TEXTURAL AND CATALYTIC CHARACTERISTICS OF DECATIONIZED MORDENITE AND ZSM-5 ZEOLITE

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Abstract: The textural characteristics of acid forms of mordenite and ZSM-5 zeolite (HM and HZSM-5) were described based on the experiments of adsorption of nitrogen at 77 K in a specially constructed apparatus.

The specific surface (SP) of catalysts was determined by applying BET-equation (SP_{BET}), Langmuir adsorption isotherm (SP_{LANG}) and t-method. The „t-method" was used to determine the outer specific surface (SP_{ext}^{t}) and the volume of micropores ($V_{\mu p}^{t}$) of zeolite. The volume of micropores ($V_{\mu p}^{DR}$) was additionally determined also based on Dubinin-Radushkevich method. The reactions of diethyl ether dehydration in the temperature interval from 400 to 480 K got sped up in time on both zeolites (HM and HZSM-5) and did not fully follow the kinetics of the first order reaction. The initial period registered by the experiment (increase of reaction rate in time) is interpreted by the slow reaction of water occurrence in the reaction of dehydration, which is necessary for the occurrence of Brönsted acid centers, where diethyl ether dehydration takes place. Now the overall rate of the dehydration reaction is determined by the rate of water occurrence. When there is a sufficient number of acid centers, the rate of diethyl ether dehydration is determined by the surface reaction and the „initial period" gradually disappears. In the reaction of diethyl ether dehydration on HZSM-5 catalyst, the reaction is slower, even water (which is a product of dehydration) occurs more slowly, and therefore in the observed temperature interval the reaction was not transferred to the first order reaction. By the adsorption of diethyl ether from gas phase on HM and HZSM-5 zeolite at 300 K, the insight was provided into hydrophilic-hydrophobic characteristics of the surface, as well as the insight into the character and strength of active centers of these zeolites. As the test reaction for determining acidity of the catalyst, the one selected was the reaction of isomerization of 3,3-dimethyl butene-1 (3,3-DMB-1), which takes place on Brönsted acid centers by the mechanism of carbonium ion. The results obtained by the experiments of adsorption of nitrogen and diethyl ether from gas phase are in accordance with the kinetic data of the diethyl ether dehydration reaction.

Keywords: zeolites, mordenite, ZSM-5 zeolite, dehydration, diethyl ether, isomerization, 3,3-dimethyl butene-1, nitrogen adsorption, adsorption from gas phase.

1. INTRODUCTION

Zeolites are crystallic microporous solid materials of a very regular crystal structure [1]. The structure defined in this manner represents a threedimensional network of arranged channels and cavities, and since these channels are of molecule dimensions, they represent the so-called molecular sieves.

Zeolites are characterized by a large specific surface, they have a capacity of adsorbing hydrocarbons and accepting foreign ions in their crystal structure. These materials are of extreme importance for many industrial processes as catalysts.

The exquisite activity and selectivity of zeolite catalysts is achieved by modifying the basic cha-

racteristics of these catalysts by an adequate chemical treatment.

The catalytic active centers of zeolites have acid character. The knowledge of textural characteristics of catalysts [2,3] is a precondition for understanding the phenomenon of adsorption in heterogeneous catalysis, because the adsorption of reactants on the catalyst surface as a phase (stage) of the heterogeneous-catalytic process preceding the chemical reaction to a great extent influences the further course of the reaction.

The study examined the catalytic activity of acid forms of mordenite (HM) and ZSM-5 zeolite (HZSM-5) for the process of diethyl ether dehydration as a heterogeneous catalyzed reaction.

The textural characteristics of these zeolite catalysts were determined by the adsorption of nitrogen at 77 K, and the reaction of isomerization of 3,3-DMB-1 served as a criterion of active centers acidity, while the hydrophilic-hydrophobic characteristics of the mentioned zeolites were examined by the adsorption of diethyl ether from the gas phase.

2. EXPERIMENTAL

The study used the zeolite of mordenite with the ratio Si/Al=13, synthesized at the Faculty of Natural Sciences and Mathematics in Belgrade, and ZSM-5 zeolite (with the ratio Si/Al = 25)
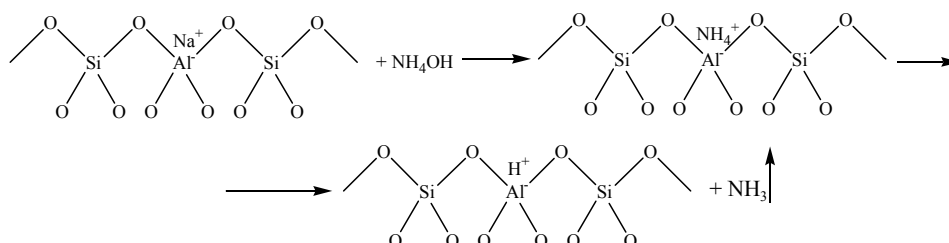
synthesized in the factory „Alkaloid" Skoplje. H-forms of both zeolites (HM and HZSM-5) were obtained by the method of ion exchange through NH_4^+ -form.

NH_4^+ -forms of both zeolites were obtained by multiple ion exchange of cations in the original zeolite (Na^+-ions) with the ammonium ion from the solution of ammonium chloride $\left(C_{NH_4Cl} = 1.0 mol / dm^3\right)$ along with the constant mixing at the room temperature. The ratio solid substance/solution was 2g/0.020 dm^3. After each processing that lasted for 12 hours, the zeolite sample was filtered and rinsed out with a smaller quantity of distilled water (until the negative reaction on Cl^-ions) and then treated again. Three rounds of processing were conducted in total. After the treatment zeolite was filtered and rinsed out with distilled water. The sample obtained in such a manner is NH_4^+ -form of zeolite. The samples of NH_4^+ -form of both zeolites were then heated for 4 hours at 673±2 K. After 4 hours of calcination one can assume that all ammonia was removed and that H-form of zeolite was upgraded. Schematic presentation of thermal dissolution of NH_4^+ -form of zeolite is given in Figure 1.

Specific surfaces (SP) of zeolite were determined by the BET-method, by the adsorption of nitrogen at the temperature of liquid nitrogen (77 K), and the results of these determinations are presented in Table 1. Table 1 also presents an overview of textural characteristics of HM and HZSM-5 zeolite.

Figure 1. Ion exchange in zeolite in function of creation of Brønsted acid center

The adsorption experiments were performed on the apparatus that otherwise serves for determining a specific surface by the BET-method adapted for the measurement of adsorption between solid-gas. The detailed description of the apparatus and work on this apparatus was presented earlier [4, 5]. For the adsorption experiment the sample used was a

fresh zeolite sample (≈0.0500 g) formerly activated by heating for 2 hours at 673±2 K along with the pressure of cca 10^{-6} kPa.

Both for the adsorption experiments and for the kinetic experiments the substance used was diethyl ether with a high degree of purity (99.5 %, production of the „Merck" company).

Table 1. Overview of textural characteristics of HM and HZSM-5 zeolite

Zeolite	SP_{BET} (m^2/g)	C_{BET}	SP_{LANG} (m^2/g)	K_{LANG}	SP_{ext}^t (m^2/g)	$V_{\mu p}^t$ (cm^3/g)	$V_{\mu p}^{DR}$ (cm^3/g)	SP_{BET}- SP_{ext}^t (m^2/g)
NaM	402,54	−112,35	602,08	32,60	62,21	0,1451	0,1828	340,33
HM	447,90	−88,43	658,90	38,93	49,66	0,1860	0,2171	398,24
NaZSM-5	314,05	−104,45	523,96	20,45	91,36	0,1018	0,1497	222,69
HZSM-5	303,52	−92,03	620,94	11,84	68,47	0,1380	0,1775	235,05

The test reaction for determining the catalyst acidity was the reaction of isomerization of 3,3-dimethyl butene-1 (3,3-DMB-1), which takes place on Brönsted acid centers by the mechanism of carbonium ion. It takes place in several stages, protonation of olefins and formation of carbonium ion, reorganization of carbonium ion encompassing the transformation from a less stable secondary to a more stable tertiary carbonium ion, which represents the slowest step of the reaction determining the overall speed of the process.

Apart from the reaction of isomerization, olefins may be transformed into a series of secondary reactions, such as: cracking, polymerization, cyclization, etc., which depends on the strength and number of catalyst acid centers.

The proposed scheme of the process of isomerization is presented in Figure 2.
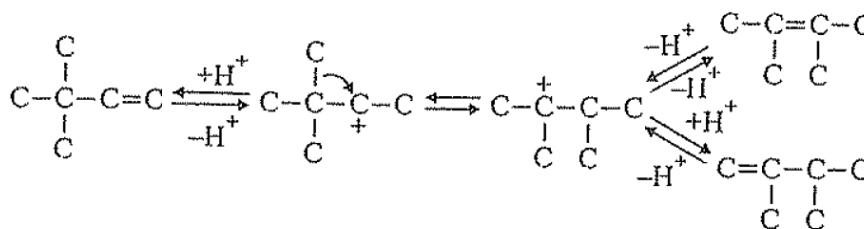

Figure 2. Isomerization of olefins by the mechanism of carbonium ion [1]

The overview of kinetic data for the reaction of isomerization of 3,3-DMB-1 on mordenite catalysts is presented in Table 2.

Table 2. The overview of kinetic parameters for the reaction of isomerization of 3,3-DMB-1 for the mordenite catalysts

Catalyst	T (K)	$k \cdot 10^4$ (s⁻¹)	$k_{373K} \cdot 10^4$ (s⁻¹)
NaM	545	4,10	0,04
HM	430	6,80	5,10

Isomerization of 3,3-DMB-1 on NaM registers as products, except for 2,3-dimethyl butene-1 (2,3-DMB-1) and 2,3-dimethyl butene-2 (2,3-DMB-2), also butane and propene. Around 3% of butane occurs in the overall mass, and very little of propene, below 1%.

On HM, propene as a product of the reaction does not occur, and the quantity of butane is around 1% and gets increased with the increasing reaction temperature.

Isomerization of 3,3-DMB-1 on ZSM-5 and HZSM-5 zeolite as a catalyst leads this reaction towards the formation of just isomers 2,3-DMB-1 and 2,3-DMB-2 as products, and at the higher temperature of more than 600 K there occur also ethene, propene and butene in the reaction mixture. The kinetic data, constant of this reaction speed on NaZSM-5 and HZSM-5 catalysts, are presented in Table 3.

Table 3. Overview of kinetic parameters for the reaction of isomerization of 3,3-DMB-1 for ZSM-5 catalysts

Catalyst	T (K)	$k_{373K} \cdot 10^4$ (s⁻¹)	SP (m²/g)	(k/SP) 10^6 (g/m²s)
NaZSM-5	620	3,20	314,05	1,02
HZSM-5	370	7,45	303,52	2,45

Kinetic experiments were conducted in the static system at the high-vacuum line for observing the reaction in the gas phase-gas line. The detailed description of the apparatus-gas line and work on the apparatus was presented earlier [4]. For the kinetic experiments the sample used always was a fresh sample of catalyst (≈0.1000 g), which was previously activated by heating for 4 hours at 673±2 K along with the pressure of cca 10^{-6} kPa. By heating the catalyst for 4 hours at the temperature of 673±2 K along with the high vacuum there occurs a drastic fall of the water content in the zeolite and a portion of Brønsted acid centers gets transformed into Lewis acid centers (Figure 3).

The analysis of the gas mixture during the reaction was conducted by the method of gas chromatography on the gas chromatograph „Perkin Elmer" with the flame ionization detector and nitrogen as the gas carrier. Gas chromatographic column was filled with Carbovax 20M 2.25 m in length (T_{column} = 323 K; $p_{N_2} = 160 kPa$) and was applied for the analysis. A fresh sample of the catalyst was used for each kinetic experiment [4,19].
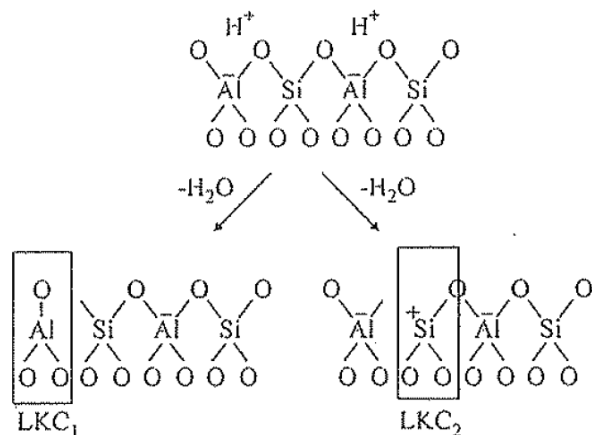
Figure 3. Formation of Lewis acid centers of different strength by dihydroxylation of two Brønsted acid centers [1]

Table 4. Survey of kinetic parameters for the reaction of dehydration of diethyl ether on HM and HZSM-5 zeolites as catalysts

Catalyst	SP (m^2/g)	T (K)	$k \cdot 10^4$ (s^{-1})	$k^1 \cdot 10^4$ (s^{-1})	E_a (kJ/mol)	$k_{450K} \cdot 10^4$ (s^{-1})
HM	453.70	407	2,7590	0,4317	67,10	18,3559
		418	3,7654	1,2637		
		428	6,8782	3,2933		
		473	40,9060	−		
HZSM-5	303,52	427	1,2991	0,4667	77,60	3,9703
		455	2,5862	1.3750		
		480	14,1818	7,8000		

The experimentally obtained results were analyzed graphically as the mixture composition-time and as the logarithm of change of the reactant concentration-time.

In the conditions when the reaction of dehydration of diethyl ether developed as the first order reaction, the reaction rate constant was calculated based on the relations for the rate constant of that first order reaction. In the cases when the reaction rate changed in time, the rate constants of the initial reactions were calculated, but again as the rate constants of the first order reaction. The rate constant of the initial reaction was approximated by drawing the line through several first dots in the diagram of functional dependency of lnc_0/c_t on time.

The experimental energies of activation were determined from the functional dependency of lnk on $1/T$. The obtained kinetic data are presented in Table 1.

3. RESULTS AND DISCUSSION

The adsorption isotherms of nitrogen at 77 K on HM and HZSM-5 zeolite are presented in Picture 4. The obtained adsorption isotherms are of Type I in accordance with IUPAC classification [7] and are reversible in the observed area of relative pressure.

The adsorption isotherms of Type I are produced by the microporous materials with a small outer surface. The classical interpretation of the Type I isotherm is that the rapid increase of isotherm in the area of a lower relative pressure corresponds to the process of filling micropores, while the occurrence of plateaus is linked with the completely filled micropores and adsorption on the outer surface. The textural characteristics obtained by the analysis of adsorption isotherms of nitrogen for all zeolite samples are presented in Table 1.

The introduction of protons in the mordenite structure resulted in an increase of specific surface so that HM has a bigger value of specific surface compared to NaM, while the introduction of protons in the structure of ZSM-5 zeolite did not result in a more significant change of the specific surface of HZSM-5 zeolite compared to NaZSM-5 zeolite.

It is assumed that the introduction of protons in the mordenite structure resulted in deblocking of relatively long, narrow and tubular channels of mordenite, which provided a more open, accessible and porous structure resulting in the increase of the specific surface of HM compared with NaM. The fact that also goes in favor of the above mentioned is that the quantity of adsorbed nitrogen is bigger on HM than on NaM.
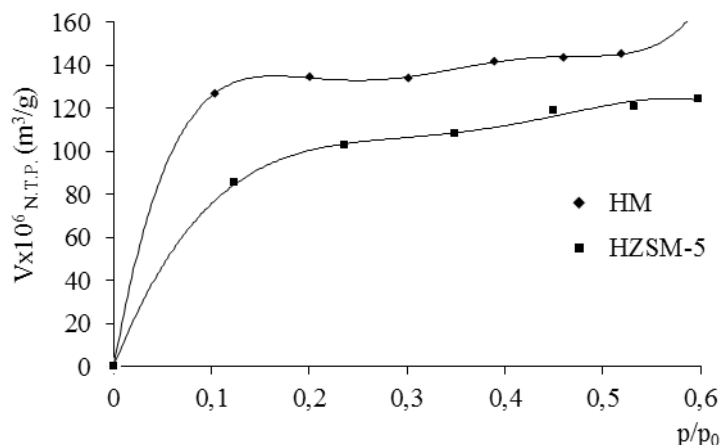
Figure 4. Adsorption isotherm of nitrogen at 77 K on HM and HZSM-5 zeolite

Unlike mordenite, the introduction of protons in the structure of ZSM-5 zeolite did not result in a more significant change of specific surface of HZSM-5 zeolite compared to NaZSM-5 zeolite. A minor change of specific surface, which was caused by the introduction of protons in the structure of ZSM-5 zeolite, could also be explained by the porous structure of this zeolite. It is known that ZSM-5 zeolite possesses two-dimensional system of channels composed of two type channels perpendicular to each other: one type of channels is flat, and the other one is sinusoidal, the so-called „zig-zag", so that the cations introduced in the structure of ZSM-5 zeolite have access to two-dimensional system of channels, i.e. two types of channels (with mordenite just one type of channels – twelve-member channels), i.e. the structure that is more open, accessible and porous, through which the circulation of adsorbate molecules is also slower than with mordenite, so that the value of the obtained SP_{BET} for HZSM-5 zeolite is insignificantly smaller than the value of SP_{BET} for NaZSM-5.

The specific surfaces obtained by the use of t-method (SP_{ext}^t) represent the outer surface of microporous materials, which is based on noticing that after the process of complete filling of micropores (corresponds to the rapid increase of adsorption on the Type I isotherm) only the adsorption on outer surface affects the experimental isotherm (corresponds to the plateau on the Type I isotherm). Therefore, the coefficient of the direction of linear part of t-curve is directly proportional to the outer surface, while the section for t = 0 gives the volume of adsorbates in micropores ($V_{\mu p}^t$). As the use of BET-method results in getting the overall specific surface (the sum of the inner and outer specific surface), and the use of t-method results in getting the outer specific surface (SP_{ext}^t), this means that for all samples of zeolite the inner specific surface (SP_{inner}) is obtained as a difference between SP_{BET} and SP_{ext}^t (values pre-sented in Table 1). Based on the obtained values: SP_{BET}, SP_{ext}^t and SP_{inner} for HM and HZSM-5 zeolite, one may say that the presence of protons in the structure of mordenite and ZSM-5 zeolite brings about the increase of an porous character of both zeolites.

The volume of micropores for HM and HZSM-5 zeolite was obtained by the use of t-method ($V_{\mu p}^t$) and DR-equation (Dubinin-Radushkevic equation; $V_{\mu p}^{DR}$); the obtained values are presented in Table 1. The volumes of micropores at HM and HZSM-5 zeolite obtained by the use of both methods are bigger than the volumes of micropores of the original forms. The volume of micropores of HM obtained by the use of both methods is in accordance with the literature data [8,9].

The obtained values $V_{\mu p}^t$ for HZSM-5 zeolite are in accordance with the literature data [10,11], while the values of $V_{\mu p}^{DR}$ are bigger than the data stated in literature. Similar remarks presented before [11] are ascribed to the fact that DR-equation (and DR-diagram accordingly) is not appropriate for the adsorption on the outer surface.

The reaction of dehydration of diethyl ether (which develops by the mechanism of carbonium ion) was observed in the gas phase on H-form of mordenite (HM) and ZSM-5 (HZSM-5) zeolite as catalysts in the temperature interval from 407 to 480 K. The presentation of the obtained kinetic parameters for this reaction is given in Table 4. The products of the reaction are always ethene and water, whose concentration in the course of the reaction was not observed.

The analysis of the kinetic course of the reaction of diethyl ether on the mentioned zeolites proved that the reaction of dehydration on both catalysts at the observed temperatures (except at HM at T = 473 K) was not of the first order, had an initial period and got sped up in time (Figures 5 and 6).
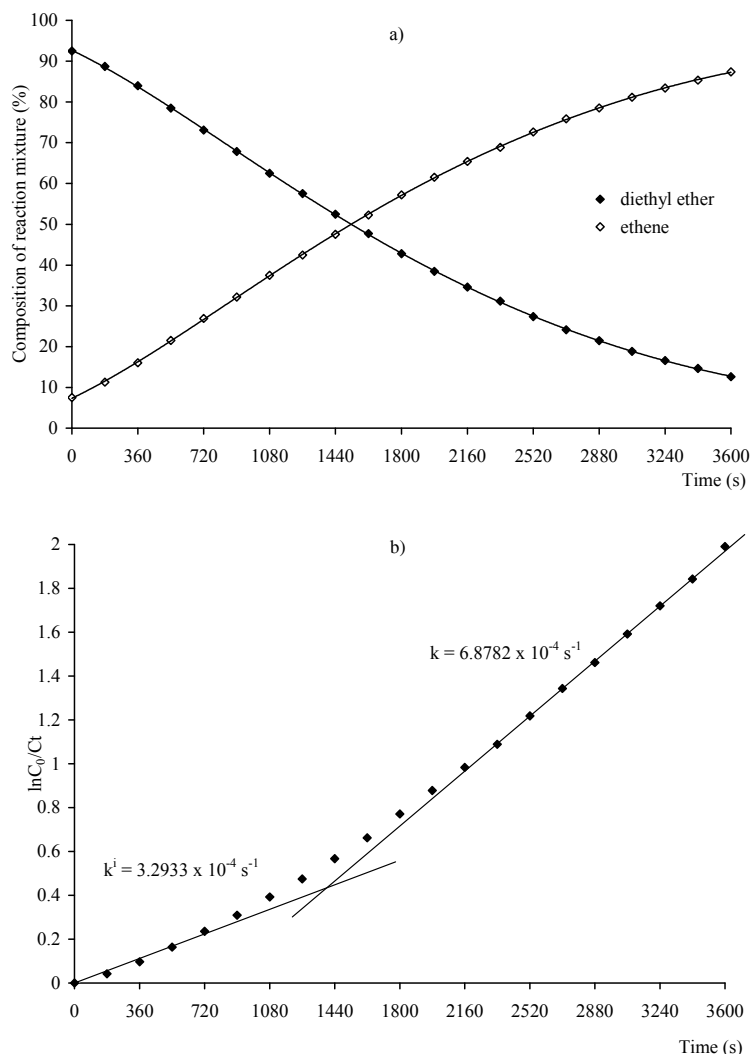
Figure. 5. Dehydration of diethyl ether on HM as catalyst at 428K;
a) dependency of the composition of reaction mixture – time; b) dependency of lnc_0/c_t on time

The previous research with ethers as substrates on the zeolites of faujasite and mordenite type gave similar data for the kinetic course of the reaction of dehydration [12−17]. This research indicated that those effects were connected with the slow origination of Brønsted acid centers in the reaction of water (produced by the diethyl ether conversion) and zeolite surface. It is known that the reactions of dehydration already take place on weak and medium strong acid centers. The „lack" of Brønsted acid centers in the initial period of the reaction is a consequence of the process of thermal activation of catalysts. Namely, before each kinetic experiment, the zeolite catalyst sample gets heated for 4 hours at 673 K in the high vacuum, when a drastic fall of the water content in the zeolite occurs and a portion of Brønsted acid centers gets transformed into Lewis acid centers (Figure 3). The reaction of dehydration of diethyl ether then starts on the small number of Brønsted acid centers and therefore develops slowly. The water resulting from the reaction reacts with the zeolite surface according to the already described scheme of transformation of Lewis into Brønsted acid centers (Figure 3) and in this way the new Brønsted acid centers get created on which this reaction takes place and the reaction gets more and more sped up in time. The rate of the process of origination of Brønsted acid centers on the zeolite surface is a step that determines the overall rate in this stadium of the process („first" direction on the diagram of functional dependency of lnc_0/c_t on time).
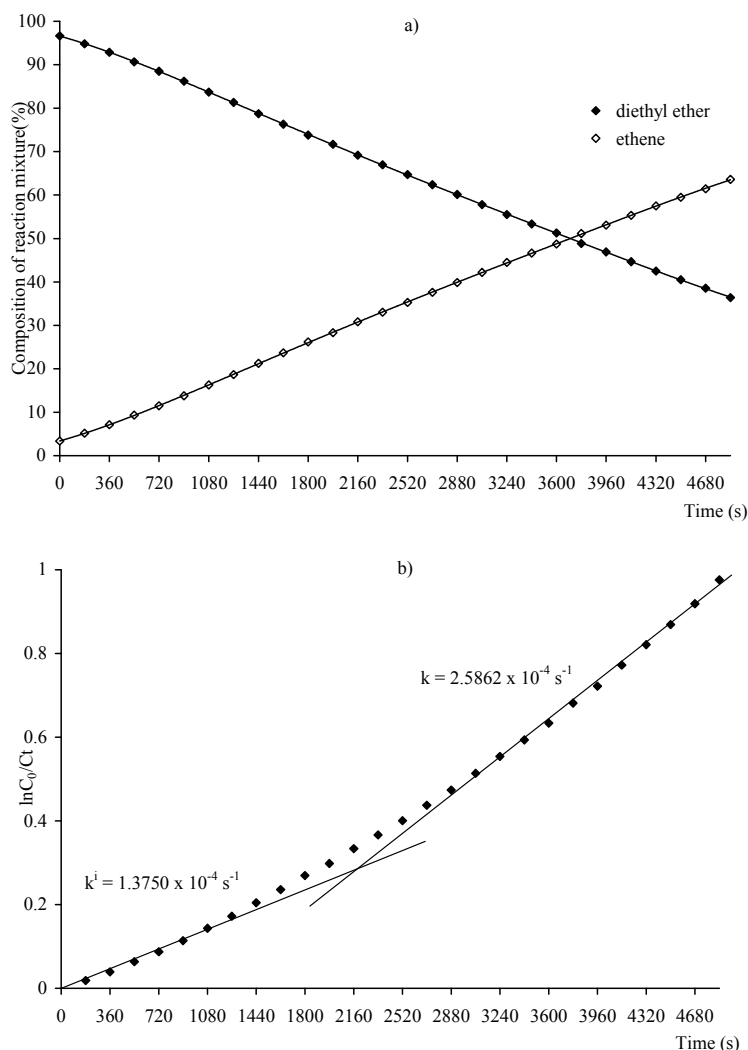
Figure. 6. Dehydration of diethyl ether on HZSM-5 as catalyst at 455K;
a) dependency of the composition of reaction mixture – time; b) dependency of lnc₀/c_t on time

After a certain period of time the number of Brønsted acid centers becomes sufficient not to block the reaction, the creation of these centers stops being a deciding step for the overall reaction rate and that role is taken by the surface reaction of diethyl ether dehydration, becoming the slowest step (the „second" direction on the diagram of functional dependency of lnc_0/c_t on time). At the higher temperature, the ratio between the rate of occurrence of Brönsted acid centers and the rate of surface reaction, gets such numerous values so that the reaction practically becomes the first order reaction, and that happens at the temperature of 473 K on HM as a catalyst, while on HZSM-5 zeolite as a catalyst at all observed temperatures the reaction has an initial period.

By the introduction of protons into the zeolite structure, the zeolite becomes a strong „solid acid", so that the presence of protons in the zeolite structure results in an increase of both the overall number and acidity of the active centers. Further, HM pos-

sesses ≈1.5 times bigger specific surface than HZSM-5 zeolite, while HZSM-5 zeolite has a higher Si/Al ratio than HM (higher Si/Al ratio means also higher hydrophobic character of the surface. A higher SiO_2/Al_2O_3 ratio in zeolite means also a smaller overall number of acid centers (because the number of acid centers is usually connected with the number of aluminium ions), [18].

When we compare the rate constants for this reaction at 450 K, we get that the reaction of diethyl ether dehydration on HM as a catalyst is 4.62 times faster than the reaction conducted on HZSM-5 zeolite as a catalyst. Since the reactions of dehydration take place already on weak and medium strong acid centers, the obtained kinetic data indicate that HM possesses (except for bigger SP) a higher total number of acid centers, which are also more accessible for the molecules of diethyl ether than HZSM-5 zeolite, and the rate of the reaction of diethyl ether dehydration on HM is higher than on HZSM-5 zeoli-

te as well. We should also mention here the difference in the porous structure of these two zeolites. The porous structure of ZSM-5 zeolite consists of two types of mutually orthogonal channels: one type of channels is flat, while the other one is sinusoidal, the so-called „zig-zag" channels, (the entrance into both channels is determined by ten-member rings of oxygen atoms), so therefore it is possible that the circulation of substrate molecules through the porous structure of HZSM-5 zeolite is somewhat hard and slow due to the presence of „zig-zag" channels. In mordenites the substrate molecules have available the one-dimensional system of relatively long, narrow and parallel channels whose entrance is determined by twelve-member rings of oxygen atoms (twelve-member channels), so that it is assumed that the circulation of the substrate molecules through the porous structure of HM is less slow.

By the adsorption of diethyl ether from the gas phase on HM and HZSM-5 zeolite at 300 K we got an insight into the hydrophilic-hydrophobic characteristics of the surface, as well as the insight into the nature and the strength of active centers of these zeolites. Adsorption isotherms of diethyl ether on HM and HZSM-5 zeolite are presented in Figure 7 and are reversible in the observed area of relative pressure. The obtained adsorption isotherms are of a „mixed" character and represent a combination of adsorption isotherms of Type III and Type V [19].
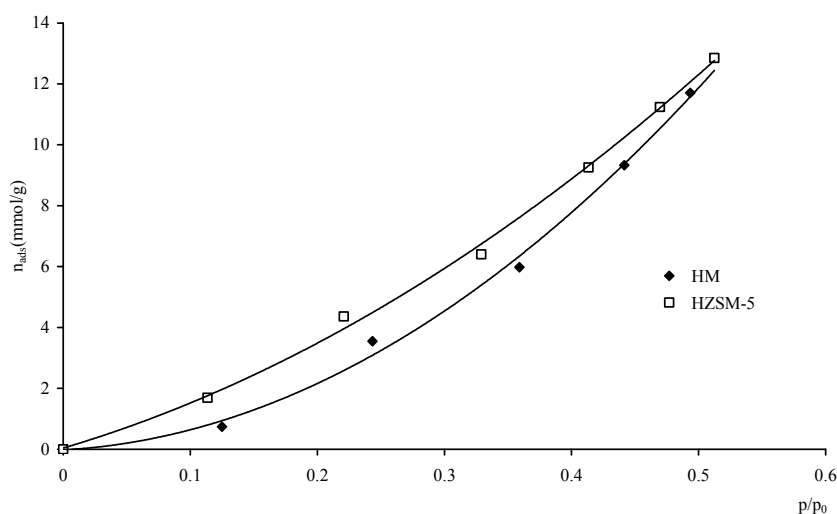

Figure 7. Adsorption isotherms of diethyl ether on HM and HZSM-5 zeolite at 300 K

Isotherms of Type III and Type V are relatively rare and are characteristic of a weak adsorbate –adsorbent interaction. Classic interpretation of Isotherm Type III (TypeV) is that the weak adsorbate-adsorbent interaction causes a small amount of adsorption at low relative pressure, but when the adsorbate molecules once get adsorbed, the adsorbate-adsorbate forces support adsorption of the next adsorbate molecules by a cooperative process, so that the isotherms become a concave pressure axis. The type of obtained adsorption isotherms diethyletheres on the mentioned zeolites at 300 K, which indicates that both the inner and outer surface of these zeolites is to a significant degree hydrophobic.

It is known that ethers are relatively inactive compounds and that „ether oxygen" possesses free electron pairs, so that the ether molecules (diethyl ether) are to a certain degree also polar, but „a lot less" polar than e.g. molecules of water and alcohol. Because of that the molecules of diethyl ether are more „susceptible" to the „degree of hydrophilic character" of the surface than the molecules of more polar adsorptives (e.g. water and alcohol), so that for the ether (diethyl ether) adsorption the presence of stronger acid centers is more needed than for the adsorption of the molecules of more polar adsorptives, which is also indicated by the type of obtained adsorption isotherms. Accordingly, the molecules of diethyl ether prefer more acid centers for adsorption and the adsorption takes place first on the strongest and then gradually on weaker and weaker centers.

The quantity of adsorbed diethyl ether on HZSM-5 zeolite is insignificantly higher than on HM. Knowing that diethyl ether is a „less" polar adsorptive, and since it prefers stronger acid centers for adsorption, i.e. it is „susceptible" to the strength of different acid active centers, we can say that HM possesses a higher number of acid centers, but not of the stronger acid centers compared to HZSM-5 zeolite (and it has already been stated that the reactions of dehydration take place already on weak and

medium strong acid centers), so that the rate of the dehydration reaction on HM is higher and the quantity of the adsorbed diethyl ether is smaller than on HZSM-5 zeolite.

The diethyl ether molecules get tied to the zeolite surface by the hydrogen bonds realized through „ether oxygen" and acid surface hydroxyl groups (Brønsted acid centers) and/or coordinate bonds for the compensation cation of the zeolite lattice. Thus primarily adsorbed diethyl ether molecules get into the interaction by the cooperative process with the subsequent diethyl ether molecules from the gas phase, i.e. the bonds created among the adsorbed diethyl ether molecules support adsorption, so that with the increase of the relative pressure there also increases the quantity of the adsorbed substance.

4. CONCLUSION

− Based on the obtained kinetic data for the reaction of diethyl ether dehydration when it is conducted in the static system on H-forms of mordenite (HM) and ZSM-5 (HZSM-5) zeolites as catalysts, we conclude that HM shows a higher catalytic activity for this reaction than HZSM-5 zeolite; the products of this reaction on both catalysts are always ethene and water.

− Since the dehydration reactions take place already on weak and medium strong acid centers, the obtained kinetic data indicate that HM possesses a higher overall number of acid centers than HZSM-5 zeolite.

− This theory is also supported by the kinetic results of the reaction of isomerization of 2,3-DMB-1, since on HM and NaM except for 2,3-DMB-1 and 2,3-DMB-2 other olefins occur as well, which is possible only if there was an increase in the number and strength of acid centers of catalysts.

− On both catalysts (except on HM at 473 K) the reaction of diethyl ether dehydration is not of the first order and gets accelerated in time, but is a consequence of the interaction in the reaction of the resulting water with the zeolite surface, and the result is an increase of the number of acid active centers and acceleration of the reaction.

− At the increased temperature the ratio between the rate of origination of Brønsted acid centers and the rate of the surface reaction gets such numerous values so that the reaction becomes the first order reaction, and that happens at the temperature of 473 K on HM as a catalyst, while on HZSM-5 zeolite as a catalyst at all observed temperatures the reaction has an initial period.

− By the adsorption of diethyl ether from the gas phase at 300 K on HM and HZSM-5 zeolite we got an insight into the hydrophilic-hydrophobic characteristics of the surface of these zeolites; the obtained type of the adsorption isotherm of diethyl ether on both zeolites indicates that both inner and outer surface of these zeolites are to a certain degree hydrophobic.

− The quantity of the adsorbed diethyl ether is higher on HZSM-5 zeolite than on HM; since diethyl ether for adsorption prefers stronger acid centers, i.e. is „susceptible" to the strength of different acid active centers, based on the quantity of the adsorbed diethyl ether we can conclude that HZSM-5 zeolite possesses stronger acid centers than HM.

− The obtained kinetic data are in accordance with the obtained adsorption data.

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ТЕКСТУРНЕ И КАТАЛИТИЧКЕ КАРАКТЕРИСТИКЕ ДЕКАТИОНИЗИРАНОГ МОДЕРНИТА И ZSM-5 ЗЕОЛИТА

Сажетак: Текстурне карактеристике киселих форми мордена и ZSM-5 зеолита (HM и HZSM-5) описани су на основу експеримената адсорпције душика на 77 К у специјално конструисаном апарату. Специфична површина (SP) катализатора одређена је примјеном BET-једначине (SP_{BET}), Лангмирове адсорпцијске изотерме (SP_{LANG}) и т-методе. „Т-метода" је коришћена да би се одредила спољна специфична површина (SP_{ext}^t) и запремина микропора ($V_{\mu p}^t$) зеолита. Запремина микропора ($V_{\mu p}^{DR}$) је додатно одређивана такође на основу Дубинин−Радушкевичеве методе.

Реакције дехидрације диетил-етера у температурном интервалу од 400 до 480 К су се убрзавале с временом код оба зеолита (HM и HZSM-5), те нису у потпуности пратиле кинетику реакције првог реда. Почетни период регистрован експериментом (повећање брзине реакције у времену) тумачи се спором реакцијом појаве воде у реакцији дехидрације, што је потребно за појаву центара Бронштедових киселина, гдје се одвија дехидрација диетил-етера. Сада се укупна брзина реакције дехидрације одређује брзином појаве воде. Када постоји довољан број центара киселине, брзина дехидрације диетил-етера одређује се површинском реакцијом, а „почетни период" постепено нестаје. У реакцији дехидрације диетил-етера на катализатору HZSM-5 реакција је спорија, те чак и вода (која је производ дехидрације) настаје спорије, па стога у посматраном температурном интервалу реакција није била пренесена на реакцију првог реда.

Адсорпцијом диетил етера из фазе гаса на HM и HZSM-5 зеолиту на 300 К, омогућен је увид у хидрофилно−хидрофобне карактеристике површине, као и увид у карактер и јачину активних центара ових зеолита. Као тест реакција за одређивање киселости катализатора изабрана је реакција изомеризације 3,3-диметил бутена-1 (3,3-DMB-1), која се одвија у центрима Бронштедове киселине механизмом карбенијум јона. Резултати добијени из експеримената адсорпције нитрогена и диетил-етера из гасне фазе су у складу са кинетичким подацима реакције дехидрације диетил-етера.

Кључне ријечи: зеолити, мордерит, ZSM-5 зеолит, дехидрација, диетил-етер, изомеризација, 3,3-диметил-бутен-1, адсорпција нитрогена, адсорпција из гасне фазе.

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