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Original scientific paper

ROLE OF WATER IN DIETHYL ETHER DEHYDRATION REACTION

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Abstract: The study examined catalytic conversion of diethyl ether in a gas phase in the static system on the synthetic mordenite (NaM) and the mordenite which the bivalent cobalt cation was introduced into (CoM). The reaction was observed in the temperature range from 424 K to 653 K, and the reaction products on both catalysts were ethene and water, and on NaM a small quantity of butene.

The reaction of diethyl ether dehydration in the observed temperature interval is accelerate in time. The initial reaction is registered at the very beginning of the reaction followed by the water occurrence. The water originating from the reaction is generated on the surface of the zeolite catalyst the active centers that is favorable for the dehydration reaction. With the temperature growth the initial period on NaM catalyst gradually disappears and the reaction becomes the first order reaction (temperature is 653 K), while on CoM catalyst the initial period is registered at all observed temperatures. The explanation of the role of water in the occurrence of active centers needed for diethyl ether hydrolysis was obtained by experiments in which water was also added to the reaction mixture of diethyl ether – catalyst.

Key words: mordenite, diethyl ether, dehydration.

Introduction

Dehydration is one of the reactions that require acid catalysts, and in practice different types of catalysts are used for this reaction, like alumina (Zhang et al., 2008), zeolites (Phillips and Datta, 1997; Barthos et al., 2006; Takahara et al., 2005; Ermakov and Plakhotnik, 2008; Inaba et al., 2006), mesoporous materials (Zhang et al., 2008), etc., and the catalysts most frequently used for this type of reaction are zeolite catalysts. It is known that the dehydration reactions already take place on weak and medium-strong acid centers on the catalyst surface, and zeolites possess this type of active centers on their surface. The acidity of the zeolite surface is expressed as Brønsted (active centers of weaker acidity) and Lewis (more acid active centers) acidity. Brønsted active centers (BKC) act as proton donors, while those of Lewis`s ones (LKC) act as an acceptor of electron pair. The characteristics of zeolites that make them extraordinary catalysts are: three-dimensional, very well defined and open network structure with a series of channels, cavities and extremely fine pores of molecular dimensions, and accessible only to those molecules whose dimensions are smaller than critical ones, high value of specific surface, high mechanical resilience and thermal stability, as well as the possibility of modification of electron characteristics of active areas.

Mordenite is often used in industry as a catalyst in the processes of transformation of simple alcohols into carbon hydrogens and possesses high selectiveness for this type of reaction and extraordinary thermal stability.

The study examines the rate of the diethyl ether dehydration reaction on the synthetic mordenite NaM and the mordenite which the bivalent cobalt cation was introduced into (CoM), as catalysts.

Experimental

PREPARATION OF CATALYSTS

The initial catalyst used was the synthetic mordenite (NaM, Si/Al=13) obtained from the Faculty of Mathematics and Natural Sciences (PMF) in Belgrade. The catalytic characteristics of mordenite were modified by introducing the bivalent cobalt cation into the mordenite structure. The introduction of Co^{2+}-ion to the mordenite structure was performed by the method of ion exchange. In doing that, the first form that was prepared fromNH$_4^+$-form of mordenite, and then also H-form of mordenite which Co^{2+} -ion was introduced into.

NH$_4^+$-form of mordenite was prepared by a multiple ion exchange of Na$^+$-ions in the initial zeolite with ammonia ions from the aqueous solution of NH$_4$Cl (). By the thermal treatment of NH$_4^+$ -form of mordenite, heating it for 4 hours at a temperature of 673±2 K, there occurthe elimination of the gas NH$_3$ and origination of the H-form of mordenite (HM).

The introduction of Co^{2+}-ions in the H-form of mordenite was conducted by the method of ion exchange from the aqueous solution of Co(NO$_3$)$_2$, (). The ion exchange was even now performed at room temperature, in the course of 24 hours and with mixing. The obtained sample was Co-mordenite (CoM), (Petrović et al., 2014).

Characterization of catalysts

X ray diffraction analysis was applied for determining the phase composition of samples. The samples were analyzed at the PHILIPS PW-1710 x ray diffractometer by using CuKα radiation (voltage 40 kV, amperage 50 mA, angle scope 5-60º).

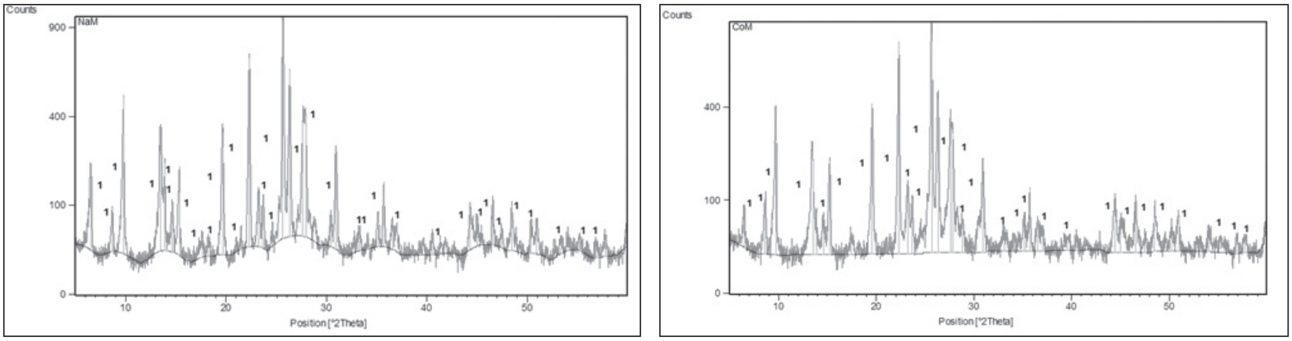


Figure 1. X ray diffractogram of NaM and CoM powder

The results obtained by x ray analysis of NaM and CoM proved that with both samples there occurred the peaks characteristic of the mordenite zeolite, which would mean that modification does not significantly change the crystal structure of the initial zeolite sample.

The degree of exchange expressed as a percentage of Na$^+$-ions exchanged with Co^{2+} cations was established for the catalyst prepared in this manner by determining the quantity of the introduced cations into mordenite and also by determining its quantity in the filtrate after the exchange. These determinations were performed by the method of atomic absorption spectrophotometry.

The specific surfaces (SP) of NaM and CoM were determined by the BET-method of nitrogen adsorption at the temperature of liquid nitrogen.

The characteristics of catalysts are presented in table 1.

The results of kinetic measurements

The experiments of diethyl ether conversion on NaM and CoM zeolites as catalysts were conducted in the static system in a gas phase on the apparatus previously described (Petrović et al., 2011). The composition of the reaction mixture was determined by gas chromatography along with flame ionization detector and nitrogen as a gas carrier. The method applied for the analysis was gas chromatography column of Carbovax 20M filling, length of 2.25 m (T_{column} = 323 K; = 160 kPa). For each kinetic experiment a fresh catalyst sample was used (weight note≈0.1000 g). The catalysts were activated before each experiment at 673±2K in a high vacuum over the course of 2 hours. The kinetic data obtained are presented in table 1.

For kinetic experiments, the diethyl ether used was the type with a high degree of purity (99.5 %, a product of the Merck Company).

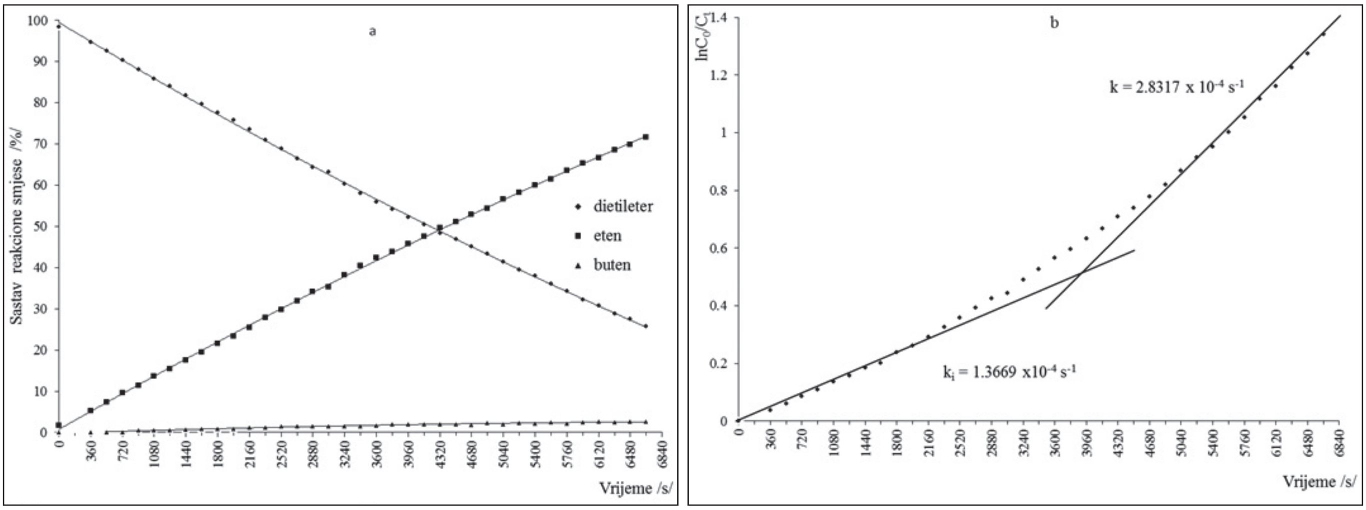
Table 1. The review of kinetic data for diethyl ether conversion on NaM and CoM catalysts

Catalyst	Degree of exchange (%)	SP (m^2/g)	Temperature (K)	$k/10^4$ (s^{-1})	$k_i/10^4$ (s^{-1})	$k_{450K}/10^4$ (s^{-1})	Ea (kJ/mol)
NaM	-	403,4	593	2,83	1,37	0,003	105,97
			603	3,95	2,08		
			610	3,97	2,26		
			617	5,28	2,85		
			631	13,02	7,54		
			653	17,37	-		
CoM	46,86	469,5	424	4,49	1,26	9,24	47,18
			438	6,28	1,74		
			450	9,24	3,30		
			438,5	12,37	-		

Processing of experimental results

The experimentally obtained data are graphically presented as a relationship of mixture composition versus time and as a logarithm of reactant concentration change versus time. In the conditions when the diethyl ether dehydration reaction unfolded as the first order reaction, the rate constant was calculated based on the relations for the first order reaction. When the reaction rate, i.e. reaction rate constant changed in time, the rate constant of the initial reaction was calculated but again as the rate constant of the first order reaction. The rate constant of the initial reaction was approximated by drawing a line through several first points in the diagram of functional dependency $\ln C_0/C_t$-time. The experimental energies of activation were determined graphically from the functional dependency of the rate constant dependency and reciprocal temperature value (Arrhenius plot).

Figure 2. Diethyl ether dehydration on NaM as a catalyst at 593 K



a) The dependence of reaction mixture composition - time b) The dependence of $\ln C_0/C_t$- time

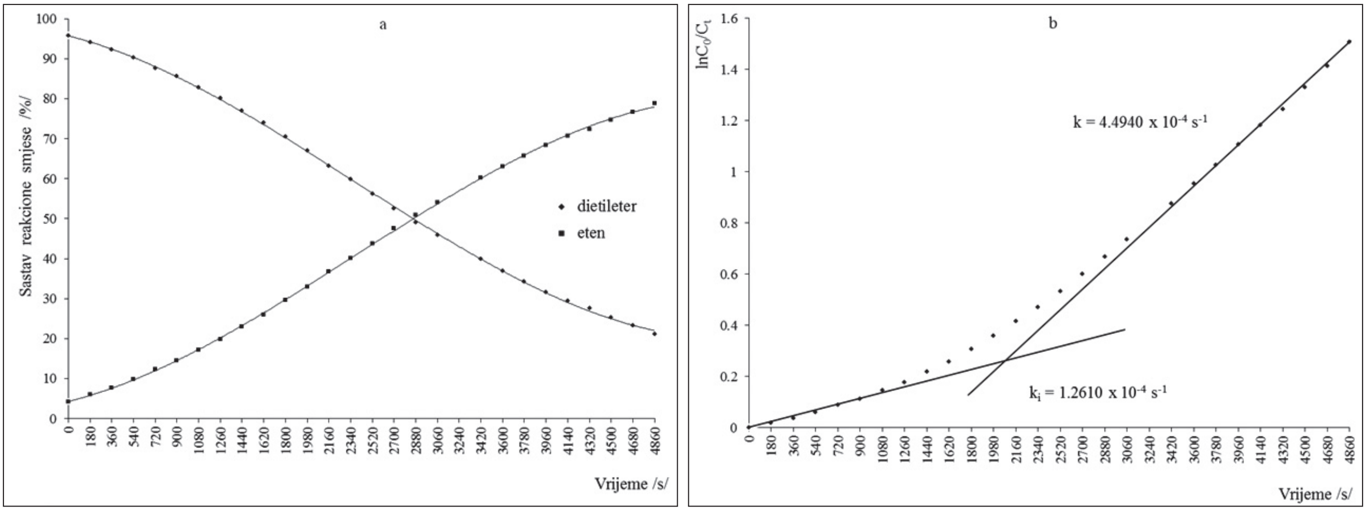


Figure 3. Diethyl ether dehydration on CoM as a catalyst at 424 K

a) The dependence of reaction mixture composition - time b) The dependence of $\ln C_0/C_t$- time

Discussion of Results

Diethyl ether dehydration on NaM and CoM

The catalytic diethyl ether conversion was examined in the temperature range of from 424 K to 653 K on NaM and CoM as catalysts. The results of kinetic measurements are presented in table 1. and in figures 2-5. The products of the reaction are just ethene and water. Only with NaM, the origination of small quantities of butene (2.64 – 0.55%) was also registered, but its concentration gets decreased with the increase of the temperature at which the reaction takes place. At the highest temperature of the reaction on this catalyst (653 K), the percentage of butene is smallest and amounts to 0.55%, while at the lowest temperature of the reaction (593 K), that percentage is highest and amounts to 2.64 %, so that at even lower temperatures of reaction there would be significantly more C_4 carbon hydrogen in the products of this reaction (and that reaction would also have a significantly smaller rate, which is in accordance with the temperature dependency of the equilibrium constant of this reaction).

The diethyl ether dehydration reaction was observed in the temperature range of 593 K to 653 K on NaM, while with CoM, due to the higher reaction rate, the optimal area for observing the reaction was 420 – 450 K.

It can be concluded already from the graphical presentation of the diethyl ether dehydration kinetics on NaM (figure 2.) and on CoM (figure 3.) that the reaction under these conditions of conducting of the experiment, in the whole time interval in which it was observed, did not follow the first order kinetics, but starts accelerated in time. The effect of acceleration is more distinct as the reaction temperature is increased. The previous research (with ethers and alcohols as substrates' on the zeolites of faujasite and mordenite type which also contained the cations of interim metals (Škundrić et al., 1996; Škundrić et al., 2004a; Škundrić et al., 2004b; Škundrić et al., 2016; Čegar et al., 2005; Čegar et al., 2011; Petrović et al., 2014; Penavin-Škundrić et al., 2016) gave similar data for the kinetic course of the dehydration reaction. The analysis of this phenomenon resulted in the conclusion that the water originated in the reaction creates new acid centers (BKC) sufficiently active for this reaction, so that it itself unfolds on all the higher number of active centers which has a consequence of becoming faster in time. It is known that the dehydration reaction take place on BKC. For this reaction poorly acid active centers are sufficient enough and in most cases for the rate of reaction the number of acid centers is applicable and not the strength of their acidity. On the occasion of thermal activation of catalysts (at a high temperature and with a high vacuum) before the kinetic experiment, there comes a drastic decrease of the content of water in zeolite, but together with this there also occurs dehydroxylation of the surface and the structural oxygen gets transferred into the water molecule. In this process the number of BKC (which are less acidic) decreases, and LKC (which are more acidic) grows. That's why at the beginning of the reaction, the number of active centers on which the dehydration reaction takes place is small, so that the reaction rate is also small. However, as the reaction continues, the reaction product-water reacts with the zeolite surface and creates new BKC on which this reaction takes place and the reaction in time becomes more and more accelerated. Therefore, on the diagram of functional dependency $\ln C_0/C_t$ – time (figure 2. and figure 3.) there is a „break" which indicates the fact that there were two reactions taking place at the same time at different rates, so that two constants of the reaction rate could have been calculated, k_i and k (where $k_i<k$ at all times). „The first" direction on the plot of functional dependency $\ln C_0/C_t$ – time corresponds to the rate of BKC origination, and at this stage it is the step that determines the overall reaction rate. After some time the number of BKC centers becomes sufficient and does not hinder the reaction any more, the origination of these centers stops being a decisive step for the rate of the overall reaction and that role is taken over by the surface reaction of diethyl ether dehydration and it becomes the slowest step („the second" direction on the diagram of functional dependency $\ln C_0/C_t$ – time). At a higher temperature the ratio between the rate of BKC origination and the rate of surface reaction gets such numerical values that the reaction becomes the first order reaction without the initial period, and that happens for the diethyl ether dehydration reaction at the temperature of 653 K (that is also the highest temperature of the reaction at which the reaction was observed on the NaM catalyst, figure 4.). The reaction of diethyl ether dehydration on CoM as a catalyst at all observed temperatures has the initial period.

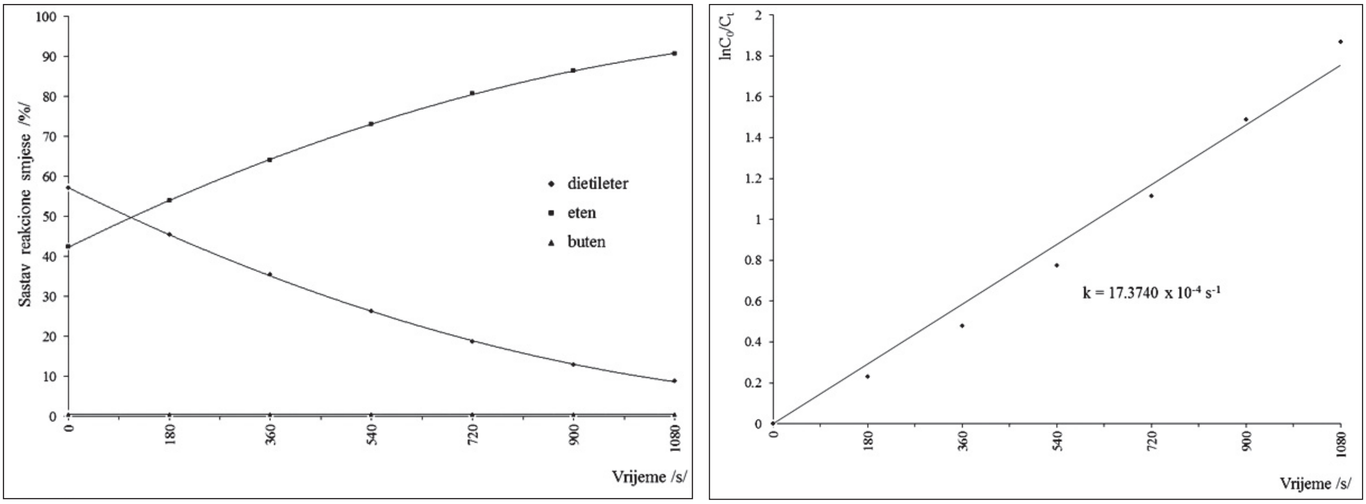


Figure 4. Diethyl ether dehydration on NaM as a catalyst at 653 K

a) The dependence of reaction mixture composition - time b) The dependence of $\ln C_0/C_t$- time

In support of this postulate on the role of water in the origination of BKC the experiment was conducted where water was added in the initial reaction mixture. Such experiment was conducted on CoM as a catalyst at 438.5 K where the proportion of diethyl ether and water was 1:2 (DEE: water = 1:2), figure 5. The added portion of this quantity of water to the reaction mixture was sufficient to remove the initial period, so that the first order reaction was obtained, which could be considered as a confirmation of the assumption on the role of water in the occurrence of the initial period.

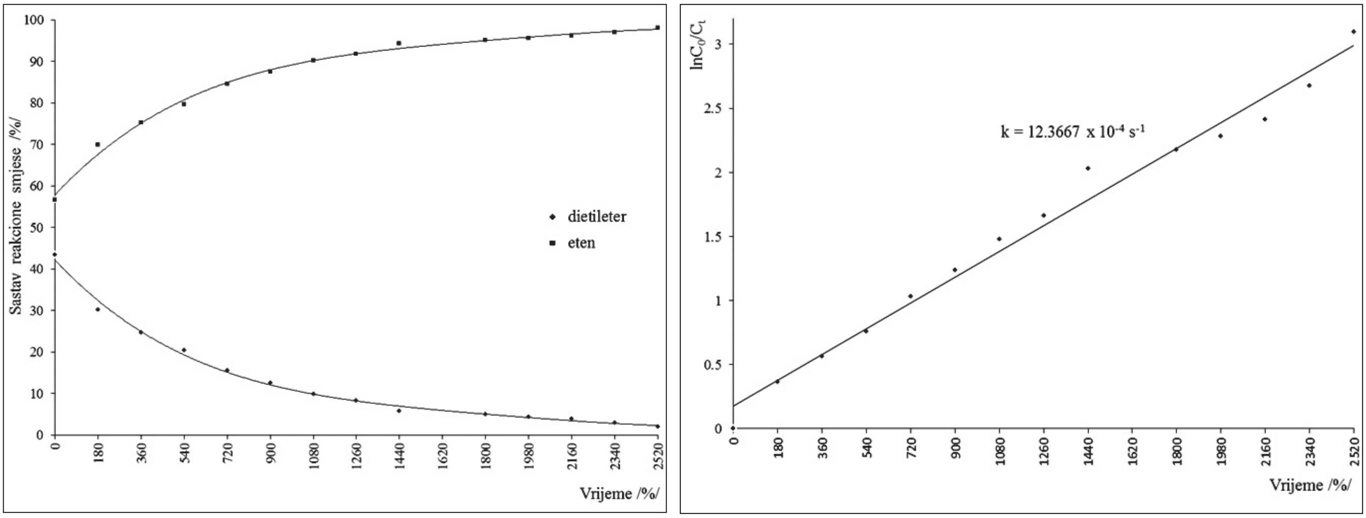


Figure 5. Diethyl ether dehydration on CoM as a catalyst with the addition of water (diethyl ether: water = 1:2) at 438.5 K

a) The dependence of reaction mixture composition-time b) The dependence of $\ln C_0/C_t$-time

The examination of the reaction on NaM catalyst proved that even at such high temperatures the dehydration reaction on this catalyst unfolds slowly. The characteristics of this catalyst are that it is the zeolite whose porous structure is made up of a two-dimensional system of relatively long and narrow channels that do not intersect, with elliptical pores of different diameters. Along the channel walls at periodical distances there occur cavities („pockets“) which are not completely open from one channel to the other, which prevents circulation of the reactant molecules so that the number of active centers accessible to the reactant molecules is smaller than it would be in a more open zeolite structure. Besides, with NaM the compensation cation is Na^+-ion, the electrostatic field of this cation is weak and that is why the electrostatic polarizing activity towards the protons of structural hydroxyl groups bonded to silicium and aluminium atoms of the zeolite surface is also small, and therefore the overall number of surface hydroxyls representing BKC is small. After introducing of cation Co^{2+} to the mordenite structure, the activity of catalyst significantly increased, so that the reaction takes place at significantly lower temperatures (≈200 K), i.e. the reaction rate increased by a factor $3 \cdot 10^3$ times if the rate constants are compared at the same temperature (k at 450 K, table 1). By the preparation of CoM the catalyst was obtained of a „more open“ structure, where the access to the reactant molecules was made easier to the inner structure. The consequence of opening of the mordenite structure is that CoM also possesses a higher value of the specific surface compared to NaM (increase by 14 %), so that the reactant molecules have access to a much larger surface. The electrostatic field of Co^{2+} cation that has a smaller ion radius compared with Na^+ cation is bigger and therefore the electrostatic polarizing activity of this cation towards the protons of structural hydroxyl groups bonded to silicium and aluminium atoms of the zeolite surface is much more distinct, so that the number and acidity of active centers of the zeolite surface increases compared with NaM. All these effects together lead towards the increase of catalytic activity of CoM compared with NaM.

It was earlier mentioned (see figure 3.) that on CoM catalyst in the whole observed temperature range the „break“ remained, i.e. the initial reaction does not disappear even with the temperature increase. The reason for such behavior is to observe the reaction at significantly lower temperatures than it was the case for the dehydration reaction on NaM catalyst, and therefore in the observed temperature interval the origination of BKC was too slow. The increase of dehydration in the experiment where water was added to the reaction mixture, is connected with the change in the zeolite structure, because the added water together with the water originated in the reaction results in the increase of the number of BKC active centers on which the surface reaction takes place.

Conclusions

- Diethyl ether dehydration on NaM and CoM catalysts observed in the gas phase gets accelerated in time. It is possible to determine two rate constants for this reaction that kinetically correspond to the first order reaction.
- With the temperature increase the initial reaction period disappears on the catalyst NaM (T=653 K), while the initial period of the reaction on the catalyst CoM remains in the whole temperature range in which the reactions on this catalyst are examined, i.e. from 424 K to 450 K.
- The products of diethyl ether dehydration on both catalysts are ethene and water, and on the original mordenite NaM a small quantity of butene was also registered.
- The water originated in the reaction participates in the creation of Brønsted acid centers on the surface of mordenite catalysts, which results in acceleration of this reaction in time, i.e. as the quantity of the originated water (reaction product) increases, the number of Brønsted acid centers also increases and therefore the rate of the reaction as well, since the reaction of diethyl ether dehydration takes place on Brønsted acid centers.
- At a higher temperature the ratio of the rate of origination of Brønsted acid centers and rate of surface reaction is such that the initial period disappears on the catalyst NaM (which follows the origination of Brønsted acid centers) and the reaction of diethyl ether dehydration completely becomes the first order reaction.
- CoM shows a larger catalytic activity for the reaction of diethyl ether dehydration than NaM, and therefore the dehydration reaction on CoM takes place in the temperatures range of 150 to 200 K lower than on NaM. The increase of catalytic activity of CoM compared to NaM is the result of removing of Na^+-ions in the initial zeolite NaM, and therefore a more acidic catalyst is obtained, which contains a larger number of acid catalytic active centers and of an increased strength compared with NaM.

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