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SYNTHESIS OF KAOLIN-BASED ZEOLITE Y AND ITS APPLICATION FOR ADSORPTION OF TWO CARBONYL COMPOUND GASES

The aim of the study was to synthesize zeolite Y based on natural clay mineral and to determine its potential for adsorption of carbonyl compounds. The synthesis route consisted of four steps: thermal activation of kaolin into metakaolin; aging of reaction mixtures at ambient temperature; crystallization of the reaction mixture; washing and drying of the final product. The reaction mixture consisted of metakaolin silica gel (SiO_2), sodium chloride (NaCl) and sodium hydroxide (NaOH). All substrates were used at an intended molar ratio. The physicochemical properties of the synthesized adsorbent were attained through the advanced instrumental analysis. The adsorption of acetone and methyl ethyl ketone (MEK) on synthesized zeolite as well as on four commercially available adsorbents and three natural materials was examined in a dedicated home-made installation. The results showed, that the synthesized zeolite Y has the highest affinity for acetone over other adsorbents, while its affinity for MEK is only a little lower then AC. Additionally, adsorption isotherms of acetone and MEK on zeolite Y were measured on a gravimetric balance. Experimental binding isotherms were fitted by a non-linear regression to five empirical equations. In both acetone and MEK cases, the best results of statistical tests were obtained for the Marczewski-Jaroniec model.

Keywords: adsorption, acetone, methyl ethyl ketone, Y zeolites

1. Introduction

Carbonyl compounds are one of the most common volatile organics (VOCs) emitted by industrial processes into the atmosphere [19, 21]. Their primary emission sources are vehicle exhausts, industrial processes, cook stoves, household commodities and solvent evaporation. Other source of carbonyl compounds is

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photochemical oxidation of atmospheric hydrocarbons [13, 41]. Ketone group of VOCs are usually toxic or carcinogenic and their elimination, at a reasonable cost, is a serious challenge for many industrial processes [6, 35]. To meet the stringent regulations of pollutants emission two methods have been mainly investigated in industrial applications (95%): thermal and catalytic oxidation. Both processes are highly energy consuming and produce huge amount of combustion by-products (NOx, CO_2). In the contrary adsorption based processes are considered as an effective and low-cost technique. Activated carbons (AC) are the most abundantly used adsorbents in industry mainly due to their high surface area and high adsorption capacity. However, the application of AC has some obstacles. AC is flammable, difficult to regenerate for high boiling point solvents, requires humidity control and promotes polymerization or oxidation of some solvents to toxic or insoluble compounds. One should also keep in mind that ACs has low affinity for polar organics.

Hydrophobic, thermo-stable zeolites are considered as an effective alternative to active carbons, essentially because they possess a large range of surface polarities [21, 28, 34]. Their first definitive synthesis was reported in 1948, when an analog of natural zeolite mineral, mordenite, was synthesized by R.M. Barrer [13]. A little later, Milton and Breck discovered a number of zeolites, types A, X and Y [40] which next, in 1954, the Union Carbide commercialized as a new class of industrial materials for separation and purification processes [22]. Currently more than 600 zeolites have been identified and more than 119 types of zeolitic structures have been cataloged by the Structure Committee of the International Zeolite Association [5, 37].

Faujasitic zeolite has gained immense popularity within the research community and in industry [3]. Its basic structural units are sodalite cages which form supercages and can accommodate spheres up to 1.2 nm in diameter [12]. The synthesis of faujasite is quite expensive if it is based on pure silica and alumina sources, i.e. colloidal silica and aluminium isopropoxide [2, 31] or water glass and sodium aluminate [26]. To reduce the production cost, it is possible to use for its synthesis a natural clay mineral [20, 30]. Among the clays, several investigators have studied the preparation of zeolite from kaolin and have been successful in the synthesis of zeolites [15]. Kaolin has unique properties and can be easy transformed into amorphous phase. The present study was therefore undertaken aiming at synthesis of zeolite Y from metakaolin. The obtained zeolitic product was characterized by some instrumental techniques and was applied for adsorption of acetone and methyl ethyl ketone (MEK) gases.

2. Experimental

2.1. Reagents

NaOH was purchased from Polskie Odczynniki Chemiczne (analytical grade), NaCl and silica gel were supplied by Chempur (analytical grade). The starting material of kaolin was purchased from BioDrain, Poland. Two gaseous mixtures,

acetone in nitrogen and methylethylketone (MEK) in nitrogen, at a concentrations of 0.48 and 0.6 mg/m^3 respectively, were supplied by AirLiquide.

2.2. Synthesis of the zeolite

The Y zeolite precursor (metakaolin) was obtained by thermal activation of kaolin at 800°C for 6h (muffle furnance SNOL 8:2/1000). During this process crystalline kaolin was converted to chemically reactive amorphous metakaolin according to the reaction [4, 36]:

$$2Al_2Si_2O_5(OH)_4 \xrightarrow{>500°C} 2Al_2Si_2O_7 + 4H_2O$$
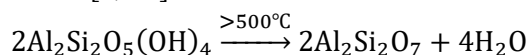
Metakaolin was mixed with appropriate volume of NaOH (20%) solution and mass of SiO_2 to keep molar composition of the mixture as follow: $SiO_2/Al_2O_3 = 10$, $Na_2O/SiO_2 = 1$, $H_2O/Na_2O = 20$ [7]. Reaction mixture was aged at ambient temperature for 10 days and then kept in laboratory dryer (POLEKO SLW32 EKO) at 100°C for 24 h for crystallization [20]. After that, the mixture was washed with distilled water until pH was equal 7. Finally the sample was filtrated by laboratory filters and dried at 120°C for 2 h [38].

2.3. Characterization of the synthesized material

2.3.1. Chemical composition

The chemical composition was determined by Wavelength Dispersive X-Ray Fluorescence Spectroscopy (WDXRF), using the AxiosMAX PANalytical spectrometer. Measurements were made from the pellet (diameter of 32 mm) pressed from the ground, dried and homogenised material. Elemental analysis (measurement of average concentration of elements in the bulk phase) was made using a semi-quantitative method.

2.3.2. Phase composition

Zeolite sample was analyzed by X-ray powder diffraction (XRD) using an Empyrean PANalytical diffractometer with Cu Kα radiation. The tube voltage was 40 kV and the current was 25 mA. The diffractograms were recorded in 0.0263° 2θ. The diffraction data were analyzed by Rietveld method using HighScore Plus 3.0 software.

2.3.3. Specific surface area

The specific surface area, pore volume and pore size distribution of the synthesized zeolite were determined by N_2 adsorption/desorption at -196°C, on a Micromeritics ASAP 2420M instrument. Zeolite was outgassed at 200°C before analysis. The specific surface area was calculated using BET model (Brunauer-Emmett-Teller). The external surface area and micropore volume were determined

from *t*-plot analysis. The total volumes of mesopores and micropores were calculated from the amounts of N_2 adsorbed at P/P_0=1. The pore size distribution of the zeolite was calculated using the BJH method (Barrett-Joyner-Halenda).

2.3.4. Thermal analysis

TG, DTG and DTA analyses were done by using a Derivatograph-C (Paulik-Paulik & Erdey) thermal analyzer where the samples of about 10 mg in silica crucibles were heated starting from 20°C up to 1,200°C at a heating rate of 10°C min^{-1} under an air atmosphere.

2.4. Adsorption study in home-made installation

The efficiency of acetone and MEK adsorption on synthesized zeolite Y as well as on other commercially available adsorbents was performed in dedicated home-made installation provided by the Otto Engineering Poland Sp. o.o. company, shown in Fig. 1 [27]. The adsorbent sample was at first dried in an oven at 473 K, weighted out (0.25 g) and located in the middle of the column (3) of 1 cm inner diameter. A thin layer of glass wool was placed at both ends of the bed to hold packing in a right position. Gas flow rate equal to 0.0001 m^3/min at p 0.04 MPa and T 393 K were regulated by using a Defender flow controller (2) supplied by MassLabs. Nitrogen was used as a carrier gas for both carbon contaminants (CC). About 200 ppm of CC was passed through the column. Its concentration in the outlet of the column was monitored on-line by using gas chromatograph (Thermo Scientific 1300 TRACE GC) and recorded by a computer to obtain the breakthrough curves. The experiment ended when the outlet concentration equaled the inlet concentration.

GAS CHROMATOGRAPH

1 - cylinder with a mixture of a carbonyl compound in nitrogen
2 - regulating valve
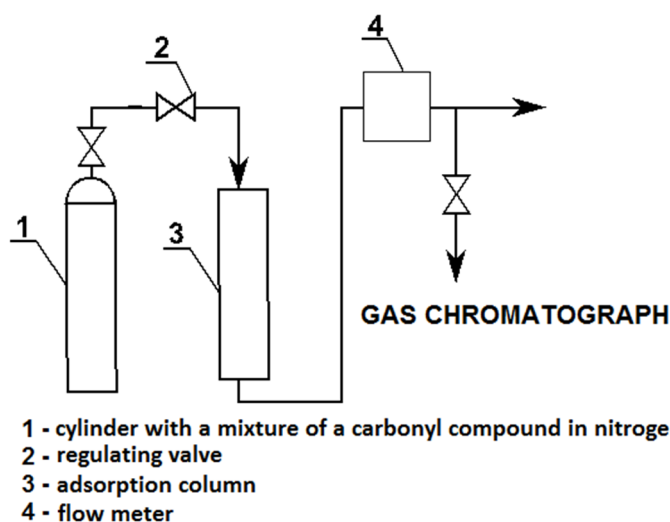3 - adsorption column
4 - flow meter

Fig. 1. Scheme of the installation for adsorption of acetone and MEK

The adsorption loading of gases was obtained by integration of the area behind the breakthrough curve. The amount of carbonyl compound adsorbed, q_e [mg/g] was calculated from Eq. (1). and Eq. (2).

$$m = \left[\frac{max(\dot{m}_{i=0} : \dot{m}_n) - (\dot{m}_i + \dot{m}_{i+1})}{2}\right] \cdot (t_{i+1} - t_i) \tag{1}$$

$$q_e = \frac{\sum_{i=0}^{n} m}{m_{zeolite}} \tag{2}$$

where: $\dot{m}_{i=0}$, $\dot{m}_n$, $\dot{m}_i$, $\dot{m}_{i+1}$ is the mass flow rate of CC in the outlet stream, respectively, at the time t=0, t=n, t=i, t=i+1 [mg/min]; t_i, t_{i+1} – is the duration of the adsorption process; and $m_{zeolite}$ is the mass of zeolite packed in column.

2.5. Determination of adsorption isotherms

The adsorption isotherms of acetone and MEK on zeolite Y were estimated on an IGA-002 gravimetric instrument (Hiden-Isochema) at 293°C and pressure up to 0.902 atm. The apparatus possesses an ultra-high vacuum system and can accurately control the subtle weight changes of the samples by changing the pressure [40]. Prior to the measurements, the sample of approximately 75 mg of zeolite was degassed in high vacuum (10^{-6} Pa) at 180°C by 2 hours to remove the excess water and impurities adsorbed in the pores. During adsorption measurements, the pressure was altered with the set pressure points and the mass uptake was measured in real time using the Real Time Processor (RTP).

The determined isotherms were examined by fitting the experimental data to the following isotherms models:

Langmuir:
$$q_e = \frac{q_m \cdot K \cdot (C_e)}{1 + K \cdot (C_e)} \tag{3}$$

Freundlich:
$$q_e = K \cdot (C_e)^{\frac{1}{n}} \tag{4}$$

Dubinin-Radushkevic:
$$q_e = 10^{\log_{10} q - n \cdot \log_{10}[K \cdot (C_e)]^2} \tag{5}$$

Aranovich and Donohue:
$$q_e = \frac{q_m \cdot K \cdot (C_e)^n}{(1 + K) \cdot [1 - (C_e)]^n} \tag{6}$$

Marczewski-Jaroniec:
$$q_e = \frac{q_m \cdot [K \cdot (C_e)]^m}{1 + [K \cdot (C_e)]^n} \tag{7}$$

where: q_e [mmol/g] is the solid phase adsorption quantity of carbonyl compound (acetone or MEK) at equilibrium; q_m [mmol/g] is the carbonyl compound

off

off off

main product of the synthesis is faujasite (77%) and the minor by-products are unreacted quartz (10%) and zeolite P (12%).

Depending on the SiO_2/Al_2O_3 molar ratio, faujasites can be considered as a zeolites X if $SiO_2/Al_2O_3 = 2$–3 or zeolite Y if $SiO_2/Al_2O_3 > 3$ [10]. The obtained molar ratio of SiO_2/Al_2O_3 is 3.80 (Tab. 1), thus the final product is zeolite Y. It is worth to emphasized that zeolite Y, in opposite to zeolite X, can have hydrophobic properties, because zeolites are hydrophobic when molar ratio SiO_2/Al_2O_3 is bigger then 20 [18].

Table 2. Phase characterization of the zeolite (mass %)

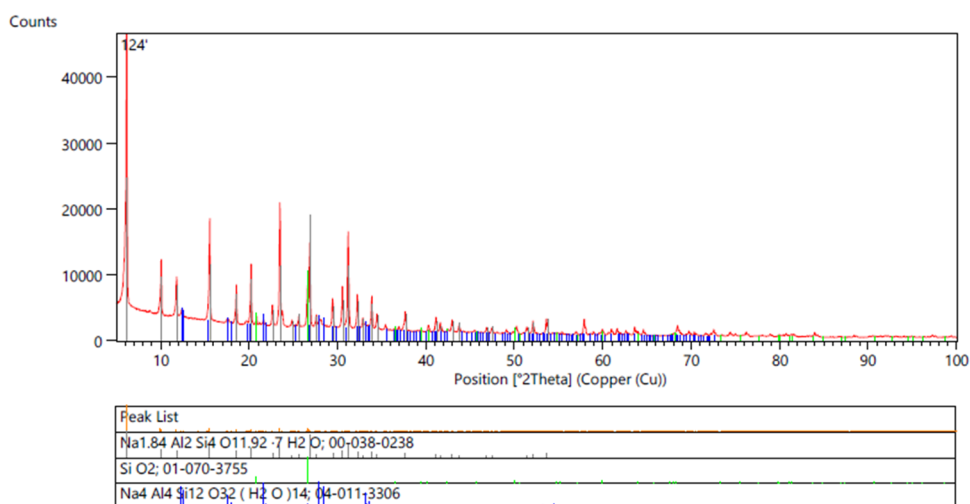| Chemical formula	Substance	Mineral	Standard deviation
$Na_{1.84}Al_2Si_4O_{11.92} \cdot 7H_2O$	Sodium Aluminium Silicate Hydrate	Faujasite	$77 \pm 3\%$
SiO_2	Silicon Oxide	Quartz	$10 \pm 1\%$
$Na_4Al_4Si_{12}O_{32}(H_2O)_{14}$	Sodium Aluminium Silicate Hydrate	-	$12 \pm 2\%$

Fig. 2. Diffractogram of zeolite along with the alignment results against the diffraction ICDD PDF4+ database

3.2. Thermal analysis

Thermal analysis of the obtained zeolite, presented in Fig. 3A, reveals a little more than 10% loss of weight associated with the dehydration of the zeolite sample during heating from room temperature up to 200°C. It is worth to mention that a maximum temperature of 200°C is used for desorption of pollutants under real conditions. Further loss of weight observed in the range 400–700°C corresponds to the dehydroxylation of the structural -OH groups [2, 14]. The results of DTA analysis (Fig. 3B) identified the presence of

endothermic peak having maximum effect at temperature 200°C (due to the loss of adsorbed water), and exothermic peak at 900°C indicating recrystallization of zeolite.
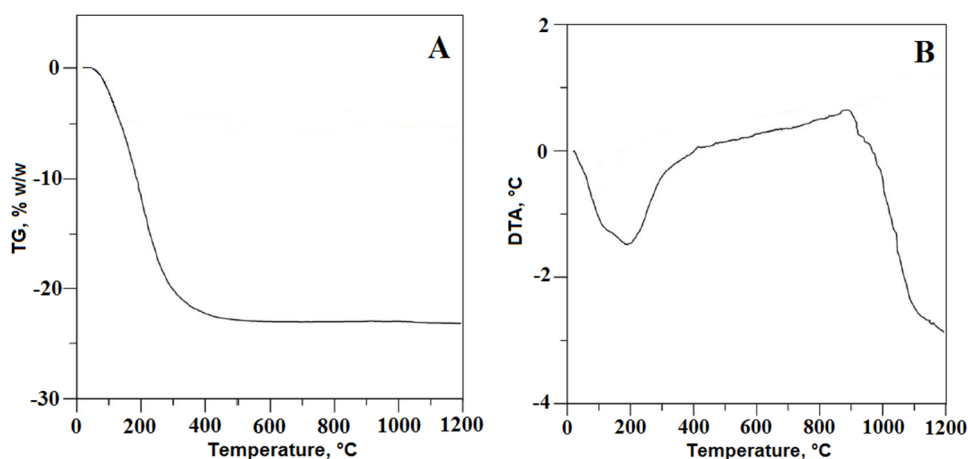

Fig. 3. (A) TG and (B) DTA curves of the zeolite Y

3.3. Textural properties analysis

The estimated specific surface areas (BET areas), pore volume and diameter of the zeolite sample are depicted in Table 3. Additionally, N_2 adsorption-desorption isotherm of the zeolite is shown in Fig. 4. At $P/Po = 0.8$, the sample shows substantial increase of nitrogen adsorption. The zeolite Y exhibited type IV isotherms, which is characteristic for mesoporous materials with H-IV hysteresis loops [17, 33]. This type of loop is usually attributed to the slip-shaped pores [24]. As shown in Fig. 4. the pore size distribution of zeolite exhibits a bimodal distribution; two peaks appear at ca. 2 and 90 nm., which indicates the presence of meso- and microporous structure. Thus, no molecular sieve effect affects adsorption of acetone (4.3 Å) and MEK (5.2 Å).

Table 3. Textural parameters of the zeolite

Surface area (m^2/g)			Pore volume (cm^3/g)		D_{mean} [b] (nm)
S_{BET}	S_{micro} [a]	S_{ext} [a]	V_{total}	V_{micro} [a]	
685,85	590,59	35,26	0,30	0,26	1,76

[a] Calculated from *t*-plot curve
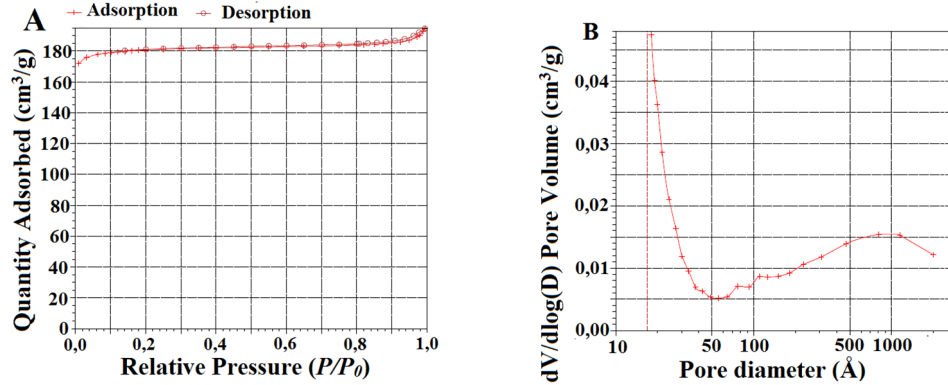[b] Adsorption average pore width (4V/A by BET)

Fig. 4. (A) N2 adsorption-desorption isotherm and (B) Pore size distribution of the zeolite

3.4. Adsorption isotherms

The adsorption isotherms of acetone and MEK are given in Figs. 5 and 6, respectively. Both depicted isotherms have long horizontal plateau, which extends up to relatively high P/P_0 ratio. This characteristic shape of the isotherms allows for their allocation to the type-I of the IUPAC classification [32]. Type I of isotherm proofs microporosity of the zeolite and suggests micropole filling mechanism of adsorption [42]. It is partially confirmed by the best approximation of the value of maximum adsorption capacity ($q_{m,exp}$) obtained for the Dubinin-Radushkevich model (Table 4). Slightly worse approximation of $q_{m,exp}$ was obtained for the Langmiur model but with a better result of statistical tests. Nevertheless, in both acetone and MEK cases, the best results of statistical tests were obtained for the Marczewski-Jaroniec model. It probably results from the biggest number ($p = 4$) of estimated parameters.
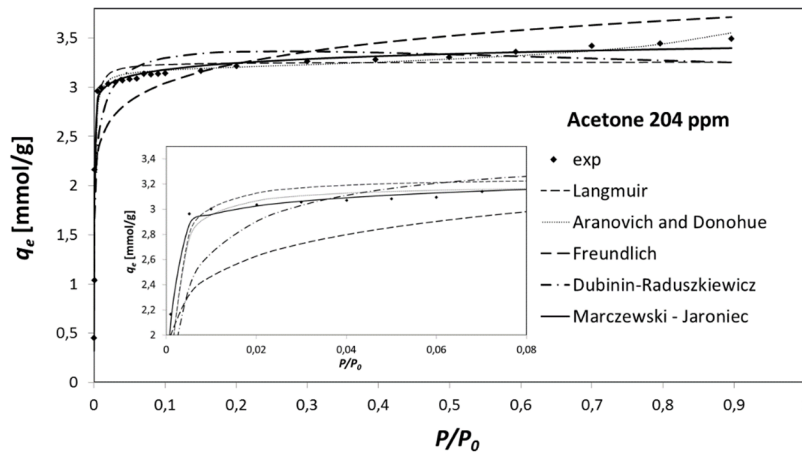

Fig. 5. Comparison of models prediction and experimental data obtained for acetone adsorption on zeolite
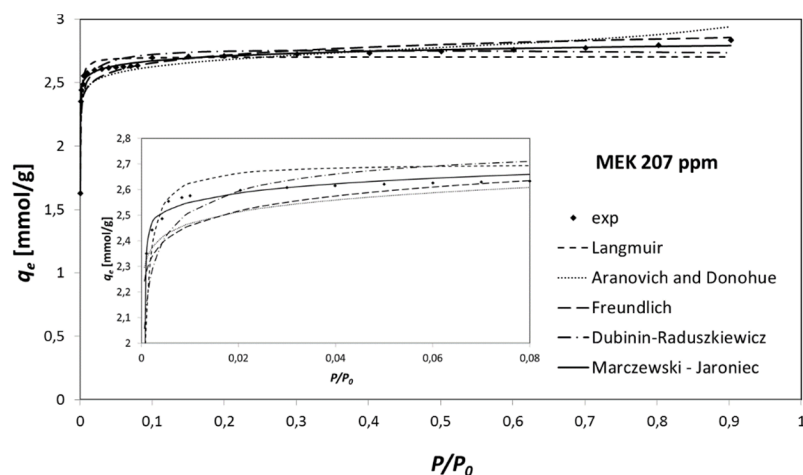
Fig. 6. Comparison of models prediction and experimental data obtained for MEK adsorption on zeolite

Table 4. Models parameters and statistical tests results for acetone and MEK adsorption on zeolite Y

Model	Parameters				Statistical tests		
	K	q_m[mmol/g]	N	m	TF	ME	σ
acetone $q_{m.exp}$ =3.50 (mmol/g)							
Langmuir	1 207	3.257	-	-	21.52	7.001	0.160
Freundlich	3.751	-	10.99	-	2.949	22.59	0.432
Dubinin-Radushkevich	3.832	3.366	0.052	-	7.031	13.01	0.280
Aranovich Donohue	1 295	3.182	0.049	-	31.53	5.806	0.132
Marczewski-Jaroniec	1 691	2.720	2.181	2.212	144.1	2.860	0.062
MEK $q_{m.exp}$=2.83(mmol/g)							
Langmuir	3 336	2.704	-	-	6.807	2.720	0.091
Freundlich	2.865	-	30.16	-	2.549	3.598	0.148
Dubinin-Radushkevich	2.840	2.754	0.018	-	3.623	3.380	0.124
Aranovich Donohue	9 174	2.778	0.026	-	2.122	3.888	0.162
Marczewski-Jaroniec	1 864	2.405	5.038	5.058	128.9	0.590	0.021

The comparison of the efficiency of acetone and MEK adsorption onto: synthesized zeolite Y, four commercial adsorbents (X13 India, AC Desotec, AC Norit and zeolite ZSM-5) and three natural clay minerals (montmorilonite, bentonite, haloizyte) are shown in Fig. 7. The ZSM-5 based zeolite is widely used as adsorbent in zeolite concentrators (temperature swing adsorbers) for continuous VOCs adsorption and desorption [8]. 13X zeolite has been studied to

adsorb various VOCs with pressure swing adsorption (PSA) [11, 39]. Natural minerals are cost-effective alternative adsorbents to widely used ACs [9, 29]. As can be seen, the synthesized zeolite Y has the highest affinity for acetone over other adsorbents, while its affinity for MEK is only a little lower then AC. Both organics have similar polarity (acetone 2.76 D, MEK 2.78 D), thus the observed difference in their adsorption can steam from different molar volume of both molecules (acetone 70.4 cm^3/mol, MEK 90.1 cm^3/mol at 25°C [23]).
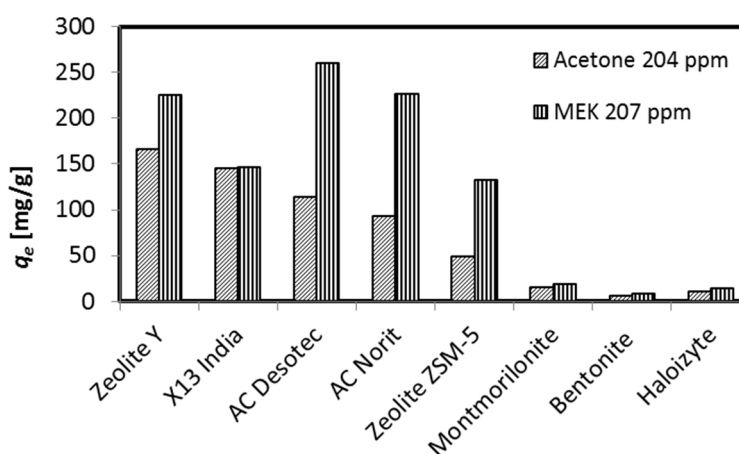

Fig. 7. Comparison of acetone and MEk adsorption efficiency of different adsorbents

4. Conclusions

The use of kaolin as an aluminum and silica source for the synthesis of Y-type zeolite allows obtaining an effective adsorbent of polar organics. The relatively big dimension of the aperture of the zeolite channels can favor the entrance of the small organics molecules. Thus, their adsorption can follow a micropore filling what was further confirm by characteristic shape of isotherm curves and by the results of model calculations. The determined adsorption capacity of the two tested carbonyl compounds reached about 170 $mg_{acetone}$/g and about 225 mg_{MEK}/g.

Despite the fact that the synthesized zeolite Y has relatively low specific surface area (380–750 m^2/g) in comparison to ACs (800–1,500 m^2/g), its affinity for polar acetone is higher than any other commercially available adsorbent. Furthermore, it's high thermal stability up to 200°C allows safety thermal regeneration and zeolite reuse. Thus, the synthesized zeolite Y comprises attractive and competitive solution for cleaning of wasted gases towards commercially available adsorbents.

References

[1] Adeoye J. B., Omoleye J. A., Ojewumi M. E., Babalola R.: Synthesis of Zeolite Y from Kaolin Using Novel Method of Dealumination, International Journal of Applied Engineering Research, 5/12, 2017, 755–760.

[2] Ahmedzeki N.S., Yilmaz S., Al-Tabbakh B.A.: Synthesis and Characterization of Nanocrystalline Zeolite Y, Al-Khwarizmi Engineering Journal, 1/12, 2016, 79–89.

[3] Alaba P.A., Sani Y.M., Daud W.M.A.W.: Synthesis and characterization of hierarchical nanoporous HY zeolites from acid-activated kaolin, Chinese Journal of Catalysis, 36, 2015, 1846–1851.

[4] Ayele L., Perez-Pariente J., Chebude Y., Diaz I.: Synthesis of zeolite A from Etiopian kaolin, Microporous and Mesoporous Materials, 215, 2015, 29–36.

[5] Bortolatto L.B., Boca Santa R.A.A., Moreira J.C., Machado D.B., Martins M.A.P.M., Fiori M.A., Kuhnen N.C., Riella H.G.: Synthesis and characterization of Y zeolites from alternative silicon and aluminium sources, Microporous and Mesoporous Materials, 248, 2017, 214–221.

[6] Bradberry S.: Acetone, Medicine, 3/44, 2016, 127.

[7] Chandrasekhar S., Pramada P.N.: Kaolin-based zeolite Y, a precursor for cordierite ceramics, Applied Clay Science, 27, 2004, 187–198.

[8] Chang F.T., Lin Y.C., Bai H.L., Pei B.S.: Adsorption and desorption characteristic of semiconductor volatile organic compounds on the thermal swing honeycomb zeolite concentrator, Journal of Air & Waste Management Association, 53, 2003, 1384–1390.

[9] Dobre T., Parvulescu O.C., Iavorschi G., Stroescu M., Stoica A.: EXPERIMENTAL STUDY OF VOCs ADSORPTION ONTO FIXED BED ACTIVATED CARBON, Analele Universităŉii din Oradea Fascicula: Ecotoxicologie, Zootehnie si Tehnologii de Industrie Alimentară, 2010, 1241 – 1246.

[10] Falth L., Hakansson U., Hansen S.: Structure of synthetic zeolite Na-P2, Acta Crystallographica Section C: Crystal Structure Communications, 46, 1990, 1361–1362.

[11] Gangil S., Mewar Ch., Jha R., Kumar J., Malviya L., Modhera B.: Performance of 13X Zeolite for Volatile Organic Compound Adsorption by Pressure Swing Adsorption, Int. Conf. on Advances in Chemical Engineering and Technology, ICACE TKMCE, 2014, 41–44.

[12] Garcia G., Cardenas E., Cabrera S., Hedlund J., Mouzon J.: Synthesis of zeolite Y from diatomite as silica source, Microporous and Mesoporous Materials, 219, 2016, 29–37.

[13] Hellen H., Hakola H., Reissell A., Ruuskanen T.M.: Corbonyl compounds in boreal coniferous forest air in Hyytiala, Southern Finland, Atmospheric Chemistry and Physics, 4, 2004, 1771–1780.

[14] Hilal G.: Liquid Phase Hydrogenation of Citral on Zeolite Supported Monometallic (Ni,Pt) and Bimetallic (Ni, Sn), (Pt-Sn) Catalysts, MSc Thesis, Izmir Institute of Technology, 2005.

[15] Hildebrando E.A., Bastos Andrade Ch.G., Ferreira da Rocha Junior C.A., Angélica R.S., Valenzuela-Diaz F.R., de Freitas Neves R.: Synthesis and Characterization of Zeolite NaP Using Kaolin Waste as a Source of Silicon and Aluminum, Materials Research, 17(1), 2014, 174–179.

[16] Htay M.M., Oo M.M.: Preparation of Zeolite Y Catalyst for Petroleum Cracking. World Aademy of Science, Engineering and Technology, 48, 2008, 114–120.

[17] Huang W.L., Liu B.J., Sun F.M., Zhang Z.H., Bao X.J.: Synthesis and characterization of thermally stable MCM-41/γ-Al2O3 composite materials, Microporous and Mesoporous Materials, 94, 2006, 254.

[18] Jha B., Singh D.N.: Fly Ash Zeolites, Advanced Structured Materials, 78, 2015, 5–31.

[19] Jiang Ch., Li S., Zhang P., Wang J.: Pollution level and seasonal variations of carbonyl compounds, aromatic hydrocarbons and TVOC in a furniture mall in Beijing, China, Building and Environment, 69, 2013, 227–232.

[20] Kazemimoghadam M., Mohammadi T.: Preparation of nano pore hydroxysodalite zeolite membranes using of kaolin clay and chemical sources, Desalination, 278, 2011, 438–442.

[21] Khan F.I., Ghoshal A.Kr.: Removal of Volatile Organic Compounds from polluted air, Journal of Loss Prevention in the Process Industries, 13, 2000, 527–545.

[22] Kulprathipanja S., Flanigen E.M., Broach R.W., Wilson S.T.: Zeolites in Industrial Separation and Catalysis, Chapter 1. Introduction. Wiley-VCH Verlag GmbH & Co. KGaA, 2010, 1–26.

[23] Mark J.E.: Physical Properties of Polymers Handbook: Edition, Springer Science & Business Media, Berlin, 2007, 296–298.

[24] Meng Q., Liu B., Piao J., Liu Q.: Synthesis of the composite material Y/ASA and its catalytic performance for the cracking of n-decane. Journal of Catalysis, 290, 2012, 55–64.

[25] Omoleye J. A., Hymore F.K., Babalola R., Adefila S. S., Ajayi O.A.: Comparative Analysis of Zeolite Y From Nigerian Clay and Standard Grade. International Conference on African Development Issues (CU-ICADI) 2015: Materials Technology Track, 2015, 179–182.

[26] Penkaj S., Su-Jung J., Moon-Hee H., Churl-Hee Ch.: Influence of the silica precursors on octahedron shaped nano NaY zeolite crystal synthesis, Journal of the Taiwan Institute of Chemical Engineers, 000, 2015, 1–7.

[27] Pliś I., Prokop W., Petrus R., Warchoł J.: Sorption of acetone onto clay materials, 12 Scientific Conference POL-EMIS, Karpacz 4-7 June 2014.

[28] Qi J., Li J., Li Y., Fang X., Sun X., Shen J., Han W., Wang L.: Synthesis of porous carbon beds with controllable pore structure for volatile organic compounds removal, Chemical Engineering Journal, 307, 2017, 989–998.

[29] Qiu W., Dou K., Zhou Y., Huang H., Chen Y., Lu H.: Accepted Manuscript. Hierarchical pore structure of activated carbon fabricated by CO2/microwave for VOCs adsorption, Chinese Journal of Chemical Engineering, 2017.

[30] San Cristobal A.G., Castello R., Martin Luengo M.A., Vizcayno C.: Zeolites prepared from calcined and mechanically modified kaolins. A comparative study, Applied Clay Science, 49, 2010, 239–246.

[31] Sang S., Liu Z., Tian P., Liu Z., Qu L., Zhang Y.: Synthesis of small crystals zeolite NaY, Material Letters, 60, 2006, 1131–1133.

[32] Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquerol J., Siemieniewska T.: Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosit, Pure and Applied Chemistry, Vol. 57, No. 4, 1985, 603–619.

[33] Tan Q.F., Bao X.J., Song T.C., Fan Y., Shi G., Shen B.J., Liu C.H., Gao X.H.: Synthesis, characterization, and *catalytic* properties of hydrothermally stable macro-meso-micro-porous composite materials synthesized via in situ assembly of preformed zeolite *Y* nanoclusters on kaolin, Journal of Catalysis, 251, 2007, 69.

[34] Tang L., Li L., Chen R., Wang Ch., Ma W., Ma X.: Adsorption of acetone and isopropanol on organic acid modified activated carbons, Journal of Environmental Chemical Engineering, 4, 2016, 2045–2051.

[35] Tittarelli F., Giosue C., Mobili A., Ruello M.L.: Influence of binders and aggregates on VOCs adsorption and moisture buffering activity of mortars for indoor applications, Cement and Concrete Composites, 57, 2015, 75–83.

[36] Ugal J.R., Hassan K.H., Ali I.H.: Preparation of type 4A zeolite from Iraqi kaolin: Characterization and properties measurements, Journal of the Association of Arab Universities for Basic and Applied Sciences, 9, 2010, 2–5.

[37] United States Environmental Agency, Office of Air Quality, Technical bulletin, Zeolite a versatile air pollutant adsorber, 1998, http://www.epa.gov/ttn/catc.

[38] Warzybok M., Chverenchuk A., Warchoł J.: Acetone adsorption on synthesized zeolite from natural clay material, Czasopismo Inżynierii Lądowej, Środowiska i Architektury – Journal of Civil Engineering, Environment and Architecture, JCEEA, z. 62, t. XXXII (3/I/15), 2015, 487–495, DOI:10.7862/rb.2015.132.

[39] White D.H.: Compressed Air and Gas Purification and Fractionation for High Purity Applications by Improved PSA Processes, Separation Science and Technology, 43, 2008, 2298–2306.

[40] Yuan W., Yuan P., Liu D., Deng L., Zhou J., Yu W., Chen F.: A hierarchically porous diatomite/silicalite-1 composite for benzene adsorption/desorption fabricated a facile pre-modification in situ synthesis route, Chemical Engineering Journal, 294, 2016, 333–342.

[41] Zhang M., An T., Fu J., Sheng G., Wang X., Hu X., Ding X.: Photocatalytic degradation of mixed gaseous carbonyl compounds at low level on adsorptive TiO_2/SiO_2 photocatalyst using a fluidized bed reactor, Chemosphere, 64, 2006, 423–431.

[42] Zhang P.: Adsorption and Desorption Isotherms, KE Group, 2016.