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Application of the clustering-based LBET class adsorption models to the analysis of the microporous structure of silica membranes

Mirosław Kwiatkowski[1], Magda Ziółkowska[2]

AGH University of Science and Technology, Faculty of Energy and Fuels

al. A. Mickiewicza 30, 30-059 Krakow, Poland

kwiatkow@agh.edu.pl

Abstract. This paper presents the application research results of the clustering-based *LBET* class adsorption models as a tool for the analysis of the porous structure of silica membranes. This research provides information on possible significant advantages that can be drawn while applying the new proposed method of microporous structure description in comparison with the conventional approaches. Furthermore, the obtained calculation results and additional information from adsorption isotherms analysis using *LBET* class models as well as their interpretation are shown. In particular, in the presented method it is possible to easily acquire not only information regarding the values of the obtained structure parameters, but also, more importantly, precise information on the reliability of these parameter calculations.

1. Introduction

A growing interest in gas phase separation with the application of ceramic membranes is mainly caused by the well-known stability of chemical and thermal parameters of this materials [1-2]. Furthermore, in comparison with polymeric membranes it turns out that ceramic membranes have higher gas flux and also high specific selectivity, which is related to pore size and occurs for the pores having less than 2 nm in diameter in accordance with the IUPAC definition [3-5]. Microporous silica, one of the commonly used ceramic materials, is chemically stable and does not expand while firing. Earlier studies concerning its catalytic properties also provide important additional information about the gas transport mechanism [6]. This makes silica an interesting material that can be used as a ceramic membrane.

Sol-gel processes are employed most commonly in order to obtain microporous silica. Two techniques can be distinguished within these processes: polymeric and particulate [6]. In the first technique, chainlike macromolecules are formed in the sol, which enables the preparation of low-cracking silica coatings having pore sizes within the range of micropore [4]. However, in order to better control pore volume and pore size distribution, the particle technique is commonly employed. In this technique the colloidal suspension of uniform particles is involved in membrane preparation containing uniformly distributed pores of a large volume. Moreover, in comparison with polymeric silica membranes, particulate membranes typically have higher gas flow and high surface cracking ratio. The formation of cracks is the result of tensile stress during liquid evaporation, which is difficult to avoid

during the drying process. In many cases, the key step in avoiding these surface cracks in the course of silica membrane preparation is the application of coating process [7].

Practical application of silica membranes to the gas phase separation is related to their adsorption properties, which are directly resultant from their porous structure and chemical properties of the surface. In order to get information about these materials, porous structure adsorption techniques based on experimental adsorption isotherm measurements can be employed. However, the interpretation of the adsorption data requires an assumption of the mathematical model describing the adsorption equilibrium. A number of equations have already been proposed for this purpose. The ones used most commonly for the description of microporous materials include the *BET* equation [8] as well as *Dubinin-Raduskievitch* (*DR*) and *Dubinin-Astachow* (*DA*) equations [9,10]. Also, the *Density Functional Theory* (*DFT*) has recently become a strongly recommended tool for this purpose [11-14]. Nevertheless, our team developed an alternative approach to the analysis of microporous materials, employing the clustering-based adsorption theory (*uniBET*) with the *LBET* class models [15-26]. The *LBET* class models are applied to the examination of random porous structure adsorbents and can be viewed as an alternative to the classical techniques based on *BET* or *DR* equations and to the recently recommended *DFT*-based techniques [11-14].

2. Theoretical basis of the LBET class models

The *LBET* class adsorption models are based on the *uniBET* theory, described in our previous papers [15-19]. They are aimed at drawing information on pore structure and capacity by analysis of adsorption isotherms of small molecule adsorbates.

The heterogeneous adsorption *LBET* class models have the following form [20-25]:

$$\frac{m_a}{m_{hA}} = (1-\alpha)\left\{1 - \frac{1}{\ln(B_A/B_{f1})}\cdot\ln\left(\frac{B_A+\pi}{B_{f1}+\pi}\right)\right\} +$$

$$+ d\cdot\alpha(1-\alpha)(1+\beta\theta_2)\left\{1 - \frac{1}{\ln(B_{A2}/B_{f2})}\ln\left(\frac{B_{A2}(1-\theta_2)^\beta+\pi}{B_{f2}(1-\theta_2)^\beta+\pi}\right)\right\} + \quad (1)$$

$$+ \alpha^{d+1}\left[d+(\beta\theta)^d\left(1+\frac{\beta\theta}{1-\alpha\beta\theta}\right)\right]\left\{1 - \frac{1}{\ln(B_{A2+d}/B_{f\theta})}\ln\left(\frac{B_{A2+d}(1-\theta)^\beta+\pi}{B_{f\theta}(1-\theta)^\beta+\pi}\right)\right\},$$

where: m_a is the total adsorption [mmol/g], m_{hA} is the total number of the adsorption primary sites, $m_{hA}=V_{hA}/V_a$, V_{hA} is the first adsorption layer capacity [mm^3/g], V_a is the molar volume of adsorbate [mm^3/mmol], θ_{kj} and θ are the coverage ratio of *j*-th - layer at *k*-th - type cluster and mean coverage ratio of layers *n* >1 respectively, π is the relative pressure p/p_0, α and β are parameters of the geometrical and pore shape porous structure respectively. B_{Ak}, B_{fk} are both energetic parameters, Q_A is the first layer adsorption energy [J/mol] and B_C is the energetic parameter for adsorption layer *n* > 1 [20-25].

The *LBET* models involves five parameters: V_{hA} [mm^3/g], Z_A, α, β, B_C which can be adjusted by fitting Eq. (1) to empirical adsorption isotherm, with a chosen variant of the surface energy distribution function [20-25]. In the presented approach two types of adsorption at the top layer *k* are considered, corresponding to different nature of restrictions for the adsorbate clusters size represented by *k*. The first type adsorption, assuming the restrictions of formal nature, implies $\theta = \pi/(B_c(1-\theta)\beta-1)$ and may results in more compact or flat end large pores. For the second type adsorption (the restrictions are of geometrical nature, which is likely in small or narrow pores) the ratio θ averaged over the layers *n*=2, …, *k*, *k*=2+*d*, …, ∞ is taken [20-25].

The reliability of identification was assessed on the basis of residual dispersion σ_e and relative errors of parameters calculated for all 30 variants. To make possible a final choice of the best variant, the detailed results were presented for the three best fittings. Moreover, the 10 of well fitted variants

from 30 ones were treated as acceptable ones. In order to get a measure of the identification uncertainty, the identifiability index w_{id} was defined [20-25]:

$$w_{id} = 1 - \frac{\sigma_{e\,min}}{\frac{1}{10}\sum_{opt=1}^{10}\sigma_{e\,opt}} \qquad (2)$$

where: σ_{emin} and σ_{eopt} denotes respectively dispersion error of the best fitting and the sequence of increasing dispersion errors of the ten well fitted models.

3. Numerical calculations

The purpose of the reported research was to evaluate the application of *LBET* class adsorption models to the porous structure analysis of crack-free unsupported silica membranes with different polyvinyl alcohol (PVA) and silica ratios on the basis of nitrogen isotherms at 77 K, obtained by Chu and Anderson [26]. The crack-free unsupported silica membranes with different PVA additive ratios were obtained by the sol-gel technique. Chu and Anderson employed the interfacial hydrolysis method to obtain silica sol by mixing tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS) with ammonia solution (0.4 - 0.5 M silica concentration) [26]. After obtaining a homogenous mixture, sol was dialyzed and then diluted by adding nitric acid until the pH was 3, whereas PVA, used to improve support coating as an organic binder, was prepared by mixing PVA - water solution with previously obtained sol. Final unsupported silica membranes with different PVA/silica ratio by weight (10/100; 20/100; 30/100 respectively) were obtained after solvent evaporation and heating for 1 h at 500°C. The examination was concluded with the measurement of nitrogen adsorption isotherms at 77 K. Adsorbent preparation is described more precisely in paper [26]. The results of numerically calculated nitrogen isotherm for the best-fitted variants are illustrated in Figs. 1-3. Each figure presents the set of fitting results (subfigure in the first row) and adsorption energy distribution (subfigure in the second row) corresponding to the upper subfigure. The first row of subfigures presents the results of simultaneously fitted calculated isotherms (solid lines) to experimental data (marked with dots "∘"), and the theoretical coverage of the first adsorption layer is additionally presented (dotted lines). The headlines contain adsorbate and adsorbent name with PVA/silica ratio described in brackets, and the slash is followed by the best-fitted model name and the number of *LBET* class models. The values of identifiability index w_{id}, fitting error dispersion σ_e, fitted adsorption model type and variants (h, d, η) are also presented. The second row of subfigures presents adsorption energy distribution and the values of numerically calculated parameters Q_A, B_C, Z_A, V_{hA}, α and β.

4. Discussion of the results of numerical analysis

On the basis of the measurements of nitrogen adsorption isotherms on crack-free unsupported silica membranes with different PVA/silica ratios, it can be concluded that adsorption systems are well identifiable by way of the fitting of a *LBET* class model. It seems to confirm the abovementioned high applicability of the *LBET* class models with multivariant fitting procedure as a tool for the analysis of the microporous structure of silica membranes [26].

During the numerical calculations the dependence of preparation techniques of silica membranes on the obtained microstructure was considered. In particular, the PVA additive ratio influence on the formation of the microporous structure of silica membranes in sol-gel preparation techniques was considered. The obtained isotherm fitting results, presented in the subfigure in the first row (Fig. 1), show that silica membrane structure, with the PVA/silica ratio of 10/100 [26], is highly heterogeneous, as evidenced by the values of parameter $h = 7$. The porous structure consists of high stack-like adsorbate clusters ($\alpha = 1.00$, $\beta = 1.00$), whose enlargement is determined by a preassigned distance to another cluster – competing clusterisation, first type. Moreover, the subfigure showing adsorption energy distribution on the first layer (Fig. 1) indicates a wide spectrum of the primary adsorption sites.
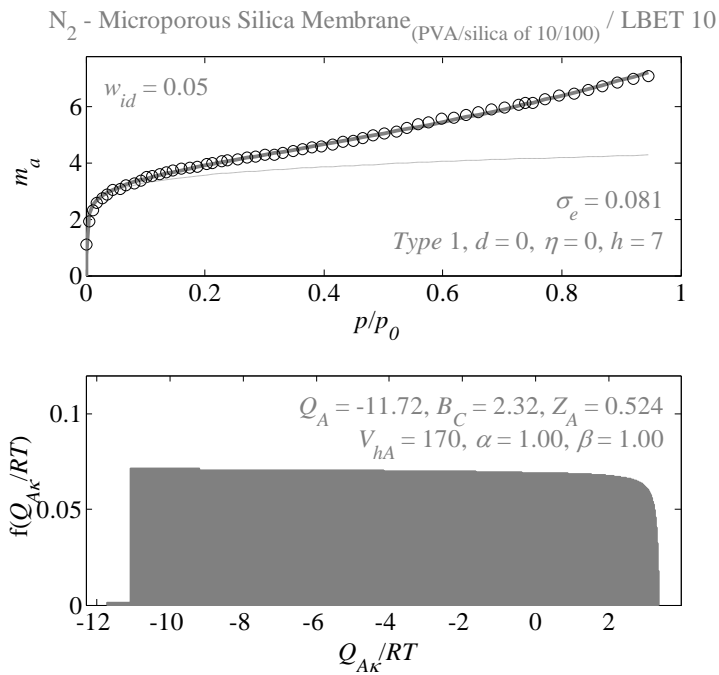
Fig. 1. The results of multivariant identification for nitrogen adsorption isotherms on crack-free unsupported silica membranes with PVA/silica ratio by weight of 10/100 [26]. The subfigure in the first row: fitted isotherm, the subfigure in the second row: adsorption energy distribution.
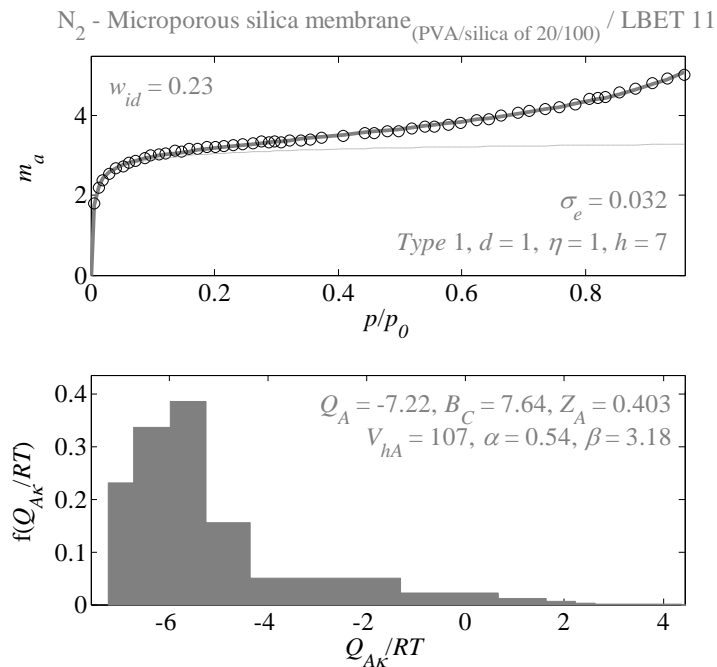

Fig. 2. The results of multivariant identification for nitrogen adsorption isotherms on crack-free unsupported silica membranes with PVA/silica ratio by weight of 20/100 [26].
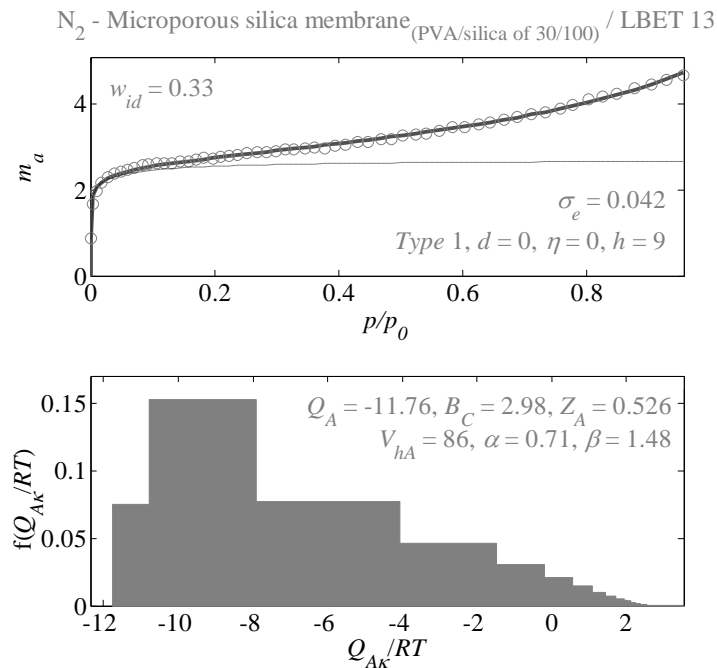
Fig. 3. The results of multivariant identification for nitrogen adsorption isotherms on crack-free unsupported silica membranes with PVA/silica ratio by weight of 30/100 [26].

An analysis of the results presented in the second figure, for silica membranes with the PVA/silica ratio of 20/100 [26], shows that – similarly to the case of the earlier results – silica membrane structure is highly heterogeneous (h parameter value is the same). However, further fitted parameter analysis indicates differences in the porous structure. The porous structure of the analyzed silica membranes consists of medium-sized branched adsorbate clusters, whose enlargement is determined by competing clusterisation ($\alpha = 0.54$, $\beta = 3.18$). It should be noticed that particular values of the parameter V_{hA} (first adsorption layer volume, $V_{hA} = 107$ [mm^3/g]) are smaller, as in the case of the previously analyzed sample. Also, the adsorption energy distribution on the first layer occurs with a narrower spectrum of the primary adsorption sites as compared with the first analyzed membrane (Fig. 2). Some interesting results were obtained for the third sample of silica membrane. It was found that higher PVA additive results in increasing surface heterogeneity ($h = 9$) and first adsorption layer volume reduction ($V_{hA} = 86$ [mm^3/g]). Particular values of the geometric parameters indicate the creation of high and branched adsorbate clusters ($\alpha = 0.71$, $\beta = 1.48$), in case of the silica membranes PVA/silica ratio of 30/100 [26]. First layer adsorption energy distribution subfigure (Fig. 3) indicates a wide spectrum of the primary adsorption sites, but with the dominant fraction of the highly energetic primary adsorption sites.

5. Conclusions

The results of the numerical analysis presented in this paper indicate complicated relationships between preparation techniques of crack-free unsupported silica membranes obtained at different PVA/silica ratios and microporous structure formation. Silica membranes structure identification requires an application of advanced numerical tools. Also, reliable identification was obtained while applying *LBET* class models. To sum up, the obtained results confirm the applicability of *LBET* class models to the silica membranes structure analysis as an efficient tool to evaluate surface capacity, monolayer adsorption energy, and outline pore geometry. Moreover, it gives an insight into the properties of the proposed identification technique presented in earlier papers by the author's team.

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