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Examination of zeolites as fragrance carriers

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ABSTRACT

Zeolites are well-known as very good adsorbents used, e.g. for water purification, gas drying and removal of harmful compounds. They are also used as molecular sieves for separation of mixtures of different compounds. Zeolites may also serve as fragrance carriers. This paper presents surface properties of natural and synthetic zeolites and influence of these properties on the ability to adsorb several fragrance compounds: citral, p-cymene, geraniol, menthol. The enthalpy, entropy and energy of adsorption of these compounds on the surface of studied zeolites were estimated using of inverse gas chromatography (IGC). Activity of the zeolites surface was expressed by the value of the dispersive component of the free surface energy γ_S^D. γ_S^D parameter was determined by means of inverse gas chromatography at 35 °C and various humidity. Zeolite structure was determined by XRD and nitrogen sorption. IGC derived experimental data concerning adsorption of fragrance on zeolites have been discussed using structural and affinity QSAR characteristics obtained by from DFT and Hyperchem procedures. Obtained results prove that both studied zeolites can be successfully applied as fragrance carrier.

1. Introduction

Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimension. The primary structural units of zeolites are the tetrahedra of silicon and aluminum ($[SiO_4]^{4-}$and$[AlO_4]^{4-}$). The framework contains well organized and regular system of channels and cages. Inside these voids are water molecules and small cations which compensate the negative framework charge and can be easily exchanged by other ions. In these solids dominate adsorption of molecules that fit snugly inside the pores and exclude molecules that are too large. Thus, zeolites act as sieves on a molecular scale and belong to the family of molecular sieves [1]. They are very good matrices for hosting nanosized particles because of large variety of crystalline structures with different pore sizes and shapes. Zeolites can absorb large amounts of molecules both in the gas and in liquid phases. Moreover, they are nontoxic and have good thermal and chemical stability. Due to this, they became very popular in different areas of chemical research and are widely used in industrial, agricultural, environmental and biological technology. They are applied for water purification, gas drying, separation of mixtures of different compounds. The use of zeolites as fragrance carriers is relatively poorly known because adsorption behaviour of these compounds on molecular sieves is still under investigation. However, this issue seems to be very promising [2].

Surface properties of solids are crucial to adsorption process. Inverse Gas Chromatography (IGC) was used as main technique for studying surface characteristics of zeolites. IGC is an extension of conventional gas chromatography. In this method the examined material is placed in the chromatographic column and its properties are concluded based on retention behaviour of carefully selected test compounds [3–6]. Thanks to IGC method it was also possible to describe adsorption process on zeolites of fragrance compounds: citral, p-cymene, geraniol, menthol. Adsorption of these fragrance compounds on the zeolite surface was examined in thermodesorption experiment [7,8]. The use of retention data of test solutes allowed the calculation of the Gibbs free energy, enthalpy and entropy of adsorption of fragrance compounds on the zeolites surface. These parameters give information e.g. on the nature and magnitude of the interactions.

2. Inverse gas chromatography – calculations

2.1. Dispersive properties

γ_S^D parameter was calculated according to Schultz and Lavielle method based on the Eq. (1) [3–4,9–11]:

$$R \cdot T \cdot \ln V_N = 2 \cdot N \cdot a \cdot \sqrt{\gamma_S^D \cdot \gamma_L^D} + C \tag{1}$$

where:
R – the gas constant, 8.314 [J/mol·K];
T – temperature of measurement [K];
V_N – net retention volume [m^3];

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N – the number of Avogadro, 6.023×10^{23} [1/mol];
a – cross sectional area of the adsorbate [m^2];
γ_S^D – the dispersive component of surface free energy [mJ/m^2];
γ_L^D – the dispersive component of the surface tension of the probe molecule in liquid state [mJ/m^2];
C – constant.

This is the straight line equation ($y = a_1x + b$), in which:

$$R \cdot T \cdot \ln V_N = y \quad a \cdot \sqrt{\gamma_L^D} = x \quad 2 \cdot N \cdot \sqrt{\gamma_S^D} = a_1 \quad C = b$$

and γ_S^D is determined from the slope.

2.2. Characterization of fragrance interactions with zeolites

The magnitude of interactions of the fragrance compounds with the examined zeolites might be expressed by the thermodynamic functions as Gibbs free energy, enthalpy and entropy of adsorption. This might be obtained through IGC experiments where the fragrances are used as very specific test solutes. Such results should allow better understanding of the adsorption mechanism of these compounds on the studied solids.

ΔG^o values the free energy of adsorption might be determined from retention data of test solutes according to the following relationship [4,12–15]:

$$\Delta G^0 = -RT\ln\frac{BV_N}{Sg} \tag{2}$$

where:

$B = 2.99 \times 10^8$ [1/m] (according to definition of de Boer), S – surface area of adsorbent [m^2/g], g – adsorbent mass in chromatographic column [g], V_N – net retention volume [m^3].

The enthalpy of adsorption ΔH^o was calculated from ΔG^o dependence on temperature:

$$\Delta G^o = \Delta H^o - T \cdot \Delta S^o \tag{3}$$

where:

ΔG^o – the free energy of adsorption [J/mol], ΔS^o – the entropy of adsorption [J/(mol K)]. Plotting $\Delta G^o/T$ versus $1/T$ the values of ΔH^o and ΔS^o can be deduced from the slope and the intercept, respectively.

3. Experimental

3.1. Materials

Two adsorbents were examined: natural zeolite Micro20 (Certech Niedomice, Poland) and synthetic molecular sieve (MSU-S) which was prepared as described in [16,17]. However, Aerosil 200 V was used as silicon source instead sodium silicate. The procedure of MSU-S synthesis was as follows:

NaOH (cz.d.a, Chempur) and sodium aluminate (30% Na_2O, 44% Al_2O_3, POCH) were dissolved in distilled water. Aerosil200 V (Degussa, Germany) was added to NaOH solution with vigorous stirring. The mixture was stirred at room temperature for about 1 h and then heated under reflux with moderate stirring at 100 °C overnight. The second step of the synthesis was addition of "zeolite seeds" solution to a solution of CTAB (hexadecyltrimethylammonium bromide, Sigma Aldrich) in distilled water at room temperature. After 1 h stirring the appropriate amount of sulfuric acid was added to obtain pH = 9–10 and then stirring was continued overnight. The gel was crystallized for 42 h at 100 °C under static conditions. The final solid products was separated by filtration, washed with distilled water and dried in air overnight. Then the samples were calcinated in air at 540 °C for 7 h to remove the template.

3.2. Characterization of zeolites

3.2.1. Inverse gas chromatography experiments

In the present work IGC measurements were carried out by using two gas chromatographs:

- iGC (Surface Measurements Systems Ltd., London, U.K.) with flame-ionization detector; chromatographic columns – glass, silanized inside, I.D. 4 mm, length 30 cm; this equipment gave possibility to study zeolites surface at different relative humidity,
- SRI 8610C gas chromatograph produced by SRI Instruments (USA) equipped with flame-ionization detector; chromatographic columns – teflon, I.D. 4 mm, length 30 cm, the temperature of injector and detector – 220 °C.

In both cases carrier gas was helium (flow rate was 35 ml/min for MSU-S for the sake of long retention time and 15 ml/min for zeolite Micro20) and measurements were undertaken at infinite dilution which means that very small amount of test compounds was injected onto the chromatographic column with examined material in order to preserve Henry's law. The presence of symmetrical peaks and repeatability of retention time assured the achievement of equilibrium conditions in the bed of tested material.

To determine dispersive component of the free surface energy, γ_S^D (at temperature $T = 35$ °C and humidity RH = 0%, RH = 40%, RH = 80%) nonpolar test compounds were used:

- pentane (p.a., POCH S.A.),
- hexane (99%, Chempur),
- heptane (99%, Sigma–Aldrich),
- octane (99%, Fluka) and
- nonane (99%, Acros Organic).

Retention data for these alkanes were recalculated according to Eq. (1).

Four fragrance molecules:

- citral: mixture of neral (*Z*-isomer) and geranial (*E*-isomer) (95%, Sigma Aldrich),
- geraniol (98%, Sigma Aldrich),
- p-cymene (99%, Sigma Aldrich),
- menthol (99%, Sigma Aldrich),

were used to determine Gibbs free energy, ΔG^o at various temperature ($T = 35$; 60; 100; 120; 160; 180 °C) from Eq. (2) and the enthalpy, ΔH and entropy ΔS^o of adsorption from Eq. (3).

Thermodesorption experiments were carried out to explain adsorption mechanism of fragrance compounds on zeolites surface and to determine the type of solid structure and estimate the contributions of micropores, mesopores and outer surface area to the adsorption process. Thielmann's procedure was applied here [7,8]. The measurement consisted of two steps. In the first, elution carried out at 35 °C. After recording the peak, which represents the mesopore adsorption according to [7,8] and reaching again the baseline, column was rapidly heated to 100 °C. Then, thermodesorption from micropores took place and the second peak was observed. In case of the strong interactions total amount of adsorbate cannot be released at 100 °C due to the slow desorption kinetics of such interactions [8]. Therefore, it is also possible that at higher temperature adsorbate might be retained in micropores by both dispersive and hydrogen bonding