ammonium chloride solution and dryed at 270°C. The ammonium type of clinoptilolite was used to prepare the cobalt zeolite modification. 700 g of the NH_4^+ zeolite was washed with a 0.5 mol·dm^{-3} solution of $CoCl_2$ for 24 hours at 24°C. The Cu^{2+} clinoptilolite modification was prepared in a similar way. Another 700 g of the zeolite sample was decanted with distilled water, and the NH^{4+} zeolite type was prepared. The NH^{4+} zeolite was dried at 270°C, allowed to cool and washed with a 0.5 mol·dm^{-3} $CuSO_4$ solution. After drying at 270°C, the samples were preapared for experimental measurements.

All the samples of thermally-activated and chemically-modified zeolites with a mass of 650 g intended for PAH analysis were subsequently placed into the filter-sorption apparatus and exposed to exhaust gases under identical conditions (1500 rev/min). Contamination for PAH analysis began with the cold start and continued for 15 minutes. The apparatus had a stainless steel coat in which a net pipe was placed. The exhaust gases could flow through the net pipe which was filled with granular zeolite. After unscrewing the flange, another sample could be exposed to the exhaust gases. The filter sorption apparatus was placed at the end of the exhaust system of the mobile source of exhaust gases.

1.3. Extraction procedure

30 g of each contaminated and uncontaminated zeolite sample were used for the PAHs multiple ultrasonic extraction (4 × 25 ml toluene, 1 hour). The resulting extract solutions were dried using a rotary evaporator, and the residues were dissolved in 2-propanol for the subsequent solid-phase extraction (Kicinski et al. 1989; Götze et al. 1991).

The solid-phase extraction was performed using C18 solid-phase cartridges (Strata 500 mg, Phenomenex, USA). After elution by an acetonitrile-methanol mixture, the solution was ready for chromatographic analysis. For the fluorescence analysis, the extract was diluted with methanol at a ratio of 1:10 000.

2. Analysis

The GC analysis of PAHs was accomplished with a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector. The carrier gas was nitrogen at a constant flow of 1 ml/min. A capillary column SPB-5 (Supelco, Switzerland) 30 × 0,75 mm, 1 μm film thickness was used as an analytical column. Initial column temperature was held for 2 min at 60°C, programmed at 10°C/min to 320°C which was held for 5 min. The injector and detector temperatures were maintained at 220°C and 320°C, respectively. Injection of 2 μl of the extract was performed with a microsyringe (Hamilton, USA).

HPLC separation was performed on Thermo Separation Products AS 3000, USA liquid chromatograph equipped with a fluorescence detector (Spectra System FL 3000, USA) at 40°C. Lichrospher PAH column (25 cm × 4 mm, 5 μm, Merck) was used for chromatographic separation.

Mixtures of acetonitrile-methanol-water (20 : 40 : 20, v/v/v) (A) and acetonitrile (B) of varying compositions were used as mobile phases at a flow rate of 1 ml/min. The elution profile was: A for 1 min, then linear gradient to 100% B over 30 min.

Synchronous spectra were scaned by a luminescent spectrofluorimeter Perkin Elmer LS55 in the range of excitant wavelengths 250–500 nm simultaneously with the movement of the excitant and emissive monochromator with the wavelength difference $\Delta\lambda = 10 - 200$ nm, increment $\Delta\lambda = 10$ nm, crevice Ex/Em = 5/10 nm, with silica cuvette 1 cm, monochromator scan speed 1200 nm/min. Synchronous spectra were presented as contour maps as the dependence of the fluorescence intensity on the excitant wavelength and the defined difference in wavelength between the monochromators $F = f(\lambda_{ex}; \Delta\lambda)$. The same fluorescence intensity points link the contours. The value of the contours representes 5% of the global fluorescence.

3. Results and discusion

Polycyclic aromatic hydrocarbons (PAHs) are an excelent group of compounds for investigation by fluorescent spectroscopy because of their strong fluorescence (Andrade et al. 2000; Luo et al. 2005). Contour maps (Fig. 1) of the contaminated and clean zeolite extracts were distinctively different. The more abundant contour map refers to the presence of polycyclic aromatic hydrocarbons which were absorbed by ammonium modification of zeolite. Fluorescence centres ($\lambda_{ex}/\Delta\lambda$) 280–300/140 nm, 298/120 nm, 398/70 nm correspond to their fluorescence. The contour map of zeolite modified by ions Co^{2+} and Cu^{2+} does not apart the noncontaminate. The respective polycyclic aromatic hydrocarbons were analysed by HPLC and GC methods. The sorptive ability of natural zeolite for some PAHs present in exhaust gases was proved. The extracts of noncontaminated zeolite and zeolite exposed to exhaust gases were compared. The contaminated zeolite extract contained some polycyclic aromatic hydrocarbon-phenanthrene, pyrene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene.

The analysis of the extract was repeated after the zeolite chemical treatment to NH_4^+ type and after its contamination. On the basis of GC and HPLC analysis of the extract, it is possible to state that the treatment increased the sorption properties towards PAHs. In the extract of the contaminated NH_4^+ zeolite type, the polyaromatics with high molecular weight were found-fluorene, phenanthrene, pyrene, benzo(a)anthracene, chrysene benzo(b)-fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(ghi)-perylene.

The following experiments focused on the influence of chemical modification of zeolites by copper sulfate and cobalt chloride on their sorptive properties. After contamination of the chemically-modified zeolites placed in the filter-sorption apparatus, the gas chromatography analysis was carried out using the previously described procedure. Comparison of results showed that no carcinogenic polycyclic aromatic hydrocarbons, present in extracts of natural

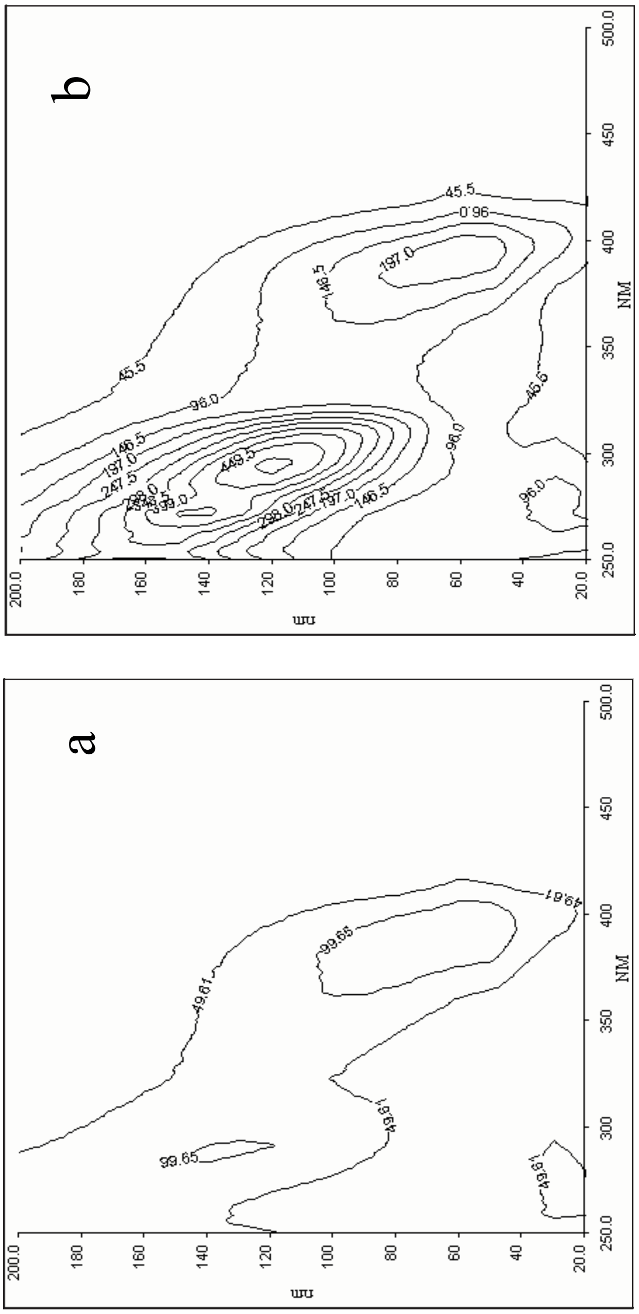

Fig. 1. Contours maps of the noncontaminated zeolite NH_4^+ extract (a), contaminated zeolite NH_4^+ extract (b)

Rys. 1. Mapy konturowe niezanieczyszczonego ekstraktu NH_4^+ zeolitu (a) zanieczyszczonego ekstraktu NH_4^+ zeolitu (b) and NH_4^+ type of zeolite, were found in the Co^{2+} and Cu^{2+} extracts. The subsequent experiment investigated sorption of nitrogen monooxide on natural and modified zeolites and their presumed catalytic activity. The level of NO was measured in exhaust gases which passed through the filter-sorption apparatus filled with natural zeolite and thermically- and chemically-modified zeolites. The initial measurements were carried out with natural zeolite samples. After the preliminary measurements, the zeolite samples were thermally activated and chemically modified by ammonium chloride, cobalt chloride and copper sulfate. All the measurements of NO concentration were conducted using the vehicle SKODA 120 with an internal combustion engine as a source of exhaust gases.

The concentration of NO was recorded in periodic time intervals at the inlet and outlet of the filter-sorption apparatus, filled with zeolite of grain size 5–8 mm, under identical conditions (800 rev/min). The registered values allowed us to calculate the efficiency of the filter-sorption apparatus. The efficiency determined was presented in a graphical form (Fig. 2, 3, 4, 5). The efficiency of natural zeolite ranged between 19% and 25%. The mean efficiency of the filter-sorption apparatus with thermally-activated zeolite (270°C) was 31%. After the modification with NH_4Cl the efficiency increased to 59%. The dependence of the filter-sorption apparatus on the time after the modification of natural zeolite is evident from

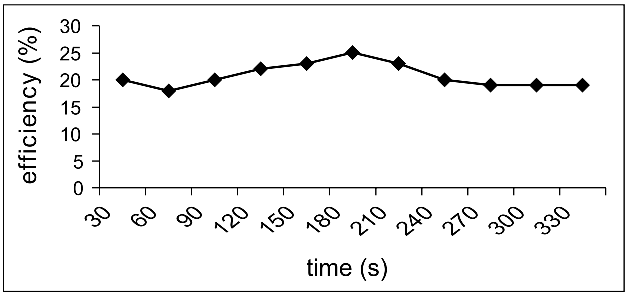

Fig. 2. Time dependence of the filter-sorption apparatus efficiency with natural zeolite

Rys. 2. Zależność urządzenia z filtrem sorpcyjnym z naturalnym zeolitem od czasu wydajności

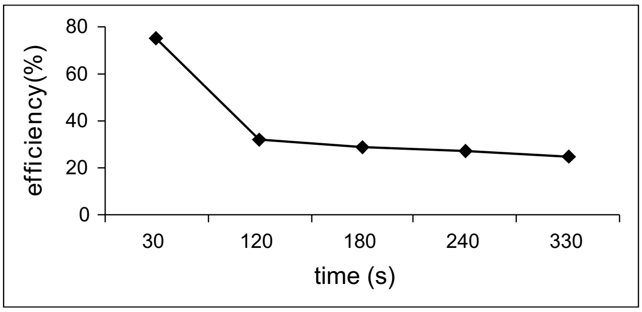

Fig. 3. Time dependence of the filter-sorption apparatus efficiency with thermally-activated zeolite

Rys. 3. Zależność urządzenia z filtrem sorpcyjnym z termicznie aktywowanym zeolitem od czasu wydajności

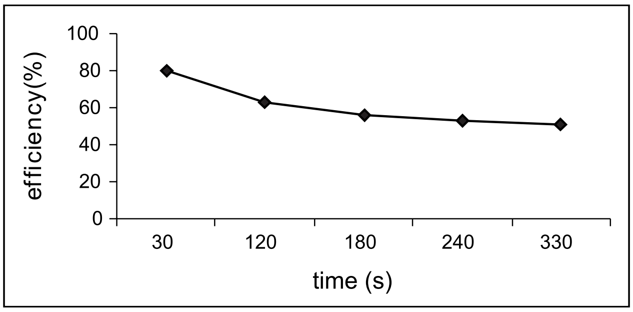

Fig. 4. Time dependence of the filter-sorption apparatus efficiency after the zeolite chemical treatment by NH_4Cl

Rys. 4. Zależność urządzenia z filtrem sorpcyjnym z zeolitem po obróbce chemicznej przez NH_4Cl od czasu wydajności

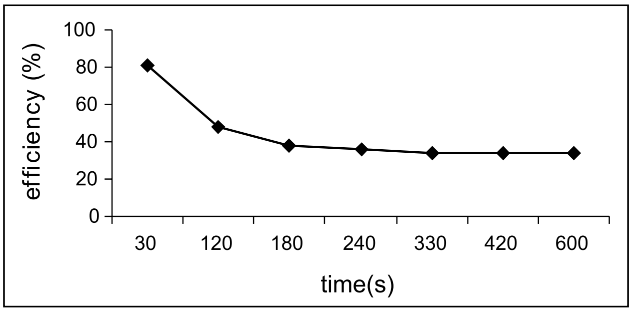

Fig. 5. Time dependence of the filter-sorption apparatus efficiency after the zeolite chemical treatment by $CoCl_2$

Rys. 5. Zależność urządzenia z filtrem sorpcyjnym z zeolitem po obróbce chemicznej przez $CoCl_2$ od czasu wydajności

Figure 4. After 30 seconds, the curve shows a descending trend. The peak efficiency at 30 sec was 80%. Table 1 presents efficiency values for various zeolite samples. It shows that with the untreated zeolite, the highest efficiency (25%) was reached at 180 seconds, and then showed a gradual decrease. A moderate increase in mean efficiency was achieved by thermal treatment. A relatively high efficiency (75%) was recorded at 30 seconds, with a subsesquent, rapid decrease to only 25% at 270 seconds. The ammonium chloride treatment caused a marked increase in efficiency to 59%.

The highest mean values were recorded for the ammonium form of zeolite. Additional experiments investigated the influence of incorporating cobalt cations to zeolite structure. The mean efficiency reached with this modification was 46.4%. We can assume that in this case, under the influence of cobalt cations incorporated in the pores of zeolite, not only NO sorption but also conversion of nitrogen oxide to nitrogen could be expected.

$$2\,NO \rightarrow N_2 + O_2$$

TABLE 1

Efficiency of NO adsorption from exhaust gas using various zeolite samples as a function of time

TABELA 1

Zmiana wydajności w czasie adsorpcji NO z gazów spalinowych przy wykorzystaniu różnych próbek zeolitu

Efficiency of NO adsorption by zeolite (%)				
time (s)	natural	thermally activated	NH_4-form	Co-modified
30	20	75	80	81
69	18	54	69	69
90	20	32	65	59
120	22	32	63	48
150	23	30	59	42
180	25	29	56	38
210	23	29	55	36
240	20	27	53	36
270	19	25	52	34
300	19	25	51	34
330	19	25	51	34
360	19	25	51	34

According to the literary sources (Obalová, Bernauer 2003), if a catalyst is present, N_2O produced at combustion is converted according to the following formula before its oxidation to NO:

$$N_2O \rightarrow N_2 + 1/2O_2$$

$$N^{2+} \leftrightarrow N^0$$

$$Co^{2+} \leftrightarrow Co^{3+}$$

The highest efficiency (87%) of the filter-sorption apparatus was registered at 15 seconds. Between 15 and 270 seconds, the efficiency was maintained at 34%. After that, the efficiency showed no further changes. NO measurements using the $CuSO_4$ zeolite modification showed that, contrary to the previous measurements, the concentration of nitrogen monooxide in exhaust gases was increased at the apparatus outlet. There is an explanation for this fact. Deamonization of the sample at 270°C is not complete. Some residual NH_4^+ cations remain in zeolite channels and are oxidized to nitrogen monooxide by the catalytic effect of Cu^{2+}.

Our experiments confirmed the ability of natural zeolite-clinoptilolite to absorb some polycyclical aromatic hydrocarbons. The results obtained allow us to to state that natural zeolite-clinoptilolite is a prospective material for reducing PAHs and nitrogen monooxide levels in combustion engine exhaust gases.

As far as the ability of zeolite to reduce the content of NO in exhaust gases is concerned, the best results were reached for zeolite treated with amonnium chloride and cobalt chloride. Based on the results of this study and the reasonable price of natural zeolite, one can envisage its use in the automobile industry for the purpose of reducing the content of PAHs and NO in the exhaust gases, particularly during the cold-start period of engine operation when the conventional catalyst is not effective.

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REDUKCJA WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH I TLENKÓW AZOTU W GAZACH WYDECHOWYCH SILNIKA SPALINOWEGO PRZY UŻYCIU KLINOPTYLOLITU

Słowa kluczowe

Klinoptylit, wielopierścieniowe węglowodory aromatyczne (WWA), szkodliwe gazy, tlenek azotu, chromatografia gazowa, chromatografia cieczowa, widmo fluorescencyjne

Streszczenie

Przedmiotem niniejszej pracy było zbadanie zeolitu jako sorbentu toksycznych gazów. Wystąpienia dwóch warstw zeolitu zawierających wtrącenia aktywnego klinoptylitu można spotkać w okolicach Nižnego Hrabovca w Republice Słowackiej. Przedstawione badania dotyczą zdolności tego naturalnego zeolitu do redukcji wielopierścieniowych węglowodorów aromatycznych (WWA) i redukcji emisji tlenków azotu z układu wydechowego silnika. Gazy wydechowe z silników spalinowych zawierają toksyczne składniki, takie jak tlenek węgla, tlenki azotu i węglowodory. Wielopierścieniowe węglowodory aromatyczne (WWA) wywierają szkodliwy wpływ na zdrowie istot żywych. Wykonane eksperymenty koncentrowały się na ocenie potencjalnej redukcji tych toksycznych gazów poprzez sorpcję i właściwości katalityczne naturalnego zeolitu. Obserwowano także możliwości korekty procesu chemicznego, w tym poprzez zastosowanie niektórych związków pierwiastków metalicznych. Prowadzone analizy chemiczne z wykorzystaniem niezależnych technologii miały na celu obserwację sorpcji WWA o kancerogennych właściwościach na testowanym naturalnym zeolicie. Doświadczenia wykazały, że chemiczna modyfikacja poprawia właściwości sorpcyjne i katalityczne natualnego zeolitu. Analizowano WWA w zanieczyszczonym, termicznie aktywowanym naturalnym zeolicie oraz w modyfikowanym zeolicie powstałym po jego przepłukaniu w chlorku amonu, chlorku kobaltu i siarczanie miedzi. W pracy przedstawiono również wyniki pomiarów NO uzyskanych z badań filtra sorpcyjnego samochodu.

REDUCTION OF POLYCYCLIC AROMATIC HYDROCARBONS AND NITROGEN MONOOXIDE IN COMBUSTION ENGINE EXHAUST GASES BY CLINOPTILOLITE

Key words

Clinoptilolite, polycyclic aromatic hydrocarbons (PAHs), noxious gases, nitrogen oxide, gas chromatography, liquid chromatography, fluorescence spectrum

Abstract

The subject of this work was the investigation of zeolite as a sorbent of toxic gases. In Nizny Hrabovec in the Slovak republic, two layers of zeolite with the active component clinoptilolite can be found. The study presented here investigated the ability of this natural zeolite to reduce polycyclic aromatic hydrocarbons (PAH) and NO emissions from engine exhaust. Exhaust gases from combustion engines include toxic components such as carbon monoxide, nitrogen oxides and hydrocarbons. Polycyclic aromatic hydrocarbons (PAH) are a component of hydrocarbons causing harmful influence on life forms. The experiments focused on the potential reduction of these toxic gases based on the sorption and catalytic properties of natural zeolite. Also observed was the influence of chemical adjustment including incorporation of certain metal elements. Chemical analysis by mutually independent technologies served to observe the sorption of PAH with carcinogenic properties on the natural zeolite tested. The experiments showed that chemical modification improved the sorption and catalytic properties of natural zeolite. The PAH were analysed in an extract of the contaminated, thermally-activated natural zeolite and modified zeolite after washing with ammonium chloride, cobalt chloride and copper sulphate. The study also presents results of NO measurements obtained by testing the filter-sorptive automobile system.