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Clinoptilolite as a mineral usable for cleaning of exhaust gases

Introduction

Natural zeolites have been the subject of continuous scientific research due to their unique physical and chemical properties. Recently, they have been employed in various areas of industrial technologies and environmental protection (Šamajová 1988; Reháková 2003).

Zeolites belong to the group of inclusion compounds. They are microcrystalline, hydrated aluminosilicates, consisting of a three-dimensional framework of SiO_4^{4-} and AlO_4^{5-} tetraheders linked through oxygen atoms, with characteristic cavities and pores. The literature presents various types of chemical formulas characterising general composition of zeolites (Šamajová 1988; Reháková 2003; Miller 2004). The characteristic features of zeolites include ion exchange, sorption and catalytic properties. By absorption in their cavities zeolites may bind various substances – inorganic, organic, biologically active, and others, which may in turn modify their physico-chemical properties. A typical property of zeolites is their ability to exchange metal ions in their crystal structure which leads to formation of modified zeolites. As a result of modification reactions, diameters of pores or electric field may be changed and lead to altered molecular sieve and sorption-selective properties. By incorporation of some elements in the structure of zeolite its catalytic properties can be improved. The sorption capacity and catalytic properties of zeolites are influenced by contact with solutions of various metal ions (Jacobs 1991; Erga 1996; Obalová 2003).

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One of the most widespread zeolites is the clinoptilolite. Slovak clinoptilolite from the deposit in Nizny Hrabovec is the K-Ca type with additional Fe, Mg and Na ions and other ions present in trace amounts. Its detailed mineralogical and chemical analysis as well as the study of its morphological properties were described in the literature (Čeliščev 1987; Jacobs 1991; Kozáč 1989).

TABLE 1

Chemical composition of natural zeolite from the deposit in Nizny Hrabovec

TABELA 1

Skład chemiczny naturalnego zeolitu ze złoża Nizny Hrabovec

Type of the chemical component	Percentage proportion	Type of the chemical component	Percentage proportion
SiO ₂	65.0 to 71.3	Fe ₂ O ₃	0.7 to 1.9
Al ₂ O ₃	11.5 to 13.1	MgO	0.6 to 1.2
CaO	2.7 to 5.2	Na ₂ O	0.2 to 1.3
K ₂ O	2.2 to 3.4	TiO ₂	0.1 to 0.3
P ₂ O ₅	0.02	Si/Al	4.5 to 5.4

Other elements, such as Li, B, V, Zr, Bi, Sc, Cu, Sn, Cr, Ga, Y, Yb and Ni are present in this zeolite in trace amounts. Some undesirable admixtures intergrown in clinoptilolite cannot be separated from by current physical and chemical methods. Clinoptilolite is a nontoxic, natural, ecologically and economically advantageous material that is used in various areas of industry. One of its important uses is in environmental protection. It has been widely recognized that combustion engines contribute to substantially to air pollution. They are a source of harmful emissions. They consist mainly of carbon monoxide, hydrocarbons and nitrogen oxides (NO_x) emissions. To reduce the level of toxic compounds in exhaust gases from combustion engines we employ presently three-way catalytic converters. However, they starts working only after reaching an optimum temperature. Prior to warming of the converter, during the cold start period, a large volume of harmful substances is produced and emitted into the air without undergoing any change. Studies conducted by various research teams tried to deal with this problem by using zeolites. Application of these materials as adsorbents or minerals with catalytic properties for the purpose of decreasing the levels of toxic compounds in car exhaust gasses, particularly during the cold start period, have been tested. This research resulted in catalytic converters based on chemically modified zeolites. Zeolite is usually applied to the surface of monolithic carrier in the form of thin coating. Synthetic zeolites, such as ZSM-5, beta zeolites, X or Y-type zeolites, and also natural zeolites, such as ferrierit, mordenit, pentasil faujasit were used most frequently (Miller 1993). These zeolites were modified by means of acids and solutions of metal cations.

After this modification, the channels must contain ion-exchangeable cations of catalytic metals (Miller 1993; Caputo 2004; Bulow 2000). In 1993, the Japanese company Mazda introduced a zeolite-based catalytic converter that reduced the content of NO_x . The aim of the present study was to test the capability of natural zeolite clinoptilolite, mined in eastern Slovakia near Nizny Hrabovec, to reduce the amount of hydrocarbons and nitrogen oxides in exhaust gasses produced by combustion engines. At the same time, the effect of chemical modification of zeolite, including implantation of selected metal elements, on its sorption properties as well as on potential gaining catalytic properties was investigated.

1. Natural zeolite modification methods

The sorption and catalytic properties of natural zeolites can be influenced by chemical modification methods. This chemical modification encompasses either de-alumination by weak acids or incorporation of metal elements into zeolite structure on the basis of ion exchange, using suitable solutions. The ion exchange allows one to prepare monoionic forms either directly or indirectly. The de-alumination approach, based on the action of weak acids, removes aluminium from the tetrahedral zeolite skeleton and increases the silicon to aluminium ratio. Organic matter is adsorbed more advantageously on material with higher silicon content, therefore on the sorbent exhibiting higher acidity. Action of diluted acids results in partial de-alumination and increased number of active centres. Such modification of natural zeolite is carried out under conditions that do not result in destruction of this material. It is a goal-directed process. The action of H_2SO_4 at a concentration of 0.03% causes partial extraction of Na^+ cations while Ca^{2+} and K^+ cations are not extracted at all. Application of H_2SO_4 at a concentration of 0.3%, sodium cations are removed completely and calcium and potassium ions only partially. The application of 3% H_2SO_4 causes removal of cations and de-alumination of clinoptilolite (Kozáč 1989). Wet extraction with concentrated H_3PO_4 at boiling temperature causes neither decomposition nor structural changes and increases sorption capacity of the material by increasing the number of active centres. Boiling concentrated HCl causes complete decomposition of clinoptilolite, aluminium and exchange ions pass to the solution while SiO_2 remains in insoluble form.

According to literature, the ratio of silicon to aluminium can be increased by three methods, i.e. thermally, hydrothermally, by chemical de-alumination and combination of chemical and thermal de-alumination (Kozáč 1989). Chemical de-alumination is carried out by using several types of chemicals either in solution or in gaseous form. Chemical reagents in the form of solution are preferred to the gaseous form and of them the most suitable are acids and their salts. When using the gaseous form, de-alumination takes place at high temperatures. After de-alumination, it is recommended to wash the zeolite with de-ionized water to remove the retained acid.

In the first stage, during which cations are exchanged for hydrogen originating from acid, hydroxonium ion (H_3O^+) is formed by reaction between H^+ and zeolite water and the

so-called hydrogenium form is produced. Due to the following action of protons and oxygen radicals the centres of cation exchange are destroyed which results in decreased charge of the matrix and production of the hydroxide. This process is irreversible.

Preparation of basic zeolites is based on common ion-exchange techniques. One can use aqueous solutions containing cations of alkaline metals and metals of alkaline earths, most frequently nitrates, chlorides and sulphates, which are allowed to act for sufficiently long time at appropriate temperature. Exchange capacity of zeolites depends particularly on the content of active ingredients (clinoptilolite), affinity to various cations, concentration of the ion-exchange solution, duration of action, temperature, pressure and grain size of the zeolite.

Ammonium form may be useful when preparing cobalt modifications by means of solution of cobalt salt, namely in the form chlorides, nitrates, sulphates or acetates. The most effective approach is to adjust zeolite with the cobalt salt so as to obtain zeolite with molar quantity of cobalt 0.9 to 1.6 fold higher compared to molar quantity of aluminium. The most suitable appears to be zeolite with molar ratio of SiO_2 to Al_2O_3 not lower than 15, with no upper limit for this ratio (Obalová 2003). This allows one to obtain zeolite with catalytic action and acceptable thermal resistance and stability. Incorporation of cobalt into zeolitic structure can be accomplished by two methods, namely by impregnation or washing (ion exchange). With both methods cobalt is used in the form of solution of its salt, e.g. chloride, nitrate, acetate or sulphate.

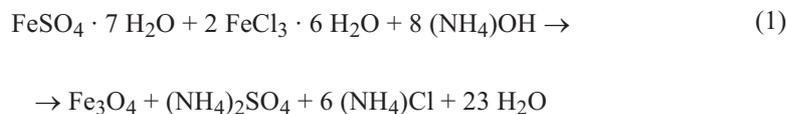
An alternative method is hydrophobisation of zeolite surface by coating it with organic substances capable of anion binding. By applying water solution of octadecylamine to zeolite, the substance adsorbs to its surface and enables adsorption of anions from water solution, removal of cations from zeolite lattice and their replacement by other cations (Erga 1996).

Magnetic particles can also be used to prepare zeolite modifications. This method of modification produces zeolite not only with increased sorption capacity but also with magnetic properties. Such zeolite offers the advantage of simple separation in magnetic field which is very important from the point of view of adsorbent regeneration. The best known methods of zeolite modification by magnetic particles include surface treatment of natural zeolite by means of magnetic nanoparticles (Fe, Co, Ni) and treatment based on colloidal magnetite particles.

The advantage of modification by magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$ is relatively high chemical and thermal stability of the product. According to literature (Feng 2000) impregnation of zeolite Y with maghemite occurs in three stages:

1. Introduction of Fe^{3+} into the Na^+ form of zeolite Y by immersion of zeolite in the melt of $\text{Fe} \cdot 9 \text{H}_2\text{O}/\text{NaNO}_3$,
2. Chemisorption of vapours of formic acid to Fe^{3+} centres,
3. Pyrolysis of the resultant material by ignition in the air at 400°C .

Modified clinoptilolite – clinoptilolite – magnetite- $\text{Fe}(\text{OH})_3$ was used to remove Pb^{2+} , Cd^{2+} and Cu^{2+} ions (Feng 2000).



This way modified zeolite can be used to absorb lead from water solution and the zeolite with magnetic properties may be separated from solution using magnetic field forces.

2. Experimental

Our experiments investigated the suitability of application of natural zeolite clinoptilolite for the purpose of decreasing the level of toxic compounds present in exhaust gases produced by combustion engines utilizing the sorption, ion-exchange and catalytic properties of this material. The measurements focused on the use of zeolite clinoptilolite as a sorbent for removal of nitrogen monoxide and hydrocarbons from combustion engine exhaust gases. The influence of chemical modification of zeolite, including incorporation of selected metal elements, on its sorption properties was investigated in parallel. Nitrogen monoxide is a gas contributing to global warming and its increased concentration in the atmosphere causes damage to the ozone layer. Combustion processes are important sources of nitrogen monoxide among them those which take place in combustion engines.

To carry out the measurements, we invented and constructed a sorption-filtration device consisting of a steel case filled with zeolite. The scheme of this device is on the figure 1. Construction of the device allowed us to remove and replace the filling material. The experiment was carried out on zeolite of grain size between 5.0 mm and 8.0 mm. The aim of the experiment was to observe the ability of clinoptilolite to adsorb nitrogen monoxide from

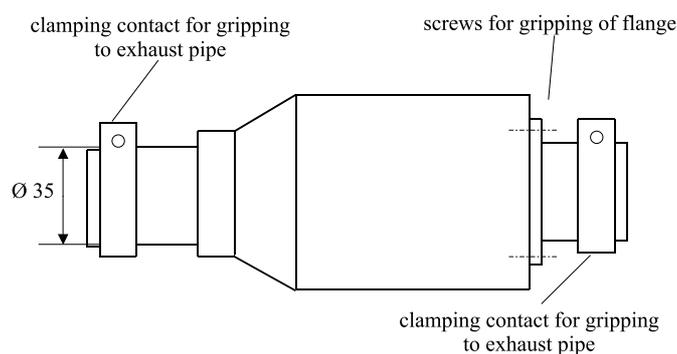


Fig. 1. Sorption-filtration device

Rys. 1. Urządzenie sorpcyjno-filtrujące

exhaust gases produced by combustion engine before chemical treatment and after its modification to the ammonium form.

The initial treatment of clinoptilolite samples consisted in multiple decantation with distilled water and subsequent drying at 270°C. The chemical modification was based on ion-exchange achieved by washing the clinoptilolite with ammonium chloride solution for 24 hours and subsequent drying at 270°C. This way prepared sample was subjected again to measurements and used for preparation of cobalt modification with presumed catalytic properties. The incorporation of cobalt into zeolitic structure was accomplished by ion exchange method. The ammonium form of the zeolite was washed by solution of the cobalt chloride with concentration 1 mol·dm⁻³ for 24 hours. After them the sample was drying at 270°C.

3. Results and discussion

Observation of sorption of nitrogen monoxide on natural zeolite included measurements of process kinetics using heat activated natural zeolite and ammonium modified zeolite. In these experiments we used automobile Favorit. We measured concentration of adsorbed nitrogen monoxide in predetermined intervals of exposure to exhaust gases at constant temperature. The adsorbed nitrogen monoxide was extracted from the adsorbent by sodium hydroxide. Subsequently the content of nitrogen monoxide was determined quantitatively, indirectly in the form of nitrites present in the eluate. The reaction below (2) describes the chemical process. Temporal dependence of nitrogen monoxide sorption to zeolite was determined indirectly on the basis of quantitative mass balance of nitrites in the eluate after extraction with sodium hydroxide.



Figure 2 shows a graphical illustration of nitrogen monoxide sorption on heat-activated natural zeolite. After obtaining ammonium modification of zeolite, kinetics of the adsorption process is illustrated in the same way. The sorption curve obtained is depicted in Figure 3.

Time behaviour of nitrogen monoxide sorption on ammonium-modified form of zeolite shows that the curve reached higher level than that obtained for the heat activated natural form. With the natural form the maximum sorption was 11 mg·g⁻¹, while with the ammonium form the sorption reached 25 mg·g⁻¹. More reliable quantification requires sorption isotherms that may be constructed in the future.

According to literary sources, the nitrogen monoxide molecules, retained by zeolite, exhibit characteristic reactivity. There is an assumption, that after adsorption inside pores nitrogen monoxide is subject to the following reaction (Monticelli 1999):



While dinitrogen monoxide may be desorbed easily, dinitrogen trioxide is retained in pores and undergoes partial decomposition to NO^+ and NO_2^- .

In addition to sorption kinetics we also investigated the changes in the level of nitrogen monoxide in exhaust gases before and after the filtering-sorption device. For this purpose we used a flow analyzer Smart Logger. The apparatus consists from the draw of pipe, filter system for fixation of the solid particles, condensator of water vaper, pumping device and analyzer. Experimental measurements were carried out in relation to both natural and modified samples. For these experiments we prepared also cobalt modification by means of cobalt chloride solution of concentration $0.5 \text{ mol}\cdot\text{dm}^{-3}$ acting on ammonium modification. Zeolites with ion-exchangeable transitional metals act as active catalysers of NO decomposition.

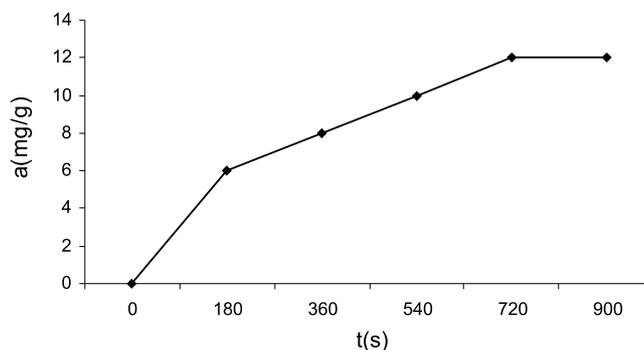


Fig. 2. Time dependence of nitrogen monoxide sorption on natural clinoptilolite

Rys. 2. Zależność od czasu sorpcji tlenku azotu na naturalnym klinoptilolicie

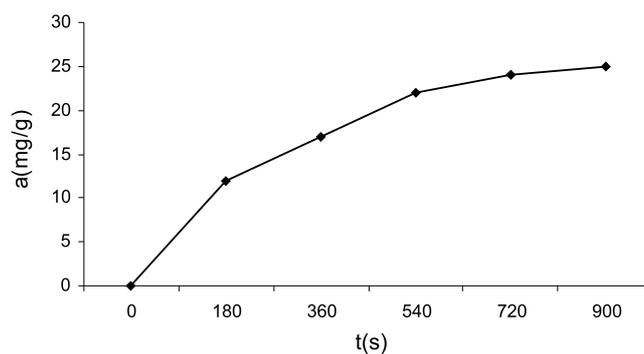


Fig. 3. Time dependence of nitrogen monoxide sorption on ammonium form of clinoptilolite

Rys. 3. Zależność od czasu sorpcji tlenku azotu na amonowej formie klinoptylolitu



According to literature, the presence of catalyser supports decomposition of N_2O according to (5) in advance of its oxidation to NO (Obalová 2003).



Measurements with the cobalt-modified forms were carried out before and after the sorption-filtration device. The results allowed us to calculate the effectiveness of this device and are summarised in Table 2. The effectiveness of the sorption-filtration device filled with natural zeolite was in the range 19–25%. The highest effectiveness was observed at 180 sec and then it had a decreasing trend. The computed values of effectiveness were used to calculate average effectiveness. The mean sorption effectiveness observed with untreated natural zeolite was 20.7% and with the heat treated zeolite it reached 34%. When testing the heat-treated zeolite the highest effectiveness (75%) was reached at 30 sec and then it decreased sharply to 32% at 90 sec. Essential increase in the effectiveness of the device was observed when the natural zeolite was replaced with its ammonium modification. With this sample the mean effectiveness reached 59%. When using cobalt modification we observed an opposite trend. In comparison with the ammonium form the mean effectiveness decreased to 45% but after 270 sec the effectiveness showed no further changes.

TABLE 2

Time dependence of the effectiveness of NO adsorption from exhaust gases by various zeolite samples

TABELA 2

Zależność od czasu efektywności adsorpcji NO z gazów spalinowych w różnych próbkach zeolitu

Time [sec]	Efficiency of NO adsorption by zeolite [%]			
	natural	heat-activated	NH ₄ -form	Co-modified
30	20	75	80	81
60	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

Conclusions

The aim of our experiments was to investigate the potential use of natural clinoptilolite for reduction of nitrogen monoxide concentration in exhaust gases produced by combustion engines. We examined untreated and heat-activated natural zeolite clinoptilolite and its ammonium and cobalt modified forms. Our results showed that modification to ammonium form increased the sorptive capacity of natural clinoptilolite for nitrogen monoxide. While the heat-activated natural form showed sorptive capacity of $11 \text{ mg}\cdot\text{g}^{-1}$, the ammonium modification increased sorption capacity to $24 \text{ mg}\cdot\text{g}^{-1}$. The effectiveness of our sorption-filtration apparatus increased by using modified samples. In comparison with the natural form, the average effectiveness increased from 20% to 59% with the ammonium form and to 45% with the Co-modified form. The results obtained allowed us to state that clinoptilolite is a prospective material for application in the treatment of exhaust gasses from combustion engines, particularly in the period of cold start, during which considerable volume of harmful pollutants can be released to atmosphere before the conventional three way catalyst converter warms up to the optimal temperature.

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CLINOPTILOLITE AS A MINERAL USABLE FOR CLEANING OF EXHAUST GASES

Key words

Zeolites, clinoptilolite, sorption properties, combustion engines, exhaust gasses

Abstract

Natural and synthetic zeolites have been the subject of worldwide scientific research for several decades. Increased attention is paid to utilization of zeolites in environmental protection. The interest in zeolites is related to their unique structure and the related chemical and physical properties which form the basis of their potential ecological, industrial and agricultural applications. The paper presents partial results of research focused on the use of natural zeolite clinoptilolite for reduction of nitrogen monoxide, the component of combustion engines exhaust gases. Experiments were carried out with natural zeolite and also its modified forms. The results obtained allowed us to state that clinoptilolite is a prospective material for application in the treatment of exhaust gasses from combustion engines.

KLINOPTILOLIT JAKO MINERAŁ PRZYDATNY DO OCZYSZCZANIA GAZÓW SPALINOWYCH

Słowa kluczowe

Zeolity, klinoptylolit, własności sorpcyjne, silniki spalinowe, gazy spalinowe

Streszczenie

Naturalne i syntetyczne zeolity badane są od kilku już dekad przed grona naukowców na całym świecie. Coraz więcej uwagi przywiązuje się do wykorzystania zeolitów do celów ochrony środowiska. Zainteresowanie zeolitami związane jest z ich unikalną strukturą i właściwościami chemicznymi i fizycznymi, które stanowią podstawę do potencjalnego ich zastosowanie w ekologii, przemyśle i rolnictwie. Artykuł przedstawia częściowe wyniki badań dotyczące przydatności naturalnego zeolitu – klinoptilolitu do redukcji tlenu azotu, który jest składnikiem gazów spalinowych powstających podczas pracy silnika spalinowego. Przeprowadzono eksperymenty z naturalnym zeolitem oraz z jego zmodyfikowanymi formami. Uzyskane wyniki pozwalają na stwierdzenie, że klinoptilolit jest obiecującym materiałem, który może być zastosowany do oczyszczania gazów powstających podczas pracy silników spalinowych.