

Temperature-programmed equilibrated desorption of *n*-hexane as a tool for characterization of the microporous structure of zeolites

Wacław Makowski^{a,*}, Dorota Majda^b

^a Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

^b Regional Laboratory for Physicochemical Analyses and Structural Research, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

Received 16 June 2003; received in revised form 15 September 2003; accepted 16 September 2003

Abstract

Temperature-programmed desorption (TPD) of *n*-hexane from the commercial ZSM-5 and Y zeolites, performed in a flow system using carrier gas saturated with *n*-hexane vapor, was studied by means of TG. It has been shown that the desorption is controlled by the gas–adsorbate equilibrium. The desorption profiles were fitted with the model functions based on the Langmuir adsorption model. The adsorption enthalpy and entropy values estimated as the model parameters agree with the previously reported data. Micropore volume determined from the desorption data is close to that obtained from low-temperature N₂ adsorption isotherms. Application of temperature-programmed equilibrated desorption of *n*-hexane as a method for probing micropores in zeolites was proposed.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Micropores; Zeolites; Adsorption; Temperature-programmed desorption; *n*-Hexane

1. Introduction

Zeolites, often referred to as “molecular sieves” or “shape selective catalysts”, are widely used in catalytic and separation technologies. The unique properties of zeolites result mainly from their well-defined structure, comprising microporous channels and cavities as well as from their ability of formation catalytic or adsorption centers inside the micropores. The specific pore volume and pores size distribution are essential parts of physicochemical characteristics of zeolites [1]. Adsorption of gas (usually N₂ or Ar) measured at low temperatures is a method most often used to characterize micropores (<2 nm) and mesopores (2–5) in porous solids. Several computational methods of determination of the pore sizes distributions in zeolites from the adsorption data have been developed, e.g. the Horvath–Kawazoe method [2] and the BJH method [3]. The micropore volume may be determined using the *t*-plot and the α_s -plot methods. The exact assessment of micropores from the adsorption isotherms is quite difficult [4], therefore other experimental methods for probing the porous structure of zeolites are still needed.

Since zeolites are used in separation of hydrocarbons, their sorption properties for alkanes on has been extensively studied [5]. Special attention was paid to unusual sorption properties of MFI type molecular sieves (ZSM-5 and silicalite-1). Sorption isotherms and isobars of light paraffins (*n*-C₄–*n*-C₁₀) on these materials exhibit complex profiles that may be explained in terms of dual-site Langmuir adsorption model [6–9]. Monte Carlo simulations revealed so called “commensurate freezing,” i.e. ordering of the sorbate molecules in channels of the MFI structure at high partial pressures and low temperatures [10–13].

Temperature-programmed desorption (TPD) that is a well known experimental technique, widely used for determination of concentration and strength of active sites in heterogeneous catalysts [14]. TPD measurements are typically performed under kinetic control, but the influence of readsorption or diffusion may not always be eliminated. Despite this, TPD results are often used for determination of the activation energy of desorption. TPD studies in equilibrium conditions are quite rare. Measurements of the temperature-programmed equilibrated desorption of linear alkanes on silicalite-1 [7] yielded complex profiles, closely related to the porous structure of this material. Basing on these results and the Langmuir adsorption model values of the adsorption, enthalpy and entropy were determined. The aim of this work is development of thermogravimetric

* Corresponding author. Tel.: +48-12-6324888-2245; fax: +48-12-6340515.

E-mail addresses: makowski@chemia.uj.edu.pl (W. Makowski), majda@chemia.uj.edu.pl (D. Majda).

TPED of *n*-hexane as a method for characterization of the adsorptive properties of selected zeolites, related to their microporous structure.

2. Experimental

The studies were performed using the commercial zeolites Y (Degussa, dealuminated, Si/Al = 17) and ZSM-5 (Akzo Nobel, Si/Al = 66) that were both delivered in H-exchanged form. Sodium forms of the zeolites were prepared by ion exchange in aqueous solutions of NaNO₃, the exchange ratio was about 100%. Analytical pure *n*-hexane (POCH) was used as a sorbate. Before the experiments the zeolites were pressed, crushed into small particles and sieved. Samples of about 10–20 mg of the sieve fraction 0.355–0.500 mm were used. Prior each experiment the zeolite sample was activated in situ by heating in a flow of pure Ar (ramp: 30 °C/min and 30 min at 400 °C).

Desorption measurements were performed using the TGA/SDTA851^e thermogravimeter (Mettler-Toledo). For additional TPD experiments, the differential scanning calorimeter DSC821^e (Mettler-Toledo) was employed. Porous structure of zeolites was characterized by means of nitrogen adsorption at 77 K with use of the automatic sorptometer ASAP2010 (Micromeritics).

The TPED experiments were performed at the constant partial pressure of the sorbate. The carrier gas flowing through the furnace (above the sample container) could be saturated with the vapor of the hydrocarbon, using a simple glass saturator filled with the liquid hydrocarbon and cooled using water–ice mixture. The partial pressure of the vapor determined from the Antoine equation as the vapor–liquid equilibrium pressure at 0 °C was equal to 0.06 bar [15]. After the activation, the sample was cooled to 20 °C, then a

flow of the carrier gas through the saturator was switched on and the sorption in situ started. When the mass of the sample stabilized (typically after 20 min of sorption), the TPED measurement was performed. Two types of temperature programs were applied—either the classical linear program (with the constant heating rate of 5 °C/min, up to 400 °C) or the stepwise program, consisting of several ramps (1 min at 20 °C/min) followed by isothermal segments (10 min each). Efforts have been made to suppress effects of diffusion. The fastest stabilization of the sample mass was observed when particles of the sample formed a single loose layer on the bottom of the 0.9 ml Al₂O₃ crucible.

A series of additional TPD experiments was performed using the samples with preadsorbed *n*-hexane. The activated sample was placed for ca. 20 h in a desiccator containing the liquid hydrocarbon in an open vessel and a drying agent (CaCl₂). After the sorption the sample was placed in the TG or in the DSC apparatus, and the TPD experiment with use of the linear program was immediately started. Various sample containers were used, either 0.9 ml Al₂O₃ crucibles without the cover, 0.15 ml Al₂O₃ crucibles or 0.04 ml Al DSC sample cells—both having a cover with a hole. Volumes of the smaller cells and the rate of effusion through the hole were relatively low, so that the partial pressure of the hydrocarbon quickly increased to such a level that it could control the desorption process.

3. Results

Isotherms of low-temperature N₂ adsorption for HY and HZSM-5 and the corresponding pore volume distributions calculated basing on the Horvath–Kawazoe model are presented in Fig. 1. The isotherms exhibit rapid increase in low pressure range resulting from the adsorption of N₂ in

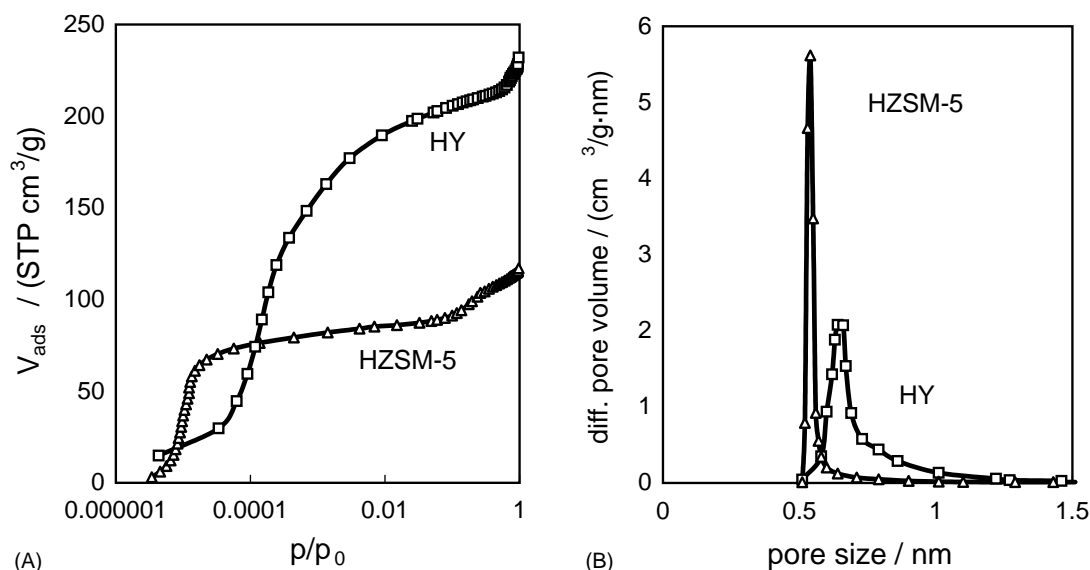


Fig. 1. Isotherms of N₂ adsorption at 78 K and the corresponding Horvath–Kawazoe differential pore volume distributions.

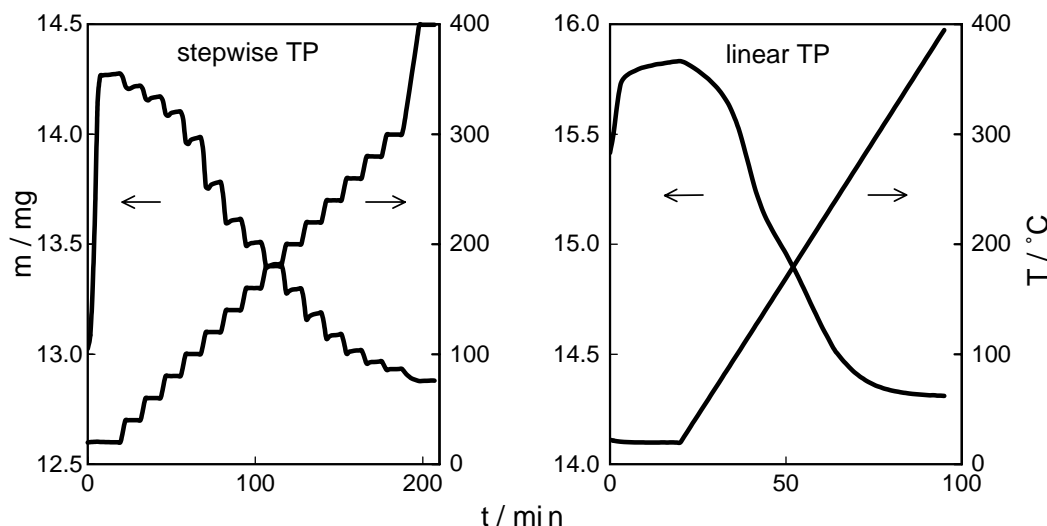


Fig. 2. Examples of the constant-pressure TPED data of *n*-hexane on HZSM-5, obtained using either the stepwise or the linear temperature program.

the micropores and very small contribution of meso- and macropores at higher pressures. Uniform pores volume distributions with maxima at 0.5 nm for HZSM-5 and 0.7 nm for HY are consistent with the pore sizes expected for the ideal MFI and FAU structures (0.53–0.55 and 0.71 nm [16], respectively).

Examples of raw data obtained in the TPED experiments (i.e. temperature profiles and the corresponding mass profiles) are presented in Fig. 2. It should be noticed that when the stepwise temperature program was used the mass of the sample stabilized during each 10 min isothermal segment—the change of the relative adsorption in the last minute was less than 0.0001, i.e. less than 0.1% of the total adsorption capacity (for HZSM-5).

The TPED results for the hydrogen exchanged zeolites are presented in Fig. 3. The profiles obtained using the

linear heating program are almost the same as the profiles measured with use of the stepwise temperature program. These curves may be regarded as isobars since they were measured at the constant pressure of the hydrocarbon and the adsorption values were not controlled by the kinetic parameters (desorption rate or diffusion). The desorption profiles of *n*-hexane for HY show one inflexion point, whereas those for HZSM-5 exhibit three inflexion points. The maximum adsorption for HY is about 70% higher than for HZSM-5.

Better representation of the desorption profiles is provided by the temperature derivatives of the adsorption profiles, presented in Fig. 4. In these curves one minimum for HY (at 150 °C) and two minima for HZSM-5 (at 114 and 196 °C) are observed. These minima may be attributed to different adsorptions sites within the porous structure of the

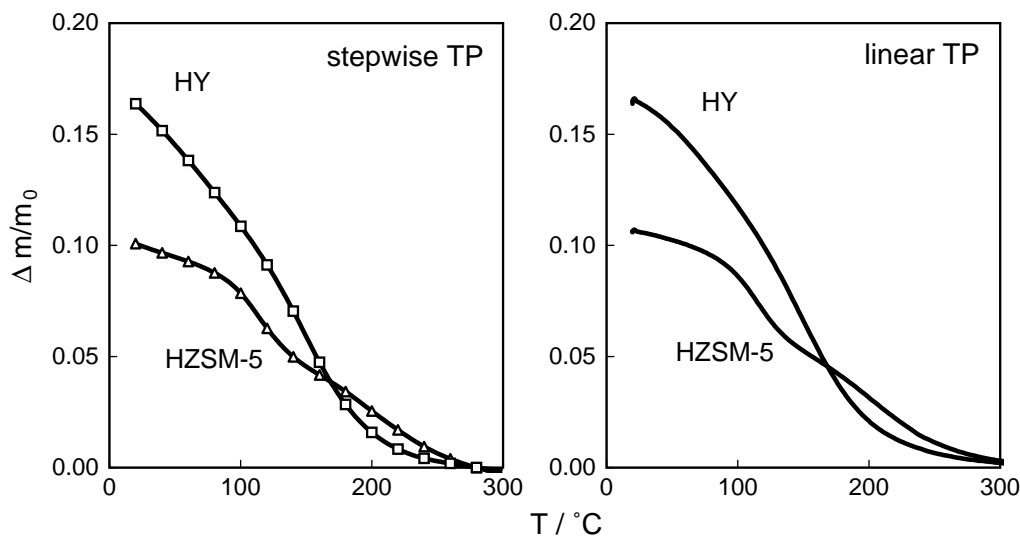


Fig. 3. Desorption profiles of *n*-hexane measured using the constant-pressure TPED. The points in A and the lines in B correspond to the experimental values. The lines in A result from the interpolation of the experimental points with a spline function.

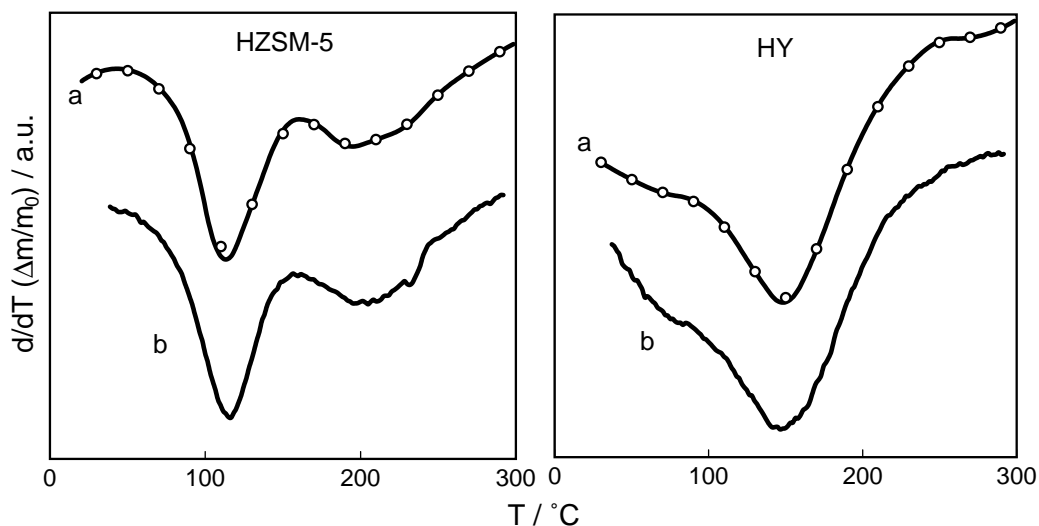


Fig. 4. Temperature derivatives of the TPED profiles of *n*-hexane (a: the stepwise TP, b: the linear TP). Values corresponding to the points in the profiles (a) were calculated as difference quotients of the experimental data. Values corresponding to the lines in the profiles (a) were obtained by numerical differentiation of the interpolation data. The profiles (b) result from numerical differentiation of the smoothed experimental data.

zeolite. It should be pointed out that the differential desorption profiles of *n*-hexane obtained with use of both temperature programs are almost the same. This indicates that its desorption is controlled by the equilibrium not only in the isothermal conditions but also while the temperature is being increased, provided that the heating rate is slow enough. The same effect has been reported by Millot et al. [7].

In order to check the effect of acidity of the zeolite on the adsorption of *n*-hexane, the TPED profiles for hydrogen and sodium exchanged zeolites were compared (Fig. 5). For both forms of ZSM-5, the desorption profiles are practically identical, whereas the intensity of the desorption peak of NaY is only slightly lower than that of HY. These results indicate that cracking of *n*-hexane, the catalytic reaction typical for acidic zeolites, did not influence the TPED

results. Although detection of the cracking products was not attempted, it may be assumed that this reaction did not take place on the studied samples, since no coke formation could be observed during the TPED measurements—neither their mass increased nor the color changed.

Results of additional TPD measurements of the preadsorbed hexane are similar to the TPED profiles (Fig. 6). Two overlapping thermodesorption peaks were observed for HZSM-5 and one peak was found for HY. The positions of the TPD peak depend on the value partial pressure of hexane above the sample. It increases with the decreasing volume of the sample cell and rate of effusion of hexane vapor from this cell, shifting TPD peak to higher temperatures. Profile TPD (c) observed for HZSM-5 obtained with the use the smallest sample cell is very similar to that of

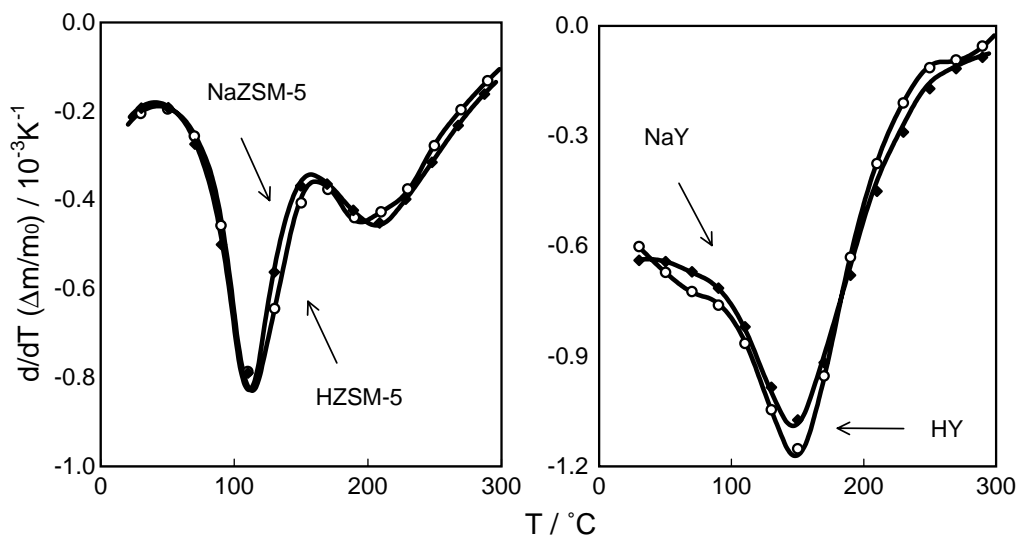


Fig. 5. Effect of ion exchange on the differential TPED profiles of *n*-hexane.

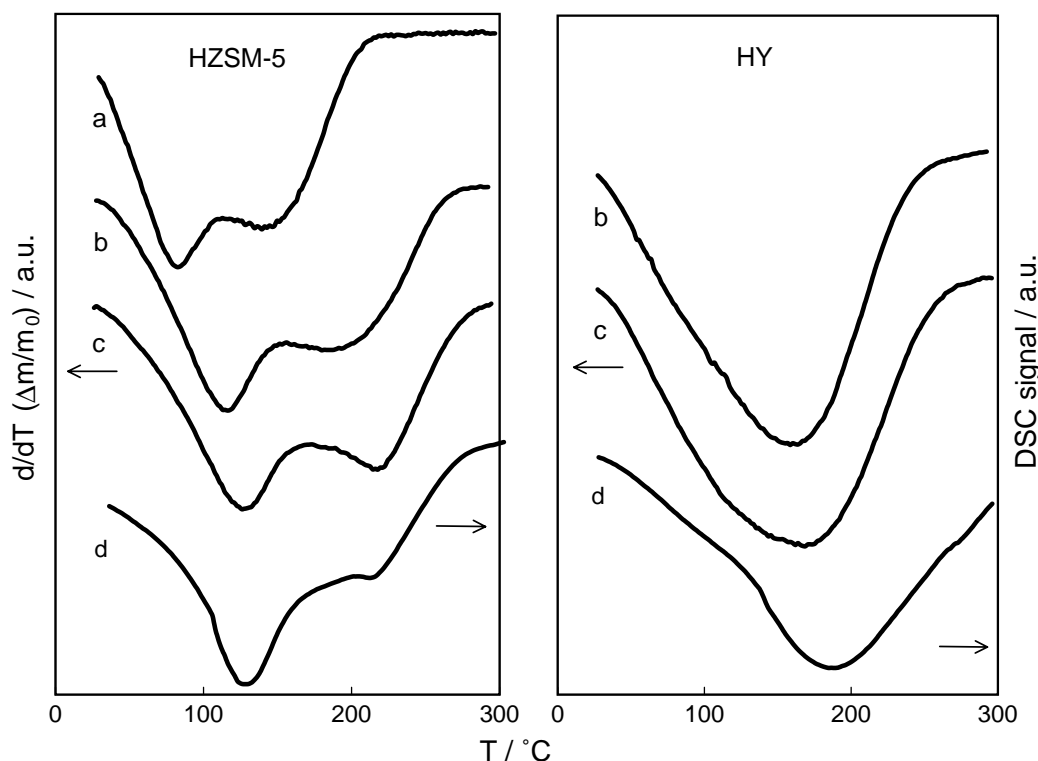


Fig. 6. Results of the additional TPD measurements, obtained after preadsorption of *n*-hexane in a dessicator, performed using different sample containers: (a) 0.9 ml crucible (Al_2O_3) without cover, (b) 0.15 ml crucible (Al_2O_3) with cover with a small hole, (c) 0.04 ml DSC sample cell (Al) with cover with a small hole—the same as used in DSC measurement (d).

TPED. Profile (d) for HZSM-5 that was measured in a DSC apparatus in the same sample cell exhibit two peaks in the same positions as in profile (c) but the relative intensity of the low-temperature peak is substantially higher.

4. Discussion

Differential TPED profiles observed for ZSM-5 are very similar to the results reported for silicalite-1 [7,17], as well as to derivatives of adsorption isobars for high silica ZSM-5 [6]. All these results fit well the generally accepted dual-site Langmuir adsorption model, assuming adsorption equilibrium between the sorbate and two independent pools of the adsorption sites. The isotherms or isobars derived from this model may reproduce well experimental profiles exhibiting “kinks” or “steps” [13].

For quantitative analysis of the differential profiles a formalism proposed by Millot et al. was adopted [7,8]. If adsorption for a given pool of adsorption sites is described by the Langmuir isotherm equation

$$\frac{a}{a_m} = \frac{Kp}{Kp + 1}$$

where a is the actual and a_m the maximum adsorption value, p the partial pressure of the sorbate, and K the adsorption

equilibrium constant depending on temperature

$$K = \exp\left(-\frac{\Delta G^{\text{ads}}}{RT}\right)$$

One may derive temperature derivative of the adsorption isobar as

$$\frac{d}{dT} \left(\frac{a}{a_m} \right) = \frac{p\Delta H^{\text{ads}} \exp(\Delta S^{\text{ads}}/R) \exp(-\Delta H^{\text{ads}}/RT)}{[p \exp(\Delta S^{\text{ads}}/R) \exp(-\Delta H^{\text{ads}}/RT) + 1]^2 RT^2}$$

assuming that $\Delta G^{\text{ads}} = \Delta H^{\text{ads}} - T\Delta S^{\text{ads}}$ and the enthalpy and entropy of adsorption do not depend on temperature. Such model functions were fitted to the differential TPED profiles obtained using the stepwise temperature program (Fig. 7). Very good agreement of the experimental data and the model function was observed, especially in the high temperature range. All estimated parameters of the model functions (presented in Table 1) have reasonable values.

Contribution of low-temperature desorption (observed below 100 °C, especially for HY) could not be fitted with the model function. In this temperature range adsorption in the wide pores or at the external surface may occur, not being limited to the “monolayer” of the adsorbate. For multi-layer adsorption the Langmuir model is no longer valid. Substantial distortion of the ideal porous structure with formation of the secondary meso- and macropores is expected for the dealuminated HY zeolite.

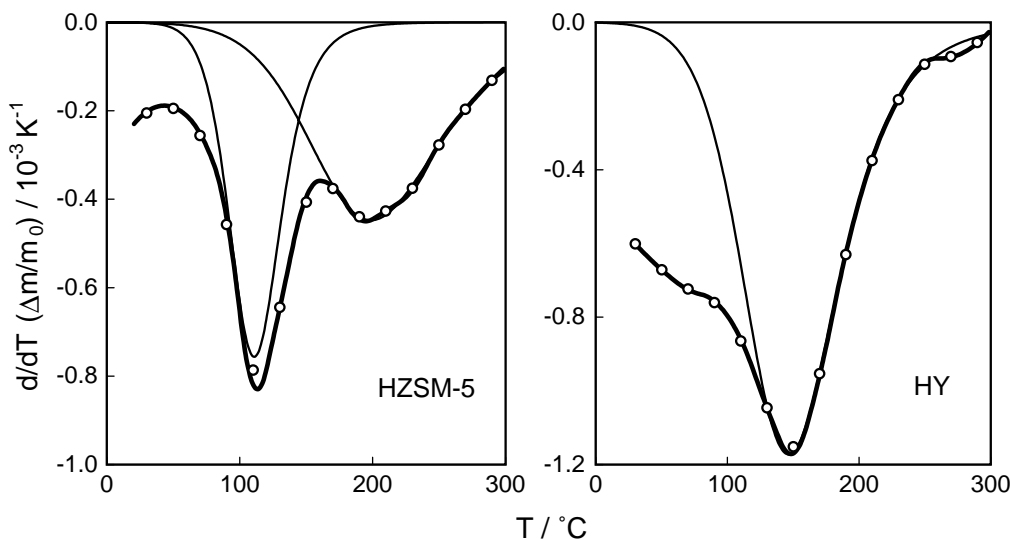


Fig. 7. Fitting the Langmuir model equation to the differential TPD profiles of *n*-hexane. The estimated model parameters are shown in Table 1.

The estimated values of the adsorption enthalpy of *n*-hexane are close to the experimental adsorption heats reported for ZSM-5 (60–82 kJ/mol, data collected by Vlucht [13], p. 66) and for FAU (47–65 kJ/mol [18]) as well as to the heats of desorption determined in the additional TPD measurements using DSC (85 kJ/mol for HZSM-5 and 80 kJ/mol for HY). However, the latter data are not very accurate due to low sensitivity of the instrument in that type of measurements—the relative error exceeds 10%.

It has been reported that the heat of adsorption of *n*-hexane on ZSM-5 increases with the growing coverage [5]. The estimated adsorption enthalpies reveal the same behavior—for the low-temperature peak (corresponding to high coverage) higher value of the adsorption enthalpy was found. The same dependence may be seen in the TPD results obtained using DSC method. Higher relative intensity of the low-temperature peak indicates higher desorption heat for higher coverage values.

This effect may be explained in terms of the adsorption entropy that increases due to ordering of the hydrocarbon molecules in the channels of MFI zeolite [6,10,13]. The estimated values of the adsorption entropy confirm this explanation. The adsorption entropy values calculated for Y

and for the high temperature desorption peak observed for ZSM-5 correspond to the standard entropy of vaporization of *n*-hexane (94 J/mol K [15]). Much higher adsorption entropy of the low-temperature desorption peak for ZSM may be compared with the sum of the vaporization entropy and the entropy of fusion (72 J/mol K at 178 K [15]). This indicates high degree of ordering of hexane molecules in ZSM-5 at high coverage, similar to that in solid phase.

According to Jentys and Lercher the relation between the adsorption enthalpy and entropy of alkanes adsorbed in zeolites may provide a means to assess the effective pore sizes [1]. For a series of *n*-alkanes a linear dependence between the adsorption enthalpy and entropy was found, indicating that for the stronger bound molecule also the adsorption entropy is higher. The slope in this linear relation depends on the pore size of a zeolite—for narrow pore zeolites higher changes of the adsorption entropy with the adsorption enthalpy are observed. However, no model allowing determination of the pore size from the adsorption data has been proposed yet.

Values of the total sorption capacity were equal to 106 mg/g for HZSM-5 and 164 for HY. The value found for HZSM-5 corresponds to seven hexane molecules per

Table 1
Parameters determined from the TPD profiles of *n*-hexane (obtained using the stepwise temperature program)

Zeolite	T_{\max} (°C)	ΔH^{ads} (kJ/mol)	ΔS^{ads} (J/mol K)	Sorption capacity (mg/g)		Total pore volume (cm ³ /g)	
				Model	Total	TPED	Adsorbed N ₂
HZSM-5	114	−95	−223	43	106	0.16	0.16
	196	−56	−92	56			
NaZSM-5	114	−99	−234	37	100	0.15	–
	209	−56	−91	63			
HY	150	−60	−118	117	164	0.25	0.32
NaY	150	−50	−96	127	164	0.25	–

unit cell and is close to the theoretical loading limit of eight molecules per unit cell [13]. The pore volumes calculated assuming density of the adsorbate the same as of the liquid hexane (0.65 g/cm^3) were equal to $0.16 \text{ cm}^3/\text{g}$ for HZSM-5 and $0.25 \text{ cm}^3/\text{g}$ for HY. These values fit well those determined from N_2 adsorption (0.16 and $0.32 \text{ cm}^3/\text{g}$, respectively). For HZSM-5 with complete coverage even slightly higher value of the pore volume could be expected, however in this zeolite the density of the adsorbed hexane is probably higher than that of the liquid, due to high degree of ordering of the adsorbed molecules. Difference in both pore volume values determined for HY result most probably from lower size of N_2 molecules that may be more efficiently fill the supercages of FAU structure.

Our results indicate that TPED of hexane may be used as a method for characterization of the microporosity of zeolites, complimentary to the low-temperature adsorption of N_2 . Nevertheless, further studies on development of the adsorption models allowing direct determination of the pore size distribution from the TPED data are necessary.

5. Conclusions

Desorption of light linear alkanes from MFI and FAU zeolites may be performed under equilibrium control conditions. It has been shown that temperature-programmed equilibrated desorption (TPED) of *n*-hexane studied gravimetrically in a flow system is a simple and fast experimental method yielding desorption data closely related to the porous structure of the zeolite. Derivative TPED desorption profiles fit well the model functions derived assuming Langmuir adsorption model. Micropore volume as well as the adsorption enthalpy

and entropy values determined from the TPED data provide valuable characteristics of the microporous structure of zeolites.

References

- [1] A. Jentys, J.A. Lercher, Techniques of zeolite characterization, in: H. van Bekkum, et al. (Eds.), *Introduction to Zeolites Science and Practice, Studies in Surface Science and Catalysis* 137, Elsevier, Amsterdam, 2001, pp. 345–386.
- [2] G. Horvath, K. Kawazoe, *J. Chem. Eng. Jpn.* 16 (1983) 470–475.
- [3] E.P. Barrett, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.* 61 (1951) 373–380.
- [4] S. Storck, H. Bretinger, W.F. Maier, *Appl. Catal. A* 174 (1998) 137–146.
- [5] L.V.C. Rees, D. Shen, Adsorption of gases in zeolite molecular sieves, in: H. van Bekkum, et al. (Eds.), *Introduction to Zeolites Science and Practice, Studies in Surface Science and Catalysis* 137, Elsevier, Amsterdam, 2001, pp. 579–631.
- [6] D.H. Olson, P.T. Reischman, *Zeolites* 17 (1996) 434–436.
- [7] B. Millot, A. Methivier, H. Jobic, *J. Phys. Chem.* 102 (1998) 3210–3215.
- [8] B. Millot, A. Methivier, H. Jobic, I. Clemencon, B. Rebours, *Langmuir* 15 (1999) 2534–2539.
- [9] W. Makowski, D. Majda, R. Dziembaj, *Przem. Chem.* 82 (3) (2003) 226–229.
- [10] B. Smit, T.L.M. Maesen, *Nature* 374 (1995) 42–44.
- [11] R. Krishna, S. Calero, B. Smit, *Chem. Eng. J.* 88 (2002) 81–94.
- [12] R. Krishna, D. Paschek, *Phys. Chem. Chem. Phys.* 3 (2001) 453–462.
- [13] T.J.H. Vlugt, Adsorption and Diffusion in Zeolites—A Computational Study, PhD thesis, University of Amsterdam, Amsterdam, 2000 (<http://www.molsim.chem.uva.nl/publications>).
- [14] R.J. Gorte, *Catal. Today* 28 (1996) 405–414.
- [15] NIST Chemistry WebBook, <http://www.webbook.nist.gov/chemistry/>.
- [16] Database of Zeolite Structures, <http://www.iza-structure.org/databases/>.
- [17] Y. Yang, L.V.C. Rees, *Microporous Mater.* 12 (1997) 223–228.
- [18] F. Eder, J.A. Lercher, *Zeolites* 18 (1997) 75–81.