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GASEOUS HYDROCARBON ADSORPTION ON A GRANULATED ACTIVATED CARBON. EXOTHERMIC EFFECTS.

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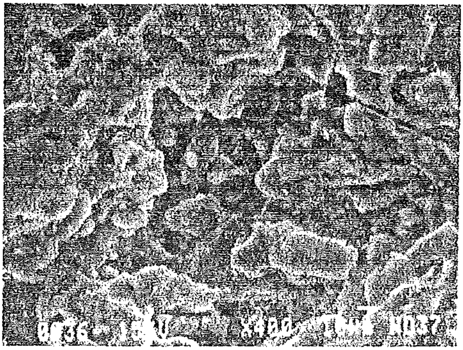
ABSTRACT

The adsorption of n-butane on an extruded cylindrical activated carbon was studied providing two kinds of information: the influence of the temperature and the hydrocarbon partial pressure on the adsorption dynamics (kinetic study) and on the carbon adsorption capacities (thermodynamic study). The activated carbon used showed a bimodal porous distribution (micropores and large macropores) and a rather homogeneous site distribution. The thermodynamical aspect could be interpreted by a Langmuir model. Generally, adsorption kinetic curves are described by diffusion models which often assume isothermal and isobaric conditions (1,2,3). Nevertheless, we have experimentally proved in this paper that strong temperature variations occur inside the particles during the adsorption. In our case, we have showed that experimental kinetic curves were found to be in good agreement with the predictions of a kinetic Langmuir law which corresponds to an interfacial limiting step and which takes into account the inner temperature variations.

1 - INTRODUCTION

One of the main characteristics of active carbons is the great diversity of their geometrical and chemical properties. They depend on the origin of the raw material and on the conditions under which this material has been prepared. Thus, from a chemical point of view, the activation makes possible the creation of organic groups which act as adsorption sites on the solid surface. From a geometrical point of view, depending on the natural origin



Photography 1. SEM photograph of the extruded active carbon surface.

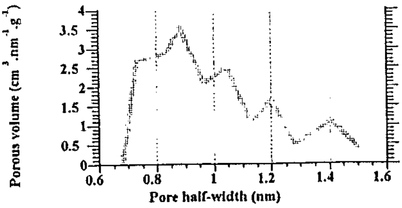


Figure 1. Pore size distribution from nitrogen adsorption.

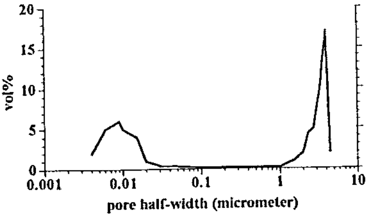


Figure 2. Pore size distribution from mercury porosimetry.

of the carbon and the activation process, active carbons will possess a pore size distribution centered on one or several particular sizes (4). This solid also presents the particularity of containing an important microporous texture. The whole surface area of the solid is developped in these micropores, usually considered as slit-shaped pores separating disordered aromatic sheets (5).

The wide range of physicochemical active carbon properties offers the opportunity of using these materials in numerous industrial fields: for instance water treatment, precious metal recovery (6) or sugar refining. The particular case of gas treatment and more precisely the removal of fuel vapours evolved from automotive vehicle tanks is the industrial application which has motivated the following work. These vapours exhibit harmful effects on human health: carcinogenic agents, smog formation agents (7)...

Our objective consists of following the behaviour of an active carbon placed in contact with gaseous n-butane, a major compound of fuel vapours. Two kinds of information are expected in this study: the influence of temperature and hydrocarbon partial pressure on the adsorption dynamics (kinetic study) and on the carbon adsorption capacities (thermodynamic study) will be examined and discussed.

2 - EXPERIMENTAL SECTION

2.1 - Features of our active carbon

The active carbon used is composed of extruded cylindrical granules (5 mm high; 2 mm diameter). The density ρ_s, the porosity ε and the porous volume V_p have been measured by helium pycnometry (MICROMERITICS AccuPyc 1330 apparatus):

$\rho_s = 1.6\ \text{g.cm}^{-3}$

$\varepsilon = 0.65$

$V_p = 1.15\ \text{cm}^3.\text{g}^{-1}$

Specific surface area and porous distribution were obtained from the 77 K nitrogen adsorption isotherm (MICROMERITICS Asap 2000 apparatus). The shape of this isotherm is characteristic of microporous materials. By using the BET conventional method, the specific surface area is estimated at 1665 m^2.g^{-1} whereas the De Boer t curve, more suited for microporous materials, gives a value of 1550 m^2.g^{-1}. The use of the Brunauer method shows the presence of micropores around an average half-width of 0.9 nm (figure 1). Moreover, this active carbon extruded granules possess macropores (dimension around

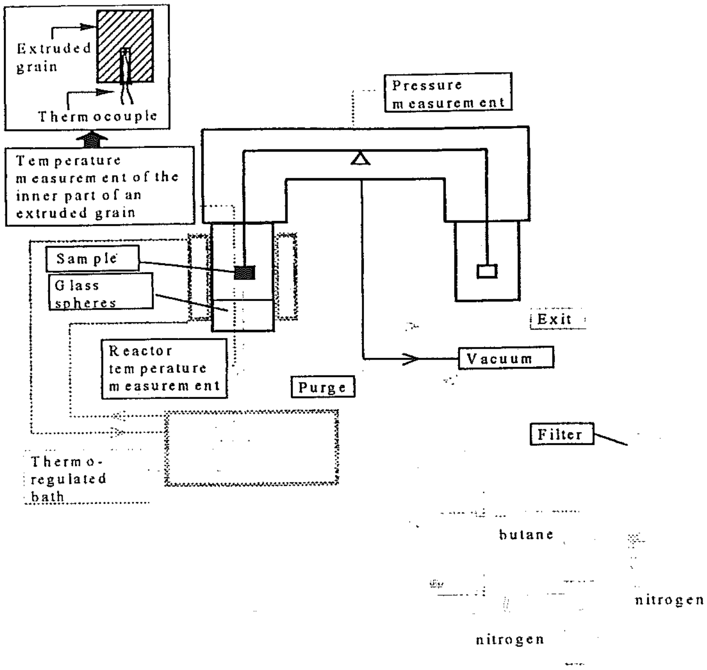


Figure 3. TGA: experimental apparatus.

20 μm) which can be seen by Scanning Electron Microscopy (photograph 1) and which allow the entrance into the inner microporous texture. On the other hand, these observations are confirmed by mercury porosimetry results (CARLO ERBA Porosimeter 2000 apparatus) which show a bimodal distribution (figure 2).

Chemically speaking, X-ray fluorescence, spectrometry and elementary organic analyses show obviously the presence of a majority of carbon atoms (62 moles%), hydrogen atoms (25 moles%) and oxygen atoms (12 moles%) at the basis of several organic functions contained in the active carbon.

2.2 -Adsorption of n-butane: experimental conditions

Experimentally, the adsorption on active carbon is followed by thermogravimetric analysis (TGA); n-butane is diluted in an inert carrier gas (nitrogen) under atmospheric pressure. Nitrogen and n-butane are mixed by using a bank of thermal mass flowmeters. Figure 3 schematizes the TGA apparatus. The thermobalance is a SETARAM MTB 10-8 one. Before each experience, adsorbed gases are removed from the samples (mass = 30 mg) by a vacuum pump and then the balance is pressurized under high-purity nitrogen (pressure: 1 atmosphere). After being heated at the same temperature as the reactor one, the n-butane / nitrogen mixture is introduced through a small cylindrical tube (2 mm in diameter) just 2 cm under the solid sample (lying on a metal wired squared 1 cm x 1 cm vessel). The distance between the n-butane / nitrogen mixture inlet and the sample as well as the gaseous mixture velocity are chosen so that no dilution occurs. The sample mass gain is monitored continuously until equilibrium. n-butane adsorption experiments were achieved for 6 values of hydrocarbon partial pressures (from 0.01 atm to 0.9 atm) and 7 values of temperatures (from -5°C to 85°C).

Since the adsorption on our active carbon presents a very high adsorption rate, it should produce strong exothermic effects. Thus, we have measured the temperature variations of the inner central part of an extruded granule during the adsorption thanks to a microthermocouple.

3 - GASEOUS n-BUTANE ADSORPTION - RESULTS & DISCUSSION

3.1 - Equilibrium adsorption capacities

Classical results are obtained in the case of n-butane fixation on our extruded activated carbon: the quantity of n-butane mass adsorbed when the equilibrium is reached increases as the hydrocarbon partial pressure increases or as the temperature decreases. These experimental results are in a fairly good agreement with the Langmuirian expression (figure 4):

$$m_e = m_{tot}\left(\frac{KP}{1+KP}\right) \qquad \text{(E1)}$$

where m_e = mass of n-butane adsorbed at the thermodynamic equilibrium per unit mass of active carbon $[g.g^{-1}]$

m_{tot} = mass of n-butane that can be fixed in the whole porous system per unit mass of active carbon $[g.g^{-1}]$. Constant whatever P and T.

P = n-butane relative partial pressure (relative to 1 atm)

K = thermodynamic constant which follows Van't Hoff equation :

$$K = \exp\left(\frac{\Delta_a S^0}{R}\right)\exp\left(\frac{-\Delta_a H^0}{RT}\right) = K_0 \exp\left(\frac{-\Delta_a H^0}{RT}\right) \qquad \text{(E2)}$$

where $\Delta_a H^0$ = adsorption standard enthalpy variation $[J.mol^{-1}]$

$\Delta_a S^0$ = adsorption standard entropy variation $[J.mol^{-1}.K^{-1}]$

The good fits of the Langmuirian thermodynamic model (E1) provide m_{tot} and K = f(T) parameters. A value of 0.389 $g.g^{-1}$ is obtained for m_{tot}. The thermodynamic constants are summarized in Table 1. Thermodynamic constants should also verify the Van't Hoff equation (E2). Figure 5 shows the variations of ln K versus 1/RT. A straight line is effectively obtained; thus, $\Delta_a H^0$ and $\Delta_a S^0$ can be deduced: $\Delta_a H^0$ = -22 $kJ.mol^{-1}$ and $\Delta_a S^0$ = -55.5 $J.mol^{-1}\ K^{-1}$.

T(K)	268	283	298	313	328	343	358
K	18.6	10	5.72	4.05	2.8	2.05	1.41

Table 1. Langmuir model thermodynamic constants for n-butane adsorption between -5°C and 85°C.

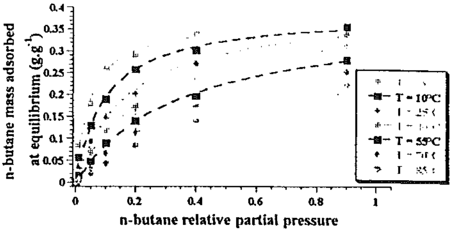


Figure 4. Isotherms for n-butane adsorption compared to Langmuir isotherm predictions

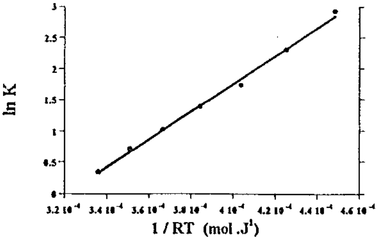


Figure 5. Verification of the Van't Hoff equation.

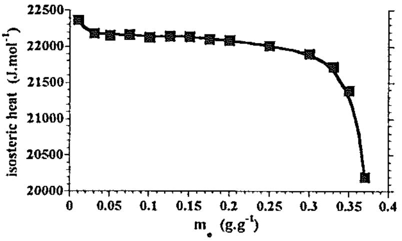


Figure 6. Variations of the isosteric heat with m_e.

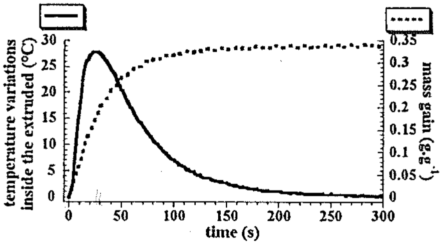


Figure 7. Example of an uptake curve with thermal effects measured in extruded particles.
P = 0.4 ; T = 268 K.

It is noticeable that $\Delta_aH^0 < 0$ and $\Delta_aS^0 < 0$ are respectively consistent with the fact that the adsorption phenomenon is exothermic and that n-butane changes from a gaseous state to a condensed matter. Moreover, according to the Clausius-Clapeyron equation, isosteric adsorption heats (q_{iso}) can be calculated versus the mass of n-butane adsorbed at the thermodynamic equilibrium m_e (figure 6), from the slopes of ln P = f (1/T) at fixed values of m_e. Over the whole range of m_e, the isosteric heat of adsorption value is nearly constant which means that each site is characterized by only one binding energy and this value is close to the standard enthalpy variation of n-butane vaporization (21 kJ.mol^{-1}) and the adsorption standard enthalpy variation deduced from the Van't Hoff law.

3.2 - Adsorption kinetics

Results. The experimental apparatus described in section 2 enables the simultaneous measurements of sample mass variations and temperature variations of the inner part of the granulated active carbon during the n-butane adsorption. A characteristic example is given on figure 7. In most cases, the n-butane adsorption is rather fast and occurs within a few minutes. In addition, an important temperature increase inside the grains has been observed. If the difference between the reactor and the inner part of the granule temperatures is generally negligible when P = 0.01 whatever the temperature might be, it can reach 40°C when P = 0.9 and T = 10°C. Therefore, the n-butane adsorption on the extruded active carbon used can not be considered as being isothermal.

Discussion. A kinetic model is required for interpretation of the experimental kinetic results. From several experimental observations, we have proposed some assumptions about the physicochemical mechanisms which occur during the adsorption of n-butane:

(a) Only three activated carbon grains have been used so that no bed effect can undergo.

(b) The gas velocity is high enough to avoid any adsorption rate limitation by the n-butane external diffusion.

(c) In a former work (8), by comparing the kinetic curves of adsorption on the used extruded activated carbon and on three sieved size fractions of a powder obtained by a grinding of the extruded grains, we have concluded that it is reasonable to think that no n-butane diffusion limitation should occur in the macroporous system. Consequently, the access to microcristallites which are separated by the macropores and which contain the microporous network should be fast.

(d) Kinetic results show that the n-butane adsorption is a very fast phenomenon. We will suppose that, after the gas arrives at the microcristallite level, the adsorption rate is limited by the interfacial reaction rate and we will also suppose that this step is governed by a kinetic law deduced from the Langmuir model. This kinetic law can therefore be linked to the thermodynamic model which was developped in section 3.1.

(e) Very important temperature variations have been measured inside the grains (ΔT_i) during the adsorption experiments. The non-isothermal aspect of the adsorption in the extruded grains of activated carbon must be taken into account in the kinetic modeling. In some cases, the temperature was also measured at the surface of the extruded grains during the adsorption (ΔT_s). The surface temperature variations are always almost equal to the ones of the inner part of the grain: $0.7\ \Delta T_i < \Delta T_s < \Delta T_i$ (in °C) (figure 8). This can be explained by the fact that the n-butane/nitrogen gaseous flux tends to slightly cool the grain surface. Thus, it can be roughly assumed that the temperature inside the grains is uniform and equal to the one measured at the center of the grains.

The adsorption specific rate [$\text{mol}_{\text{butane}}.\text{s}^{-1}.\text{m}^{-2}$] provided by the Langmuir model is :

$$v = k\,N\,(1-\theta)\,P - k'\,N\,\theta \qquad \text{(E3)}$$

where k, k' = respectively kinetic constants for adsorption and desorption [$\text{mol}_{\text{butane}}.\text{s}^{-1}.\text{mol}_{\text{site}}^{-1}$]

N = site density [$\text{mol}_{\text{site}}.\text{m}^{-2}$]

k and k' are kinetic constants verifying the Arrhenius law:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \qquad k' = k'_0 \exp\left(\frac{-E'}{RT}\right) \qquad \text{(E4) and (E5)}$$

E and E' respectively refer to energies of activation for adsorption and desorption [J.mol^{-1}]

On the other hand, the experimental rate [g.s^{-1}] measured by TGA is :

$$V_{ATG} = \frac{dm}{dt} = v\ m_0\ S\ M_{butane} \qquad \text{(E6)}$$

where m_0 = sample mass [g]

S = specific surface area [$\text{m}^2.\text{g}^{-1}$]

M_{butane} = butane molar mass [g.mol^{-1}]

By combining equations (E5) and (E6), the n-butane mass fixed on the active carbon is:

$$m = m_e\left(1 - \exp(-\alpha t)\right) \qquad \text{(E7)}$$

$$\text{where } \alpha = k\,P + k' \qquad \text{(E8)}$$

According to (E1) and (E2), m_e (called thermodynamic factor) depends on the temperature and as the grain temperature evolves with time, this factor which is obviously constant in case of an isothermal adsorption will vary with time in our case. According to (E4), (E5) and (E8), (1-exp(-αt)) (called kinetic factor) is a function of time and of temperature which varies with time. Temperature variations will have opposite effects upon the thermodynamic factor m_e and upon the kinetic factor (1-exp(-αt)): if the temperature increases, m_e decreases and (1-exp(-αt)) increases.

E and E' and k_0 and k'_0 are not independant since they are respectively linked to $\Delta_a H^0$ and K_0 determined from the thermodynamical modeling:

$$\Delta_a H^0 = E - E' \text{ and } K_0 = k_0 / k'_0 \qquad \text{(E9) and (E10)}$$

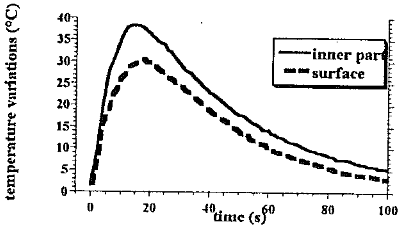


Figure 8. Comparison of the temperature variations inside and at the surface of a particle during the adsorption.
P = 0.9 ; T = 10°C.

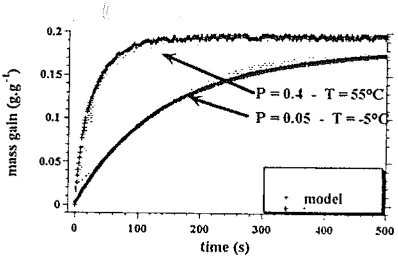


Figure 9. Experimental and modeled uptake curves.
P = 0.4 ; T = 55°C: E' = 23 kJ.mol^{-1}
P = 0.05 ; T = -5°C: E' = 22.5 kJ.mol^{-1}

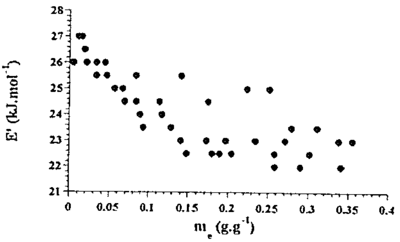


Figure 10. Variations of the fitted values of E' versus m_e.

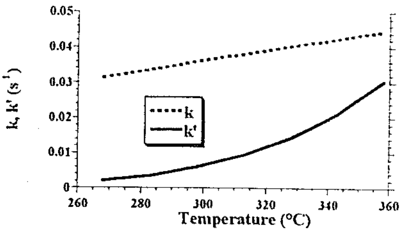


Figure 11. Variations of k and k' versus time when $k'_0 = 100$ s^{-1}, $k_0 = 0.126$ s^{-1}, E' = 24.1 kJ.mol^{-1} and E = 2.1 kJ.mol^{-1}

Hence only two parameters have to be calculated. They should be determinated so that, being constant, they allow the model equation (E7) to correctly describe each adsorption kinetic curve. If $k'_0 = 100\ s^{-1}$ ($k_0 = 0.126\ s^{-1}$), the fitted values of E' are nearly constant around an average of 24.1 $kJ.mol^{-1}$ (E = 2.1 $kJ.mol^{-1}$) for the non isotherm Langmuir kinetic model to be in good agreement with 41 adsorption kinetic curves. Figure 9 compares the experimental and modeled uptake curves in the case of two very different P-T conditions. The variations of the fitted values of E' versus m_e are plotted on figure 10: little variations of E' around 24.1 $kJ.mol^{-1}$ seem to be due to the slight heterogeneity observed on the active carbon (see figure 6) since E' calculated values decrease (as q_{iso} values do) when m_e increases.

Thus it is possible to predict kinetic curves for the adsorption of n-butane on an extruded activated carbon with a Langmuir model which takes into account the temperature variations measured inside the particles during the adsorption. Here the energy of activation is very poor as E is close to 0 and the variations of k and k' with temperature according to (E4) and (E5) are reported on figure 11. This poor value for the energy of activation is in agreement with a gas fixation looking like a physical adsorption (fast rates, adsorption enthalpies close to the gas condensation enthalpy).

CONCLUSION

The adsorption of n-butane was studied on an activated carbon showing a bimodal porous distribution and a fairly homogeneous site distribution, for a wide range of temperature and n-butane pressure conditions. Experimental data were obtained by using a thermogravimetric apparatus adapted to follow the temperature in the inner part of activated particules during the adsorption.

The Langmuir model applied to experimental results could explain the thermodynamical aspects of the adsorption. From a kinetic point of view, as the Langmuir model constants (K, k, k') depend on the temperature, the measured strong temperature variations inside the grains during the adsorption modify both kinetic constants k and k' and local thermodynamic constant K at every time. By assuming that the grain temperature is uniform and equal to the one measured inside the grain, good agreement is found between experimental uptake curves and the predictions provided by the kinetic Langmuir model including the grain temperature variations. The slight heterogeneity of the used activated carbon seems to cause little variations of E' and the adsorption is poorly activated.

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