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Evaluation of adsorption properties of zeolites using inverse gas chromatography: comparison with immersion calorimetry

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Abstract

Adsorption properties (enthalpy of adsorption, free energy of adsorption as well as the dispersive and specific components of free energy of adsorption) of several hydrocarbons on zeolites 13X and 5A have been evaluated by inverse gas chromatography (IGC). A parallelism between the effects of the molecular diameter on the enthalpy of immersion and the parameter of specific interaction was found for series of hydrocarbon with the same number of carbon atoms. For polar compounds, dipolar moment presents a key role on the relationship between calorimetric and chromatographic data.

Keywords: Inverse gas chromatography; Immersion calorimetry; Zeolite 13X; Zeolite 5A

1. Introduction

The understanding of adsorption phenomena at the solid/gas and solid/liquid interfaces requires experimental methods able to characterize the solid surface in terms of surface area, porosity, nature and energy of active sites. Sorption measurements are very common in the characterization of solid/gas interfaces for various materials. These measurements can provide thermodynamic information (for instance surface energy or heat of adsorption) as well as kinetic information, such as diffusion rates. The thermodynamic data can be used to estimate and compare the relative strengths of intermolecular forces between the adsorbent and different adsorbates and to study the interactions between the adsorbate and the adsorbent. In gas adsorption studies, inverse gas chromatography (IGC) is the most common method to obtain heats of adsorption [1]. Surface free energy of the adsorbent, obtained by IGC, allows the exhaustive study of surfaces since it can be divided into dispersive and specific component, the latter due to adsorbates other than *n*-alkanes [2,3].

IGC offers an alternative to the conventional gravimetric or volumetric methods for determining adsorption equilibrium isotherms, due to its simplicity, the shorter measurement time and a wider range of experimental possibilities. IGC has been widely utilized in the last years to study adsorbents [3,4], foods [5], carbon blacks [6] and fibers [7].

On the other hand, when a solid is immersed into a non-reacting liquid a given amount of heat is evolved. This heat, related to the formation of an adsorbed layer of liquid molecules on the solid surface, is called ‘heat of immersion’ or ‘heat of wetting’. The heats of immersion of a given solid into different liquids are usually different, and they are not related only to the surface area available to the liquid, but also to the physico-chemical interaction between the solid surface and the probe liquid. The measurement of heats of immersion into liquids with different molecular sizes is a widely used technique to determine the pore size distribution of solids with similar surface chemistry. When polar surfaces are analyzed, the total value of heat of immersion is due to both the surface accessibility of the immersion liquid and the specific interactions between the solid surface and the liquid molecules. Moreover, immersion calorimetry has also been applied to the characterization of acidic and basic sites, through the determination of the enthalpies of

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neutralization of acidic and basic groups by titrated solutions of NaOH, $NaHCO_3$ and HCl [8] and correlations between the enthalpy of immersion and various surface groups characterized by direct titration have been established. Recent applications of immersion calorimetry for surface studies are applied to microporous adsorbents, such as carbon surfaces [9–11] and zeolites [12]. Immersion calorimetry data for the wetting of a solid in a pure liquid could be obtained by two different procedures. Either the dry solid is immersed into a liquid or it is first covered by an adsorbed layer of the corresponding vapour and then immersed in the liquid.

The scope of this work is to find a relationship between parameters of adsorption obtained by IGC and the enthalpy of immersion taking the data reported in the literature [13]. These studies have been carried out with two kinds of zeolites, and using *n*-hexane, cyclohexane and benzene, as well as chlorinated compounds (chloroform, trichloroethylene and tetrachloroethylene), as adsorbates.

Zeolites, crystalline aluminosilicates with empirical formula $M_{2/n}O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$, where M is an exchangeable cation of valence *n*, are widely used as adsorbents and catalysts due to: (i) their molecular sieve ability due to their internal structure, composed by cavities and channels with uniform dimensions, (ii) their catalytic function, attributed to their surface acidity (presence of Al^{3+} ions replacing some Si^{4+} ions in the framework), (iii) their capacity to exchange cations to transition metals, that can act as catalysts themselves. Molecular sieve zeolites such as 13X zeolite (also known as NaX) have been used for hydrocarbon adsorption [14], and more recently, molecular sieves of 5A type (CaA) [15,16].

2. Experimental

Zeolites 13X and 5A were used in this work, both supplied by Alltech, and available in the range 40–60 mesh. Solutes employed in adsorption studies were hexane from Fluka (>99.5% purity), and cyclohexane, benzene, chloroform, trichloroethylene and tetrachloroethylene from Panreac (>99% purity), in order to study thermodynamics of the adsorption of several kinds of common volatile organic compounds (VOCs). Helium (>99.9995% purity) was supplied by Air Liquide.

Basically, chromatographic measurements were carried out in a Varian 3800 gas chromatograph with a thermal conductivity detector, as described elsewhere [17,18]. The zeolite (0.6 g) was placed into a 27 cm length of stainless steel column, with passivated inner walls and an inside diameter of 5.3 mm (o.d. 1/4 in.). Packing of the catalyst was accomplished with mechanical vibration, and the two ends of the column were plugged with silane-treated glass wool. The columns were then stabilized on the GC system at 300 °C overnight under a helium flow rate of 30 mL/min.

Measurements were carried out in the temperature range of 200–270 °C, and the thermodynamic equilibrium in adsorption measurements is ensured employing the flow rate of carrier gas for which there was no contribution of molecular diffusion: 50 mL/min was found to be the proper carrier gas flow rate for cyclohexane, benzene, trichloroethylene and tetrachloroethylene over zeolite 13X, whereas for chloroform and *n*-hexane in the case of the same zeolite 13X and for all the compounds studied for the zeolite 5A, at 30 mL/min have reached constant specific retention volume, V_g:

$$V_g = Fj\frac{t_R - t_M}{m}\left(\frac{p_o - p_w}{p_o}\right)\left(\frac{T}{T_{meter}}\right) \tag{1}$$

where t_R is the retention time in min, t_M the retention time of non-adsorbing marker (hold up time), p_o the outlet column pressure, p_w the vapour pressure of water at the flowmeter temperature in Pa, T the column temperature, T_{meter} the ambient temperature in K, and j the James-Martin compressibility factor.

3. Results and discussion

3.1. Enthalpy of adsorption

Commercial zeolites used in chromatographic study were characterized by nitrogen adsorption, obtaining a Langmuir surface area of 571 m^2/g (13X) and 550 m^2/g (5A). Moreover, their mesopores pore volume were 0.165 and 0.062 cm^3/g for 13X and 5A and micropores pore volume 0.170 and 0.176 cm^3/g, respectively.

Silvestre-Albero et al. [13] claim that immersion calorimetry is able to evaluate the microporous network of zeolites by using liquids with similar chemical interaction but different molecular size. Since diameter of molecules is known, it is possible to establish pore size distribution. The experimental values of enthalpy of adsorption obtained in this work and derived with Eq. (2), for both types of investigated zeolites as adsorbents, and for *n*-hexane, cyclohexane and benzene, as adsorbates, and compared with the enthalpy of immersion into the same liquids at 30 °C [13], in J/g (gram of zeolite), Fig. 1:

$$\Delta H_{ads} = -R\frac{\partial(\ln V_g)}{\partial(1/T)} \tag{2}$$

Zeolite 13X, which has an entrance window of about 0.75 nm, allows three adsorbates studied here (*n*-hexane, 0.43 nm; cyclohexane, 0.48 nm; benzene, 0.57 nm [13]) to penetrate into its supercage. Enthalpies of immersion follow exactly the same trend as the enthalpies of adsorption. In the case of zeolite 5A, *n*-hexane can enter the microporosity of the zeolite, but the entrance of about 0.44 nm is restricted to cyclohexane and benzene. However, the fact that the molecules cannot penetrate the zeolitic structure does not impede to maintain values of enthalpy of adsorption nearly as those obtained in the case of zeolite 13X.

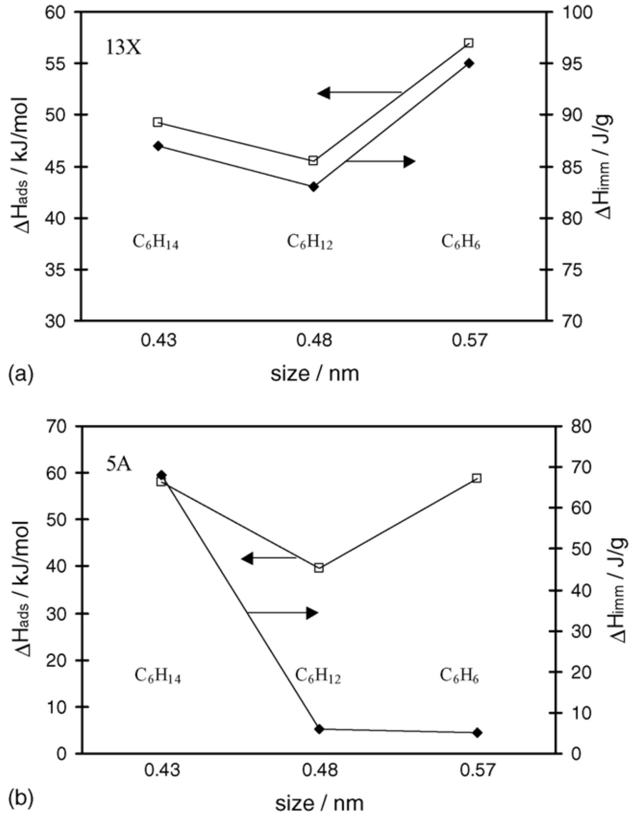

Fig. 1. Representation of enthalpy of adsorption and enthalpy of immersion vs. size of molecules of adsorbates for (a) zeolite 13X and (b) zeolite 5A.

It is important to note that the diffusion of molecules through the pores of zeolite crystal has been minimized at the conditions of IGC experiments [18]. On the other hand, both diffusion and capillarity forces play an important role in the enthalpy of immersion. The diffusion of molecules in the pores can be classified into different regimes depending on pore diameter. For macropores, collisions between the molecules occur much more frequently than collisions with the wall, and molecular diffusion is the dominant mechanism. As the size of the pores decreases, the number of the collisions with the wall increases until it finally becomes smaller than the mean free path. At this point, Knudsen diffusion takes over and the mobility starts to depend on the dimensions of the pore. At even smaller pore sizes, in the range of 2 nm and smaller, when the pore diameter becomes comparable to the size of the molecules diffusion takes place in the micropores of zeolites and is called configurational diffusion. Due to the small distance between the molecules and the pore wall, the molecules are more or less physically bonded to it, and the mechanism is comparable to a surface diffusion. In this regime, diffusion will depend strongly on the pore diameter, the structure of the pore wall, the interactions between the surface atoms and the diffusing molecules and the way the channels are connected. Uryadov and Skirda [19] have studied the system 13X/*n*-decane and they find self-diffusion as the channel diameters and diameters of fluid molecules are similar. This process is an equilibrium process (whereas the transport diffusion requires a chemical potential gradient), and satisfies the single-file diffusion regime (molecules diffuse through a zeolite with a one-dimensional channel network), characterized by a dramatic decrease in mobility of the molecules. Likewise, the capillarity forces play an important role; in fact, the immersion calorimetry in its standard form is well suited for wetting systems. However, the transition from capillarity to diffusion phenomena is not completely understood [20]. So, as it was shown in Fig. 1, both the interaction between the liquid molecule and the adsorbent and the enthalpy of immersion increase as the pore aperture increases. Likewise, the enthalpies of adsorption, less affected by the diffusion of molecules into the zeolitic structure and by the capillarity forces are not so influenced by the pore diameter.

3.2. Dispersive and specific components of surface free energy

For a given adsorbate, the free energy of adsorption is the sum of energies of adsorption attributed to dispersive and specific interactions. As in the case of the free energy of adsorption, the surface free energy of the adsorbent, γ_{S} (J/m^2), may be split into dispersion, $\gamma_{\mathrm{S}}^{\mathrm{D}}$, and specific, $\gamma_{\mathrm{S}}^{\mathrm{S}}$, contributions, corresponding to the dispersion and specific interactions, respectively [21]:

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}^{\mathrm{S}} + \gamma_{\mathrm{S}}^{\mathrm{D}} \tag{3}$$

The dispersive component, intrinsic and unspecific for all molecules, is due to London forces. The specific component of the surface free energy is closely related with the parameter of specific interaction of polar solutes (I^{sp}). This parameter involves the surface properties in terms of potential and acid–base interactions and may be determined from the difference of free energy of adsorption, $\Delta(\Delta G)$, between a polar solute and the real or hypothetical *n*-alkane with the same surface area [22], so it could be calculated for all molecules with the exception of *n*-alkanes:

$$I^{\mathrm{sp}} = \frac{\Delta(\Delta G)}{Na_{\mathrm{p}}} \tag{4}$$

where a_{p} is the polar solute surface area.

Fig. 2 shows the parallelism between the parameter of specific interaction of polar solutes, I^{sp} and the enthalpies of immersion for *n*-hexane, cyclohexane and benzene.

When the structure of the zeolite allows the entrance of the molecules of the liquid (zeolite 13X), there is a lineal relationship between enthalpy of immersion and the diameter of the molecule of the liquid for the same number of carbon atoms. Moreover, the slope of the straight line of the evolution of I^{sp} and ΔH_{im} with molecular size of the adsorbate is almost equal to that of the representation of the parameter of specific interaction versus the size of the adsorbate. The evolution of the parameter of specific interaction with the size of the adsorbate for zeolite 5A exhibits a similar behaviour as in the

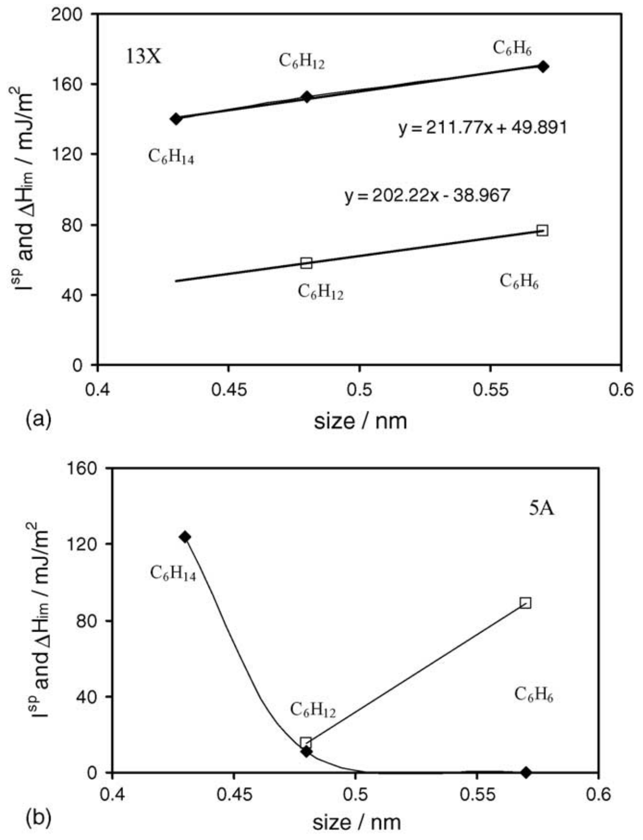

Fig. 2. Representation of the parameter of specific interaction of cyclohexane and benzene (☐) and the enthalpies of immersion (◆) for *n*-hexane, cyclohexane and benzene on (a) zeolite 13X and (b) zeolite 5A.

case of the zeolite 13X, however the enthalpy of immersion is nearly null for those molecules whose diameters are higher than the aperture diameter of the zeolite.

The three molecules tested up to now, *n*-hexane, cyclohexane and benzene are apolar molecules. However, in order to study the polarity of the zeolitic surface, polar molecules must be used for establishing the specific interactions between the surface and the wetting molecule or adsorbate. Representation of enthalpy of immersion versus diameter of wetting molecule (from [13]) for polar ones gives a curve (not shown). Chessick et al. [23] and Zettlemeyer et al. [24] aimed that if data of immersion calorimetry are plotted as a function of the dipole moment of the wetting molecule, they could fit them reasonably well to a straight line. They aimed that the slope of this straight line allowed estimating the average field strength of the surface and the intercept gave the non-specific contribution to the interaction energy. On the other hand, Silvestre-Albero et al. [13] indicated that there is a relationship between the enthalpy of immersion into chlorinated compounds and the dipole moment, but the intercept gives a positive value, which would mean that the process is endothermic, which is not possible.

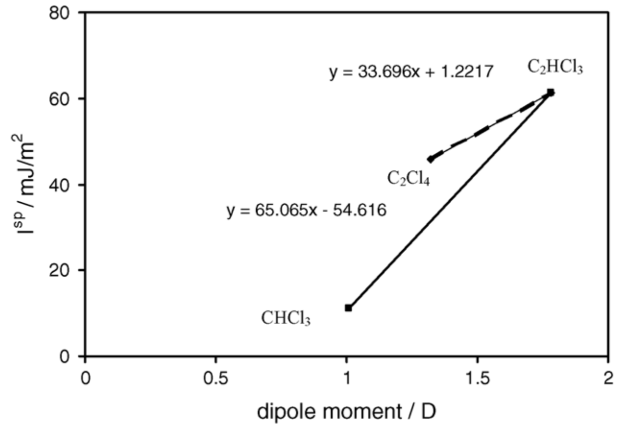

Fig. 3. Evolution of parameter of specific interaction of zeolite 13X at 250 °C for chloroform, trichloroethylene and tetrachloroethylene as function of dipolar moment: compounds with the same number of carbon atoms (discontinuous line) and compounds with the same number of chlorine atoms (continuous line).

The evolution of the parameter of specific interaction of polar compounds, obtained by IGC, as function of dipole moment (chloroform, 1.01 D; trichloroethylene, 1.78 D; and tetrachloroethylene, 1.32 D) is depicted in Fig. 3. The evolution of I^{sp} versus the dipole moment is represented as function of the number of carbon atoms and the number of chlorine atoms. The representation according to the number of carbon atoms gives also a positive value of the intercept, however, the representation as function of the number of chlorine atoms leads to a reasonable value of non-specific interaction.

The dispersive component, intrinsic and unspecific for all molecules, is given from chromatographic data by:

$$\gamma_S^D = \frac{1}{4}\frac{\Delta G_{CH_2}^2}{\gamma_{CH_2} N^2 a_{CH_2}^2} \qquad (5)$$

where N is the Avogadro number, a_{CH_2} is the area occupied by a $-CH_2$ group (0.06 nm^2), and γ_{CH_2} (mJ/m^2) the surface tension of a surface consisting of CH_2 groups, which is a function of temperature in °C:

$$\gamma_{CH_2} = 35.6 + 0.058(20 - T) \qquad (6)$$

In order to explain the relationship between the negative intercept, due to non-specific interaction (if we assumed that the aim of Chessick and Zettlemoyer is also appropriate in the representation of parameter of specific interaction obtained by IGC instead of the enthalpy of immersion), and the dispersive component of the surface free energy of the adsorbent, both are represented as function of temperature, Fig. 4.

The same trend is observed between both representations: they decrease as temperature increases, although there exist a high difference between two series of values (the first series is multiplied by 2) and the variation of γ_S^D is much slighter.

On the other hand, with the aim to find a relationship between the slope of the straight line of Fig. 3 with the strength of the interaction between the adsorbate and the adsorbent, data of the slope of I^{sp} of zeolite 13X versus dipolar moment for compounds with the same number of chlorine atoms

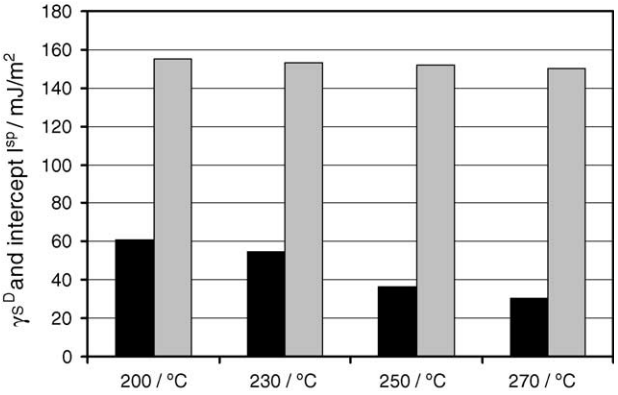

Fig. 4. Relationship between intercept I^{sp} of zeolite 13X vs. dipolar moment for compounds with the same number of carbon atoms (black) and the dispersive component of surface energy, γ_S^D (grey).

are represented as function of temperature, Fig. 5. Likewise, data of the free energy of adsorption are represented versus temperature for chloroform and trichloroethylene, both compounds implied in the study.

From chromatographic data, the standard free energy of adsorption at infinite dilution, ΔG_{ads} (J/mol), can be expressed as [2,3,16]:

$$\Delta G_{\text{ads}} = -RT \ln\left[\frac{p_0 V_g}{\pi_0 A}\right] \tag{7}$$

where A is the specific surface area, and π_0 is the spreading pressure of the adsorbed gas in the De Boer standard state, which was taken as 338 μN/m [25].

Fig. 5 shows an unexpected coincidence between the shape of the curves, which represent the evolution of the free energy of adsorption, and the parameter, which would represent the strength of the interaction between adsorbate and adsorbent (slope of I^{sp} versus dipolar moment). Furthermore, although the unit of measure is different for both parameters to consider, the sum of the slopes corresponding to free energy of adsorption as function of temperature for chloroform (−2.124) and trichloroethylene (−1.395), is approximately the slope of the first parameter (−3.552).

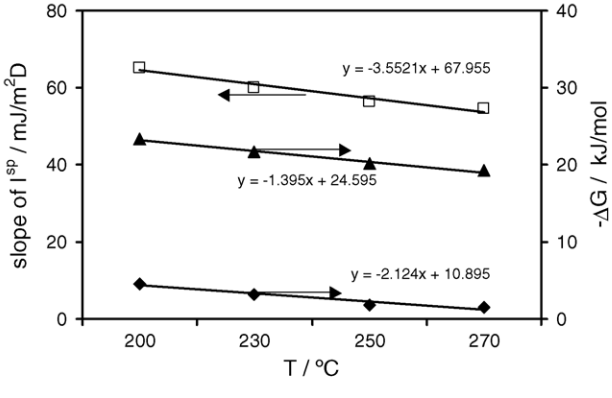

Fig. 5. Relationship between free energy of adsorption (kJ/mol), chloroform (♦) and trichloroethylene (▲) and the slope of I^{sp} vs. dipolar moment as function of temperature (□).

4. Conclusions

Adsorption parameters obtained by IGC on zeolites 13X and 5A have been compared and related to data obtained by calorimetry of immersion. The following conclusions were reached:

(1) For series of hydrocarbons (null dipolar moment) with the same number of carbon atoms (*n*-hexane, cyclohexane and benzene), there is a constant difference between the enthalpy of adsorption and the enthalpy of immersion when they are represented as function of the size of the molecules, as long as the aperture diameter of the zeolite allows to penetrate into its structure the wetting liquid. Moreover, representations of enthalpies of immersion versus size of molecules of wetting liquid gives a straight line whose slope is equal to that resulting of representing the parameter of specific interaction, I^{sp}, as function of the size of adsorbate.

(2) In the case of polar molecules (chlorinated compounds), a representation of ΔH_{imm} versus dipolar moment leads to a straight line, however its intercept, which would mean the non-specific interaction, gives a positive value when compounds of the same number of carbon atoms are used. If compounds of the same number of chlorine atoms are represented, the intercept gives a negative value. It follows the same trend with temperature that the dispersive component of surface energy obtained by chromatography, however its variation is much more pronounced.

(3) The slope of the straight line resulting of representing ΔH_{imm} versus dipolar moment means the strength of interaction between the solid and the wetting liquid. For series of chlorinated compounds with the same number of chlorine atoms, its evolution as function of temperature reveals that its slope is the sum of the slopes of the lines, which represent $-\Delta G_{\text{ads}}$ versus temperature.

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References

[1] J. Jagiello, T.S. Bandos, J.A. Schwarz, Carbon 30 (1992) 63–69.
[2] S.K. Milonjic, Colloids Surf. 149 (1999) 461–466.
[3] J. Xie, M. Bousmina, G. Xu, S. Kaliaguine, J. Mol. Catal. 135 (1998) 187–197.

[4] M.P. Elizalde-González, R. Ruíz-Palma, J. Chromatogr. A 845 (1999) 373–379.
[5] A. Boutboul, F. Lenfant, P. Giampaoli, A. Feigenbaum, V. Ducret, J. Chromatogr. A 969 (2002) 9–16.
[6] E. Papirer, E. Brendle, F. Ozil, H. Balard, Carbon 37 (1999) 1265–1274.
[7] A. Vega, F.V. Díez, P. Hurtado, J. Coca, J. Chromatogr. A 962 (2002) 153–160.
[8] M.V. López-Ramón, F. Stoeckli, C. Moreno-Castilla, F. Carrascoso Marín, Carbon 37 (1999) 1215–1221.
[9] F. Rodríguez-Reinoso, M. Molina-Sabio, Adv. Colloid Interf. Sci. 76/77 (1998) 271–294.
[10] M.V. López-Ramón, F. Stoeckli, C. Moreno-Castilla, F. Carrascoso Marín, Carbon 38 (2000) 825–829.
[11] G.S. Szymanski, S. Biniak, G. Rychlicki, Fuel Process. Technol. 79 (2002) 217–223.
[12] B. Garrot, G. Coudeerc, M.-H. Simonot-Grange, F. Stoeckli, Micropor. Mesopor. Mater. 52 (2002) 199–206.
[13] J. Silvestre-Albero, C. Gómez de Salazar, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, Colloids Surf. 187/188 (2001) 151–165.
[14] O. İnel, D. Topaloğlu, A. Aşkin, F. Tümsek, Chem. Eng. J. 88 (2002) 255–262.
[15] F. Tümsek, O. Inel, Chem. Eng. J. 94 (2003) 57–66.
[16] C. Bilgiç, A. Aşkin, J. Chromatogr. A 1005 (2003) 281–286.
[17] E. Díaz, S. Ordóñez, A. Vega, J. Coca, Micropor. Mesopor. Mater. 70 (2004) 109–118.
[18] E. Díaz, S. Ordóñez, A. Vega, J. Coca, J. Chromatogr. A 1049 (2004) 139–146.
[19] A.V. Uryadov, V.D. Skirda, Magn. Reson. Imaging 19 (2001) 429–432.
[20] V.N. Bogomolov, Phys. Rev. B 51 (1995) 17040–17045.
[21] R.A. Bailey, K.C. Persaud, Anal. Chem. Acta 363 (1998) 147–156.
[22] J. Xie, Q. Zhang, K.T. Chuang, J. Catal. 191 (2000) 86–92.
[23] J.J. Chessick, A.C. Zettlemoyer, F.H. Healey, G.J. Young, Can. J. Chem. 33 (1955) 251–258.
[24] A.C. Zettlemeyer, J.J. Chessick, C.M. Hollabaugh, J. Phys. Chem. 62 (1958) 489–490.
[25] J.H. De Boer, The Dynamical Character of Adsorption, Clarendon, Oxford, 1953.