Adsorption (2011) 17: 287–292
DOI 10.1007/s10450-010-9283-5

Heats of adsorption from the Dubinin-Astakhov model applied to the characterization of pillared interlayered clays (PILCs)

João Pires · Moisés L. Pinto · José M. Guil

Received: 10 December 2008 / Accepted: 18 October 2010 / Published online: 3 November 2010

Abstract Heats of adsorption of organic molecules are a useful tool for the characterization of porosity and surface chemistry of microporous materials. This work describes the possibility of using heats of adsorption of organic molecules, estimated from a methodology derived from the Dubinin-Astakhov equation, for the characterization of Pillared Interlayered Clays. The estimated heats were compared with data determined directly by adsorption microcalorimetry. It is shown that the chemical nature of the organic probe molecule strongly conditions the obtained results. The best agreement between calculated and experimental values, amongst the probe molecules studied, was found for toluene.

Keywords Vapour adsorption · Adsorption heats · Microcalorimetry · Pillared-Clays · PILCs

1 Introduction

The applications of microporous materials—pore widths less than 2 nm (Sing et al. 1985)—are well known as these solids have a major impact in technological fields such as adsorption or catalysis (Lu and Zhao 2004). The characterization of microporous materials can obviously be made by a large number of techniques depending on the particular objective, but techniques that involve adsorption are between those more informative. By adsorption techniques it is intended to include not only the standard nitrogen adsorption at −196 °C for the characterization of surface area and porosity (Gregg and Sing 1982) but also the adsorption of other probe molecules as, for instance in the case of catalysts characterization, the adsorption of probe molecules that are reactants or products of a given catalytic reaction. The measurement of not only the adsorbed amounts but also of properties such as the heat of adsorption can provide additional useful information for the characterization of properties such as acidity-basicity, surface heterogeneity, or pore confinement. Heats of adsorption can be estimated from adsorption isotherms or directly measured by calorimetry (Létoquart et al. 1973; Rouquerol et al. 1999). Heats of adsorption are also an important quantity in chemical engineering, where heat balances and temperature changes are important, for instance in adsorption or catalytic processes.

The amount of different molecules adsorbed on microporous materials can be successfully described by the Dubinin-Astakhov (DA) equation in many adsorbate/adsorbent systems (Dubinin 1961, 1979; Bansal et al. 1988 and Stoeckli et al. 1994). This equation is: $w = w_0 \exp[-(A/E)^n]$; where the occupied adsorption volume w is related to the limiting adsorption volume w_0. The magnitude A is the adsorption potential: $A = RT \ln(p^0/p)$, being p^0 and p the saturation and equilibrium pressures, respectively. The constant E (the characteristic energy of adsorption) and n are temperature invariant parameters. The values of E and n in this work were obtained by fitting the DA equation to the experimental data (adsorption isotherms). The characteristic energy (E) being a parameter related to the adsorption energy, has been compared with the heats of adsorption measured by calorimetry

J. Pires (✉) · M.L. Pinto
Department of Chemistry and Biochemistry and CQB, Faculty of Sciences, Building C8, University of Lisbon, Campo Grande, Lisbon, Portugal
e-mail: jpsilva@fc.ul.pt

J.M. Guil
Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain

Table 1 Values for the coefficient of thermal expansion and the enthalpy of condensation used in (1)

	n-hexane	mesitylene	toluene
Coefficient of thermal expansion (K^{-1})	1.1×10^{-3}	9.4×10^{-4}	1.07×10^{-3}
Enthalpy of condensation (kJ mol^{-1})	29.12	47.51	37.10

(Stoeckli et al. 1994; Gauden et al. 2004; Terzyk et al. 2006). As shown elsewhere (Dubinin 1979; Stoeckli et al. 1994; Terzyk et al. 2006) the isosteric heat of adsorption (q^{st}) can be related to parameters from the DA equation by:

$$q^{st} = E[(\ln 1/\theta)^{1/n} + (\alpha T/n)(\ln 1/\theta)^{1/n-1}] + L \quad (1)$$

where α and L are the coefficient of thermal expansion and the enthalpy of condensation of the adsorptive (Table 1), respectively and θ is the fraction of coverage ($\theta = w/w_0$).

The possibility of a viable methodology to estimate heats of adsorption from one adsorption isotherm only is relevant to the characterization of microporous materials, as well as in the design of adsorbers, catalytic reactors and process development. Some works have related the DA equation and the calorimetric heats of adsorption (Stoeckli et al. 1994; Gauden et al. 2004). Nevertheless, only very few studies were made on this subject and, more important, the studies are, to our knowledge, limited to only one type of microporous materials, namely activated carbons. However, other families of microporous materials are also relevant. This is the case of the solids prepared from clays, namely the Pillared Interlayered Clays (PILCs). The detailed description of the characteristics of PILCs is beyond the scope of this text, and was reviewed elsewhere (Gil et al. 2000; Vaughan 1988). Briefly, PILCs are prepared by the intercalation of oligomeric cationic species between the clay layers which, upon heating, are transformed in rigid pillars of the corresponding oxide. The more studied PILCs are those made of zirconium oxide or aluminium oxide pillars. PILCs are essentially microporous materials, frequently of 1–2 nm pore size; some of them can even present mesoporosity—pore widths between 2 and 50 nm (Sing et al. 1985) with potential applications in adsorption and in catalysis. In this work we discuss, to our knowledge for the first time, the relation between heats of adsorption determined directly by microcalorimetry, and those estimated from the DA equation, for the adsorption of organic vapours in PILCs. The organic vapours used in this study as probe molecules are reactants or products of various catalytic reactions. For instance, ethyl benzene was recommended for the characterization of acidity in microporous materials by the test reaction of ethylbenzene disproportiontion (De Vos et al. 2002), n-hexane is often used as reactant for testing the cracking properties of zeolitic materials (Selvam et al. 2003), toluene is one important reactant in alkylation reactions (Prokesova et al. 2005) from which mesitylene can be one undesired reaction product. Toluene also plays an important role in various adsorption processes (Ruthven 1984).

2 Experimental

2.1 Materials and methods

The pillared interlayered clays (PILCs) were prepared from natural clays collected in three different locations namely a clay from Wyoming, USA, which will be identified by WYO and two Portuguese clays, labeled BEN and PTS. The characterization of these parent clays, as well as the methodologies of preparation of the PILCs, was extensively described in previous works (Carvalho et al. 1996; Guil et al. 2002; Jerónimo et al. 2007). Relevant characteristics of the prepared materials are given in Table 2. Surface areas and micropore volumes were obtained from nitrogen adsorption at −196 °C using automatic apparatus either from Coulter (mod. Omnisorp 100 CX) or from Micromeritics (Asap 2010). Chemical analysis (to obtain the density of pillars) was made by ICP. The calculation of the numeric values of the density of pillars was discussed detailed in the literature (Pires et al. 1997). Briefly the values were obtained by considering the number of Al_{13} oxide pillars or tetramic Zr oxide pillars (obtained by ICP), divided by half of the total area of the initial smectite caly, which is near 750 $m^2\,g^{-1}$(Mott, 1988). To evaluate the basal spacing of the PILCs, X-ray diffractograms were obtained in a Philips PX 1820 diffractometer. Heats of adsorption of organic vapors were measured in a Tian-Calvet type microcalorimeter from Setaram (mod. BT) (Guil et al. 2002; Jerónimo et al. 2007). The microcalorimeter was coupled to a volumetric adsorption apparatus, so the adsorption isotherms of the organic vapours were determined simultaneously with the calorimetric measurements.

3 Results and discussion

Figure 1 shows the results for adsorption of ethylbenzene on PILC-1 and PILC-2 prepared from the same parent clay but with two types of pillars namely aluminium oxide (PILC-1) and zirconium oxide (PILC-2). As previously discussed namely from the results of pyridine adsorption (which are in line also with catalytic results) the PILC with zirconium oxide is somewhat more acidic (Jerónimo et al. 2007). The acid groups on the surface interact with the ethylbenzene molecule being responsible for the higher calorimetric heats (circles) at low coverage; they are higher than those for the aluminium oxide PILC. As coverage increases, the heat of adsorption tends to decrease, since the more energetic sites had

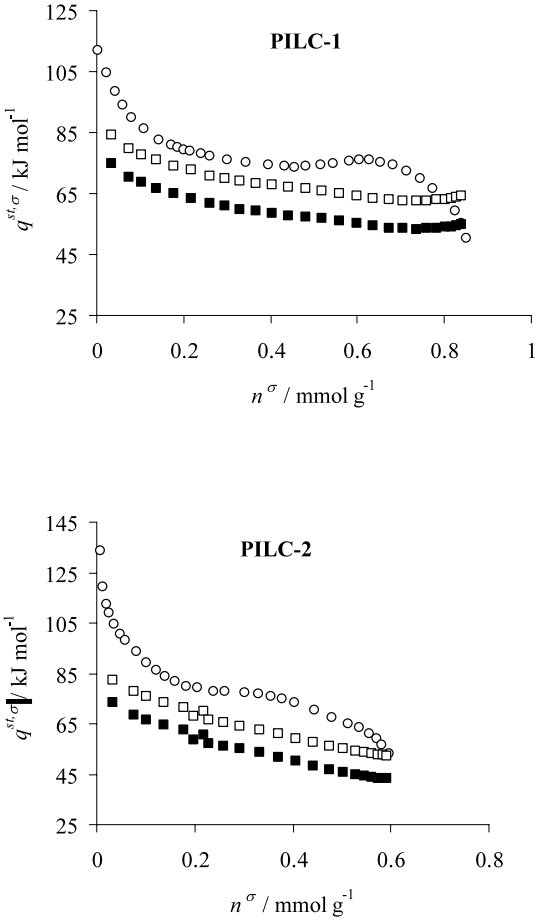

Fig. 1 Heats of adsorption of ethylbenzene at 80 °C in the indicated samples. ○—experimental, from Jerónimo et al. (2007); ■—equation (1); □—equation (1) corrected by adding the heat of fusion

been already occupied. At higher coverage an increase can be noticed (for instance around 0.6 mmol·g^{-1} for PILC-1) which is ascribed to the increase of lateral interactions between the adsorbed molecules (Pope 1986).

Comparison between the calorimetric heats and those obtained from the DA theory (closed squares), which is the focus of the present work, Fig. 1, shows that the values from DA theory are lower than the calorimetric heats. Various authors have proposed modifications to (1) (Terzyk 2006). In the present work we tested to add to the right side of (1), which already includes a term for the heat of condensation (L), the heat of fusion. The heat of fusion is the energy adsorbed (or evolved) for one mole of a substance to change from a liquid to a solid. The values after this correction are given as open squares (Figs. 1 to 4). This correction implicitly assumes that the adsorbed molecules are, energetically, in a quasi-solid state. Nevertheless, even in this case, the values for ethylbenzene adsorption (Fig. 1) are below the calorimetric data, the difference with the experimental values, being the highest for the sample with zirconium oxide pillars, that is, the more acidic sample.

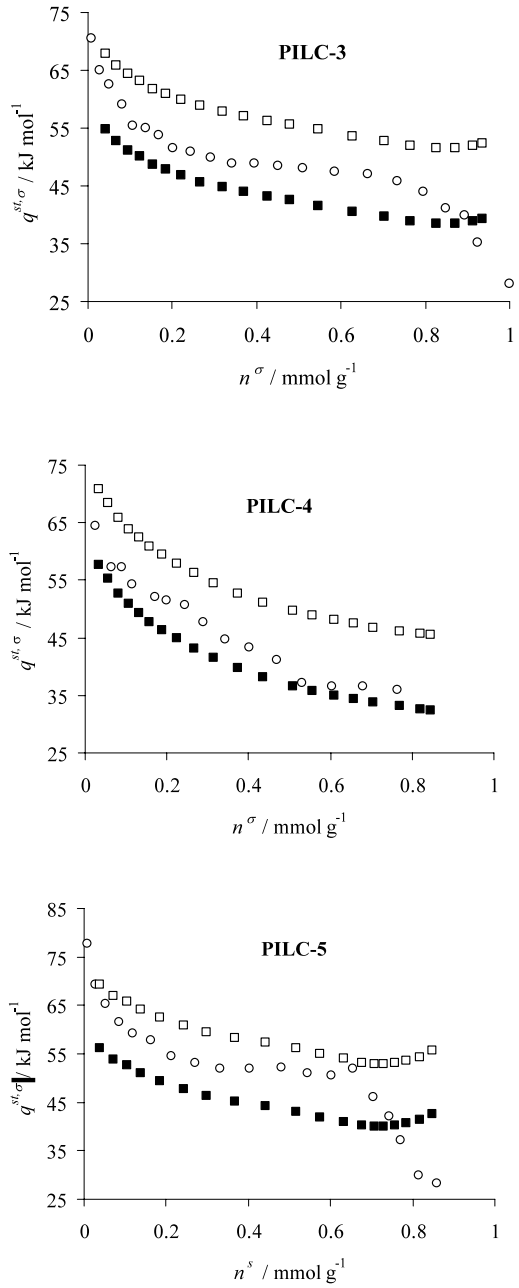

Fig. 2 Heats of adsorption of n-hexane at 4 °C in the indicated samples. Symbols as in Fig. 1. Experimental data from Guil et al. (2002)

Figure 2 gives the heats, calorimetric and from the DA theory, for the adsorption of n-hexane on three PILCs with aluminum oxide pillars, prepared with clays from three origins, as described in the experimental part (see also Table 2). As a general comment, it can be seen that the values for n-hexane are lower than those obtained for ethylbenzene (Fig. 1; PILC-1) which is in line with the fact that the specific adsorption sites, such as the acid sites, have stronger interactions with the π-electrons of the aromatic ring of the ethylbenzene molecule. Additionally, dispersion forces are

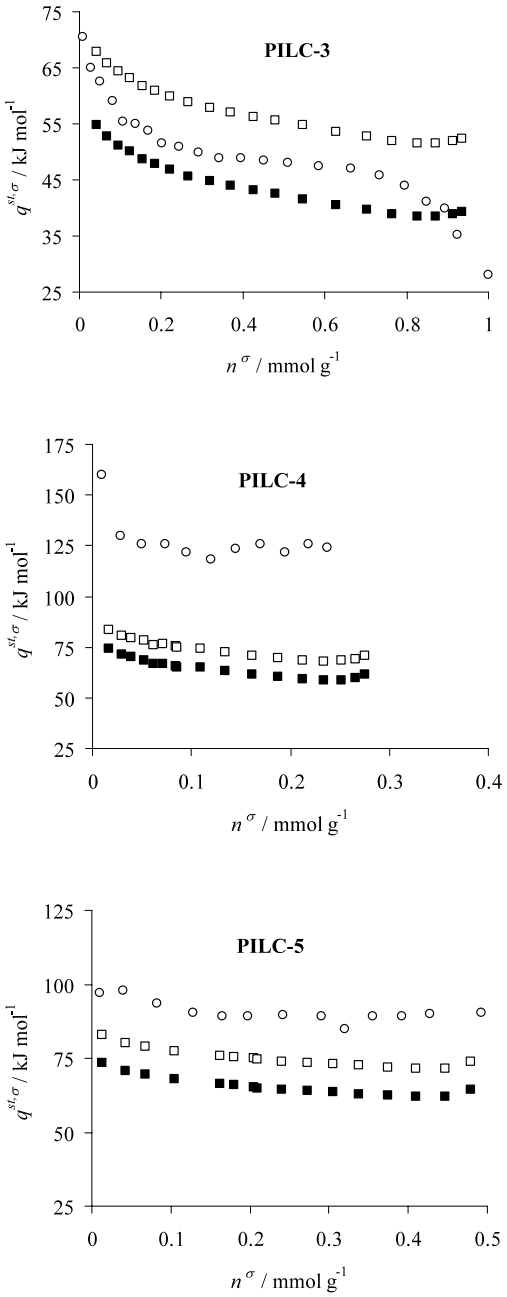

Fig. 3 Heats of adsorption of mesitylene at 57 °C in the indicated samples. Symbols as in Fig. 1. Experimental data from Guil et al. (2002)

also expected to be more relevant for ethylbenzene than for n-hexane, due to the higher number of carbon atoms. In the case of n-hexane adsorption the experimental heats of adsorption lie between the values estimated from the DA theory considering only the heat of condensation and considering the heats of condensation plus the heat of fusion.

As an extreme case, we also tested the adsorption of mesitylene (1,3,5-trimethylbenzene)—Fig. 3. This bulky molecule is highly susceptive to steric effects and the interactions with the surface groups are necessarily strong due

Table 2 Properties of the PILCs: basal spacing (d_{001}) in nm; density of pillars (np) per nm^2; specific surface area (A_{BET}) in m^2 g^{-1} and microporous volume (V_{micro}) in cm^3 g^{-1}

Sample	Parent clay	Pillars	d_{001}	np	A_{BET}	V_{micro}
PILC-1	PTS	Al_2O_3	1.77	0.48	252	0.093
PILC-2	PTS	ZrO_2	1.59	0.8	234	0.081
PILC-3	WYO	Al_2O_3	1.83	0.68	270	0.106
PILC-4	PTS	Al_2O_3	1.63	0.60	250	0.078
PILC-5	BEN	Al_2O_3	1.73	0.68	302	0.118

to the aromatic ring plus the three methyl groups. The calorimetric values are higher than the values from the DA theory (irrespectively of the approximation made). The highest difference corresponds to PILC-4 sample. To obtain the heights of the galleries the dimension of the clay sheets—0.96 nm—(Grim 1968) must be subtracted from the d_{001} in Table 2. Since the heights of the galleries are lower than the diameter of mesitylene (Guil et al. 2002), mesitylene molecules have to adsorb parallel to the clay sheets. That allows total interaction of all CH groups of the molecule with the layer surface to take place enhancing to maximum solid-molecule interactions. It should be noticed that, apparently, a relation between the porous structure (particularly the d_{001} values) and the dimension of the molecules seems to be noticed essentially for the larger mesitylene molecules. In this case, Fig. 3, for comparable adsorbed amounts, the highest heats correspond to the samples with lowest d_{001} values.

In the case of toluene adsorption in the same three samples (Fig. 4), except for the region of very low adsorbed amounts, where adsorption on the most energetic sites is predominant, the calorimetric data agree relatively well in a wide range of amounts adsorbed with the results from the DA theory when the heat of fusion is considered. That is, the energetics of the adsorption process of toluene in clays pillared with the more commonly used oxide pillars (Gil et al. 2000) (aluminum oxide and zirconium oxide) can be described with the DA equation with a certain degree of confidence. In this way, toluene adsorption heats at a given temperature can be estimated from one adsorption isotherm only.

It is interesting to note that the limiting adsorbed amounts from the DA equation (w_0) expressed as liquid volume approach the total microporous volume obtained from low temperature nitrogen adsorption (Guil et al. 2002), except for mesitylene due to the reasons discussed above. This seems to indicate that, although in terms of packing the adsorption of the studied molecules approach the liquid state, in energetic terms the adsorbed phase is closer to the solid phase.

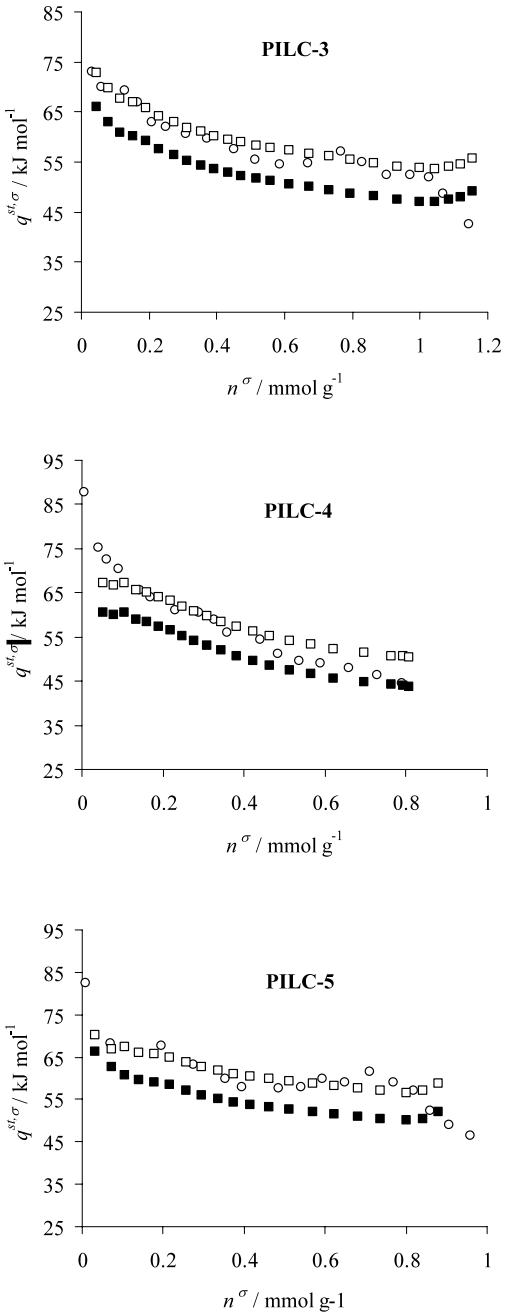

Fig. 4 Heats of adsorption of toluene at 42 °C in the indicated samples. Symbols as in Fig. 1. Experimental data from Guil et al. (2002)

4 Conclusion

The estimation of the heats of adsorption is an important tool in the characterization of the porosity and the surface chemistry of microporous materials and for the design of adsorbers and catalytic reactors. Few methodologies allow the estimation of the heats of adsorption, with a reduced number of experiments particularly when a microcalorimeter is not available. The well-known Dubinin-Astakhov equation allows an estimation of the heats of adsorption, from the results of one adsorption isotherm only. In this way, this method was applied to the adsorption of various organic molecules in three pillared interlayered clays. In the case of a molecule such as ethylbenzene or mesitylene, which interact strongly with the surface the results from the DA theory were always below the calorimetric data. In the case of n-hexane where, due to the absence of the aromatic ring and the lowest number of carbon atoms, interactions are expected to be comparatively lower, the calorimetric data was in between the results from the DA theory when only the condensation heat, or the condensation plus fusion heat were considered. Toluene revealed to be the more adequate probe molecule, except at very low coverage (less than 0.05 mmol·g^{-1}) since, when the values obtained from the DA theory are corrected by the heat of fusion the results agree with the calorimetric data within 5% in a wide range of amount adsorbed.

Acknowledgements Thanks are due to FCT, for funding CQB. MLP thanks a post-doc grant SFRH/BPD/26559/2006. JMG wish to acknowledge funding from the Comunidad Autónoma de Madrid, Spain (Program S0505/ESP/0299).

References

Bansal, R.C., Donnet, J.B., Stoeckli, H.F.: Active Carbon. Dekker, New York (1988)

Carvalho, M.B., Pires, J., Carvalho, A.P.: Characterisation of clays and aluminium pillared clays by adsorption of probe molecules. Microporous Mater. **6**, 65–77 (1996)

De Vos, D.E., Ernst, S., Perego, C., O'Connor, C.T., Stocker, M.: Standard reaction of the international zeolite association for acidity characterization: Ethylbenzene disproportionation over LaNaY. Microporous Mesoporous Mater. **56**, 185–192 (2002)

Dubinin, M.M.: The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. Chem. Rev. **60**, 235–241 (1961)

Dubinin, M.M.: Microporous structures of carbonaceous adsorbents. In: Gregg, S.J., Sing, K.S.W., Stoeckli, H.F. (eds.) Characterization of Porous Solids, pp. 1–11. Soc. of Chem. Ind., London (1979)

Gauden, P.A., Terzyk, A.P., Rychlicki, G., Kowalczyk, P., Cwiertnia, S., Garbacz, J.K.: Estimating the pore size distribution of activated carbons from adsorption data of different adsorbates by various methods. J. Colloid Interface Sci. **273**, 39–63 (2004)

Gil, A., Gandia, L.M., Vicente, M.: Recent advances in the synthesis and catalytic applications of pillared clays. Catal. Rev., Sci. Eng. **42**, 145–212 (2000)

Gregg, S.J., Sing, K.S.W.: Adsorption, Surface Area and Porosity. Academic Press, London (1982)

Grim, R.E.: Clay Mineralogy. McGraw Hill, New York (1968), p. 206

Guil, J.M., Perdigon-Melon, J.A., Carvalho, M.B., Carvalho, A.P., Pires, J.: Adsorption microcalorimetry of probe molecules of different size to characterize the microporosity of pillared clays. Microporous Mesoporous Mater. **51**, 145–154 (2002)

Jerónimo, D., Guil, J.M., Corbella, B.M., Vasques, H., Miranda, A., Silva, J.M., Lobato, A., Pires, J., Carvalho, A.P.: Acidity characterization of pillared clays through microcalorimetric measurements and catalytic ethylbenzene test reaction. Appl. Catal. **330**, 89–95 (2007)

Létoquart, C., Rouquerol, F., Rouquerol, J.: Les chaleurs d'adsorption: expression des chaleurs d'adsorption physique en terms d'energie interne a partir des donnees experimentales. J. Chim. Phys. **70**, 559–573 (1973)

Lu, G.Q., Zhao, X.S.: Nanoporous Materials. Imperial College Press, London (2004)

Pires, J., Carvalho, M.B., Carvalho, A.P.: Aluminium-pillared clays: Decomposition of the intercalating specie and textural properties. Zeolites **19**, 107–113 (1997)

Pope, C.G.: Sorption of benzene, toluene and p-xylene on silicalite and H-ZSM-5. J. Phys. Chem. **90**, 835–837 (1986)

Prokesova, P., Zilkova, N., Mintova, S., Bein, T., Cejka, J.: Catalytic activity of micro/mesoporous composites in toluene alkylation with propylene. Appl. Catal. A, Gen. **281**, 85–91 (2005)

Rouquerol, F., Rouquerol, J., Sing, K.S.W.: Adsorption by Powders & Porous Solids, Principles, Methodology and Applications. Academic Press, London (1999)

Ruthven, D.M.: Principle of Adsorption and Adsorption Processes. Wiley, New York (1984)

Selvam, T., Bandarapu, B., Mabande, G.T.P., Toufar, H., Schwieger, W.: Hydrothermal transformation of a layered sodium silicate, kanemite, into zeolite Beta (BEA). Microporous Mesoporous Mater. **64**, 41–50 (2003)

Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T.: Reporting physisorption data for gas/solid systems. Pure Appl. Chem. **57**, 603–619 (1985)

Stoeckli, F., Jakubov, T., Lavanchy, A.: Water adsorption in active carbons described by the Dubinin-Astakhov equation. J. Chem. Soc. Faraday Trans. **90**, 783–786 (1994)

Terzyk, A.P., Gauden, P.A., Rychlicki, G.: Corrected thermodynamic description of adsorption via formalism of the theory of volume filling of micropores. J. Colloid Interface Sci. **298**, 66–73 (2006)

Vaughan, D.E.W.: In: Burch, R. (ed.) Pillared Clays, Catalysis Today, pp. 187–198. Elsevier, Amsterdam (1988)