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Reversible toluene adsorption on monolithic carbon aerogels

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Abstract

Thirteen monolithic carbon aerogels with different pore textures were used as toluene adsorbents. Adsorption was carried out under both static and dynamic conditions. Under static conditions at 25 °C and at saturation, an adsorption capacity as high as $1.36 \, cm^3 \, g^{-1}$ or $1180 \, mg \, g^{-1}$ was obtained. Toluene adsorption was a reversible process in all carbon aerogels, and the adsorbed toluene was completely recovered by heating them at 400 °C. Regenerated adsorbents showed larger surface area and micropore width than the original samples, indicating that no pore blockage was produced. Adsorption under dynamic conditions at 100 °C was also completely reversible after at least three consecutive adsorption–desorption cycles. The ability of these carbon aerogels to reversibly adsorb toluene could be useful for their application in thermal swing adsorption or pressure swing adsorption equipments.
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1. Introduction

Volatile organic compounds (VOC) are air pollutants with an adverse health impact, and their emission limits have therefore been progressively restricted. Among the different technologies available for controlling gaseous emissions, adsorption on porous media is an interesting option because it offers the possibility of recovering valuable VOC. However, the porous texture of the adsorbents must be carefully optimized to ensure both an adequate adsorption capacity and an easy regeneration process to enable recovery of the VOC and reutilization of the adsorbents without loss of their adsorptive properties.

Carbon aerogels are adsorbents with considerable potential, since their textural characteristics can be tailored by controlling the concentration, proportion, and nature of reactant and catalyst in the original recipes used and at all preparation steps [1–4]. These novel carbon materials are obtained by carbonization of organic aerogels, which are generally prepared from resorcinol–formaldehyde mixtures by the sol–gel process. Once obtained, the carbon aerogel can be activated to further develop its porosity. Thus, they can be prepared with large surface area and well-developed porosity.

The aim of this study was to investigate toluene adsorption on monolithic carbon aerogels and activated carbon aerogels under static and dynamic conditions, using a wide variety of surface areas and pore textures in order to determine the influence of porosity on adsorption. The desorption process was also studied after saturating adsorbents with toluene.

2. Experimental

The method used to prepare the carbon aerogels in this study was described elsewhere [3]. The recipes of the aerogels and their carbonization and activation conditions are compiled in Table 1. Briefly, resorcinol (R) and formaldehyde (F) aqueous (W) solutions, sometimes containing metal precursors as polymerization catalysts, were stirred to obtain homogeneous solutions that were cast into glass moulds (35 cm length × 0.5 cm internal diameter) and cured. The molar ratio used were R/F = 0.50 and the R/W = 0.13 except for sample 8 where the double amount of water was used. Then, the gel rods were cut into 5 mm pellets, placed in acetone for 2 days, and super-critically dried with carbon dioxide to form the corresponding aerogels. To obtain the corresponding monolithic carbon aero-

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Table 1
Organic aerogel recipes, with amounts in moles, showing respective carbonization or activation treatments to obtain carbon or activated carbon aerogels

Sample	Polymerization catalyst	Catalyst concentration	Carbonization temperature (°C)	Steam activation B.O (%)
1	Nil	Nil	1000	–
2	Nil	Nil	1000	25
3	Ni (CH$_3$COO)$_2$	8.5×10^{-3}	1000	37
4	Ag (CH$_3$COO)	1.4×10^{-4}	1000	24
5	Na$_2$CO$_3$	1.4×10^{-4}	500	–
6	Na$_2$CO$_3$	1.4×10^{-4}	1000	–
7	Na$_2$CO$_3$	1.4×10^{-4}	1000	29
8	Na$_2$CO$_3$	3.7×10^{-4}	900	–
9	[Pt(NH$_3$)$_4$]Cl$_2$	1.4×10^{-4}	500	–
10	[Pt(NH$_3$)$_4$]Cl$_2$	1.4×10^{-4}	1000	–
11	[Pt(NH$_3$)$_4$]Cl$_2$	1.4×10^{-4}	1000	53
12	[Pt(NH$_3$)$_4$]Cl$_2$	7.5×10^{-4}	500	–
13	[Pt(NH$_3$)$_4$]Cl$_2$	7.5×10^{-4}	1000	–

gels, monolithic organic aerogels were pyrolyzed in N_2 flow at $100 \, cm^3 \, min^{-1}$, heating to either 500 or 1000 °C at a heating rate of $1.5 \, °C \, min^{-1}$, with a soaking time of 5 h. Some carbon aerogels prepared at 1000 °C were finally steam-activated at 900 °C.

Textural characterization of adsorbents was carried out by CO_2 and N_2 adsorption at 0 and −196 °C, respectively, and by mercury porosimetry. The Dubinin–Raduskevich and BET equations were used for analysis of CO_2 and N_2 adsorption isotherms, respectively. The liquid density of CO_2 at 0 °C was taken as $1.03 \, g \, cm^{-3}$ and the molecular area of N_2 at −196 °C as $0.162 \, nm^2$. Mercury porosimetry was obtained up to a pressure of $4200 \, kg \, cm^{-2}$ using Quantachrome Autoscan 60 equipment. With this technique, the following parameters were obtained: pore volume corresponding to pores with diameter between 3.7 and 50 nm, V_2, referred to as mesopore volume (note that mesopore volume range [5] is classically defined as 2–50 nm); pore volume of pores with diameter greater than 50 nm, or macropore volume, V_3.

Static adsorption measurements of toluene were carried out by exposing 0.2 g of each sample, previously dried at 120 °C, in a desiccator containing toluene at 25 °C ($P_0 = 26.7$ Torr). In these experiments, samples were in contact with a saturated atmosphere of the organic vapour until equilibrium was reached, when the total adsorption capacity of the samples was determined. Samples were weighed every day until no increase in weight was observed. Toluene-saturated samples were regenerated by heating to 400 °C in a thermobalance at $10 \, °C \, min^{-1}$ in N_2 flow ($60 \, cm^3 \, min^{-1}$).

Dynamic toluene adsorption from a toluene/air mixture was measured at different temperatures using a thermobalance. Prior to the adsorption experiments, samples were pretreated at 250 °C in air flow ($60 \, cm^3 \, min^{-1}$). All samples presented a good stability in this temperature range. Then, they were cooled down to the adsorption temperature and, after stabilization, the air flow was replaced by a similar air flow saturated with toluene at 25 °C (3.5 vol% toluene), recording the weight gained as a function of time. Finally, after saturation (constant weight), toluene was desorbed by increasing temperature to 250 °C in pure air flow. The adsorption–desorption cycle was repeated in order to determine the reversibility of the process.

3. Results and discussions

The porous texture of RF organic aerogels and their carbonized derivatives was strongly influenced by the presence of metal precursors in the initial RF mixture and by carbonization and activation conditions, as reported elsewhere [3,6,7]. The porous texture of carbon aerogels consist in a network of interconnected primary particles forming a "coral like" three dimensional structure. Micropores are located inside these primary particles and develop mainly during carbonization, while meso or macropores correspond to the space between primary particles [8]. Although the VOC adsorption capacity was associated with the narrow microporosity [9] the participation of inter-particle spaces can determine the mechanism and behaviour of adsorbents [10,11]. Some of the present carbon aerogels were previously used as catalyst supports for toluene and xylene combustion [12,13]. Thus, carbon aerogels and activated carbon aerogels studied here were previously characterized and used in catalysis, allowing the selection of a wide variety of porous textures. Textural characteristics of samples are compiled in Table 2.

Samples synthesized using Na_2CO_3 as polymerization catalysts, i.e., samples 5, 6, 7, and 8, presented a large mesopore volume. The remaining carbon aerogels were essentially macroporous although steam activation developed mesoporosity in samples 3 and 11. In general, monomodal pore size distribution was obtained by mercury porosimetry [3,4].

The microporosity of the samples was studied by gas adsorption. The mean micropore width (L_0), micropore volume (W_0), and surface area accessible to CO_2 (SCO_2) were obtained by applying [5,14] the DR equation to CO_2 adsorption isotherms and Eqs. (1) and (2):

$$L_0(\text{nm}) = \frac{10.8}{E_0(\text{kJ/mol})} - 11.4 \tag{1}$$

$$SCO_2 = 2000 \frac{W_0}{L_0} \tag{2}$$

The mean micropore width obtained ranged from 0.55 to 0.78 nm, whereas the micropore volume ranged from 0.19

Table 2
Textural characteristics of carbon and activated carbon aerogels and their toluene adsorption capacities (V_{Tol}) at saturation under static conditions at 25 °C

Sample	SCO_2 (m^2 g^{-1})	S_{BET} (m^2 g^{-1})	L_0 (nm)	W_0 (cm^3 g^{-1})	V_2 (cm^3 g^{-1})	V_3 (cm^3 g^{-1})	V_{Tol} (cm^3 g^{-1})
1	915	470	0.58	0.27	0.00	0.63	0.33
2	995	1085	0.69	0.34	0.04	0.98	0.48
3	655	550	0.60	0.20	0.25	2.23	0.57
4	1058	1140	0.78	0.41	0.00	0.46	0.38
5	760	655	0.61	0.23	0.66	0.00	0.82
6	857	531	0.58	0.25	0.62	0.00	0.72
7	877	1260	0.70	0.31	1.11	0.02	1.26
8	928	1048	0.55	0.26	1.54	0.49	1.36
9	639	523	0.61	0.19	0.00	1.27	0.14
10	874	486	0.55	0.24	0.00	0.92	0.26
11	711	699	0.65	0.23	0.33	2.67	0.78
12	689	496	0.57	0.20	0.00	0.92	0.18
13	814	483	0.59	0.24	0.00	0.91	0.23

to 0.41 cm^3 g^{-1}. Widest micropores corresponded to steam-activated carbon aerogels. For a given organic aerogel recipe, the increase in carbonization temperature produced an increase in SCO_2 value and a decrease in S_{BET} (see pairs of samples 5 and 6, 9 and 10, 12 and 13). SCO_2 was higher than S_{BET} in some cases, which indicates pore constrictions at the micropore entrance. Steam activation removed pore constrictions, resulting in similar values for both surface areas or higher S_{BET} than SCO_2 values. Thus, samples 2, 7, and 11 were obtained by steam activation from samples 1, 6, and 10, respectively.

Toluene adsorption capacities, V_{Tol}, determined by static adsorption experiments at 25 °C using a toluene density of 0.867 g cm^{-3}, are also compiled in Table 2, column 8. Very high adsorption capacities (up to 1.36 cm^3 g^{-1} or 1180 mg g^{-1}) were achieved. Experiments carried out twice showed differences of around ±8% in the total adsorption capacity as determined by direct weighing. V_{Tol} and W_0 values were very close in microporous carbon aerogels without mesopores (samples 1, 4, 9, 10, 12, and 13). This indicates that toluene at 25 °C was accessible to the microporosity determined by CO_2 adsorption, despite the presentation by some of these microporous carbon aerogels of restricted N_2 adsorption at −196 °C due to micropore constrictions. In the remaining carbon aerogels, V_{Tol} was much higher than W_0, indicating that wider pores than those determined by CO_2 adsorption at 0 °C (large micropores and mesopores) also

participated in the adsorption process. This is an important factor underlying the excellent adsorbent behaviour of these meso-microporous carbon aerogels. Thus, it was recently pointed out [10] that other specific toluene adsorbents, e.g., single-wall carbon nanotubes, only use around 40% of their N_2-accessible pore volume. The best toluene adsorption capacity of these carbon nanotubes at saturation ($P/P_0 = 0.94$) and room temperature was 456 mg g^{-1}.

On the other hand, Lillo-Ródenas [9] using a very high microporous activated carbon (AC) reached a maximum toluene adsorption of 640 mg g^{-1} at room temperature and 200 ppmv of toluene in the He flow (318 cm^3 min^{-1}). In this paper, authors review the literature and showed that the toluene adsorption capacity at room temperature for many AC ranged between 60 and 500 mg g^{-1}. Recently [15] Kim modified the chemical surface of different activated carbon with H_3PO_4 to increase their VOC adsorption capacity. The maximum toluene adsorption capacity reached was 433 mg g^{-1}.

Regeneration of carbon aerogels after toluene adsorption at 25 °C was carried out as indicated in the experimental section. Desorption profiles are shown in Fig. 1A and B for meso-microporous and microporous samples respectively; some desorption profiles are excluded for the sake of clarity. Most of the toluene adsorbed on meso-microporous samples was desorbed at around 125 °C, whereas this was not the case for
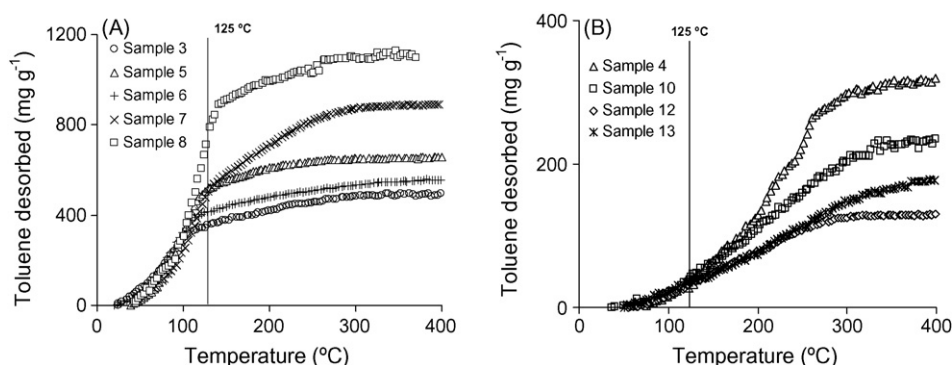

Fig. 1. Toluene desorption profiles from saturated samples at 25 °C (heating rate 10 °C min^{-1}, N_2 flow 60 cm^3 min^{-1}): (A) meso-microporous samples and (B) microporous samples.
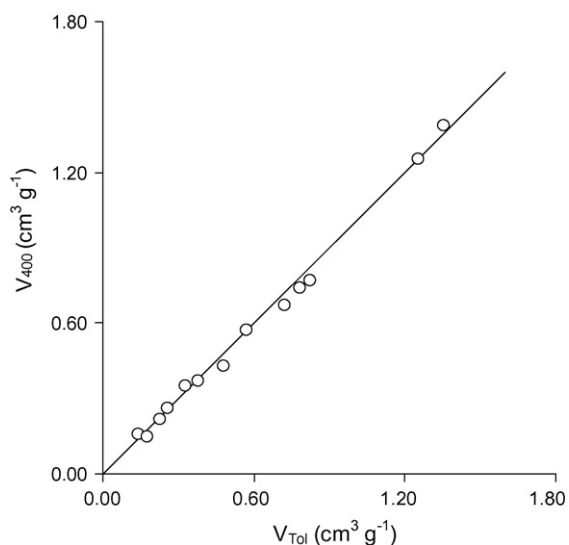
Fig. 2. Relationship between amount of toluene desorbed at 400 °C (V_{400}) and amount of toluene adsorbed at saturation at 25 °C (V_{Tol}).
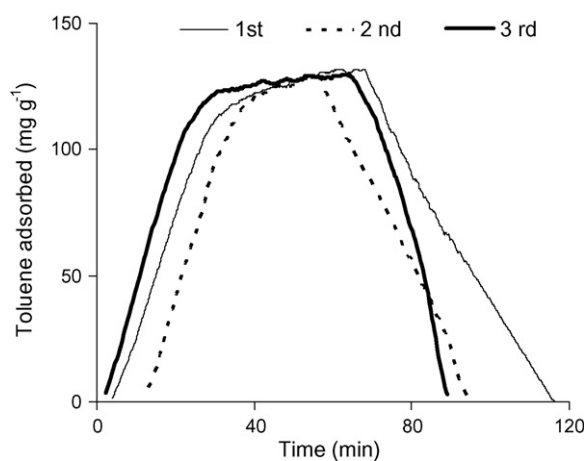

Fig. 3. Toluene adsorption–desorption cycles on sample 6. Adsorption temperature 100 °C, toluene/air flow (60 cm^3 min^{-1}) containing 3.5 vol% toluene. Desorption in air, 60 cm^3 min^{-1}, heating rate after saturation 5 °C min^{-1} (1st and 2nd cycles) and 10 °C min^{-1} (3rd cycle). Curves were shifted for clarity.

microporous samples that did not contain mesopores. This indicates that toluene desorption up to 125 °C mainly derives from that adsorbed in meso- and macropores.

Amounts desorbed up to 400 °C, V_{400}, were plotted against V_{Tol} (Fig. 2). There is a good fit between results and bisecting line, indicating that toluene adsorbed at 25 °C was completely desorbed at 400 °C. After regeneration, the microporosity of some selected samples was analyzed by CO_2 adsorption and results compared with those obtained in fresh samples (Table 3). All regenerated adsorbents had larger surface area, micropore volume, and micropore width versus fresh samples. These increases indicate that the microporosity of carbon aerogels was cleaned after desorption. The cleaning of the microporosity of solids by adsorption–desorption cycles is a well-documented phenomenon [16,17]. In addition, Gales et al. [18] found that an adsorption–desorption cycle could eliminate constrictions ham-

Table 3
Comparison of micropore characteristics determined from CO_2 adsorption isotherms between fresh and regenerated adsorbents

	SCO_2 (m^2 g^{-1})	W_0 (cm^3 g^{-1})	E_0 (kJ mol^{-1})	L_0 (nm)
Sample 2				
Fresh	995	0.34	27.1	0.69
Regenerated	1324	0.49	26.2	0.73
Sample 3				
Fresh	655	0.20	29.5	0.60
Regenerated	855	0.28	27.8	0.66
Sample 6				
Fresh	857	0.25	30.0	0.58
Regenerated	1049	0.32	29.1	0.61
Sample 8				
Fresh	928	0.26	31.0	0.55
Regenerated	1115	0.36	28.2	0.64
Sample 10				
Fresh	874	0.24	31.1	0.55
Regenerated	969	0.25	32.0	0.53

pering sorbate penetration into small pores of a BASF activated carbon recommended for VOC removal from air. Popescu et al. [19] found that volatile compounds were removed during the first adsorption–desorption run in temperature-programmed desorption of VOC from activated carbons. This led to some textural changes but the adsorption capacity was not affected.

Results obtained also indicate that no pore blockage (due to toluene adsorbed or transformed into coke) was produced during the first regeneration cycle. These results are of interest because the monolithic carbon aerogels prepared not only have a high adsorption capacity for toluene adsorption at 25 °C but can also be completely regenerated by heating at 400 °C.

Dynamic toluene adsorption was carried out on different carbon aerogels at 100 °C from a toluene/air mixture containing 3.5% (v/v). Results obtained for sample 6 are shown in Fig. 3, as an example. This figure also shows the desorption profile. As expected, the maximum amount adsorbed was smaller than that obtained at room temperature under static conditions. Three consecutive adsorption–desorption cycles are also depicted in Fig. 3. The adsorption capacity was completely recovered after desorption, demonstrating the reversibility of the process. The porous texture of the carbon aerogels was not modified by toluene adsorption or support gasification, since the profiles were alike, indicating a similar adsorption kinetics. The regeneration time can be shortened by increasing heating rate (from 5 to 10 °C min^{-1}), because desorbed toluene has no diffusion problems. In addition, toluene was the only product detected by gas-chromatography of the desorption gases.

The ability of these carbon aerogels to reversibly adsorb toluene may be useful for their application in thermal swing adsorption or pressure swing adsorption equipment. Finally, toluene adsorption under dynamic conditions decreased at temperatures higher than 100 °C, becoming negligible at 250 °C.

4. Conclusions

Microporous monolithic carbon aerogels, with or without mesopores, were excellent toluene adsorbents under either static

or dynamic conditions. Thus, under static conditions at $25\,°C$ and at saturation, both meso- and micropores were involved in toluene adsorption. Under these conditions, an adsorption capacity as high as $1.36\,cm^3\,g^{-1}$ or $1180\,mg\,g^{-1}$ was achieved. In microporous carbon aerogels (without mesopores), the volume of toluene adsorbed at $25\,°C$ matched the micropore volume obtained with CO_2 at $0\,°C$, despite the fact that some of them presented restricted N_2 adsorption at $-196\,°C$. Toluene adsorbed at $25\,°C$ was completely recovered by heating the carbon aerogels at $400\,°C$ in N_2 flow. Micropore volume and mean micropore width, determined from CO_2 adsorption at $0\,°C$, were higher in regenerated than fresh carbon aerogels, which resulted from a cleaning of the micropores. Adsorption under dynamic conditions at $100\,°C$ was also completely reversible after at least three consecutive adsorption–desorption cycles. The ability of these carbon aerogels to reversibly adsorb toluene may be useful for their application in thermal swing adsorption or pressure swing adsorption equipment.

Acknowledgment

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