

CHEMICAL ACTIVATION OF ANTHRACITES FOR METHANE STORAGE BY ADSORPTION

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Introduction

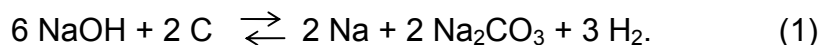
Chemical activation is probably the best method of preparing active carbons especially designed for methane storage. Indeed, pores having widths smaller than 3 nm are mostly those which are created and / or widened by such an activation process. Such pores allow a suitable and efficient densification of methane by adsorption. Moreover, the micropore size distributions (MPSDs) may be adjusted depending on the activation parameters, and only a very few mesopores, wherein methane is just compressed, are created. Materials prepared through chemical activation thus gather several features of the ideal adsorbent, as far as methane storage is concerned, namely : high micropore volumes (around 1 cm³ g⁻¹), MPSDs narrow and centred on average widths close to 0.8 nm, low mesopore volumes. As an activating agent, sodium hydroxide combines low cost, low corrosive action, easy and single-step processing. Finally, washing the NaOH-activated precursor with an acidic solution leads to a carbonaceous adsorbent of high chemical purity, with a very low ash content.

In the present work, the influence of the following activation parameters on both the pore texture and the methane storage capacities of an anthracite are investigated : temperature, mass ratio NaOH / carbon, addition of water to the activating agent, presence of a transition metal hydroxide. The first results dealing with the comparison between materials activated with different alkaline hydroxides are also given.

Experimental

A German anthracite, from the Sophia mine, was chosen as precursor. The raw material was first ground and sieved, and the grains having average sizes within the range 100 - 200 µm were simply physically mixed with sodium hydroxide beads. Several mass ratios hydroxide / anthracite, R , were tried : 1 ; 1.5 ; 2 and 3. The mixture was introduced into a nickel crucible, closed by a circular nickel sheet of the same diameter, and heat-treated in a vertical furnace under a stream of nitrogen with a flow rate of 400 ml min⁻¹. A heating rate of 5 K/min was applied up to the final activation temperature T_a which was maintained for 1 h. The crucible was then allowed to cool down to room

temperature under nitrogen flow. Dismantling of the installation was operated with extreme care, due to the presence of metallic sodium. Observation of the latter at the outlet of the reactor (transported in the vapour phase together with NaOH during the process) thus confirmed the reaction mechanism, Eq. (1) [1] :



The crucible, which cap was glued with a white soluble product identified as sodium carbonate, was submitted to atmospheric humidity for several days, during which sodium slowly oxidised. Finally, the obtained active carbon was washed with 1 M HCl first, then distilled water was used successively until its pH remains constant and close to 6. After rinsing under suction, the resultant material was dried in an oven during 24 h.

The pore textures of samples prepared under various activation conditions were investigated using the adsorption isotherms of 4 probe molecules, namely CO₂, N₂, C₆H₆ and CCl₄, having the following molecular diameters : 0.33, 0.36, 0.41 and 0.63 nm, respectively [2]. The sorption isotherms of nitrogen were obtained at 77 K with a standard commercial automatic device Sorptomatic Carlo Erba. Those of the three other adsorbates were built at 298 K using a gravimetric apparatus of the type McBain – Bakr [3,4]. The micropore volumes V(N₂, DR) and V(CO₂, DR) were calculated from application of the theory of Dubinin-Radushkevitch [5] to the adsorption isotherms of nitrogen at 77 K and carbon dioxide at 298 K, respectively. The micropore volumes V(C₆H₆, α) and V(CCl₄, α) were calculated by application of the α-plots method [6] to the adsorption isotherms of benzene and carbon tetrachloride at 298 K, respectively. The differences observed between the four calculated micropore volumes, dependent on the kind of probed pores, supply information about the pore creation or pore widening - depending on the activation temperature - occurring upon the chemical activation process.

The storage capacities of the different samples were measured at 20 °C into a classical volumetric device using highly accurate pressure transducers. For each adsorbent, the methane uptake was determined point to point by discontinuous introduction of the adsorbate into the sample holder (inner volume ≈ 1.6 cm³), up to 3.5 MPa. All the measurements were corrected from the compression of gaseous methane outside of the vessel, i.e., in the parts of the device free of adsorbent (tubes and valves). At the end of each isotherm, the maximum amount thus stored was also accurately checked by weighing the vessel before and after allowing the methane to be released at room temperature and normal pressure.

Results and Discussion

Influence of the activation temperature T_a

The effect of T_a was investigated at a constant $R = 3$. The methane storage isotherms are, as expected, of type I according to the BET classification [7]. However, at the highest equilibrium pressures (typically above 2 MPa), the isotherms are rather straight, evidencing that methane does not adsorb anymore but is just simply compressed in the

largest pores (see Fig. 1(a)). It is then interesting to calculate the true adsorption capacity Q^* of the materials, assuming that adsorption takes place within the micropores alone. For that purpose, the volume occupied by the carbon atoms and that of the micropores were subtracted from the volume of the storage vessel. The number of moles of methane purely compressed in the remaining volumes was thus calculated, and hence the amount of methane stored only in the micropores of the materials could be derived. The “corrected” storage isotherms, i.e., taking into account only the fraction of methane which is present within the micropores are presented in Fig. 1(b).

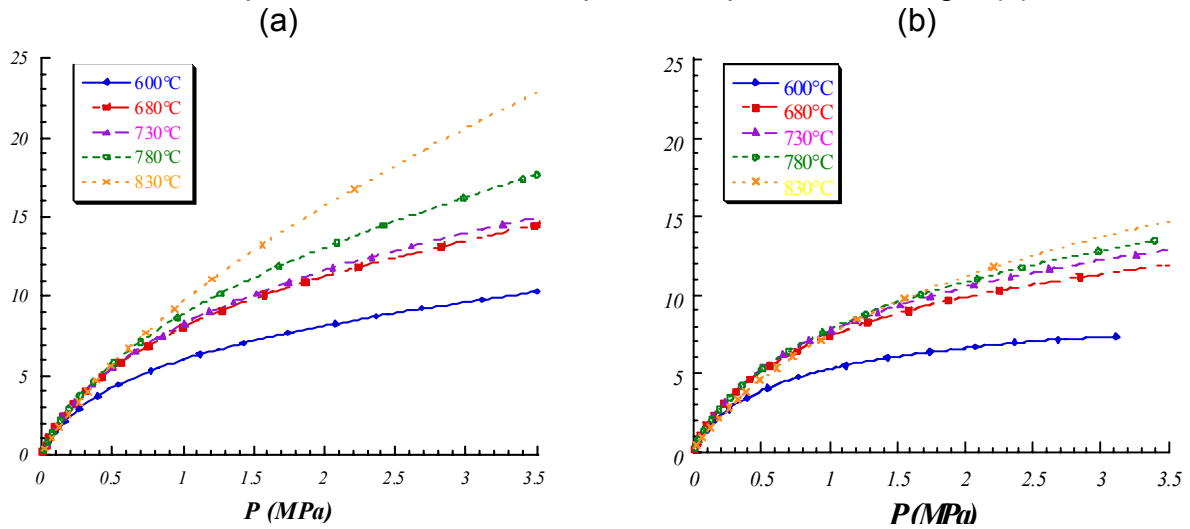


Figure 1. (a) Measured mass methane uptakes (20 °C), Q , depending on T_a . (b) Calculated mass amounts of methane, Q^* , stored only in the micropores.

The BET surface area is a linear increasing function of T_a , as seen in Fig. 2(a) ; extrapolating the straight line to the value of the area of the raw anthracite ($4 \text{ m}^2 \text{ g}^{-1}$) suggests that the activation begins at a temperature close to 450 °C. The micropore volumes, calculated from the adsorption isotherms of the 4 probe molecules, are plotted in Fig. 2(b) and evidence the following facts. Whatever the value of T_a , the ultramicropore volume ($V(\text{CO}_2, \text{DR})$, such that the width of the pore obeys $0.33 < H < 0.7 \text{ nm}$) is almost constant. $V(\text{N}_2, \text{DR})$ increases with T_a what means that, since $V(\text{CO}_2, \text{DR})$ is almost constant, the supermicropore volume ($V(\text{N}_2, \text{DR}) - V(\text{CO}_2, \text{DR})$, such that the width of the pores obeys $0.7 < H < 2 \text{ nm}$), also increases with T_a . Moreover, the volumes measured with larger probe molecules C_6H_6 and CCl_4 also increase with the temperature of the activation, thus further evidencing a widening of the supermicropores. The MPSDs were calculated by application of the Dubinin-Stoeckli (DS) method [8,9] to the nitrogen sorption isotherms measured at 77 K, and are presented in Fig. 3(a). It may be seen that increasing T_a induces both a widening of the micropores and a shift of the MPSDs towards higher values of the average micropore widths L_0 . The latter phenomenon seems to occur a little more rapidly than the widening of the full widths at half maximum (FWHMs) w , as seen in Fig. 3(b), since the slope of the straight line is slightly below 1. Another linear correlation is observed between the average micropore width L_0 and the micropore volume calculated from the nitrogen isotherms (Fig. 3(b)). Finding a slope now greater than 1 means that forming new pores occurs more rapidly than widening already existing ones.

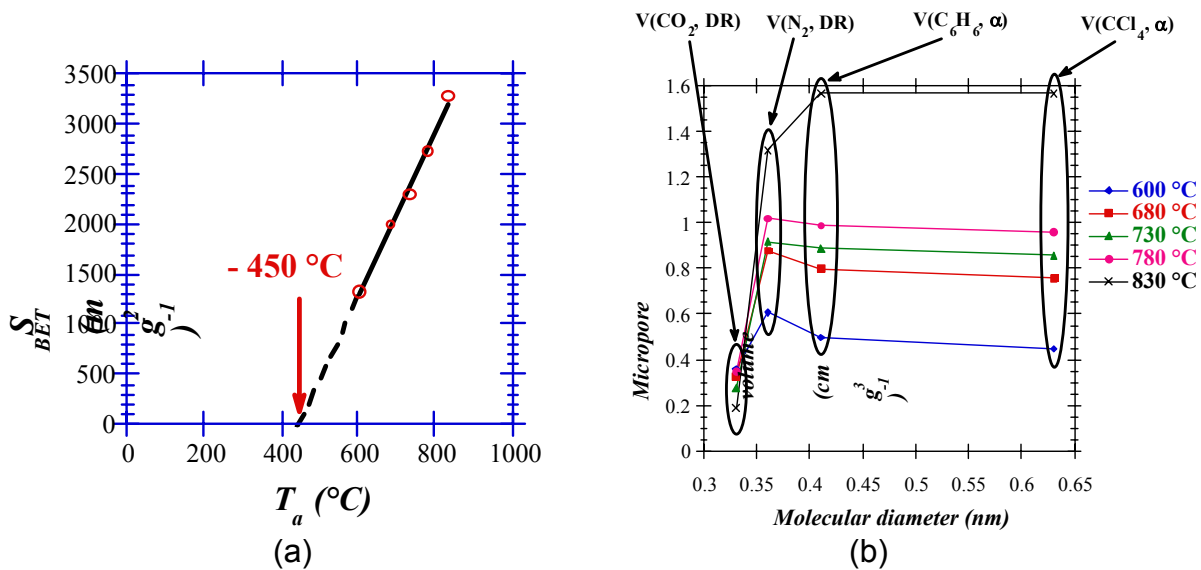


Figure 2. (a) The BET surface area vs the activation temperature T_a . (b) The micropore volume vs the diameter of the probe molecules, for several T_a .

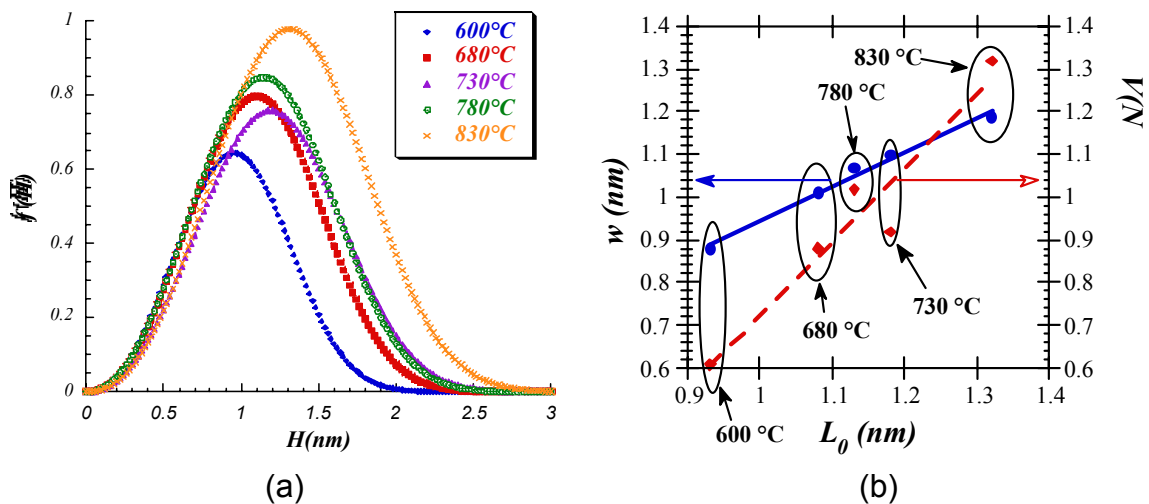


Figure 3. (a) The MPSPDs for various activation temperatures. (b) FWHMs (w) of Fig. 1(a) and micropore volumes, vs the average micropore widths (L_0).

Other results, not presented here, show that the mesopores, which are useless for an efficient storage of methane, have volumes remaining low and almost constant as far as T_a is lower than 780°C . Let us recall that methane is very strongly adsorbed within the ultramicropores, hence the deliverable amounts Q^* (3.5 MPa) - Q^{\dagger} (0.1 MPa) correspond to what is adsorbed within the supermicropores, which volume have to be optimised. Hence, since reversible methane storage is mainly due to adsorption within the supermicropores (see Fig. 4(a)), finding linear correlation between the deliverable capacities and T_a for $T_a \leq 780^{\circ}\text{C}$ (see Fig. 4(b)) is not surprising. Other linear correlation were also found between the average micropore widths L_0 and T_a , and between the fraction of micropores within the total pore volume and T_a . The latter relationship evidences that materials being more than 80 % microporous are prepared at $T_a \leq 780^{\circ}\text{C}$.

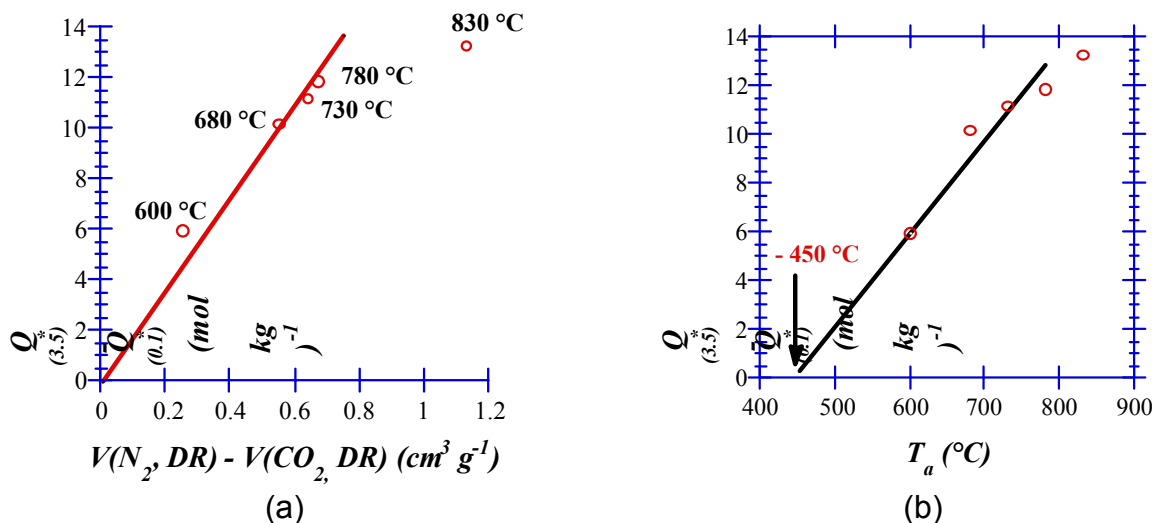


Figure 4. Deliverable mass methane capacities (within the micropores alone) (a) vs the supermicropore volumes and (b) vs the activation temperature.

Influence of the mass ratio hydroxide / anthracite R

The influence of R was investigated at a constant $T_a = 730$ °C. The methane storage isotherms are given in Fig. 5, both (a) as-measured and (b) only taking into account the adsorption within the micropores. The BET surface area is presented as a function of R in Fig.6(a). Extrapolating the curve shows that the minimum amount of NaOH for beginning of the activation is close to 0.6 g per g of raw anthracite. Again, the micropore volumes calculated from the adsorption isotherms of the 4 probe molecules are plotted in Fig. 6(b). Similar effects as those already observed while studying the influence of T_a on the pore texture are seen, namely a low effect of R on the ultramicropore volume ($V(\text{CO}_2, \text{DR})$), while the volume of the supermicropores increases with R . The MPSDs evidence a strong widening of the average micropore width L_0 at $R > 2$, while L_0 is almost constant and close to the optimum value for methane storage, i.e., 0.8 nm [10,11] (see Fig. 7(a) and (b)) for $R \leq 2$. Other results, not presented here, show that the mesopore volume increases much slower with R than the micropore one.

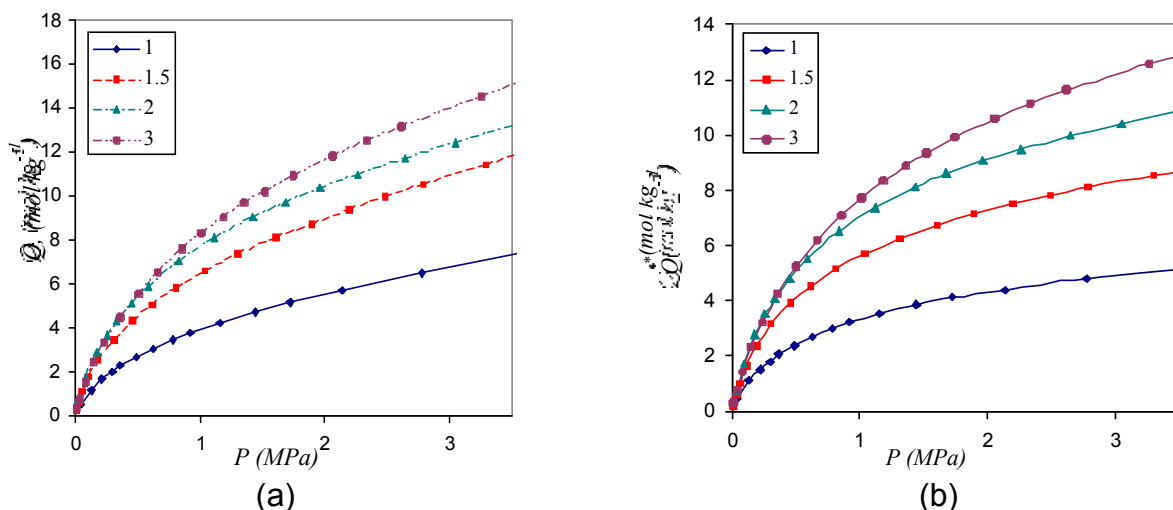


Figure 5. (a) Measured mass methane uptakes (20 °C), Q , depending on R . (b) Calculated mass amounts of methane, Q^* , stored only in the micropores.

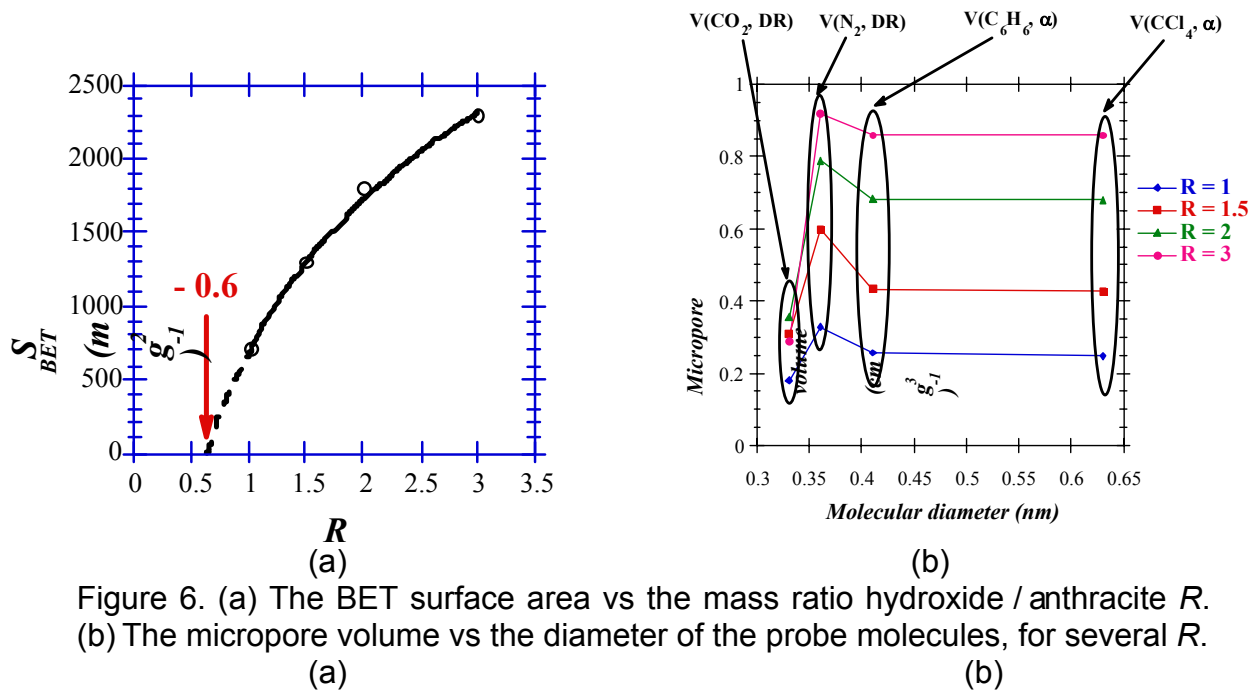


Figure 6. (a) The BET surface area vs the mass ratio hydroxide / anthracite R . (b) The micropore volume vs the diameter of the probe molecules, for several R .

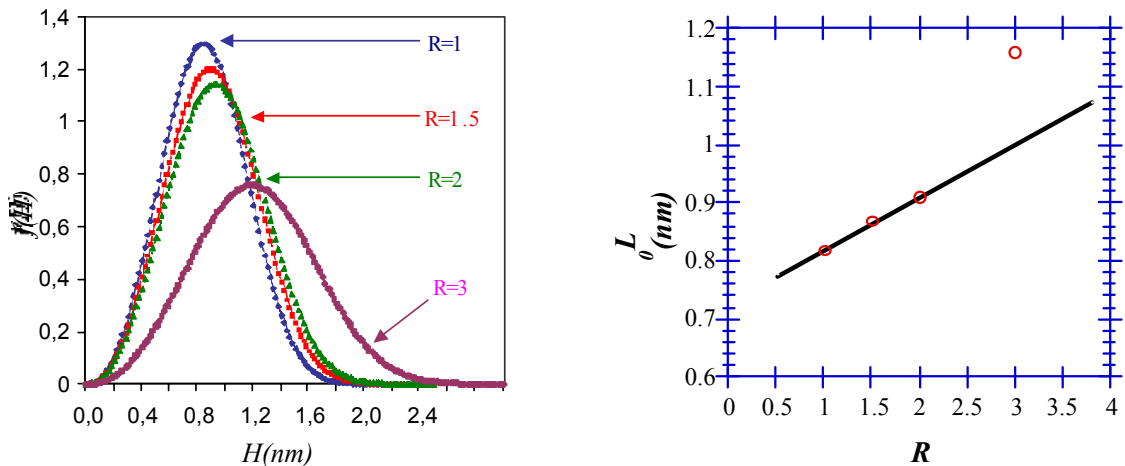


Figure 7. (a) The MPPSDs for various mass ratios hydroxide / anthracite R . (b) The average micropore widths (L_0) vs R .

The deliverable amounts of methane are plotted as a function of R in Fig. 8(a). Just like the previous case dealing with the influence of T_a , a curve similar to that of the BET surface area (Fig. 6(a)) may be seen. The quantity $Q^*(3.5 \text{ MPa}) - Q^*(0.1 \text{ MPa})$ is roughly linearly increasing with the supermicropore volume as far as R is lower than 2, see Fig. 8(b). Higher R indeed lead to wider pores, as already stated in Fig. 7(a), in which methane has a lower density, and hence deliverable capacities and supermicropore volumes are no more proportional.

Influence of the presence of water

So far, activation of the anthracite was made by physical mixing of dry sodium hydroxide beads with the carbon powder. Now, controlled amounts of water are added, resembling to the more classical impregnation technique usually encountered in chemical activation. The effect of humidity was investigated keeping constant $R = 3$ and

$T_a = 730\text{ }^\circ\text{C}$. The influence of the presence of water is shown in Fig. 9 (a) ; it may be

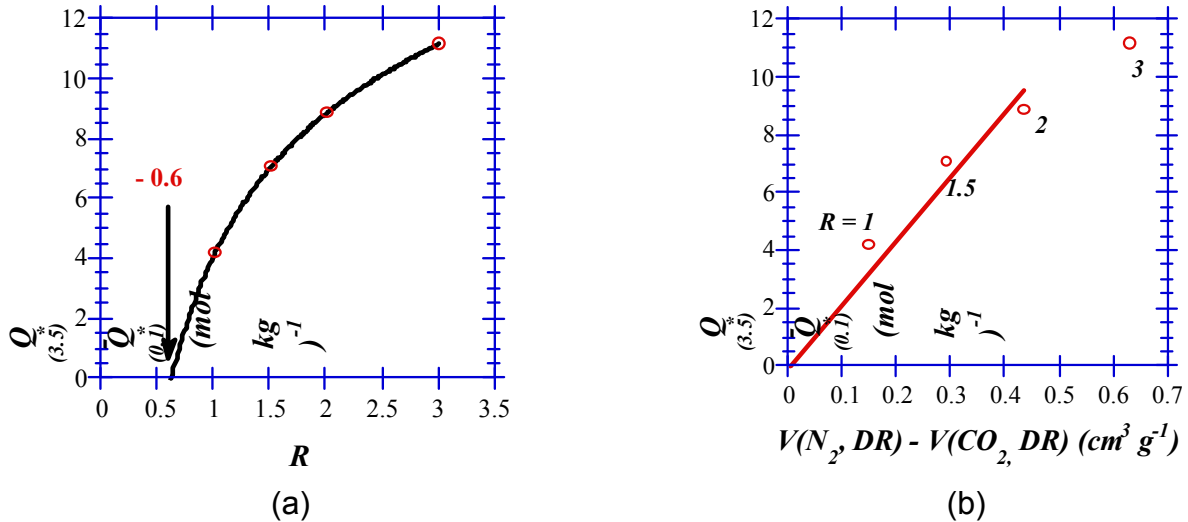


Figure 8. Deliverable mass methane capacities (within the micropores alone) (a) vs mass ratio hydroxide / anthracite R and (b) vs the supermicropore volume.

seen that the pore texture is weakly modified, with an optimum around 20 wt. % of water added to the dry anthracite. Other results, not presented here, evidence that a maximum volume of narrow mesopores (2 – 3 nm) is also generated at that definite water content. Since the supermicropore volume is the highest at 20 - 25 % of humidity, so is the reversible methane storage capacity, as seen in Fig. 9(b).

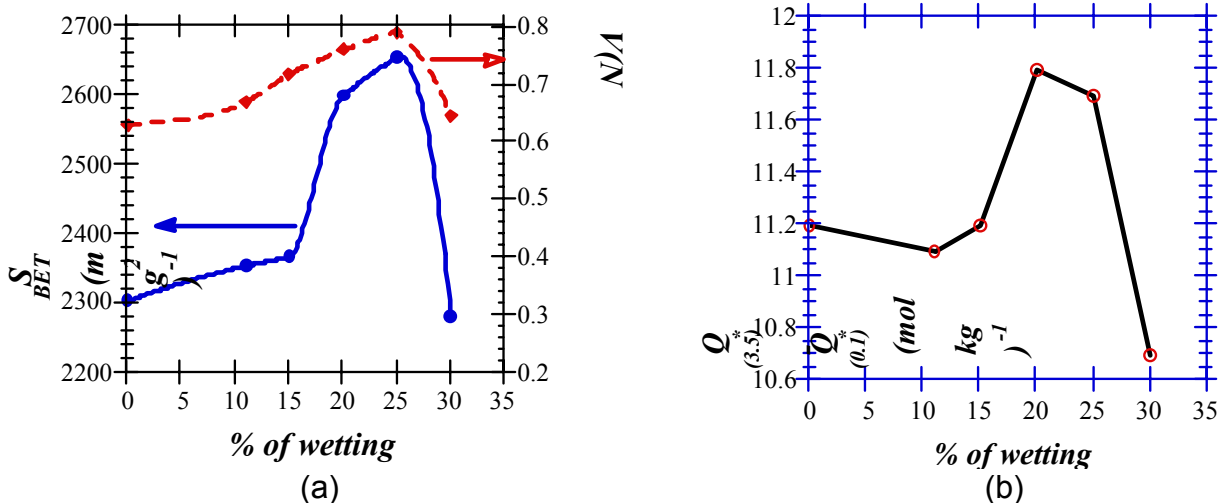


Figure 9. (a) The BET surface area and the supermicropore volume vs the wetting % (= ratio mass of water added / mass of dry anthracite). (b) The corresponding deliverable methane capacities (within the micropores alone).

Influence of the presence of nickel hydroxide

Since the activation process is performed inside a nickel crucible which is slightly attacked by molten sodium hydroxide at high temperatures, the influence of the presence of nickel hydroxide was studied. For that purpose, various controlled amounts of $\text{Ni}(\text{OH})_2$ were added (2 and 4 wt. % of the initial mass of anthracite) to NaOH in fixed

activation conditions ($T_a = 730$ °C, $R = 3$), and the pores texture were investigated accordingly. While negligible effect on the burn-off was observed, the surface area was considerably lowered by adding 4 wt. % of Ni(OH)₂. Careful study of the various pore volumes shows that such an amount leads to the creation of a very few of micropores, while much less mesopores are found. These two antagonistic effects induce no clear consequence on the methane storage capacities, which are seen to vary only very slightly. At the present time, no definite trends may be drawn, given the lack of experimental results.

Activation of the anthracite with other alkaline hydroxides

The activating action of the following alkaline hydroxides : LiOH, NaOH, KOH, and RbOH, were compared keeping a constant mass ratio $R = 2$ and using the same experimental method as before. The resultant burn-offs were found to be 10.6 ; 29.5 ; 17 and 7.3, respectively. NaOH thus appears to be the more efficient activating agent in the conditions fixed above, however the physical mixing is not necessarily adapted to hydroxides other than NaOH. Additionally, the optimum ratio R probably needs to be determined for each hydroxide, possibly being very different from what was found above for NaOH. Given what is known for KOH, i.e., higher R are required for reaching suitable burn-offs [12], $R = 2$ is probably above the optimum value for LiOH, while $R = 2$ is too low for both KOH and RbOH. Further experiments are required.

Conclusions

In the present work, the influence of several parameters of the chemical activation of an anthracite with NaOH on both the pore textures and the methane storage capacities were investigated. With such a process, adsorbents being mainly microporous with micropore widths close to the optimum required for methane storage (0.8 nm) were obtained. Increasing the activation temperature T_a lead to both a creation of new pores and a widening of already existing pores. The former phenomenon was shown to prevail for $T_a \leq 780$ °C, and materials which pore volume is microporous at 88 % at least could be prepared. Increasing the mass ratio hydroxide / carbon R lead, again, to both a creation of new pores and a widening of already existing pores. The former phenomenon was shown to prevail for $R \leq 2$, and materials which micropore width is very close to the optimum value of 0.8 nm could be obtained. The presence of water within the NaOH used for activation was shown to have favourable effects on the methane mass storage capacities, as far as the humidity content is not higher than 25 wt. %. Conversely, adding nickel hydroxide was shown to have low effects which still need to be confirmed. Finally, activation with other alkaline hydroxides lead to the conclusions that NaOH is the more efficient activating agent in the experimental conditions that were used. However, the latter were not optimised for each hydroxide, and much better results may be expected as soon as a number of other experiments will be performed.

While not presented extensively above, many correlations were found between pore texture parameters and methane adsorption performances. Hence, changing some conditions of the activation process allows the pore texture to be adjusted, with direct

consequences on the methane mass storage capacities, which can thus be predicted. However, the volume amounts of adsorbed methane, which strongly depend on the apparent density of the carbon, does not vary according to the mass capacities. Consequently, the number of volumes of methane that can be stored per volume of storage vessel is still not easily predicted.

References

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