Porosity development of the activated carbons from Japanese cypress prepared by CO$_2$ and K$_2$CO$_3$ activation and their benzene adsorption at low concentrations

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Abstract. The activated carbons (ACs) were prepared by physical (CO$_2$) and chemical (K$_2$CO$_3$) activation of wood (Japanese cypress). Porous properties of the ACs, such as BET surface area and micropore volume, were characterized by N$_2$ and CO$_2$ adsorption isotherms. Short activation times caused formation of micropores with sizes smaller than 0.7 nm, which had a restricted access for N$_2$ molecules. As a result, the ACs prepared for short time exhibited V$_{mic}$(N$_2$) smaller than V$_{mic}$(CO$_2$). The ACs were used for benzene adsorption at 5 ppmv concentration and relative humidities (RHs) of 0 % and 70 %. The largest benzene adsorption capacities at RHs 0 % and 70 % were exhibited by the AC prepared with K$_2$CO$_3$ activation at 800 °C. The benzene adsorption on the ACs was governed by V$_{mic}$(N$_2$), when it was smaller than V$_{mic}$(CO$_2$), and by V$_{mic}$(CO$_2$), when it was smaller than V$_{mic}$(N$_2$). The lower determination coefficient (R^2) for the relationship between benzene uptake by the ACs and the volume of micropores at RH 70 % compared to RH 0 % (0.59 and 0.89, respectively) was attributed to the increased influence of surface chemistry of the ACs in the presence of moisture.

Keywords: activated carbon, CO$_2$ activation, K$_2$CO$_3$ activation, benzene adsorption, humidity.

1. Introduction

Activated carbons (ACs) are widely used adsorbents for the removal of volatile organic compounds (VOCs) from air. Adsorption on ACs depends on their porous and chemical characteristics, such as micropore volume, pore size distribution, surface groups, oxygen and nitrogen contents [1-3]. Furthermore, the removal efficiency of ACs is influenced by the type of adsorbate, concentration and the presence of moisture [4].

ACs can be produced from any carbonaceous material either by physical activation with steam, CO$_2$ and air or by chemical activation with various inorganic agents (H$_3$PO$_4$, ZnCl$_2$, KOH etc.). The properties of the resulting carbons are affected by both the initial precursor and the activation conditions [5].

In the current study, Japanese cypress wood was used as a precursor for the preparation of ACs by physical (CO$_2$) and chemical (K$_2$CO$_3$) activation. The ACs were tested for benzene adsorption from air at low concentrations (5 ppmv) in dry and humid conditions. Benzene is a common VOC used in organic synthesis and is a trace component emitted from paints, exhaust gases of vehicles and cigarette smoke. Recently, much attention was paid to the development of adsorbents for benzene removal due to its toxicity and carcinogenic properties. The purposes of this study were to

- investigate the effects of temperature and time during K$_2$CO$_3$-activation on porosity formation and compare porous properties of the ACs prepared by chemical and physical activation;
- determine the influence of porous properties of the ACs on benzene adsorption in the absence and in the presence of moisture.

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2. Experimental

2.1. Preparation of the activated carbons

ACs were prepared from Japanese cypress wood. Wood chips were ground using a mixer, pelletized by pressing at room temperature and dried in oven at 110 °C for 24 h. In case of physical activation, the pellets were heated with a temperature increment of 10 °C/min to 900 °C, carbonized for 1 h in nitrogen (300 ml/min) and then activated with CO_2 (300 ml/min) for 0.25, 0.5 and 1 h. The prepared ACs were denoted as HP0.25, HP0.5 and HP1 (numbers in the name correspond to the activation time).

For chemical activation, the dried pellets were carbonized at 550 °C in nitrogen (300 ml/min) for 1 h. The char was ground and sieved in order to select the particles with sizes between 1.2 and 1.7 mm. The char particles were mixed with K_2CO_3 in a ratio of 1:3 by weight. Deionized water was added to mixture for dissolution of K_2CO_3 (15 ml of water per 1 g of char). The char was soaked in K_2CO_3 solution for 1 h at room temperature, heated in oven at 55 °C for 12 h and then at 110 °C for 24 h. The dried particles were placed into a reactor, heated with a temperature increment of 10 °C/min to 700, 800 and 900 °C and activated for 0.75 h in nitrogen (300 ml/min). The activation at 900 °C was also carried out for 1.5 and 4 h. After activation, the samples were boiled with 3 N HCl for 0.5 h, washed with cold deionized water until a neutral pH and the absence of chloride-anion in the filtrate were achieved, and then dried at 110 °C. The dried ACs were treated with nitrogen (300 ml/min) at 900 °C for 1 h in order to reduce the amount of surface functional groups. The prepared ACs were denoted as I0.75, J0.75, K0.75, K1.5 and K4 (the letters I, J and K corresponded to the activation temperatures 700, 800 and 900 °C, respectively, and the numbers in the name to the activation time).

2.2. Characterization of the activated carbons

The ACs were characterized by burn-off, N_2 (-196 °C) and CO_2 (25 °C) adsorption isotherms. The burn-off was determined as the ratio of weight loss of carbon during activation to the initial weight of char. BET surface areas S_g were measured with N_2 adsorption isotherms in the relative pressure range of 0.04-0.31. The micropore volumes $V_{mic}(N_2)$ and $V_{mic}(CO_2)$ were calculated using Dubinin-Radushkevich equation and liquefied gas densities of 0.81 and 0.85 g/ml, respectively [6]. Micropore volume $V_{mic}(CO_2)$ characterizes the adsorption in micropores smaller than 0.7 nm, while $V_{mic}(N_2)$ corresponds to the adsorption in micropores with sizes up to 2 nm. Mesopore volume V_{mes} was found from nitrogen adsorption as the difference of total pore volume calculated at the relative pressure $P/P_s = 0.96$ and micropore volume $V_{mic}(N_2)$.

2.3. Benzene adsorption experiments

The experimental setup for benzene adsorption was described elsewhere [7]. Benzene adsorption was carried out from air at 25 °C and relative humidities (RHs) of 0 or 70 %. The total gas flow was 250 ml/min and contained 5 ppmv of benzene. The tube reactor with inner diameter of 4 mm was loaded with 0.05 ml of dried AC (particle size of 0.35 mm, carbon bed height of 4 mm). The concentration of benzene was monitored by gas chromatograph equipped with flame ionization detector (without chromatographic column). Benzene adsorption capacities of the ACs were calculated when the concentration of benzene in outlet gas reached 5 and 100 % of the concentration in inlet gas using breakthrough curves ($C/C_0 = 0.05$ and 1.0, respectively).

3. Results and Discussion

3.1. Activated carbons

Table 1 illustrates the characteristics of the ACs. The burn-offs of chemically activated samples increased with activation temperature from 25 % for I0.75 to 35 % for K0.75 and longer activation time from 35 % for K0.75 to 69 % for K4. The enhancement of K_2CO_3-activation with the higher temperature and longer time was reported previously, although the preparation procedures were not exactly the same [8-9]. Activation of wood with CO_2 was more intensive than with K_2CO_3, which could be seen from the shorter activation time required for HP0.25, HP0.5 and HP1 to reach the burn-offs that are similar to those of K0.75, K1.5 and K4 samples. However, the chemically activated K0.75, K1.5 and K4 samples exhibited the larger surface areas than the samples prepared with CO_2-activation. The increase in temperature from 700 °C to

800 °C resulted in the significant enhancement of surface area in J0.75 sample compared to I0.75, while raising the temperature to 900 °C produced only slight development of surface area in K0.75 sample. The micropore volumes $V_{mic}(N_2)$ of the ACs prepared with K_2CO_3-activation at 800 °C and 900 °C were larger than at 700 °C. Similarly to surface areas, micropore volumes $V_{mic}(N_2)$ of the ACs prepared at 900 °C increased with longer activation time. Besides, the longer K_2CO_3-activation at 900 °C resulted in the formation of larger amount of mesopores (K4).

The development of micropore volume $V_{mic}(CO_2)$ was different from $V_{mic}(N_2)$. The highest $V_{mic}(CO_2)$ was exhibited by J0.75 sample prepared at 800 °C (Table 1). Since $V_{mic}(N_2)$ and V_{mes} of K0.75 increased compared to J0.75 sample, the decrease in $V_{mic}(CO_2)$ of K0.75 could be attributed to the widening of micropores with sizes smaller than 0.7 nm. Apparently, the micropore widening could also be a reason of the decrease in $V_{mic}(CO_2)$ of K0.75, K1.5 and K4 with longer activation time.

Table 1 Properties of the ACs prepared by activation with CO_2 and K_2CO_3.

Sample	Activation conditions			Burn-off [%]	S_g [m²/g]	$V_{mic}(N_2)$ [ml/g]	V_{mes} [ml/g]	$V_{mic}(CO_2)$ [ml/g]
	Activator	Temperature [°C]	Time [h]					
HP0.25	CO_2	900	0.25	21	521	0.27	0.02	0.33
HP0.5	CO_2	900	0.5	37	609	0.31	0.03	0.34
HP1	CO_2	900	1	70	852	0.43	0.05	0.35
I0.75	K_2CO_3	700	0.75	25	551	0.29	<0.01	0.41
J0.75	K_2CO_3	800	0.75	27	816	0.43	<0.01	0.50
K0.75	K_2CO_3	900	0.75	35	865	0.45	0.02	0.41
K1.5	K_2CO_3	900	1.5	39	917	0.47	0.05	0.40
K4	K_2CO_3	900	4	69	1317	0.64	0.16	0.30

3.2. Benzene adsorption

Fig. 1 depicts the examples of breakthrough curves of the ACs. The breakthrough curves obtained at RHs 0 % and 70 % were used for calculation of adsorption capacities of the ACs at $C/C_0 = 1.0$ (Fig. 2a and 2b, respectively). At RH 0 %, longer CO_2 activation improved benzene adsorption on the ACs in order of HP0.25, HP0.5 and HP1 (Fig. 2a). However, K_2CO_3 activation affected adsorption of benzene adversely and adsorption capacities of K0.75, K1.5 and K4 decreased with longer activation time. Adsorption on I0.75 was similar to HP0.5 sample, suggesting no benefits of chemical activation at 700 °C compared to physical activation. On the contrary, J0.75 and K0.75 prepared at 800 °C and 900 °C, respectively, exhibited the largest adsorption capacities at RH 0 % among the tested samples.
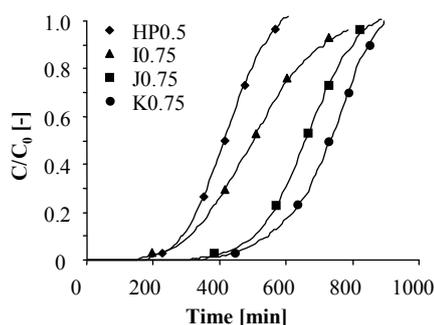

Fig. 1 Breakthrough curves of the ACs (25 °C, RH 0 %).

The decrease in benzene uptakes by K1.5 and K4 compared to K0.75 could be associated with the decrease in $V_{mic}(CO_2)$. The enhancement of $V_{mic}(N_2)$ of these ACs did not improve their benzene adsorption. In contrast, the benzene adsorption on HP0.25, HP0.5 and HP1 increased from 12.1 g/100g of AC on HP0.25 to 15.5 g/100g of AC on HP1, while their $V_{mic}(CO_2)$ were changed only from 0.33 to 0.35 ml/g, respectively (Table 1). On the other hand, these ACs exhibited an increase in $V_{mic}(N_2)$ from 0.27 ml/g in HP0.25 to 0.43 ml/g in HP1, suggesting that the enhancement of benzene adsorption was rather contributed by the development of $V_{mic}(N_2)$ than $V_{mic}(CO_2)$. Furthermore, the micropore volumes $V_{mic}(N_2)$ of HP0.25 and

HP0.5 were smaller than $V_{mic}(CO_2)$, indicating that some of the micropores with sizes smaller than 0.7 nm were not accessible for N_2 molecules (Table 1).
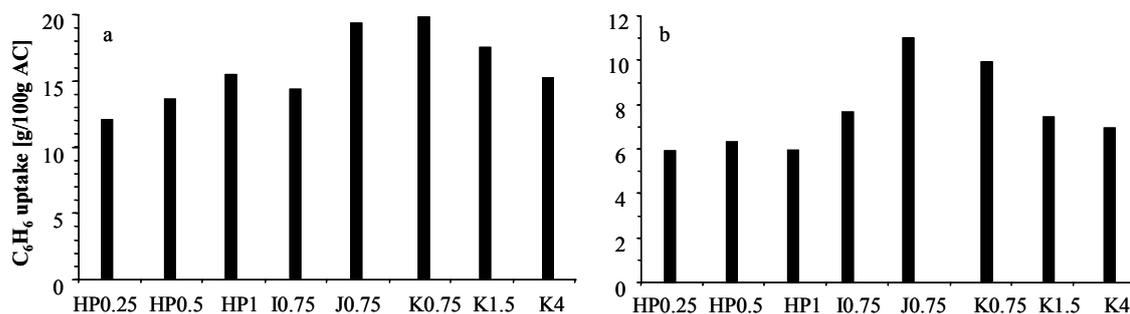

Fig. 2 Benzene adsorption capacities of the ACs at a) RH 0 % and b) RH 70 %.

The adsorption capacities of the ACs at RH 0 % plotted against their micropore volumes $V_{mic}(CO_2)$ and $V_{mic}(N_2)$ are shown in Fig. 3a and 3b, respectively. Low determination coefficients (R^2) indicated weak relationships between benzene uptakes of the ACs and their $V_{mic}(CO_2)$ and $V_{mic}(N_2)$. These results differed from previously reported ones, which showed good correlation between benzene adsorption capacities of the ACs and the amount of micropores [10]. From the benzene uptakes by the ACs and their porous properties, it was concluded that the benzene adsorption on the ACs was governed by $V_{mic}(N_2)$ when $V_{mic}(N_2)$ was smaller than $V_{mic}(CO_2)$ and by $V_{mic}(CO_2)$ when $V_{mic}(CO_2)$ was smaller than $V_{mic}(N_2)$. In other words, the amount of "effective" micropores responsible for benzene adsorption was limited by the lowest value of two micropore volumes deduced from CO_2 and N_2 adsorption (for instance, 0.27 ml/g in HP0.25 and 0.41 ml/g in K0.75). Fig. 3c illustrates a good relationship between benzene uptakes at RH 0 % and the "effective" volumes of micropores V_{mic}("effective") of the ACs ($R^2 = 0.89$).
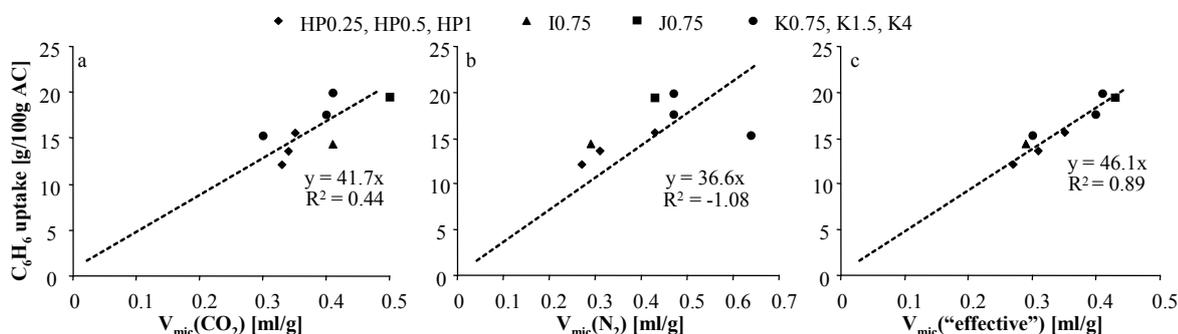

Fig. 3 Correlation between benzene uptakes at RH 0 % ($C/C_0 = 1.0$) and a) $V_{mic}(CO_2)$; b) $V_{mic}(N_2)$ and c) V_{mic}("effective").

At RH 70 %, J0.75 prepared with K_2CO_3 at 800 °C exhibited the largest benzene uptake among the tested ACs (Fig. 2b). The adsorption of benzene on HP0.25, HP0.5 and HP1 remained almost the same, while the adsorption on K0.75, K1.5 and K4 dropped with longer activation time. These results suggested that longer activation with CO_2 and K_2CO_3 did not favor benzene adsorption in the presence of moisture.

Benzene adsorption capacitites of the ACs at RH 70 % were proportional to the capacities at RH 0 % (Fig. 4a). In the presence of moisture, the adsorption of benzene at saturation ($C/C_0 = 1.0$) was of around 48 % and at breakthrough point ($C/C_0 = 0.05$) of around 28 % of the adsorption in dry conditions. These data showed that similarly as in dry conditions, the benzene uptakes at RH 70 % were determined by "effective" micropore volumes. However, the determination coefficient (R^2) for correlation between benzene adsorption capacitites of the ACs at RH 70 % and their "effective" micropore volumes was lower than at RH 0 %, indicating the increased influence of other factors on benzene adsorption (Fig. 4b). These results could be attributed to the effects of the surface chemistry of the ACs in the presence of moisture. Previously, we have shown that the influence of surface oxygen groups on benzene adsorption at RH 70 % was more pronounced

than at RH 0 % [7]. The possible explanation is that the surface oxides favored water adsorption, due to the formation of hydrogen bonds with water molecules, blocking the access of benzene into the micropores. The benzene uptakes at RH 70 % could also be affected by inorganic impurities, which favor water adsorption in a similar way to surface oxides [11].
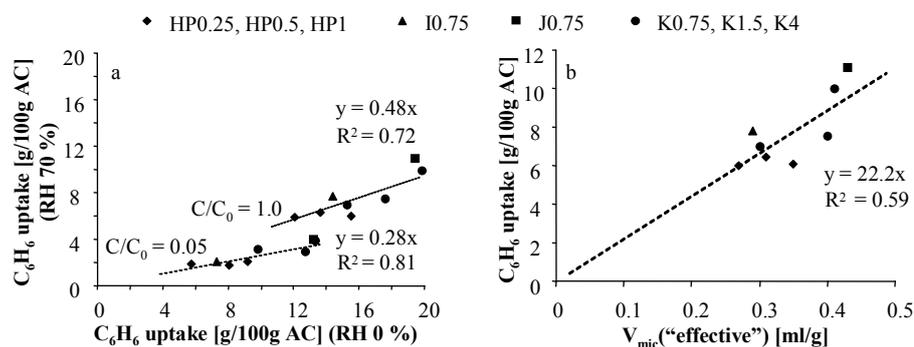

Fig. 4 Relationship between a) benzene uptakes at RH 70 % and RH 0 %; b) benzene uptakes at RH 70 % ($C/C_0 = 1.0$) and "effective" micropore volumes.

4. Acknowledgements

5. References

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