Insight into hydroxides-activated coals: chemical or physical activation?

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Abstract-

The objective of this paper is to get an insight into the chemical activation mechanism using KOH and NaOH as activated agents. Three coals have been selected as carbon precursors. It was found that KOH and NaOH develop a similar narrow microporosity, independently of the coal rank, whereas only KOH generates supermicroporosity. Temperature-programmed desorption experiments, carried out with impregnated anthracite, show differences on the gas evolved during the activated carbon preparation using the two activating agents. Thus, whereas hydrogen profiles are quite similar for both activated agents, the CO and H₂O profiles are different. It is remarkable the high amount of H₂O evolved at the maximum treatment temperature for both activating agents. The results obtained allow concluding that the chemical activation is due to a combination of different process driving the development of material porosity.

Key words: Activated carbon; Chemical activation; Thermal analysis; Microporosity.

1. INTRODUCTION

Activated carbons (AC) are porous solids with interesting properties such as high thermal stability, high hydrophobic character, high chemical resistance and potential high adsorption capacity for gas storage [1-5]. All materials that, after pyrolysis, yield a carbonized with a high carbon content could be a suitable AC precursor: coal, pitch, agricultural by-products and polymeric materials (phenol-formaldehyde resins, PAN, PVC, tires, sugar). The most industrial used precursors are coals and agricultural by-products. In order to prepare AC, two mainly groups of methods has been developed: i) physical activation (“thermal activation”) using CO_2 or steam as gasifying agents, and ii) chemical activation, using ZnCl_2 , H_3PO_4 , KOH or NaOH as activating agents. For chemical activation, the selection of the activating agent depends on the carbon precursor: ZnCl_2 and H_3PO_4 are frequently used for lignocellulosic precursors, whereas for cokes or coals KOH is widely used.

Although the mechanism of the activation processes by KOH is an old subject of study (i.e. Marsh & Walker 1979 [6]) and there are numerous reports in the literature [7-17], nowadays, it is still unclear and, as consequence, continues being under study [18]. The porosity development is strongly influence by numerous experimental parameters such as coal/KOH weight ratio, maximum treatment temperature, time at the maximum temperature, nitrogen flow and, as consequence, several mechanisms have been proposed. Some authors point out that the intercalation of metallic potassium [16,19,20] or potassium compounds [7,21,22] in the carbonaceous structure is the main cause of the porosity development. Other authors [9,10,23,24] suggest that the gasification reactions between KOH and carbon is the main activation process pathway. All these proposals can explain the experimental results, so,

all of them are acceptable. However, the challenge is to conclude which is the most realistic approach.

Thus, the objective of this paper is to get an insight into the chemical activation mechanism based on our experimental results obtained using KOH and NaOH as activated agents. In order to make easy the interpretation of the results, three coals have been selected as carbon precursor. This selection is based on the minimization of the other well-known effects produced by hydroxide activation on lignocellulosic materials, such as dehydration, degradation and polymerization of the cellulose compounds.

2. EXPERIMENTAL

Coal precursors

Three Spanish coals have been selected as carbon precursors: a lignite (denoted L), a subbituminous (B) and an anthracite (A). Proximate analysis of coals is shows on Table 1.

Table 1. Proximate analysis of coals (weight %)

Coal	Moisture	Volatile mater	Ash	Fixe Carbon
A	--	8.2	6.7	85.1
B	9.2	30	10.8	50
L	15	39	33.6	12.4

Activation treatments

Chemical activation of coals was carried out using KOH (K) and NaOH (N) as activating agents by the impregnation method [12,18]. In general, the following conditions were used: 2 g

of coal were mixed, by stirring, with a solution containing 10 cm³ of water and 4 g of the activating agent for 2 h. The slurry was dried at 110 °C overnight in an oven. Subsequently, the dry mixture was heat treated in nitrogen flow (80 cm³/min) in a horizontal cylindrical furnace (65 mm i.d.). The heating rate was 5 °C/min and the activation temperature was 700 °C, which was maintained for 2 h. The activated samples were washed repeatedly with a 5 M solution of HCl and, after that, with distilled water until free of chloride ions. Finally, the sample was dried at 110 °C for 12 h, and weighed in order to calculate the yield.. The activation yield was obtained from the weight differences between the raw coal (free ash based) and the obtained AC. On the other hand, for comparative purpose, two ACs were prepared by physical activation: one using CO₂ as activating agent at 900 °C during 10 hours, and the other using steam at 850 °C during 6 hours.

Characterization of the samples

Porous texture analysis was carried out by N₂ adsorption at 77 K and CO₂ adsorption at 273 K (Autosorb 6). The samples were degassed at 600 K under vacuum 1 Pa. The Dubinin-Radushkevich (DR) equation was used to calculate the micropore volume. The different pore volumes were calculated as follows [25]: i) the volume of the narrow micropores (< 0.7 nm) from the CO₂ DRs (relative pressures < 0.015) and ii) the total micropore volume (pore size < 2nm), which contains the volume of the previous narrow micropores and those of the supermicropores, from the N₂ DRs (relative pressures < 0.14). Apparent surface area was determined by applying the BET [26] (Brunauer-Emmett-Teller) equation.

The analysis of the weight loss and of the gases evolved during the heat treatment of impregnated coal-hydroxide was studied in Stanton Redcroft thermobalance (STA-780), by thermogravimetry analysis (TG), and in a mass spectrometer (VG quadrupoles), by temperature-

programmed desorption experiments (TPD). For TPD and TG experiments 0.1 g impregnated coal-hydroxide (1/1) were heated at 20 °C/min, under helium flow (60 cm³/min), until 700 °C, holding 30 min at this temperature.

3. RESULTS.

3.1. Porous Texture Characterization of AC.

The results corresponding to the pore texture characterization of ACs are shown in Table 2 and Figure 1. Table 2 contains the volume of micro and mesopore calculated from adsorption data and the yield (ash free based) and Figure 1 shows the micropore volume.

Table 2. Pore texture characteristic and yield of AC.

AC	S _{BET} (m ² /g)	V _{micropore} (cm ³ /g)	V _{meso} (cm ³ /g)	Yield (wt%)
AK	1806	0.64	-	53
AN	1987	0.71	-	38
BK	2100	0.75	-	51
BN	1640	0.58	-	25
LK	2587	0.92	0.10	38
LN	1325	0.52	0.05	49

The data shown in Table 2 indicate that the ACs are, essentially, microporous with values of BET surface areas around 2000 m²/g. Only ACs from low rank coal (L) shows a certain mesoporosity development. It can also be appreciated that KOH produces higher micropore development than NaOH for low rank coal; whereas, for anthracite, NaOH gives better results.

Interestingly, the evolution of the microporosity generated by both activating agents follows an opposite trend: for KOH the lower the coal rank, the higher the porosity development, whereas, for NaOH the higher the coal rank, the higher the porosity development. Regarding the yield, except lignite, the ACs obtained using NaOH show lower yields, due to its higher reactivity.. For lignite, the higher yields obtained using NaOH could be related, as reported [27], with the better efficiency of NaOH in the decrease of tarry substances. This fact is more significant for lignite due its high volatile content (see Table 1).

In order to clearly show that the microporosity development is related to the coal rank and the activating agent, Figure 1 shows the micropore volume for all the ACs prepared. For the narrow microporosity (V_{CO_2}) development a similar behaviour is observed for both activating agents: the higher the coal rank, the higher the porosity development. The main difference between both activating agents is observed on the supermicropore development. Thus, whereas NaOH produces AC with a narrow micropore size distribution independently of coal rank, using KOH the lower the coal rank, the higher the supermicropores volume.

3.2. Analysis of activation process

3.2.1. Thermogravimetry analysis.

Figure 2 shows the TG curves of the raw coal precursors and that of the KOH or NaOH coal mixture. The low rank coals (L and B) show an initial weight loss between 25-150 °C, which corresponds to the loss of adsorbed atmospheric gases (CO_2 and water). For these coals, the weight loss goes on from 300 to 700 °C due to the release of the volatile mater. The weight loss values shown by L and B samples agree with the proximate analysis of coals shown in Table

1. Coal A presents a different behaviour showing a very low weight loss at temperatures lower than 700 °C.

The weight loss shown by impregnated samples correspond to the volatile matter of raw coal, to the dehydration of activating agent and to the gaseous products generated by the chemical reaction between the activating agent (and their decomposition products) and the coal. Note that there is not a correlation between the remaining weight of TG curves and the AC yield shown in Table 2, because it is expressed in free mineral matter based. It can be observed in Figure 2 that the TG curves of impregnated samples show the same profile than the corresponding to the original coal. Hence, until temperatures close to 700 °C, the weight loss shown by impregnated samples can be related, mainly, to the release of volatile matter from the raw coal. It has to be pointed out that, in the range of temperature under study, KOH and NaOH show a similar behaviour during the heat treatment of impregnated coal. The main difference between both activating agents is observed at temperatures around 700 °C, where NaOH shows a higher reactivity than KOH. The temperature at which NaOH shows a higher reactivity than KOH is coal rank depending (700 °C to A, 650 °C to B and 600 °C L). This fact agrees with the reactivity sequence for coals gasification [28,29].

3.2.2. Evolved gas analysis.

In order to obtain more information about the activation process, the study of the gas evolution during TG experiments could be interesting. Figure 2 reveals a similar gas evolution for raw and impregnated coals in the case of coal L and B. This evolution corresponds to the release of volatile matter from these coals (Table 1). For coal A, the gases evolved by impregnated sample seem to be related to the chemical reaction between activating agent and

coal. As consequence, coal A has been selected to carry out the analysis of gas evolution during activation process.

Figures 3 and 4 feature the results of TPD experiments for AK (a) and AN (b) samples. Both, the gas evolution versus temperature during the heat treatment of samples until 700 °C (left part of figure), and the gas evolution with time at 700 °C (right part of figure) are shown. Figure 3 shows the emission of H₂, CO₂, CO and CH₄, and Figure 4 presents the H₂O and H₂ emission. As deduced from TG experiments (Figure 2), the gas evolution follows the same pattern for samples AK and AN: at low temperature is low and begins to be significant at temperatures above 500 °C. In general terms, the H₂O and CO₂ emission is observed a low temperature, the H₂ and CH₄ emission begins at temperatures close to 500 °C, and near to 600 °C starts the CO emission. The main differences between both activating agents are the onset temperature for gas evolution and the temperature for the maximum: KOH shows the lowest temperature for both onset gas evolution and the peak maximum. During the isothermal step at 700 °C, the gas evolution decreases indicating the end of chemical reactions, being this more pronounced for KOH than for NaOH.

On the other hand, the analysis of the individual gas profile gives interesting information. Firstly, it must be point out that the H₂ profile is quite similar for both activated agents. The H₂ comes from the hydroxide metal-coal reaction [23,27,29]:

The CO₂ evolved between 400-700 °C is due to the chemical interaction between oxygenated potassium (or sodium) compounds and coal. For this reaction, several pathways have been proposed in the literature [10,23,30]:

The analysis of CO profiles reveals that NaOH impregnated sample produces a higher CO amount than KOH sample, which is hold for long time during the step at 700 °C. The emission of CO has been mainly related to the gasification of carbon due to the reduction of metallic oxides and carbonates come from the activating agents [5,10,27,31,32]:

The analysis of H₂O evolved during the chemical activation of carbon has been scarcely analyzed in the literature. It must be reminded that samples has been previously impregnated using water as solvent and dried at 110 °C on an oven. Thus, the initial emission of H₂O (Figure 4) can be due to the adsorbed H₂O and, also, to the hydroxides hydrates. Interestingly, at temperatures higher than 500 °C, a high amount of H₂O is evolved by the two impregnated samples: KOH between 300 °C and 500 °C, and above 600 °C, both, KOH and NaOH. The H₂O evolved could be generated by chemical interaction between activating agents and coal, between the activating agents and evolved products and/or by decomposition of activating agents [5,10,33]:

In the case of KOH, the emission of H₂O at temperatures lower than 600 °C is not concomitant with the CO₂ emission. This fact seems to indicate that reaction (8) is taking place. In the case of NaOH, at temperature lower than 600 °C, no emission of H₂O and CO₂ is observed. So, at 600 °C, NaOH is present. Above this temperature, similar profiles for H₂O and CO₂ are shown (Figure 3 and 4) indicating that reactions (4) and (7) are taking place, without discard also reaction (8).

All the reactions above described and, in addition, reactions (1), (2) and (4) will be considered as global reactions. As example, the reaction (6) is the result of two consecutive reactions (3) and (5) [34]. On the other hand, all reactions have been proposed based on the TPD results and, for a different activating agent, others reactions can be proposed in order to explain the experimental results. As example, the reaction (2) have been proposed by Lillo et al [23] to explain the low CO₂ amount observed at 700 °C and also the high H₂ emission. It has to be considered that these authors used a MeOH/C weight ratio of 4/1 (corresponding to that used for the AC preparation). In these experimental conditions, the CO₂ evolved during the TPD could react with the MeOH through the reaction (7). In the case of our experiments, due to the lower amount of hydroxide used (1/1) most of the CO₂ evolved could flows through the previous coal bed minimizing the described reaction. Nevertheless, reaction (2) could also take place during the AC preparation.

Finally, it is noteworthy that the TG and TPD experiments cannot explain the differences in the micropore development found for the two activating agents.

4. DISCUSSION.

Development of microporosity on coal by chemical activation: unifying ideas.

The preparation of AC by chemical activation of anthracites was study by several authors [12,17,18,24,34]. In these studies, different parameters affecting the final pore texture of AC were analysed: pre-treatment of coal, activated agents, activating agent/coal ratio, maximum temperature of treatment, activation time, nitrogen flow. The analysis of the published data indicates that the micropore volume increases with activating agent/coal ratio, maximum temperature treatment, or the nitrogen flow. In this section, we are going to analyze our experimental results as well as published results in terms of the proposed reactions.

a) The influence of nitrogen flow.

One of most influent parameter on the development of microporosity, scarcely study in the literature, is the nitrogen flow. Some authors indicate that this effect is due to a diffusion control of solid phase reaction [4]. Other authors suggest that the effect could be consequence of the removal of metallic potassium (or sodium) which favours the reaction between KOH and coal to produce metallic potassium [14]. Another possibility [14] is the quicker removal of gaseous products evolved during the chemical reactions as the nitrogen flow increases. Our TPD results reveal a high H₂O emission at the maximum reaction temperature for both activating agents. H₂O is a coal gasification agent and reaction (9) can be catalyzed by alkaline compounds (hydroxides, carbonates) [32,35].

It has been reported that the coal gasification by steam can takes place at temperatures as low as 600 °C by means of water dissociation on metallic particles (10) [36].

The amount of H₂O evolved during the experiments is quite enough to allow the coal gasification. The H₂ evolution observed on TPD experiments (Figure 4) indicates that reaction (10) is taking place. In addition, this reaction could explain the influence of the nitrogen flow on the AC yield: higher nitrogen flow faster removal of H₂O, so lower coal gasification.

b) *The influence of activating agent/ coal ratio.*

It is well known that the increase of the hydroxide/coal ratio generates a higher micropore volume. Several authors related this development with the increase in the carbon gasification by potassium compounds [10,12,37]. If the chemical activation really involves carbon gasification, and considering the stoichiometry of the gasification reaction (reactions (1), (2) and (4)) and, also, that all KOH is involved in the carbon gasification, the calculate yields for 1 and 3 KOH/C ratios are 89 % and 68 %, respectively. However, the AC yields reported in the literature are higher: 1, 2 and 3 ratios gives AC yields of 86, 79 and 90 % wt, respectively. Considering these results, the following observations have to be point out: a) the development of microporosity cannot be due only to carbon gasification, b) the intercalation must play an important role on the micropore development, and c) it has to be an additional reduction mechanism for hydroxide avoiding carbon consumption.

The first observation has been already justified by the above calculated yields. Related to the second one, a comparison between chemical and physical activation has to be do. For this, two AC using CO₂ and steam as gasifying agents were prepared. The values of BET areas for comparables burn-off (BO) are: 1460 m²/g to AC prepared using CO₂ (60 % BO) and 710 m²/g

obtained with steam (65 % BO). For the sample obtained using NaOH the BO is 63 % and the BET area is 1987 m²/g. Hence, it is clear that in chemical activation the development of microporosity can not be due only to carbon gasification, so the intercalation must be taking place. This fact agrees with recent studies showing that metal intercalation can help the activation by increasing the porosity [16,19,20,22] and this seems to explain that no differences on the TG curves of two hydroxides are observed (section 3.2.1);, whereas the development of microporosity is different.

However, for intercalation metallic species are needed. These species have to be produced by reduction of potassium (or sodium) compounds (hydroxide, oxide or carbonate). Almost all of the reported reactions explain the formation of metallic species involving carbon as reductant (see reactions (2), (4)-(6)), which implies a carbon gasification that does not correspond to the higher AC yields. Another possibility, scarcely analysed in the literature, is the role that hydrogen could play in the reduction of metallic compounds. It is well known the use of hydrogen as reducing agent in the activation of metallic catalyst. During TPD a higher emission of H₂ is observed at the activation temperature. It is well known that alkaline hydroxide suffers an intense dehydrogenation, evolving H₂ comes from the hydroxide and the coal [38]. Now, the question is if the evolved H₂ is enough to reduce potassium compounds. As example, a KOH/C ratio of 3 means 0.026 mol K₂O, and from an anthracite with a low hydrogen content of a 5 wt% 0.025 mol H₂ could be released. These values indicate that there is enough hydrogen to reduce all the potassium compounds.

5. CONCLUSIONS

It was found that KOH and NaOH develop a similar narrow microporosity, independently of the coal rank, whereas only KOH generates supermicroporosity. TPD experiments, reveals that H_2 profiles are quite similar for both activated agents, whereas CO and H_2O profiles are different generating: NaOH impregnated sample the highest CO amount. The high amount of evolved H_2O at the maximum treatment temperature for both activating agents allows to explain the influence of the nitrogen flow on the AC yield; and, the large amount of evolved H_2 justifies the high AC yield obtains during the preparation of high microporous AC due its reductant role.

Based on the experimental results discussed in this paper and the revision of the previous results, it is concluded that the chemical activation of an anthracite is closer to a “physical” process of intercalation/de-intercalation than to a “chemical” carbon gasification. For low rank coals, the “chemical activation” has to be a combination of several processes: dehydration, dehydrogenation, gasification of carbon via reduction of oxygenated metallic compounds, secondary gasification by the evolved H_2O , and intercalation of metallic species. As consequence, the porosity development of carbonaceous materials by chemical activation depends on several interrelated factors: a) heteroatom contain, b) microstructure of carbonaceous precursor and c) experimental conditions. Thus, depending on the combination of these factors, the most influent activation process can be different, and, hence, the mechanism proposed for specific conditions can not be extended to others.

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Figure 1. Micropore volume calculated from N₂ and CO₂ data.

Figure 2. Thermogravimetry curves for the coal precursors (A, B and L) and their impregnated samples with KOH (K) and NaOH (N)

b)

Figure 3. H₂, CO₂, CO and CH₄ evolution on the TPD experiment over AK (a) and AN (b) samples

Figure 4. H_2 and H_2O evolution on the TPD experiment over AK (a) and AN (b) samples.