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CHARACTERISTICS OF NATURAL AND SYNTHETIC MOLECULAR SIEVES AND STUDY OF THEIR INTERACTIONS WITH FRAGRANCE COMPOUNDS

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Abstract: Structural, physicochemical and adsorption properties of two natural and one synthetic molecular sieves were investigated by various techniques: X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, low-temperature nitrogen adsorption and inverse gas chromatography. The influence of these properties on the ability to adsorb two model fragrances: *p*-cymene and menthol was studied. The free enthalpy, entropy and Gibbs free energy of adsorption of fragrance molecules on the surface of zeolite and zeolite-like materials were estimated by using inverse gas chromatography. Also, the influence of temperature on the stability of solid-fragrance compound systems as well as the release of the adsorbed fragrance compounds was studied. The obtained results exhibit that both porosity and chemical composition of molecular sieves influence the size and strength of adsorption of fragrance compounds. The study indicated different release characteristics for *p*-cymene and menthol.

Keywords: *molecular sieves, fragrance compounds, adsorption properties, thermodynamic parameters, thermal stability*

Introduction

Molecular sieves have been and continue to be very important industrial materials. They possess unique adsorption and catalytic properties and therefore they find application in environmental protection, agriculture, engineering, process industries and medicine (Murray, 2000; Weitkamp, 2000; Siriwardane et al., 2003; Canli et al., 2013). Molecular sieves are materials with a well-developed surface area and large pore volume. In these solids dominate adsorption of molecules that fit snugly inside the pores and exclude molecules that are too large. The most common natural molecular sieves are zeolites (Szostak, 1998). These minerals are a group of crystalline aluminosilicates, composed of TO_4 tetrahedra (T = Si, Al) bound by shared

oxygen atoms. Zeolites form many different crystalline structures and have large open pores (cavities) in the same size as many molecules (Roth et al., 2014). Also palygorskite (hydrated magnesium aluminum silicate mineral) exhibits the characteristics of molecular sieves. These material has high surface area and the inverted structure, which leaves parallel channels through the lattice (Murray, 2000).

Molecular sieves are characterized by high selectivity and high adsorption capacity. To increase the adsorption capacity of zeolites different activation methods (acid activation, heat activation or modification) can be applied (Canli et al., 2013). Molecular sieves are good matrices for placement in them nanosized particles with specific properties. Zeolites are effective materials for the selective adsorption and storage various gases, e.g. carbon dioxide, hydrogen (Chang et al., 2013; Chen et al., 2014; Fujiwara et al., 2014; Thang et al., 2014). Molecular sieves are also used as drug carriers (Rivera et al., 2003; Horcajada et al., 2004), matrices for pigments (Kowalak and Jankowska, 2003) or fragrance compounds carriers (Gu et al., 2008; Strzemiecka et al., 2012, Tekin et al., 2015). The effective retention of volatile aroma on a solid support is very important issue (Madene et al., 2006; Nedovic et al., 2011). Even small amounts of fragrance can be expensive and, because they are usually unstable and can degrade, preserving them is often a top concern of manufacturers. Retention of fragrance compounds on molecular sieves brings many advantages: decrease the evaporation rate of the fragrance, reduce the reactivity of the fragrance with the outside environment or stabilise and protect the fragrance during storage (Van Soest, 2007). In addition, it allows controlled release of fragrances under appropriate conditions. Molecular sieve-fragrance compound systems are applied in industry for various reasons, e.g. to increase the attractiveness of the product or to mask unpleasant smells.

Zeolites with trapped fragrance molecules in their channels or cage-like structures are used as a perfume delivery systems in laundry detergents (Pan et al., 1997; Barket Jr. et al., 1999; Marin et al., 2004; Portabales et al., 2005). Solid carrier-fragrance compound systems coated with water-soluble but perfume-insoluble material or coated both with a hydrophobic oil and a water-soluble/water-dispersible material provide effective and efficient delivery of perfume from a laundry bath onto fabric surfaces. These systems provide the benefit of continued smell release from laundered fabrics when exposed humidity or heat while being stored, dried or ironed. The perfume-loaded zeolite particles are used to impart a fragrance to a second material, such as animal litter, bath salts, carpet cleaners, room deodorizers or fabric softeners, through simple physical admixture (Dente and Weston, 2002; Dente, 2007). Molecular sieve-fragrance compound systems are also applied in scented candles that release desirable fragrances (Welch et al., 2003; 2007). These systems allow for incorporation of greater amounts of the perfume to the product. The proposed solution allows to increase the longevity of fragrance, both before and after burning, and increase fragrance intensity during burning of candles. The patent shows the loading of

fragrance onto the porous inorganic carrier molecule and adding the perfume-loaded zeolite particles to the candle manufacturing material.

Zeolite-based carriers for fragrance are reported practically only in patents and the literature lacks academic research papers on the sorption of fragrance in zeolites. This publication attempts to explain the adsorption behaviour of selected fragrance compounds on molecular sieves and to find correlations between the structure, morphology and chemical composition of molecular sieves and their adsorption properties. Very often during production or exploitation molecular sieve-fragrance compounds systems are exposed to high temperatures. Therefore, it is important to examine thermal stability of these systems and to determine fragrance release from systems at various temperatures. However, to the best of our knowledge, this issue has been poorly investigated so far.

In this research structural, physicochemical and adsorption properties of natural and synthetic molecular sieves were examined. The influence of these properties on the ability to adsorb two fragrance compounds was studied. *p*-cymene and menthol were employed as two model fragrances. Basic thermodynamic parameters (ΔH° , ΔS° , ΔG°) for adsorption of fragrance molecules on the surface of molecular sieves at infinite dilution were determined by IGC. The results presented in this paper are a continuation of the previous work (Strzemieska et al., 2012). The study was extended, the molecular sieve-fragrance compound systems were prepared and their thermal stability were examined. The release of the adsorbed terpenes at different temperatures was studied by TG and HS-GC/MS analysis.

Experimental

Three molecular sieves were used: 1. natural ZC20, 2. natural ZG (from Certech Niedomice, Poland), and synthetic material Al-MSU-F (from Sigma Aldrich, Poland). Al-MSU-F is mesoporous high-silica zeolite (Al content = 3%). Individual analysis techniques typically probe only a particular aspect of the material and, therefore, a combination of methods was necessary to give a complete description of studied materials.

X-ray powder diffraction (XRD) patterns were carried out on D8 Advance (Bruker) diffractometer using CuK α radiation ($\lambda=0.15418$ nm) and Ni filtering. The patterns were measured in the 2θ interval from 5° to 57° , with a step size of 0.03° and 2 s counting time per step. The chemical compositions of the samples were determined by X-ray photoelectron spectroscopy (XPS) analyses on multichamber UHV system (Prevac) equipped with an Mg K α source ($E=1253.6$ eV), at a pressure less than $1.5 \cdot 10^8$ mbar. The morphology of natural and synthetic materials were examined by transmission electron microscopy. The TEM images were collected on Philips EM300. The textural properties were determined by nitrogen sorption analysis at -196°C using a conventional volumetric technique on a ASAP 2420 sorptometer (Micromeritics). Before experiments the samples were outgassed at 200°C in a vacuum chamber. The

surface area was measured by BET method and the total pore volume was estimated on the basis of the amount of nitrogen adsorbed at $p/p_o = 0.98$. The t-plot method was used to calculate the micropore volume.

IGC measurements were carried out by using Varian 430GC gas chromatograph equipped with flame-ionization detector (FID). High purity helium was used as carrier gas (flow rate of 15 cm³/min). The temperature of injector and detector was 200 °C and column oven: 100 °C, 120°C, 160°C and 180°C. Chromatographic columns were from Teflon, I.D. 4 mm, length 30 cm. Measurements were carried out at infinite dilution which means that a very small amount of test compounds was injected onto the chromatographic column filled with investigated materials. To determine the dispersive component of the free surface energy γ_S^D nonpolar test compounds were used: hexane (Chempur, purity 99%), heptane (Sigma-Aldrich, purity 99%), octane (Fluka, purity 99%) and nonane (Acros Organics, purity 99%). To determine the basic thermodynamic parameters (ΔG° , ΔH° , ΔS°) two terpenes were used: menthol (Sigma-Aldrich, purity 99%) and *p*-cymene (Aldrich, purity $\geq 97\%$).

The γ_S^D parameters can be calculated (according to Schultz and Lavielle method) by Eq. (1):

$$R \cdot T \cdot \ln V_N = 2 \cdot N \cdot a_m \cdot \sqrt{\gamma_S^D \cdot \gamma_L^D} + C \quad (1)$$

where R is the gas constant; 8.314 (J/mol·K), T temperature of measurement (K), V_N net retention volume (m³), N the number of Avogadro, a_m cross sectional area of the adsorbate (m²), γ_S^D the dispersive component of surface free energy (mJ/m²), γ_L^D the dispersive component of the surface tension of the probe molecule in liquid state (mJ/m²), C constant.

A plot of $RT \ln V_N$ against $a_m(\gamma_S^D)^{0.5}$ yields a straight line and γ_S^D parameter can be obtained from the slope of this line (Schultz et al., 1987).

The magnitude of interactions of the fragrance compounds with studied molecular sieves can be expressed by the thermodynamic functions: energy, enthalpy and entropy of adsorption. The Gibbs free energy of adsorption ΔG° can be calculated (from retention data of test compounds) according to the following equation (Belgacem and Gandini, 1999):

$$\Delta G^\circ = -R \cdot T \cdot \ln \left(\frac{B \cdot V_N}{S \cdot m} \right) \quad (2)$$

where B is a constant (according to definition of De Boer equal $2,997 \cdot 10^8$ (1/m), S surface area of adsorbent (m²/g), m adsorbent mass in chromatographic column (g), V_N net retention volume (m³).

The free enthalpy, ΔG° , and free entropy, ΔS° , of adsorption can be determined using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (3)$$

A plot of $\Delta G^{\circ}/T$ against $1/T$ yields a straight line. The value of ΔH° can be obtained from the slope and ΔS° intercept.

The molecular sieve-fragrance compound systems were prepared using the adsorption processes. Terpenes (menthol or *p*-cymene) were dissolved in ethanol (POCH S.A., purity 99%) and mixed with Al-MSU-F (in ratio 1:1) or with natural materials (in ratio 2:1). Then mixture was stirred for three days at room temperature in a sealed flask. After this time solvent (ethanol) was evaporated under vacuum and the final product (molecular sieve-fragrance compound system) was achieved. The obtained systems were analyzed by Fourier transform infrared spectroscopy (FTIR) to verify the presence of functional groups. The spectra were recorded on a Vertex 70 spectrometer (Bruker) in 4000–400 cm^{-1} region. Also thermogravimetric analysis were used in this study. The measurements were conducted using TG 209 F1 Libra thermobalance (Netzsch Instruments). The samples were heated from 35 °C to 900 °C in nitrogen with a flow rate of 25 cm^3/min .

To examine the influence of temperature on stability of obtained molecular sieve-fragrance compound systems static headspace and GC/MS analysis was applied. The identification of substances that are emitted from systems after heating was performed. The experiment procedure was as follows. First, systems were placed in vials, sealed and heated in a thermostat block (Stuart Block Heater SBH200D). The heating temperature was: 35, 100, 120, 160 and 180 °C. The sealed vials were maintained at given temperature for 90 min. After this time, 0.01 cm^3 of gas phase was collected using a gas-tight syringe and manually injected into the capillary column (0.25 mm I.D., 30 m length). Than vials were opened and desorbed in these conditions volatile compounds were released into the atmosphere. After 30 min vials were again sealed and heating at higher temperature was started. The mass spectrometer (TurboMass) coupled with gas chromatograph (AutoSystem XL, Perkin Elmer) was used in the analysis. The oven temperature was 160 °C. The injection and transfer line temperature were kept at 250 °C. The EI source was kept at 200 °C. The ionization energy was 70 eV.

Results and discussion

Materials characterization

In this study XRD method was used to identify the crystalline phases present in the natural samples. Measured powder diffraction patterns (Fig. 1) were compared with standardized results collected in the ICDD database (International Centre for Diffraction Data). The mineralogical analysis of ZC20 indicated that the sample contains heulandite as the main mineral with impurities such as quartz, cristobalite, kalisilite and illite. In sample ZG palygorskite, leucite and quartz were detected.

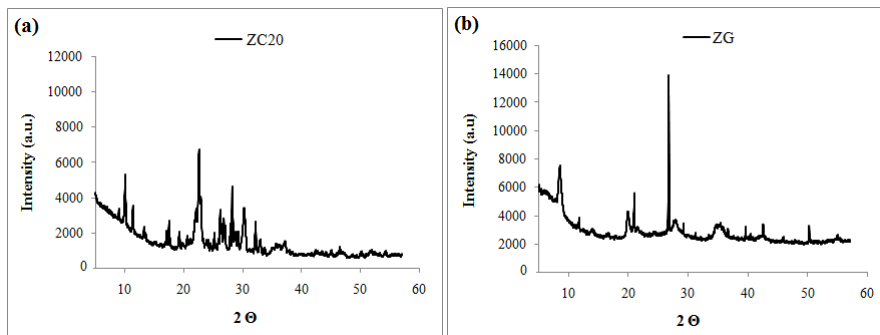


Fig. 1. XRD pattern of (a) ZC20 and (b) ZG samples

ZG possesses different phase composition than sample ZC20. These observations were also confirmed by XPS analysis which helped to determine the elemental composition of the surface layer of materials. Results indicate that ZC20 contains silicon and aluminum in addition to potassium and calcium while ZG – potassium, magnesium and iron (Table 1).

Table 1. Chemical composition of natural materials

Sample	Atomic %							
	Si	Al	Ca	K	Mg	Fe	O	C
ZC20	19.9	5.4	1.1	1.8	–	–	58.6	13.2
ZG	25.5	7.9	–	0.6	3.1	1.1	55.7	6.1

The TEM images of ZC20 and ZG (Fig. 2a and b) also proved another morphology of these two materials. Fibrous forms for ZG sample were observed. Moreover, the TEM image of Al-MSU-F (Fig. 2c) confirms that this material has cellular foam structure.

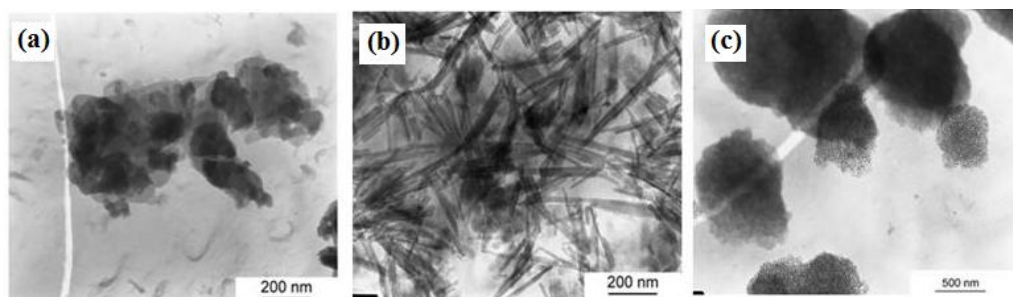


Fig. 2. TEM images of (a) ZC20, (b) ZG and (c) Al-MSU-F samples

In order to characterize the porous structure of the examined molecular sieves low-temperature, nitrogen adsorption was used. For the Al-MSU-F, the adsorption/desorption isotherm (Fig. 3c) displays a type IV of the IUPAC classification (Sing et

al., 1985) with a H1 hysteresis loop which is a typical characteristics of mesoporous material (Kim et al., 2000). A well-defined step occurs at relatively high pressure of 0.6–0.95, corresponding to capillary condensation of N₂ within mesopores. The isotherms measured for natural materials (Fig. 3a, b) also can be considered as isotherms of IV type but with the hysteresis loop of the type H3 according to IUPAC classification. For ZC20 and ZG the values of *a* parameter obtained for each *p/p*₀ were several times lower than for the synthetic aluminosilicate. The isotherms shapes of natural samples indicate the presence of mesopores in minerals. Analogous results for natural zeolite were reported in (Korkuna et al., 2006; Sprynskyy et al., 2010).

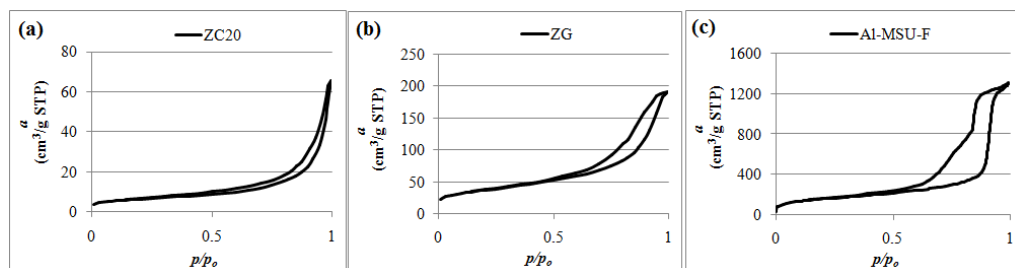


Fig. 3. Nitrogen adsorption-desorption isotherms of (a) ZC20, (b) ZG, (c) Al-MSU-F samples

Materials surface area, pore volume and pore size are summarized in Table 2. Synthetic aluminosilicate has about 4-times higher surface area than ZG and about 25-times higher than ZC20. Also the largest pore volume was found for Al-MSU-F. All tested molecular sieves contain both mesopores and micropores.

Table 2. Textural properties of tested molecular sieves

Sample	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Pore size (nm)
ZC20	22.8	0.092	0.002	22.2
ZG	130.2	0.296	0.01	10.8
Al-MSU-F	547.8	1.976	0.02	16.6

Surface properties of molecular sieves at various temperatures (100–180 °C) were studied by inverse gas chromatography. The surface energy is an important property controlling many practical applications. The surface energy can affect catalytic activity, strength of particle–particle and be crucial to adsorption processes (Yla-Maihaniemi et al., 2008; Kondor and Dallos, 2014; Mohammadi-Jam et al., 2014). The dispersive component of surface free energy was calculated by Eq. (1) and received results were presented in Fig. 4. In all temperatures the highest values of γ_S^D parameter were obtained for material ZG while the smallest for ZC20. It was observed that γ_S^D values decrease with temperature increase and this is consistent with literature (Diaz et al., 2005; Bilgic and Tumsek, 2007; Bilgic et al., 2014). This decrease is

attributed to the entropic contribution to the surface free energy change. The highest change of surface activity with temperature increase was found for sample ZG. In temperature range 100–180 °C values of γ_S^D parameter decreased from 113.6 mJ/m² to 37.6 mJ/m².

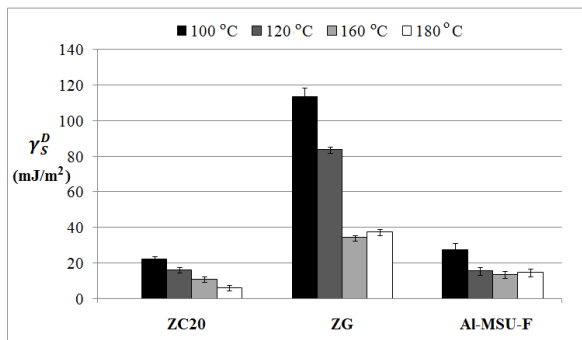


Fig. 4. The value of γ_S^D parameter for examined molecular sieves at 100 °C, 120 °C, 160 °C and 180 °C

The smallest decrease of γ_S^D value was recorded for Al-MSU-F (12.6 mJ/m²). Material ZG exhibits the highest ability to disperse interactions among the tested solids but also this mineral is the most sensitive for temperature. During the experiment surface nature of studied molecular sieves was changed: from active to semi-active for ZG and from semi-active to low-active for ZC20 and Al-MSU-F.

Characterization of fragrance compounds interactions with molecular sieves

Inverse gas chromatography was also applied for study solids ability to retain the fragrance molecules. Thermodynamic parameters (ΔG° , ΔH° , ΔS°) related to the adsorption/desorption processes are used to evaluate the physicochemical affinity between fragrance compound and examined materials (Cantergiani and Benczedi, 2002; Reutenauer and Thielmann, 2003). The obtained parameters are presented in Table 3 and in Fig. 5.

Table 3. The values of ΔG° parameter at different temperatures

Temperature (°C)	ΔG° (kJ/mol)					
	ZC20		ZG		Al-MSU-S	
	CYM	MEN	CYM	MEN	CYM	MEN
100	-29.8	-35.0	-19.8	-29.4	-22.1	-28.7
120	-29.5	-32.6	-15.7	-24.1	-20.2	-27.1
160	-29.3	-30.4	-6.8	-16.8	-17.2	-25.3
180	-29.1	-29.2	-4.5	-13.6	-16.1	-23.2

The Gibbs free energy was calculated for adsorption of *p*-cymene (CYM) and menthol (MEN) on natural and synthetic molecular sieves using Eq.(2). The ΔG° values are negative which indicates that adsorption is spontaneous. The value of ΔG° parameter increases with increasing temperature which means that adsorption of terpenes on molecular sieves is more favourable at lower temperatures. The highest decrease was recorded for ZG–menthol system (15.8 kJ/mol). For each temperatures and for each materials, the free energy of adsorption of menthol is more negative than the corresponding free energy of adsorption of *p*-cymene. This was reflected in the obtained values of ΔH° and ΔS° parameters. The values of Gibbs free energy of adsorption of *p*-cymene on ZC20 received at each temperature are similar, the differences are within the error limits. This means that for this particular system the influence of temperature on adsorption is not significant.

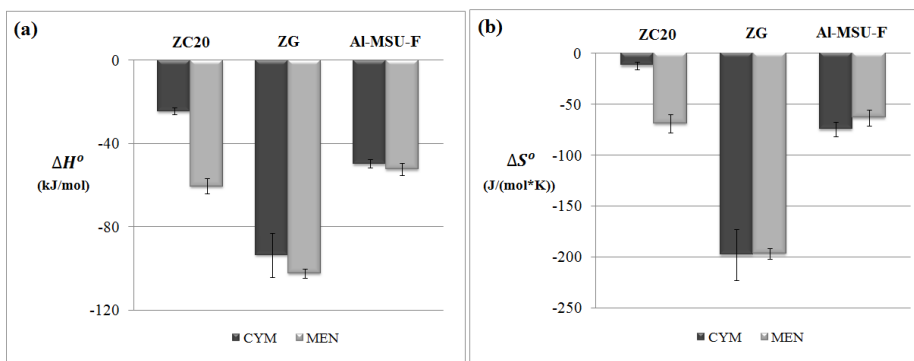


Fig. 5. Free enthalpy (a) and entropy (b) of adsorption of fragrance compounds on natural and synthetic molecular sieves

The values of ΔH° and ΔS° parameters were determined from the slope and intercept from the plot of $\Delta G^\circ/T$ versus $1/T$ given in Eq. (3), respectively. The negative values of ΔH° indicates that the adsorption processes were exothermic. The more negative value of enthalpy, the greater interaction between the fragrance compound (adsorbate) and the molecular sieve (adsorbent) (Qin et al., 2014). For all materials stronger interactions with menthol than *p*-cymene were found (Fig. 5a). Most likely, this is associated with the presence of functional group ($-\text{OH}$) in menthol molecule and formation the hydrogen bonds between fragrance and solid. However, interactions of *p*-cymene with ZG and Al-MSU-F were only slightly weaker. This indicates that the Van der Waals forces are involved in the adsorption of *p*-cymene (aromatic hydrocarbon). The magnitude of interactions is related to the hydrophilic-hydrophobic nature of the materials surface. The strongest interactions were observed for material ZG (silicate) which is more hydrophobic than the other two solids (aluminosilicates). The obtained values of ΔS° parameter suggest that the adsorption processes of terpenes on ZC20 and Al-MSU-F were more random than on ZG.

Characterisation of obtained molecular sieve-fragrance compound systems

In the initial phase of this study molecular sieve-fragrance compound systems were obtained in various proportions. Systems were weighed and solvent remaining after the process was analysed by GC (determination of not adsorbed terpenes). Loading capacity was determined using the following equation:

$$\% \text{ loading} = \left(\frac{\text{weight of adsorbed terpene}}{\text{weight of obtained system}} \right) \cdot 100\% . \quad (4)$$

Systems for which adsorption processes were the most effective have been selected for further investigations. For presented in this research systems % loading was: 11.6, 30.4, 9.4, 13.9, 46.7 and 56.5 for ZC20_CYM, ZC20_MEN, ZG_CYM, ZG_MEN, Al-MSU-F_CYM and Al-MSU-F_MEN systems, respectively. In addition, the successful preparation of molecular sieve-fragrance compound systems was confirmed by infrared spectroscopy. The selected spectra are shown in Fig. 6.

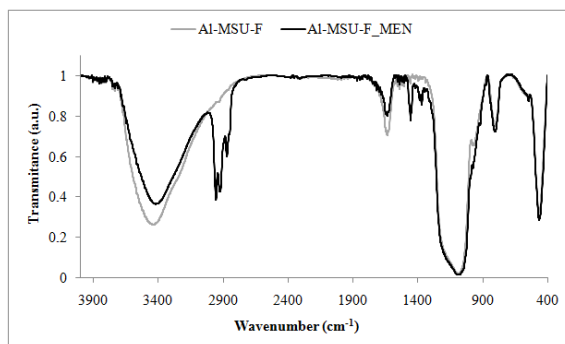


Fig. 6. The FTIR spectra of Al-MSU-F and its system with menthol (Al-MSU-F_MEN)

The spectrum obtained for Al-MSU-F_MEN system contains bands characteristic for this fragrance. The bands at 2955, 2924 and 2871 cm^{-1} are assigned to C–H stretching vibration and the bands at 1455, 1385 and 1370 cm^{-1} to C–H bending vibration.

The created molecular sieve-fragrance compounds systems were investigated by thermogravimetric analysis. TGA was used to determine the weight loss related to the release of fragrance from the sample. However, it should be noted that weight loss is also associated with water desorption. The obtained results agreed well with previous data: the higher % loading the higher mass changes observed in TG. The weight loss for systems with menthol was higher than for systems with *p*-cymene (Table 4). This indicates that less *p*-cymene was adsorbed by the studied molecular sieves and this is compatible with the conclusions drawn from the obtained values of thermodynamic parameters. Material Al-MSU-F due to the large surface area and high pore volume adsorbed more *p*-cymene and menthol than other materials (the total weight loss equals 45.0% and 59.7 % for Al-MSU-F_CYM and Al-MSU-F_MEN, respectively).

However, the interactions between terpenes and synthetic molecular sieve are weaker in comparison to the interactions between fragrances and natural materials and therefore desorption of aromatic compounds from Al-MSU-F was more rapid. For systems of natural materials with menthol the largest weight loss was recorded between 120–160 °C.

Table 4. Results of thermogravimetric analysis

Sample	Mass change (%)				
	to 100 °C	to 120 °C	to 160 °C	to 180 °C	to 900 °C
ZC20	2.7	3.5	4.7	5.1	8.6
ZC20_CYM	2.7	3.6	5.0	5.5	9.8
ZC20_MEN	4.6	9.6	31.1	31.8	35.1
ZG	4.5	6.4	9.5	10.0	17.3
ZG_CYM	4.5	6.8	9.9	10.5	19.2
ZG_MEN	5.9	17.2	25.2	25.7	33.6
Al-MSU-F	2.8	2.9	2.9	2.9	3.0
Al-MSU-F_CYM	44.6	44.9	44.9	45.0	45.0
Al-MSU-F_MEN	34.6	40.6	56.9	59.0	59.7

Mass changes for unloaded natural materials and *p*-cymene loaded ZC20 and ZG systems were close to each other. Before the adsorption of fragrance compounds, molecular sieves were dried in a balance-dryer at 160 °C in order to desorb physically bounded water and to increase the adsorption capacity of materials. It is assumed that the free spaces created after the partial desorption of water molecules were than occupied by fragrances. Therefore, the mass changes for systems are the result of the desorption of water and fragrance molecules. In contrast, unloaded molecular sieves were not dried before TG analysis thus they contain more water molecules than loaded solids. Probably, the comparable weight changes for ZC20, ZG and ZC20_CYM, ZG_CYM systems are associated with the fact that the unloaded and loaded materials release similar amounts of molecules but for the raw carriers there are only water molecules and for systems there are water and fragrance molecules.

Although results of TG analysis show that in the case of ZC20_CYM and ZG_CYM systems weight loss in the temperature range of 35–100 °C is small, the HS-GC/MS analysis suggests that the desorption of *p*-cymene in these conditions was significant. The chromatograms recorded after injection vapor from samples heated at 35 °C and 100 °C contain intense peaks of *p*-cymene (Fig. 7a). Probably, *p*-cymene is released in two stages. The part of the *p*-cymene adsorbed on the natural materials surface is released below 100 °C (this explains the intense signals of *p*-cymene on chromatograms recorded after heating systems at 35 °C and 100 °C). The remaining part of *p*-cymene strongly retained within the pores is released at higher temperatures (above 180 °C). Therefore, this was not observed by HS-GC/MS analysis but only by TG analysis. For Al-MSU-F_CYM system results of TG and HS-GC/MS analysis

were the same: intensive desorption of *p*-cymene was observed to 120 °C and only a very small percentage of *p*-cymene was released at higher temperatures. The characteristics of menthol release from the Al-MSU-F_MEN system determined by both experiments were also compatible. However, for systems of natural materials with menthol unexpected phenomenon has been noticed. After heating ZG_MEN system at 100 °C and ZC20_MEN system at 180 °C emitted vapours contain besides menthol also another substance (Fig. 7b). The analysis demonstrated that part of menthol was dehydrated to the 3-menthene (identification was made by a comparison of the measured mass spectrum with the mass spectra collected in the NIST database). Therefore, for these two systems long heating is not recommended because it causes undesirable transformation of menthol.

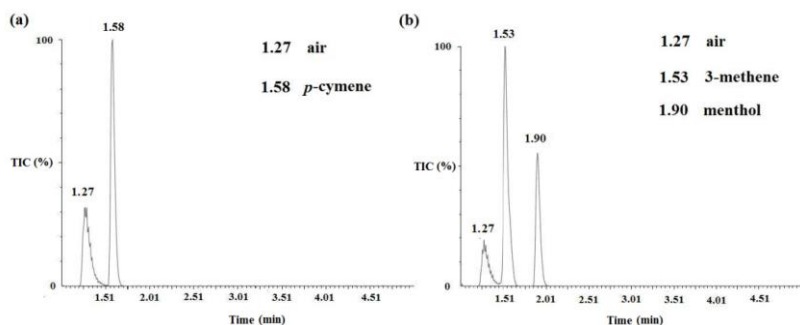


Fig. 7. Chromatograms of volatile compounds emitted from (a) ZC20_CYM system after heating at 35 °C, (b) ZG_MEN system after heating at 180 °C

Conclusions

Natural and synthetic molecular sieves having different structure, morphology and chemical composition were investigated. These differences were reflected in adsorption properties of materials. The performed study showed that both porosity and chemical composition influences the size and strength of adsorption of fragrance compounds. The largest amount of *p*-cymene and menthol was adsorbed by material Al-MSU-F which has the highest surface area and total pore volume. However, the strongest interactions between terpenes and studied materials were found for sample ZG. This solid has more hydrophobic surface and higher values of γ_S^D parameter at all temperatures than other studied molecular sieves. The release of the adsorbed fragrances, evaluated by thermogravimetric analysis and HS-GC/MS analysis, indicated different release characteristics for *p*-cymene and menthol.

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