ADSORPTION OF PROPANE ACID ON HIGH-SILICA ZSM-5 ZEOLITES OF NANOSTRUCTURE DIMENSIONS

S. Sladojevic^{*1}, *J. Penavin-Skundric*¹, *Z. Levi*¹, *D. Bodroza*¹, *D. Lazic*², *B. Skundric*³ ¹ *Faculty of Technology, University in Banja Luka, Banja Luka, RS, B&H* ²*Faculty of Technology, University in Istocno Sarajevo, Zvornik, RS, B&H* ³*Academv of Sciences and Arts of the Republic of Srpska, Banja Luka, RS, B&H*

ISSN 2232-755X

UDC: 66.063.61:549.67

DOI: 10.7251/GHTE1309001S

Original scientific paper

Physical-chemical characteristics of zeolites, among other things, depend on the ratio of silicon and aluminum in their crystal structure. What makes zeolite particularly interesting is a great possibility of its modification, which results in new materials of desired characteristics. Due to their polyfunctional characteristics and a big spectrum of application in almost all industry branches, the interest in zeolites is constantly growing. This study examined adsorption of propane acid from the aqueous solution on high-silica zeolite samples produced by the modern nanotechnologies in the American company Zeolyst International (sign: CBV 28014). The adsorbents used were

 NH_4 ZSM-5 zeolite and its modified form-HZSM-5, with the ratio of SiO₂ /AI₂ O₃ equaling 280. Adsorption was examined in the temperature interval from 283 K to 303 K. The results proved that the growth of adsorption temperature resulted in the growth of the quantity of adsorbed propane acid both on the original and on the modified form of ZSM-5 zeolite, which indicated that in addition to physical adsorption the chemisorption also occurred, where the acid molecules were bonded to active centers by stronger chemical bonds. HZSM-5 zeolite, compared with NH_4 ZSM-5 zeolite, as expected, proved to be a better adsorbent for propane acid.

Key words: adsorption, ZSM-5 zeolite, propane acid.

INTRODUCTION

The interest in zeolites is still constantly increasing due to their polyfunctional characteristics and a wide application in almost all industry branches (1-9). We can feel free to say that they are the most important inorganic polymers, three-dimensional in the structure made up of tetrahedrons of silicon and aluminum mutually bonded by oxygen atoms. The structure of ZSM-5 zeolite is composed of a configuration of tetrahedrons linked together through four-member, five-member and six-member rings (10, 11). The general gross formula of the hydrated ZSM-5 zeolite, according to Breck, is (12):

(TPA, Na) $_2$ O \cdot Al $_2$ O $_3$ \cdot 5-100 SiO $_2$ \cdot yH $_2$ O

The zeolite crystals form a whole labyrinth of channels and pores of various profiles in which cations, water and other molecules (species) may stay on. They are characterized by a high selectiveness originating from steric restrictions conditioned by the size of molecules of substrates (adsorbates), which need to reach active centers within the pores of strictly defined forms and dimensions.

What makes zeolites particularly interesting is a strong likelihood of their modification, which results in obtaining new materials of desired characteristics. Synthetic zeolites have some significant advantages compared to their natural analogues, and that is a defined crystal structure, arranged system of micropores, big specific surface

(even up to 1000 m² per gram), as well as an increased sorption potential. It is also possible to synthesize a zeolite of specific structure that does not appear in nature. The physical – chemical characteristics of zeolites, among other things, depend on the ratio of silicon and aluminum in their crystal structure. The zeolites with a low

^{*} Korespodentni autor: Slavica Sladojevic, Faculty of Technology, University in Banja Luka, Banja Luka, RS, B&H. e-mail: slavica.bl@gmail.com

Rad je izložen na međunarodnom naučnom skupu *X Savjetovanje hemičara, tehnologa i ekologa Republike Srpske* u Banjaluci, novembar 2013.

content of silicon have a distinct hydrophilic character and have a bigger affinity towards polar molecules, while those with a high content of silicon have a more distinct hydrophobic character and a bigger affinity towards nonpolar molecules. The objective of this study was, by observing the adsorption of a selected adsorbate on the high-silicate ZSM-5 zeolite, to obtain the data that represent a basis for the characterization of active surface of these adsorbents. The results of observing adsorption proved that with the increase of adsorption temperature the the quantity of adsorbed acid also increases, which indicates that physical adsorption is also followed by chemisorption in the course of which a stronger bond is realized between acid and active site in the zeolite surface. A better adsorbent for propane acid was obtained by the modification of the original zeolite characteristics.

EXPERIMENTAL PART

The adsorption of propane acid ($C_3 H_6 O_2$, p.a., *Sigma Chemical, USA*) was observed from the aqueous solution in the temperature interval from 283 K to 303 K. The adsorbents used were high silicate synthetic zeolites of ZSM-5 type (group *MFI*, products of the company *Zeolyst International, USA*). The original NH₄ ZSM-5 zeolite was before the use of thermally activated at 378 ± 1 K to the constant mass. The acidity of the zeolite surface of the original form was modified by thermal processing at the temperature of 673 K in the period of four hours, which resulted in obtaining HZSM-5. The characterization of prepared adsorbents was conducted by determining their specific surfaces by using the BET method on the Flowsorb II-2300 device. The basic characteristics of the used adsorbents are presented in table 1.

Classification against IUPACU	Zeolite type ZSM-5; CBV 28014	SiO ₂ /Al ₂ O ₃ (Mole ratio)	Weight loss by annealing / %	Spec. surface / $m^2 g^{-1}$
	NH₄ZSM-5	280.00	15.67	400.00
MFI	HZSM-5	280.00	-	380.00

Table 1. Characteristics of zeolite samples used as adsorbents

The x-ray diffraction analysis of ZSM-5 was performed (Figure 1). The x-ray structural analysis of the powder was performed on the diffractometer PHILIPS PW 1710 with the use of Cu anticathode (40kV, 50mA, K α =0.154056 nm). The recording was performed in the area 2 θ from 5 to 40⁰, and the results were processed by the use of software for automatic diffraction of powder (PC-APD) and ICDD/JCPDS PDF-2 database.

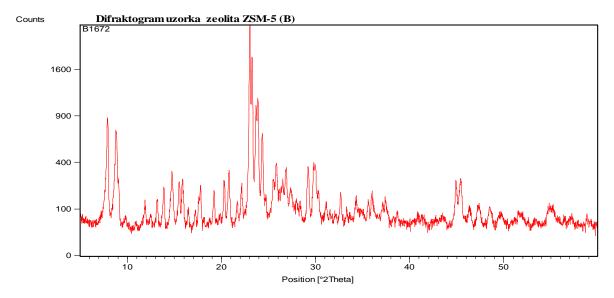


Figure 1. Diffractogram of ZSM-5 zeolite

The samples of zeolite were also electronically recorded by enlarging them from 1: 5000 to 1: 50 000, where the fractions of extremely small dimensions are visible (Figure 2). The scanning electronic microscopy (SEM analysis) was performed on the JEOL JSM 6460LV device.

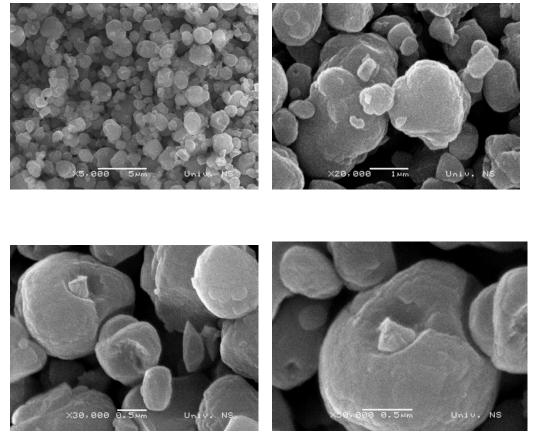


Figure 2. SEM of ZSM-5 zeolite

The solutions of adsorbates (propane acids) were prepared in the range of concentrations from 0.05 to 0.20 mol/L. The proper concentrations of acid, before and after adsorption, were determined by titration with standard solution of sodium-hydroxide, with phenolphthalein as indicator. The quantity of adsorbed acid was calculated from the difference. The ratio of adsorbent mass and adsorbate volume in the reaction system, in all experiments, was approximately 0.5 grams (exact weighed quantity) / 50.00 milliliters. The reaction mixture was thermostated and the balance state was reached in the period of three hours.

RESULTS AND DISCUSSION

The characterization of the system adsorbate-adsorbent was described by the Freundlich adsorption isotherm. The results of the experimental observation of adsorption of propane acid on ZSM-5 zeolites were presented in the tables 2-10 and diagrams 3-7.

Table 2. Adsorption of propane acid on NH4ZSM-5 at283 K

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} \ge 10^3$ / mol ⁻¹
0.0375	0.4975	1.236
0.0560	0.5004	1.199
0.0840	0.4998	1.301
0.1325	0.5014	1.247
0.1520	0.5004	1.299
0.1845	0.5000	1.250

Table 3. Adsorption of propane acid on NH₄ZSM-5 at 288 K

$c_{ravn.}$ /molL ⁻¹	m _{adsorb.} /g	$\frac{x}{m} \ge 0^3 / \text{ molg}^{-1}$
0.0380	0.5002	1.179
0.0560	0.4993	1.262
0.0860	0.5006	1.099
0.1320	0.5037	1.291
0.1510	0.4984	1.405
0.1850	0.5035	1.192

Table 4. Adsorption of propane acid on NH₄ZSM-5 at 293 K

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} \ge 0^3$ / molg ⁻¹
0.0370	0.4990	1.283
0.0570	0.4999	1.100
0.0860	0.4999	1.100
0.1320	0.5035	1.291
0.1500	0.5015	1.496
0.1855	0.5012	1.147

Table 6. Adsorption of propane acid on HZSM-5 at 283 K

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} \ge 0^3 / \text{ molg}^{-1}$
0.0371	0.5009	1.328
0.0584	0.5010	1.268
0.0881	0.4997	1.481
0.1374	0.5000	1.590
0.1576	0.4995	1.532
0.1719	0.5007	1.318
0.1889	0.4994	1.382

Table 8. Adsorption of propane acid on HZSM-5 at293 K

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} \ge 0^3 / \text{ molg}^{-1}$
0.0361	0.5000	1.430
0.0541	0.5003	1.699
0.0849	0.5005	1.798
0.1332	0.5003	2.009
0.1538	0.4996	1.912
0.1851	0.4997	1.761

Table 5. Adsorption of propane acid on NH₄ZSM-5 at 303 K

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} lpha 0^3$ / molg ⁻¹
0.0360	0.5012	1.377
0.0550	0.5016	1.296
0.0840	0.4992	1.302
0.1320	0.5012	1.297
0.1500	0.4996	1.501
0.1815	0.5006	1.548

Table 7.	Adsorption	of propane	acid	on	HZSM-5	at
288 K						

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} \ge 0^3 / \text{ molg}^{-1}$
0.0371	0.4999	1.330
0.0573	0.5005	1.379
0.0870	0.5010	1.587
0.1369	0.5000	1.640
0.1570	0.5000	1.590
0.1889	0.5012	1.377

Table 9.	Adsorption	of propane	acid d	on HZSM-5 a	at
303 K					

$c_{ravn.}/molL^{-1}$	m _{adsorb.} /g	$\frac{x}{m} \ge 0^3 / \text{ molg}^{-1}$
0.0382	0.5000	1.220
0.0578	0.4997	1.311
0.0881	0.5000	1.480
0.1369	0.5003	1.639
0.1581	0.4998	1.481
0.1883	0.4969	1.449

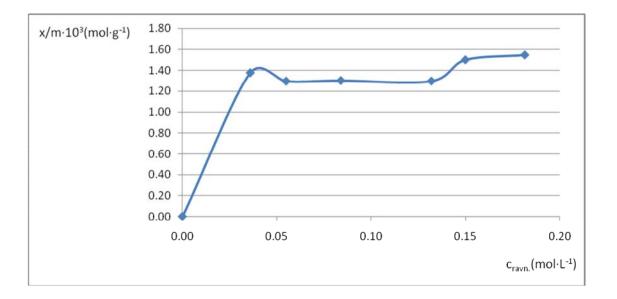


Figure 3. Adsorption of propane acid on NH₄ZSM-5 at 303 K

The adsorption isotherms for the system of propane acid - NH_4ZSM -5 are presented by the comparative diagram in Figure 4.

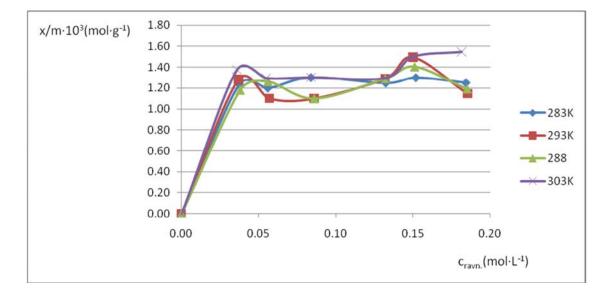


Figure 4. Adsorption isotherms for the system of propane acid-NH4ZSM-5

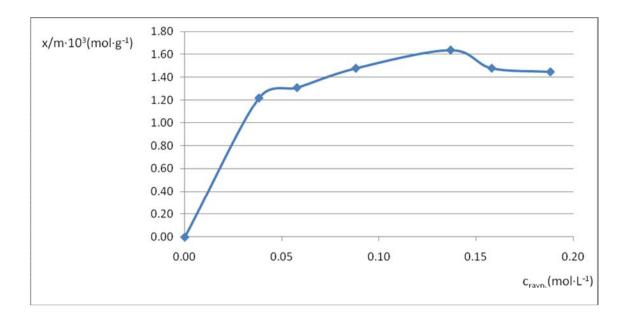


Figure 5. Adsorption of propane acid on HZSM-5 at 303 K

The adsorption isotherms for the system of propane acid - HZSM-5 are presented by the comparative diagram in figure 6.

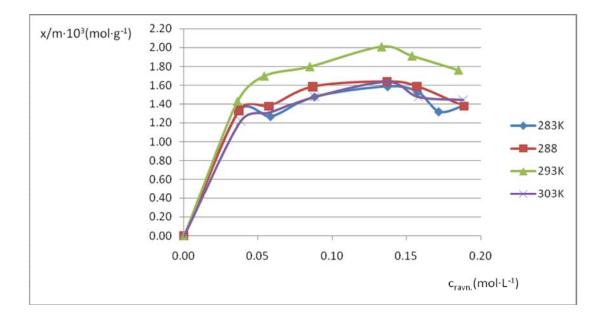


Figure 6. Adsorption isotherms for the system of propane acid-HZSM-5

Figure 7 presents the comparative diagram giving a summary survey of the adsorption isotherms of propane acid on NH_4ZSM -5 and HZSM-5 zeolite.

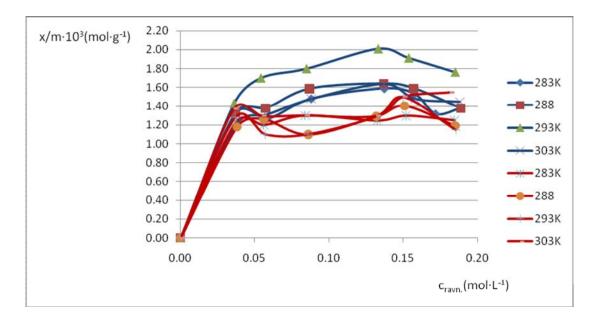


Figure 7. Adsorption isotherms for the system of propane acid-NH₄ZSM-5 and for system of propane acid-HZSM-5

Adsorbent	T _{ads.} /K	$\frac{x}{40^3}$ /molg ⁻¹	Number of adsorb. molec. of	Ratio of surface of all adsorb.
		m	propane acid / 10^{19}	acid molec. and spec.surface of adsorbent / %
	283	I – 1.217	I – 3.663	I – 1.20
		II – 1.301	II – 3.916	II – 1.28
	288	I – 1.276	I – 3.841	I – 1.26
NH₄ZSM-5		II – 1.348	II – 4.057	II – 1.33
	293	I – 1.191	I – 3.585	I – 1.17
		II – 1.400	II – 4.214	II – 1.38
	303	I – 1.300	I – 3.913	I – 1.28
		II – 1.530	II – 4.605	II – 1.51
	283	I – 1.275	I – 3.838	I – 1.32
		II – 1.514	II – 4.557	II – 1.57
HZSM-5	288	I – 1.355	I – 4.079	I – 1.41
		II – 1.615	II – 4.861	II – 1.68
	293	I – 1.875	I – 5.644	I – 1.95
	303	I – 1.523	I – 4.606	I – 1.59

Table 10. Summary presentation of the adsorption of propane acid on NH₄ZSM-5 and HZSM-5 zeolite

Based on the experimental data, the study determined constants k and n for Freundlich adsorption isotherm, as well as the heat of adsorption, Δ_{ads} H (table 11).

propane acid-ZSM-5 zeolites				
Adsorbent	T _{adsorpcije} /K	k∙10 ³	n	$\Delta_{ m ads}$ H /Jmol $^{-1}$
NH₄-ZSM-5	283	1.50	1.84	-4329
	288	1.50	1.58	-3783
	293	1.10	1.02	-2484
	303	1.70	1.08	-2720
HZSM-5	283	1.96	1.53	-3599
	288	2.40	1.67	-3999
	293	2.60	1.60	-3898
	303	2.30	1.67	-4207

Table 11. Values of constants k, n and Δ_{ads} H for Freundlich adsorption isotherm for the systems of

The obtained adsorption isotherms for the system propane acid - NH₄-ZSM-5 have two plateaus, the curve has a convex form in the beginning, which is an indicator that the zeolite surface is still not fully occupied with the propane acid molecules. The quantity of adsorbed acid, expressed by the number of acid molecules, is bigger on the second plateau by around 7 % to 17 %. Similar form and trend are also shown by the adsorption isotherms for the system propane acid - HZSM-5 at 283 and 288 K, while at the higher temperatures the isotherm gets a typical Langmuir form. The results of observing the adsorption of propane acid on zeolites, as well as other adsorbates, (6, 13, 14) can certainly give a piece of interesting information on the orientation of molecules adsorbed on the zeolite surface in its saturation. Since, with the increase of the adsorption temperature, more or less, a more efficient adsorption of propane acid was registered on NH₄-ZSM-5 and on HZSM-5 zeolite, one may conclude that the molecules of acid got bonded to the active surface of these high-silicate samples in different manners, partly by chemical bonds through functional groups, and partly by weaker van der Waals forces, getting linked vertically or by "lying" on the surface. The adsorption capacity of HZSM-5 zeolite is somewhat bigger, which is logical with regard to the distinct hydrophobic character of the modified H-form, which means a relatively bigger affinity towards propane acid, because annealing did not change the ratio Si/Al, the water molecules were removed from the cavities, decationization of zeolite occurred by removing the ammonia ion, which significantly changed electrostatic potential of the active centre, so they became less acid and probably more accessible for this organic molecule. The data obtained for constants k and n and heat of adsorption speak in favor of these conclusions.

CONCLUSION

The adsorption of propane acid (C3H6O2, p.a., Sigma Chemical, USA) was observed from the aqueous solution in

the temperature interval from 283 K to 303 K. The specific surface of the original NH₄-ZSM-5 zeolite is 400 m²/g, and specific surface of the modified form of HZSM-5 zeolite is 380 m²/g. The quantity of adsorbed acid, expressed by the number of acid molecules, is bigger on the second plateau by around 7 % to 17 %. The adsorption isotherms for the system of propane acid - HZSM-5 (at 283 and 288 K), have a similar form, while at the higher temperatures the curve gets the Langmuir form. A bigger affinity towards propane acid was shown by the modified zeolite, HZSM-5, probably because of a more distinct hydrophobic character of this zeolite compared to NH₄-ZSM-5.

LITERATURE

- Anderson, J. R., K. C. Pratt: Introduction to Characterization and Testing of Catalysts, Academic Press, London, (1985).
- 2. Csicsery, S. M.: Zeolites, 4, 202, (1984).
- 3. Greg, S. J., K.S.W. Sing: Adsorption, Surface Area and Porosity, Academic Press, London, New York, Tokyo, Toronto, (1982).
- 4. Trimm, D. L.: Design of Industrial Catalysts, Elsevier, Amsterdam, (1980).
- 5. Škundrić, B., J. Penavin i ostali: Kinetika nekih organskih reakcija na zeolitnim katalizatorima, Elaborat za SIZ nauke BiH, Banjaluka, (1981).
- Penavin-Škundrić, J. i saradnici: Uticaj hemije na površini alumosilikatnih i oksidnih materijala na adsorpciju kiselih i baznih organskih i neorganskih komponenti iz vodene sredine, Projekat Ministarstva nauke i tehnologije, Banjaluka, (2012).
- Skundric, B., J. Penavin, S. Sladojevic, N. Cegar: Kinetic Studies of Catalytic Dehydration of Diethylether and Izomerization of 3,3-DMB-1 on Clinoptilolitic Catalysts. Gazette of Chemists and Technologists of RS, 45 (2003) 27-35.
- Penavin-Skundric, J., S. Sladojevic, B. Skundric, N. Cegar: MFI Zeolites as Catalysts in Some Organic Reactions, Proceedings of 37th IOCMM, Bor Lake, Serbia and Montenegro, (2005) 515-520.
- 9. Weng, C. H., Y. F. Pan: Adsorption Characteristics of Methylene Blue from Aqueous Solution by Sludge Ash. Coloids Surf., **274** (2006).
- Yoo, W. C., X. Zhang, M. Tsapatsis, A. Stein: Synthesis of mesoporous ZSM-5 zeolites through desilication and reassembly processes. Microporous and Mesoporous Materials, 149, 1 (2012) 147-157.
- 11. Cho, <u>H. S.</u>, <u>R. Ryoo</u>: Synthesis of ordered mesoporous MFI zeolite using CMK carbon Templates. <u>Microporous</u> and <u>Mesoporous Materials</u>, **151** (2012) 107-112.
- 12. Breck, D.W.: Zeolite Molecular Sieves, Wiley Inc., New York, (1974).
- Sladojević, S., B. Škundrić, J. Penavin, N. Čegar: Adsorpcija organskih kiselina na Y Zeolitu. Glasnik hemičara i tehnologa RS, 44 (2003) 371-380 (Supplementum)
- Sladojević, S., J. Penavin-Škundrić, D. Lazić, S. Krnetić, N. Čegar, B. Škundrić:MFI zeoliti kao adsorbens kiselih i baznih primjesa u vodenom mediju. Glasnik hemičara, tehnologa i ekologa RS, 1 (2009) 11-15.

ADSORPCIJA PROPAN KISELINE NA VISOKOSILIKATNIM ZSM-5 ZEOLITIMA NANOSTRUKTURNIH DIMENZIJA

*S. Sladojević*¹ , *J. Penavin-Škundrić*¹ , *Z. Levi*¹ , *D. Bodroža*¹ , *D. Lazić*² , *B. Škundrić*³ ¹ Tehnološki fakultet, Univerzitet u Banjaluci, RS, BiH

² Tehnološki fakultet, Univerzitet u Istočnom Sarajevu, Zvornik, RS, BiH

³ Akademija nauka i umjetnosti Republike Srpske, Banjaluka, RS, BiH

U radu je praćena adsorpcija propan kiseline iz vodenog rastvora na visokosilikatim zeolitnim uzorcima, proizvedenim savremenim nanotehnologijama u američkoj kompaniji Zeolyst International (oznaka: CBV 28014). Kao adsorbensi korišteni su NH₄ ZSM-5 zeolit i njegova modifikovana forma-HZSM-5 (molski odnos SiO₂ /Al₂ O₃ iznosi 280). Adsorpcija je praćena u temperaturnom intervalu od 283 K do 303 K. Rezultati su pokazali da je sa porastom temperature adsorpcije količina adsorbovane propan kiseline rasla i na izvornoj i na modifikovanoj formi ZSM-5 zeolita, što ukazuje da se pored fizičke adsorpcije dešava i hemisorpcija, pri čemu su molekule kiseline vezane za aktivne centre i čvršćim hemijskim vezama. Modifikacijom osobina izvornog zeolita dobio se bolji adsorbens (HZSM-5 zeolit) za propan kiselinu, što je i očekivano obzirom na izražen hidrofobni karakter ove modifikovane forme.

Rad primljen:19. 11. 2013 Rad prihvaćen: 02. 12. 2013.