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Natural zeolite-clinoptilolite – raw material serviceable in the reduction of toxical components at combustion engines noxious gases

Key words

Clinoptilolite, combustion engines, noxious gases, nitrogen monooxide

Abstract

This article presents the results of the research in the area of the possibilities of the utillisation of the natural zeolite from the locality Nižný Hrabovec at reduction of combustion engines toxical gases. The combustion engines produce a lot of toxical emissions. There is an increased interest to utilize zeolites in the partial reduction of CO, NO_x and hydrocarbons in the combustion products in the world. The article contains the results of the measurements obtained by testing of the filter-sorption machinery with natural and modify zeolite. The influence of the chemical treatment on the sorptional and catalytical possibilities of natural zeolite was acknowledge with experiments.

Introduction

The combustion engines produce exhalations that contribute by great degree to the contamination of the environment. Recently there is an increased interest to utilize zeolites in the partial reduction of the NO_x, CO and hydrocarbons in the combustion products. The natural zeolite was tested in the area of the nitrogen monooxide reduction produced by vehicles. The active component of the natural zeolite from Nižný Hrabovec is a mineral

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clinoptilolite, natrium-calcic type. The structure of the clinoptilolite is comprised by tetraedric $[SiO_4]^{-4}$ and $[AlO_4]^{-5}$,which are connected one another over the oxigen atoms, while the segment of the silicon atoms is substituted by atoms of aluminium. The structure of the clinoptilolite was described at literature (Čeliščev et al. 1987). The composition of the clinoptilolite is utterable by formula:

$$(Na, K)_4\ Ca\ (Al_6\ Si_{30}\ O_{72}) \cdot 24H_2O$$

By influence of modification the size of porous of the zeolite and also electrical field can be changed in consequence of something the molecular- site and sorptive selection properties (Jacobs 1991). The properties and potencial applications of the modified zeolitic forms depend on the way of sorption and on the interaction of the guest components from the zeolitic channelsand cavities (Reháková et al. 2003).

In the consequence of the incorporation of some elements to the structure of zeolite its catalyst proporties are improve (Jacobs 1991).

1. Experimental

The experiments relate to ability of the natural zeolite-clinoptilolite from the Nižný Hrabovec to reduction a content of the nitrogen oxide from the exhaust of the combustion engines. The influence of the zeolite chemical treatment was study. The chemical treatment included the incorporation of the some metal elements after the amonnium chloride, cobalt chloride and cuprum sulfate treatment. It is possible the sorption capacity and catalytic proporties zeolites influenze.by washing with liquid compound of a methal cations.The most often the liquids of the metal cations are used (Bülow et al. 2000). The measurements of the nitrogen monooxide content at noxious gases after their crossing over the filter-sorption machinery were realised.

The experiments were aimed at study of the chemical treatment influence on the zeolite sorption power and also on catalytic zeolite activity. In experiments the samples of the zeolite from the Nizny Hrabovec in natural form and also chemicaly modify with great size 5–8 mm were used to investigate the sorption of the nitrogen monooxide and its supposed catalytic conversion.

1.1. Zeolite treatment

For experiments the clinoptilolite in natural form was used, also thermically activated at 270°C and chemically modified. For the chemical treatment following chemicals were used: ammonium chloride, hydrochloric acid and cobalt chloride.

The clinoptilolite with great size 5–8 mm from the Nižný Hrabovec was modified to ammonium form with the ion-exchange process by amonnium chloride water solution with concentration 1 mol · dm^{-1}. After the decantation by destilated water clinoptilolite was

adjusted with an amonnium chloride to obtain an NH_4^+ type ion exchanged zeolite. 700 g of the zeolite-clinoptilolite sample was washing 24 houres subsequently the sample was dried at 270°C temperature, thereby the NH_4^+ type obtained. Similarly the clinoptilolite was treated by chlorid acide. After the decantation by destilated water 700g of the zeolite sample was showed by chloride acide with the concentration 0.5 mol · dm^{-3} 24 houres. Amonnium type of the clinoptilolite was used to preparation cobalt zeolite modification. 700 g of the NH_4^+ zeolite type was washing by $CoCl_2$ with concentration 0.5 mol · dm^{-3} 24 houres at 24°C temperature. After a drying at 270° C temperature, the samples were preapared on experimentaly measurements. All the samples of the thermically activated also the chemically modified zeolites were gradually placed to the filter-sorption machine and contaminate by exhaust gasesat. The machine is composed of the rustproof steel coat in which the net pipe is placed.The pipe makes possible for exhaust gases flowing. The net pipe is fill by the zeolite in granular form. After the unscrew of a flange a exchange of the sample is possible. The filter sorption machine was placed on the output of the exhaust system of the mobile source of exhaust gases. The automobile SKODA FAVORIT withaut catalyst was used on these experiments. The content of NO was registered at periodic time intervals at the entrance and output of the filter-sorption machinery.

2. Results and discussion

At experiments the natural and modify zeolite was used to investigate the sorption of the nitrogen monooxide and its supposed catalytic conversion. At measurements of the NO at exhaust gases after their crossing across the filter-sorption machinerry, the natural zeolite and progressively the thermically and chemically modify zeolites were used. After every measurement the machinery efficiency was calculated according to formula

$$\text{efficiency } (\%) = [(c_1 - c_2)/c_1] \cdot 100$$

where:

c_1 — NO contents at exhaust gases on pipe entrance,

c_2 — NO content at exhaust gases on pipe output.

The first measurements realized with natural zeolite samples.

The registered values of the apparatus efficiency with natural zeolite were rangeing from 19 to 25%. The dependence of the efficiency was visible graphically (Fig. 1).

After the thermal activation of zeolite sample the highest efficiency was between 15 and 30 second, when 75% was registered, speedily effficiency rapidly decreased and at 90 second it dived to 32%. The average efficiency at this case was 31%.

After the orientational measurements, the zeolite samples were termically activated and gradually chemically modify by ammonium chloride, hydrochloric acid and cobalt chloride.

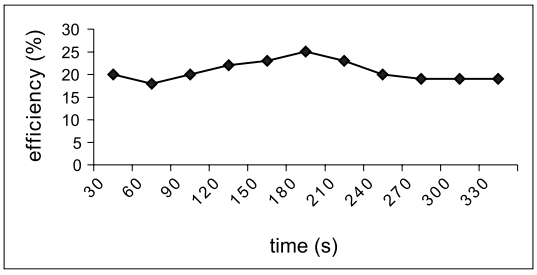

Fig. 1. Time dependence of the efficiency of the sorption-filter machinery with natural zeolite

Rys. 1. Zależność wydajności sorpcyjnej od czasu – filtr z naturalnym zeolitem

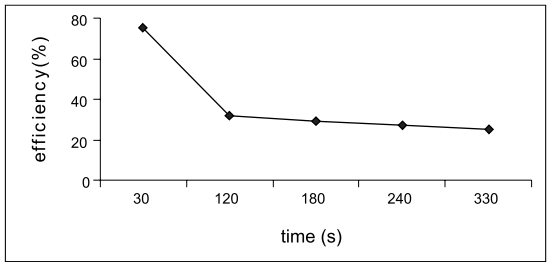

Fig. 2. Time dependence of the efficiency of the sorption-filter machinery with thermally activated zeolite

Rys. 2. Zależność wydajności sorpcyjnej od czasu – filtr z aktywowanym termicznie zeolitem

The experiments concern the influence of the zeolite chemical modification by cobalt chloride effect on the sorptive and catalytic properties.

The content of NO was registered at periodic time intervals at the entrance and output of the filter-sorption apparatus. All the measurements were realized at the same conditions, at revolutions 800 rev/min.

The dependence of the filter-sorption machinery efficiency on the time after the modification of natural zeolite by NH_4Cl is visible on the Figure 3. The curve has since 30 second the descend character. The peak efficiency at 30 second was 80%.

In Table 1, the efficiency values are stated for various samples of the zeolites.

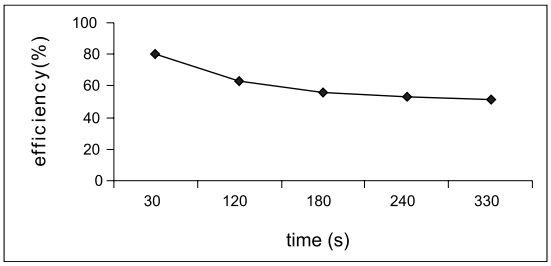

Fig. 3. The dependence of the filter-sorption machinery efficiency on the time after the zeolite chemical treatment by NH_4Cl

Rys. 3. Zależność wydajności sorpcyjnej od czasu – fitr z zeolitem po obróbce NH_4Cl

TABLE 1

Efficiency dependence on the time at various samples

TABELA 1

Zależność wydajności sorpcyjnej od czasu dla różnych sposobów przygotowania zeolitu

Time t [s]	Filter efficiency[%] natural zeolite	Filter efficiency [%] thermal treated zeolite	Filter efficiency [%] NH_4Cl modified zeolite	Filter efficiency [%] HCl modified zeolite
30	20	75	80	73
60	18	54	69	62
90	20	32	65	61
120	22	32	63	46
150	23	30	59	39
18	25	29	56	37
210	23	29	55	37
240	20	27	53	37
270	19	25	52	36
300	19	25	51	36
330	19	25	51	35

From the abduce values follows that the highest efficiency of the non treated natural zeolite 25% was registered at 180 second, subsequently gradually falled. The mild increase of the average efficiency was gained by termically adjustment. Relatively high efficiency 75% witch was registered at 30 second, subsesquently rapidly decreased and at 270 second its value was only 25%. After the adjustment by amonnium chloride the average efficiency markedly increased to 59%.

After the sample treatment by cloride acid, a weak improveing was adjusted opposite thermal treatment zeolite. After the sampel treatment by hydrochloric acid, the average efficiency of sorption-filter machinery was 44.5%.

The highest average values were registered at ammonium form of the zeolite. On the base of the results stated at the table, it is evident that treatment by NH_4Cl is more appropriate as HCl treatment.

The farther experiments were specialized in samples treatment for the purpose incorporation of the cobalt cations to the structure. After the zeolite washing by $CoCl_2$ and their driving the sample was placed to filter-sorption machinary. of exhaust gases. The content of NO was registered at periodic time intervals at the entrance and output of the filter-sorption machine.

On the base of measurement values, the average efficiency was 46.4%. We can assume, that in this case under the influence of cobalt cations incorporated in the pores of zeolite, besides NO sorption also the catalytic change nitrogen oxide to nitrogen proceedes.

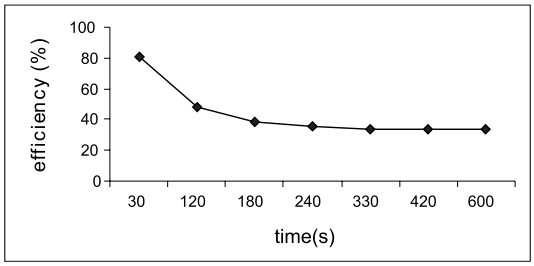

Fig. 4. The dependence of the filter-sorption machin ery efficiency on the time after the zeolite chemical treatment by $CoCl_2$

Rys. 4. Zależność wydajności sorpcyjnej od czasu – zeolit po obróbce chemicznej $CoCl_2$

The following oxidative- reductive reactions are proceeding:

$$N^{2+} \leftrightarrow N^{0}$$
$$Co^{2+} \leftrightarrow Co^{3+}$$

Similarly as in preceding cases the course of apparatus efficiency was visible graphically (Fig. 4). The highest apparatus efficiency 87% was registered at 15 second. From 15 second to 270 second the efficiency value stabilized on 34%. At father time the efficiency did not change yet.

Conclusions

On the base of results it is possibly to state, that natural zeolite-clinoptilolite from the locality Nižný Hrabovec is appropriate to reduce a content of the nitrogen monooxide arise at combustion engines by combustion of fuel. Concerning to zeolite ability to reduce a content of NO at noxious gases, the best results were adjusted by treat zeolite with amonnium chloride and cobalt chloride. Concerning to adjusted results and price accessibility of the natural zeolite it is possibility to use that for the purpose to reduce content of effective to redual a content of the nitrogen oxide by sorption and also by catalytic change. In respect to short period of fill it is necessary zeolite in natural form for practical purpose to modify. By experiments the pertinence of the elected chemical treatment for the purpose to encrease sorption capacity and to obtain catalytical properties. The modified clinoptilolite enriched with cobalt cations is appropriate on the long-term use.

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JOZEF MAČALA, IVETA PANDOVÁ

NATURALNY ZEOLIT-KLINOPTILOLIT – JAKO MATERIAŁ DO REDUKCJI TOKSYCZNYCH ZANIECZYSZCZEŃ W SPALINACH Z SILNIKÓW SPALINOWYCH

Słowa kluczowe

Klinoptilolit, zeolit, silnik spalinowy, spaliny, tlenki azotu

Streszczenie

W artykule przedstawiono wyniki badań nad możliwością wykorzystania naturalnego zeolitu-klinoptilolitu – pochodzącego z Nižnego Hrabovca na Słowacji do redukcji ilości toksycznych zanieczyszczeń w spalinach z silników spalinowych. Klinoptilolit jest to minerał z gromady krzemianów, zaliczany do grupy zeolitów, odmiana heulandytu o składzie $(Na, K)_4 Ca (Al_6 Si_{30} O_{72}) \cdot 24 H_2O$. Należy do grupy minerałów rzadkich. W świecie wzrasta zastosowanie zeolitów do częściowej redukcji CO, NO_x i węglowodorów w produktach spalania. W artykule przedstawiono wyniki badań nad sorpcją zanieczyszczeń przez zeolity w instalacji laboratoryjnej. Współczynnik efektywności sorpcyjnej okreslono zgodnie ze wzorem:

$$\text{Efektywność } (\%) = [(c_1 - c_2)/c_1] \cdot 100$$

gdzie:

c^1 — zawartość NO w gazah odlotowych na wejściu do filtra

c_2 — zawartość NO w gazach odlotowych na wyjściu filtra

Zbadano sorpcję na zeolicie naturalnym oraz modyfikowanym. Modyfikacja zeolitu polegała na obróbce termicznej, obróbce $CoCl_2$ i NH_4Cl.