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## Deep Catalytic Methane Oxidation at the Clinoptilolite

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### Abstract

Five specimens of the natural clinoptilolite-based catalysts (Sokymytsya deposit, Ukraine) have been prepared for the purpose of studying some of their physical and chemical characteristics (specific surface and its acidity, total pore space). The above catalysts have been studied in the reaction of deep methane oxidation. It has been shown that the natural clinoptilolite possesses the maximal carbon dioxide selectivity (97%), though the activity of all specimens under study remains quite low (i.e. the degree of methane transformation does not exceed 30%). It has been found that the cause of the carbon dioxide selectivity reduction at the modified specimens is the increase of the formaldehyde yield. A scheme of the deep methane oxidation at the catalysts under study has been suggested.

**Key words:** clinoptilolite, catalyst, oxidation, methane

### Introduction

The rational environmental management and protection are being the hot topics gradually occupying the leading place among the global problems of modern times. The further use of the novel technologies accelerates the ecological crisis due to the increase of contaminations involved in the environment. In accordance with the results of studies carried out by a number of economists, the influence of the technological factor on the crisis situation is determinative [1]. The more products are manufactured to satisfy the needs of the mankind, the more complicated are the environmental problems. However, in the technological production, the problem of the human work that specifies the economical expediency of the social production is only a part of the resources used. Another part of production is, as a rule, larger by its mass, these are the scrap materials that come into the environment and require for their utilization the additional financial and material expenses.

The deep methane oxidation reaction is used in a series of devices, i.e. in catalytic heaters, catalytic systems for air cleaning of the exhaust engine gases and the industrial enterprise waste etc. Methane is an extremely inert substance, therefore for the reaction of its oxidation the high temperatures, and, as a result, high energy consumption are required. In addition, at high temperatures due to the oxidation of nitrogen present in air its oxides are produced being extremely harmful for the environment [2]. Therefore, reduction of the reaction temperature to reduce the energy consumption and improve ecology is a hot topic of studies.

The catalysts made of the noble metals deposited onto different carriers [3–4] as well as mixed oxides of transition metals [5] have shown themselves well in the reaction of deep low-temperature methane oxidation. In addition, the vast studies are being carried out on investigating the possibility of the use of natural zeolites as deep oxidation catalysts [2, 6].

In this paper, the natural zeolite clinoptilolite and its modified forms have been studied in the reaction of deep oxidation of methane.

### Experimental

The natural clinoptilolite from the Sokymytsya deposit (Ukraine) [7] was chosen as the initial object of our studies. Zeolite was modified in three stages.

1. To obtain dealuminated specimens the initial natural clinoptilolite with 3–5 mm particles size was treated by the 5N solution of the chloride acid (with the solid to liquid ratio of 1:1.25) at the water bath temperature during three hours with periodical stirring. The specimen obtained was thoroughly washed by the distilled water up to complete elimination of the chlorine ions and dried in the air at room temperature.
2. The dealuminated specimen was decationized by a salt treatment using the 3M  $\text{NH}_4\text{Cl}$  solution (with the solid to liquid ratio of 1:10) during three hours. The specimen obtained was thoroughly washed by the distilled water and dried in the air at room temperature.
3. The dealuminated and decationized specimens of the clinoptilolite layer for ion exchange was treated by the 2N solutions of the  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$  salts. This treatment was also carried out three hours at the water bath. Then the specimens were thoroughly washed by the distilled water and dried in the air at room temperature.

The air-dry specimens were heated at the 393K temperature for five hours and incinerated during three hours at the 823K temperature. As a result of such treatment, five catalyst specimens were obtained: the initial natural clinoptilolite (Zeolite-natural); the specimen substituted by the  $\text{NH}_4^+$  ion (the hydrogen form (Zeolite-H)); the specimen substituted by the  $\text{Cu}^{2+}$  ion (Zeolite H- $\text{Cu}^{2+}$ ); the specimen substituted by the  $\text{Co}^{2+}$  ion (Zeolite H- $\text{Co}^{2+}$ ) and the specimen substituted by the  $\text{Cr}^{3+}$  ion (Zeolite H- $\text{Cr}^{3+}$ ).

After the thermal treatment at relevant temperatures the acidity on the catalysts surface was determined as well as their specific surface and pore space. The surface acidity was determined by amine titration of the benzene suspension of the specimen in the presence of the Hammett indicator i.e. by the Johnson's method; the specific surface was determined chromatographically by the temperature nitrogen adsorption using the BET method, while the pore space was determined by benzene vapor adsorption [8].

The kinetic experiments on the methane oxidation were carried out in the differential reactor of the flowing-type apparatus. The mixture under study comprised 87% of methane and 13% of oxygen. Reaction products were analyzed chromatographically [9]. To obtain the satisfactorily reproducible experimental data, the above apparatus was turned on for a long time of continuous work. The experiments were carried out serially. Before the beginning of each particular series the catalyst was activated under the conditions of the previous series. After reaching the stationary activity of the catalyst the control experiments were carried out.

### Results and Discussion

The clinoptilolite content in the zeolite layer of the Sokymytsya deposit is 70–90%. By its chemical composition it belongs to the aluminosilicates of the sodium-potassium type with quite low calcium content. The gross formula of zeolite is  $(\text{Na}, \text{K}, \text{Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ . The harmful

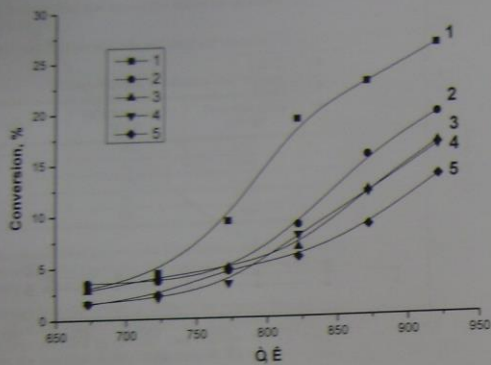


Fig. 3. Methane transformation degree as the function of temperature -  $\text{CH}_4/\text{O}_2=2:1$ ,  $\tau=6\text{c}$ , 1 - Zeolite H -  $\text{Cu}^{2+}$ ; 2 - Zeolite-natural; 3 - Zeolite H -  $\text{Cr}^{3+}$ ; 4 - Zeolite H -  $\text{Co}^{2+}$ ; 5 - Zeolite H

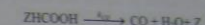
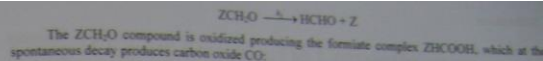
It should be noted that the natural clinoptilolite modification results in the decrease of carbon dioxide selectivity and, according to this parameter, the catalysts form the following series: Zeolite H -  $\text{Cu}^{2+}$  < Zeolite H -  $\text{Cr}^{3+}$  < Zeolite H -  $\text{Co}^{2+}$  < Zeolite-natural.

Carbon dioxide selectivity at the modified specimens decreases due to the formaldehyde yield rise. While the maximal formaldehyde selectivity at the natural clinoptilolite does not exceed 2%, at the specimen modified by the chromium ions (Zeolite H -  $\text{Cr}^{3+}$ ) is approximately 60%, whereas formaldehyde yield at the 923K temperature and the 6 s time of the reaction mixture contact with catalyst reaches 5.7%.

The methane transformation degree is not less significant characteristic of the catalyst. As seen in Fig. 3, the most active is the clinoptilolite form modified by the copper ions (Zeolite H -  $\text{Cu}^{2+}$ ), which the methane transformation degree reaches 25% (see Fig. 3, curve 1). The less active is the origin form of the clinoptilolite (Zeolite-natural) (see Fig. 3, curve 5).

It is known that the transient metal oxides push the oxidation process towards the carbon dioxide formation; therefore, the part of the zeolite surface not modified by the metal ion is, probably, suitable for the formation of the products with lower oxidation degree. At low temperatures (723K) acidity of the specimen surface has almost no effect on the carbon dioxide production rate (see Fig. curve 1). At higher temperatures (see Fig. 4, curves 2, 3) the carbon dioxide production rate is high in specimens with minimal (Zeolite-natural) and maximal (Zeolite H -  $\text{Cu}^{2+}$ ) surface acidity.

One may assume the following mechanism of a complicated multistage process of selective methane oxidation into the oxygen-containing products. Deep oxidation occurs via the formation of an intermediate compound ( $\text{ZCH}_2\text{O}$ ) (here Z being an active centre of the catalyst). Existence of such compound was proven in [10]. Formaldehyde is produced at the intermediate compound desorption on the surface into the bulk.



Carbon dioxide is produced at full oxidation of the surface complex  $\text{ZHCOOH}$  by the molecular oxygen:

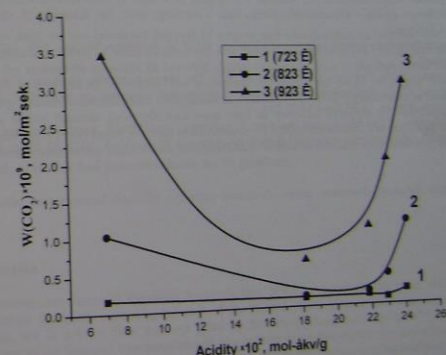


Fig. 4. Comparison of the carbon dioxide production rate with the specimen surface acidity  $[\text{CH}_4]/[\text{O}_2]=2:1$ ,  $\tau=2\text{c}$

## Conclusions

The natural clinoptilolite even without chemical modification is an active catalyst of methane oxidation. Modification of this catalyst by the transient metal ions results in the reduced methane oxidation. Modification of this catalyst by the transient metal ions results in the reduced carbon dioxide selectivity due to the formaldehyde yield increase. It should be noted that acts both the natural clinoptilolite and its modified forms is low and the natural clinoptilolite modification should be directed towards increasing the catalyst activity. Among the normal alkanes, methane is most difficult to be oxidized, therefore the reaction of its catalytic transformation may serve as a model one for any reaction of hydrocarbon oxidation by the molecular oxygen.

elements content does not exceed the following quantities: Pb -  $3 \cdot 10^{-3}\%$ , Zn -  $4 \cdot 10^{-3}\%$ , Cu -  $1.5 \cdot 10^{-3}\%$ , As -  $1 \cdot 10^{-3}\%$ .

Table 1 shows some physical and chemical characteristics of the catalysts under study.

Table 1. Physical and chemical characteristics of the catalysts under study

Catalyst	Specific surface S [m <sup>2</sup> /g]	Total pore space [cm <sup>3</sup> /g]	Surface acidity [mole ekv/g]	
			Before catalysis	After catalysis
Zeolite-natural	86	0.013	0.0696	0.0647
Zeolite H	96	0.243	0.1814	0.1794
Zeolite H - $\text{Cr}^{3+}$	527	0.121	0.2181	0.2093
Zeolite H - $\text{Co}^{2+}$	83	0.117	0.2291	0.2214
Zeolite H - $\text{Cu}^{2+}$	140	0.080	0.2401	0.2345

The clinoptilolite layer of the Sokrytsya deposit is characterized by a high thermal stability due to its strong silica properties. The optimal activation temperature is 600-700K. The water starts to excrete only at heating above 800K.

As seen from the entries of Table 1, the natural clinoptilolite modification results in the change of its physical and chemical properties, i.e. the specific surface, total pore space and surface acidity. The specimen modified by the  $\text{Cu}^{2+}$  ions (Zeolite H -  $\text{Cu}^{2+}$ ) has the maximal specific surface (140 m<sup>2</sup>/g) and the maximal acidity. Reduction of the specimen acidity after the catalysis is, probably, related to the decrease of the number of surface hydroxyl groups.

The specific catalytic activity of the catalysts under study (see Table 2) with respect to the total process of methane oxidation under the stationary conditions increases in the following series: Zeolite H -  $\text{Cu}^{2+}$  < Zeolite H -  $\text{Co}^{2+}$  < Zeolite H -  $\text{Cr}^{3+}$  < Zeolite H -  $\text{Cu}^{2+}$  < Zeolite-natural.

Table 2. Catalytic properties of the clinoptilolite forms under study ( $T=673\text{K}$ ,  $[\text{CH}_4]/[\text{O}_2]=2:1$ ,  $\tau=6\text{c}$ )

Catalyst	Specific catalytic activity $W \cdot 10^3$ [mole/(m <sup>2</sup> s)]	Selectivity S [%]		Concentration of $\text{CH}_2\text{O}$ [%]
		$S_{\text{HCHO}}$	$S_{\text{CO}}$	
Zeolite-H	1.00	11.8	68.3	0.12
Zeolite H - $\text{Cu}^{2+}$	1.17	13.5	67.3	0.14
Zeolite H - $\text{Cr}^{3+}$	1.19	57.9	31.6	1.1
Zeolite H - $\text{Co}^{2+}$	1.38	11.3	49.3	0.21
Zeolite-natural	2.69	9.1	74.6	0.22

The main product of methane oxidation at the natural clinoptilolite is carbon dioxide with concentration in the mixture at the 923K temperature of about 10 vol.% (see Fig. 1, curve 1).

At the same time, and this is very important for the deep oxidation catalysts, the total concentration of formaldehyde and carbon monoxide in the reaction products does not exceed 0.5% (Fig. 1, curves 2, 3). However, the practical application of the natural clinoptilolite is embarrassed by the fact that in the course of hydrocarbons transformation it is rapidly deactivated due to deposition of reaction products in the narrow pores of the catalyst.

To elucidate the influence of dealumination and deactivation of the natural clinoptilolite on the methane oxidation process we have used its modified forms as the catalysts (see Fig. 2). As seen from this figure, carbon dioxide selectivity at the natural clinoptilolite is maximal and reaches 97% at 923K.

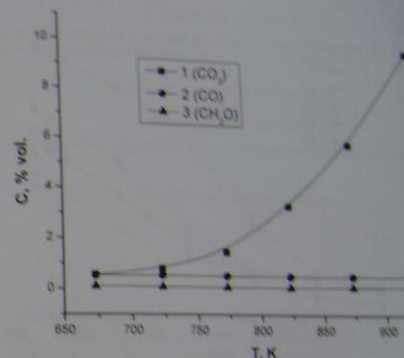


Fig. 1. Reaction product yield as the function of temperature at methane oxidation at the  $[\text{CH}_4]/[\text{O}_2]=2:1$ ,  $\tau=2\text{c}$

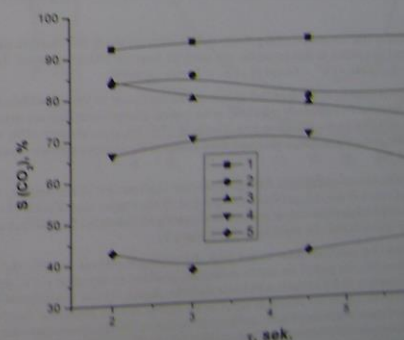


Fig. 2. Carbon dioxide selectivity as the function of time  $t$  of the reaction mixture with the catalyst at the specimen under study -  $[\text{CH}_4]/[\text{O}_2]=2:1$ ,  $T=923\text{K}$ , 1 - Zeolite H -  $\text{Cu}^{2+}$ ; 2 - Zeolite H -  $\text{Cr}^{3+}$ ; 3 - Zeolite H -  $\text{Co}^{2+}$ ; 4 - Zeolite H -  $\text{Cu}^{2+}$ ; 5 - Zeolite H - natural



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