

吴克柳, 李相方, 陈掌星。页岩纳米孔吸附气表面扩散机理和数学模型, 中国科学: 技术科学 2015年第45卷第5期: 525-540页。其中从3.1.1节起至3.1.3节中‘造成低估了体相传输, 高估了表面扩散[39]’完全照抄至斯洛伐克作者Igor Medved等人于2011年发表在 Microporous and Mesoporous Materials期刊上的‘Surface diffusion in porous media: A critical review’。<https://doi.org/10.1016/j.micromeso.2011.01.015>

以下为吴等人的原文:

3.1.1 跳跃模型

跳跃模型假设吸附气分子是从孔隙表面一吸附位跳跃到相邻吸附位, 这也视为吸附气分子的活化过程[5,42~44,46,57]。如果吸附气分子获得足够的能量, 并越过两个相邻吸附位之间的能量障碍, 则活化过程发生, 吸附气发生表面扩散(图1)。跳跃模型仅适用于单层吸附的气体表面扩散。

3.1.2 水动力学模型

水动力学模型假设吸附流体的表面扩散是由于表面液膜黏性流动形成的。该类模型最早由 Gilliland等人[58]提出; Petropoulos[59]针对介孔($2 <$ 半径 <50 nm)推导出了新模型; 之后众多学者又将该类的均质表面模型推广到非均质表面模型[60~62]。该类模型应用较少, 仅适用于多层吸附的流体表面扩散。

3.1.3 Fickian 模型

Fickian 模型假设多孔介质中流体的表面扩散和体相传输是相互独立的, 则总传输量为

$$J_{\text{tot}} = J_b + J_s, \quad (2)$$

式中, J_{tot} 为总扩散质量通量, $\text{kg}/(\text{m}^2 \text{ s})$; J_b 为体相传输质量通量, $\text{kg}/(\text{m}^2 \text{ s})$ 。由(2)式可知, 表面扩散质量通量等于总扩散质量通量减去体相传输质量通量。其中, 总扩散质量通量和体相传输质量通量均可通过理论或实验获得, 且体相传输质量通量一般是用无吸附的流体实验获得的。该类模型由于忽略了流体在多孔介质中的“解吸附-体相传输-再吸附”的物理现象, 造成低估了体相传输, 高估了表面扩散[39]。

以下为英文原文:

1. Theories based on hopping models. This category contains hopping (mechanistic) models in which the migrating particles are viewed as hopping between distinct, energetically favorable adsorption sites on the surface [11–16]. Thus, surface diffusion is viewed as an activated type of a mass transfer process: if an adsorbed particle acquires a sufficient energy, called the activation energy (Eac), it can get over the energy barrier between adsorption sites and jump to a neighboring site (see Fig. 2). Hopping models are appropriate when at most one layer of adsorbed particles is formed.

2. Theories based on hydrodynamic models. This category contains hydrodynamic models of surface diffusion in which the diffusion of adsorbed particles is due to the viscous motion of the liquid film inside the porous medium. Hydrodynamic models for surface diffusion go back to the work of Gilliland et al. [17] in which a relation for the surface diffusivity was derived. Another hydrodynamic model was proposed by Petropoulos [18] for mesoporous solids. The extensions of homogeneous hydrodynamics models to heterogeneous surfaces were proposed [19–21]. Hydrodynamic models are not used very often because the transport mechanism associated with a hydrodynamic flow appears only when at least a few layers of adsorbed particles are formed.

3. Theories based on Fickian models. Here surface diffusion is treated as the flow in excess of the flux of non-adsorbing liquid or gas, i.e., in excess of bulk diffusion. Assuming that the two fluxes are independent, the total flux becomes

$$J_{\text{tot}} = J_b + J_s \quad (1)$$

and the surface diffusion flux, J_s , is obtained (experimentally or theoretically) as the total diffusion flux of a given liquid/gas minus the analogous diffusion flux of a non-adsorbing liquid/gas. This method underestimates the bulk flux and overestimates the surface flux because the path “desorption-bulk-diffusion-re-adsorption” is neglected [9].

吴等人原文中的参考文献出现顺序:

3.1.1 跳跃模型中出现的参考文献

- 5 Kapoor A, Yang R T. Surface diffusion on energetically heterogeneous surfaces. *AIChE J*, 1989, 35: 1735–1738
42 Higashi K, Ito H, Oishi J. Surface diffusion phenomena in gaseous diffusion: I. Surface diffusion of pure gas. *J Atom Energ Soc Jpn*, 1963, 5: 846–853
43 Yang R T, Fenn J B, Haller G L. Modification to the higashi model for surface diffusion. *AIChE J*, 1973, 19: 1052–1053
44 Chen Y D, Yang R T. Concentration dependence of surface diffusion and zeolitic diffusion. *AIChE J*, 1991, 37: 1579–1582
46 Okazaki M, Tamon H, Toei R. Interpretation of surface flow phenomenon of adsorbed gases by hopping model. *AIChE J*, 1981, 27: 262–270
57 Chen Y D, Yang R T. Surface and mesoporous diffusion with multilayer adsorption. *Carbon*, 1998, 36: 1525–1537

3.1.2 水动力学模型中出现的参考文献

- 58 Gilliland E R, Baddour R F, Russell J L. Rates of flow through microporous solids. *AIChE J*, 1958, 4: 90–96
59 Petropoulos J H. Model evaluation of adsorbate transport in mesoporous media in the multilayer adsorption region. *Langmuir*, 1996, 12: 4814–4816
60 Kainourgiakis M E, Stubos A K, Konstantinou N D, et al. A network model for the permeability of condensable vapours through mesoporous media. *J Membrane Sci*, 1996, 114: 215–225
61 Kikkinides E S, Tzevelekos K P, Stubos A K, et al. Application of effective medium approximation for the determination of the permeability of condensable vapours through mesoporous media. *Chem Eng Sci*, 1997, 52: 2837–2844
62 Kainourgiakis M E, Kikkinides E S, Stubos A K, et al. Adsorption-desorption gas relative permeability through mesoporous media—Network modelling and percolation theory. *Chem Eng Sci*, 1998, 53: 2353–2364

3.1.3 Fickian 模型中出现的参考文献

- 39 Kapoor A, Yang R T, Wong C. Surface diffusion. *Cat Rev Sci Eng*, 1989, 31: 129–214

以下为英语原文中参考文献顺序:

Theories based on hopping models段落中出现的参考文献

- [11] K. Higashi, H. Ito, J. Oishi, *J. At. Energy Soc. Jpn.* 5 (1963) 846–853.
[12] R.T. Yang, J.B. Fenn, G.L. Haller, *AIChE J.* 19 (1973) 1052–1053.
[13] Y.D. Chen, R.T. Yang, *AIChE J.* 37 (1991) 1579–1582.

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Theories based on hydrodynamic models段落中出现的参考文献

- [17] E.R. Gilliland, R.F. Baddour, J.L. Russel, AIChE J. 4 (1958) 90–96.
- [18] J.H. Petropoulos, Langmuir 12 (1996) 4814–4816.
- [19] M.E. Kainourgiakis, A.K. Stubos, N.D. Konstantinou, N.K. Kanellopoulos, V.Milisic, J. Membr. Sci. 114 (1996) 215–225.
- [20] E.S. Kikkinides, K.P. Tzevelekos, A.K. Stubos, M.E. Kainourgiakis, N.K. Kanellopoulos, Chem. Eng. Sci. 52 (1997) 2837–2844.
- [21] M.E. Kainourgiakis, E.S. Kikkinides, A.K. Stubos, N.K. Kanellopoulos, Chem. Eng. Sci. 53 (1998) 2353–2363.

Theories based on Fickian models段落中出现的参考文献

- [9] A. Kapoor, R.T. Yang, C. Wong, Catal. Rev. – Sci. Eng. 31 (1989) 129–214.

综上：吴克柳，李相方，陈掌星等人发表的‘页岩纳米孔吸附气表面扩散机理和数学模型’，中国科学：技术科学 2015年第45卷第5期：525-540页，其中大段内容完全照抄至国外作者的论文。

不仅如此，同样的抄袭再次出现在吴克柳，陈掌星于2016年发表在《石油科学通报》第1卷第1期，题为‘页岩气纳米孔气体传输综述’的论文中。

对于以上内容的真实性，任何一位研究生及以上水平的人均可以轻易核实，望能严肃认真处理。