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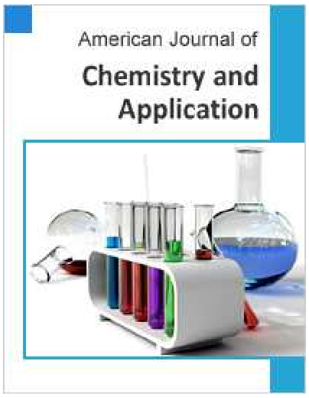

Study of Modified Forms of Natural Zeolites as Catalysts for Methanol Oxidation

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Abstract

Catalytic properties of natural zeolites in Cu-, Ni-, Co- and Mn ion-exchange forms have been studied in reaction of oxidative dehydrogenation of methanol. It was established that processes of dehydration as well as partial oxidation are going in all samples of catalysts. It has been identified a number of catalysts activity in the process of oxidative dehydrogenation of methanol: clCoX <clNiX <clFeX <clCuX. Calculations have been performed using the software package OptimMe.

1. Introduction

It has been researched the activity of natural zeolitic catalysts in the reaction of converting aliphatic alcohols [1]-[4]. Building selective catalysts on the basis of natural zeolites by their modifying are representing scientific and practical interest due to their high thermal and chemical stability, the orderly crystal structure and relatively affordable "output window".

The deposits of zeolites are known in many countries of the world, and besides the prospects for their practical use are extremely varied. We used natural zeolites - clinoptilolite deposits of Azerbaijan, where the contents of the zeolites in the rocks are ranged between 75-85%. The aim of this work is an identification of effective ion-exchanged forms of zeolite catalysts for the oxidation reaction of methanol with high activity and selectivity.

Catalytic experiments were carried out on flow unit at atmospheric pressure. The air cleared of dust and water vapor passes through the alcohol evaporator, which is heated up to the temperature corresponding to a given air saturation with alcohol. The stable operating mode of the catalyst has been set within one hour.

2. Methods and Apparatus

Samples of catalysts based on a natural clinoptilolite (clX) and its cationic form (Ni, Co, Cu, Mn) were prepared by impregnation of clX with a solution of ferric chloride and the rest by ion exchange with 0,1N; 1,0N; 0,2N - normal solutions of the corresponding salts, at temperature of 353-373 K for 4 hours to obtain the active ion exchange forms of catalysts [1].

Ion exchange catalysts have been obtained from solutions of $MnCl_2$, $NiCl_2$, $CoCl_2$, $CuCl_2$. Before the experiments, the zeolite has been treated with the current of dry air at

675 K for 6 hours. The reaction products were analyzed by chromatography. All studied clinoptilolite samples are active in the oxidative dehydrogenation of methanol. The main products of the reaction are formaldehyde, carbon dioxide and water.

A study of dependence of specific activity of the catalyst for formaldehyde on the reaction temperature and the ratio of the initial products was conducted. The degree of oxidative dehydrogenation of methanol was judged by the output of formaldehyde. On natural clX - formaldehyde yield under optimal conditions reaching values - 12.0 mol%.

All calculations to study the properties of zeolites as catalysts for methanol oxidation, including temperature dependence of the specific activity of the catalyst samples for formaldehyde on the ratio of the initial products of the reaction, the reaction rate constant were calculated from the equation of the first order in the methanol oxidation, the apparent activation energy, performed using the software package OptimMe [5] [6]. Software modules (Runge-Kutta 4th order, numerical Gear methods , etc.) of package OptimMe used in our other works, and showed accurate results that formed the basis of his choice [7] [8].

3. Results and Discussion

Introduction of relatively small amounts of cations (Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}) resulted in a rapid increase in activity of obtained catalysts. Especially active were copper form of clX, in which the yield values of formaldehyde reached 60.0 mol%. The optimum temperature of the process for all catalysts is in the temperature range 600-630 K. Partial pressure of methanol on a formaldehyde exit had also been studied. It was also studied influence of the partial pressure of methanol on a formaldehyde yield. By increasing the partial pressure of the formaldehyde yield increases and reaches a maximum at a ratio CH_3OH: O_2 = 3÷4, as shown in Fig.1 [2].

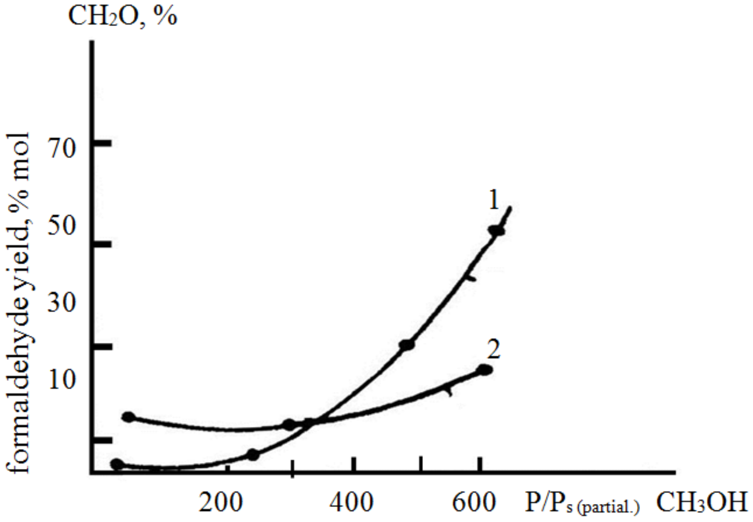

Figure 1. *Dependence of formaldehyde yield on the methanol partial pressure.*

Experimental data, conditions and results of conversion of methanol at various ion-exchanged forms of zeolite are shown in Table 1.

Table 1. *The dependence of activity of samples of zeolites on preparation methods of catalysts and reaction conditions.*

Catalysts	**Preparation method**	**The content of the substituted cations, wt.%**	**Process temperature, K**	**Yield of formaldehyde,%, mol.**	**Selectivity on formaldehyde, %, mol.**
nature. Cl	impregnation	–	610,3	12,0	48,2
clCoX	–	5,06	623,0	16,00	54,0
clNiX	–"–	8,00	600,0	20,24	60,0
clCuX	–"–	5,20	630,2	60,0	88,0
clFeX	ion exchange	10,60	650,3	10,0	84,0

The table shows that the catalytic properties depend strongly on the nature of the cations. It was found that in the oxidative dehydrogenation of methanol among investigated forms of catalysts the best proved Cu-form clX, in which the yield value of formaldehyde reached ~53,0% at 88.2% selectivity. It has been identified the number of catalysts activity: clCoX <clNiX <clFeX <clCuX.

The oxidative dehydrogenation of methanol to formaldehyde, which has great practical importance, has a leading position occupied by zeolite catalysts. All studied clinoptilolites active in the processes of oxidative dehydrogenation of methanol, however, the cobalt and copper-substituted catalyst samples, along with the main reaction products was observed the formation of small amounts of CO and CO_2. Hydrogen in these conditions was not observed. The temperature dependence of the specific activity of samples of catalysts of formaldehyde on the ratio of initial products of reaction which results are given in Figure 2 is studied.

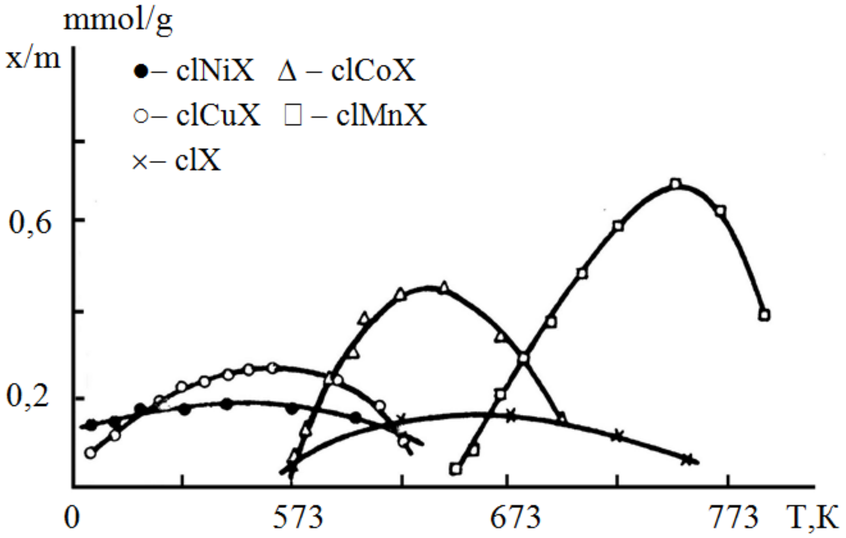

Figure 2. *The temperature dependence of the specific activity of catalysts samples of formaldehyde from the reaction temperature. x / m, mmol / g - specific activity of catalyst samples.*

As the figure shows, the introduction of copper and nickel cations shifts the process for converting methanol to CH_2O in a lower temperature region compared to the original model, although the yield of formaldehyde remains practically the same. Nickel forms of clinoptilolite to a temperature of 573 K proceeds with deep dehydration by converting the carbon skeleton, which is accompanied by a change in color of the catalyst. At increase of temperatures of reaction to 423-443 K conversion of methanol in formaldehyde on cobalt forms of clinoptilolite are 2 times higher, and forms MnCl clinoptilolite - 3 times higher compared to the initial sample. The onset temperature of complete oxidation is shifted to a higher temperature region to clCoX - 643 K for clMnX - 748 K [3].

With increasing temperature and space velocity increases not only the proportion of formaldehyde, but also increases the degree of deep oxidation, especially at high contact times. Comparative data of optimum temperatures for each shape has shown in Figure 2. The experiments that had been carried out with different amounts of methanol and oxygen, showed that the rate of oxidation is proportional to the alcohol concentration of methanol at a certain oxygen content depends on the increase in the mixture. The reaction rate constant has been calculated from the equation of the first order with respect to methanol, and the apparent activation energy have been evaluated based on the Arrhenius dependence on temperature [9]-[12].

A significant reduction in the temperature of the reaction proceeds to cationic Cu^{2+}; Ni^{2+} -forms clinoptilolite (T 473 - 423K). The significant increase (2-3 times) of activity on formation of formaldehyde is observed in these forms of clinoptilolite. The results are shown in Table 2.

Table 2. *The reaction rate constant and apparent activation energy of the oxidative dehydrogenation of methanol to formaldehyde.*

sample of zeolite	The degree of substitution of the cations,%	Process temperature, K	$K\cdot10^{-3}$ s^{-1}	E_A, kcal / mol
clCuX	21,3	483-533	6,5 (508 K)	22
clNiX	20,2	473-535	5,2 (504 K)	26
clCoX	28,4	568-623	7,9 (595 K)	21
clMnX	36,5	648-693	7,7 (671 K)	34

4. Conclusions

1. On all studied samples, dehydration process and partial oxidation process proceed.

2. The results of catalyst samples show greater activity and selectivity in the conversion of methanol than the initial sample of clinoptilolite, and can be represented as effective oxidation catalysts. A number of catalysts activity in the process of oxidative dehydrogenation of methanol: clCoX <clNiX <clFeX <clCuX.

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