

# Chemical reactions of double bonds in activated carbon: microwave and bromination methods

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The reaction of localised C=C bonds on the surface of activated carbons has been shown to be an effective method of chemical modification especially using microwave-assisted reactions.

Activated carbons (ACs) include a wide range of amorphous carbon-based materials, made from both fossil fuels and renewable resources such as wood, peat moss, coconut shell and fruit pits.<sup>1,2</sup> Their low-cost, highly porous structures and large surface areas make them useful, sustainable materials for a wide variety of applications including filtration, purification, separation, chromatography and as robust catalyst supports especially for platinum and palladium.<sup>3</sup> As with all surface-active solids, the chemical structure of the surface is fundamentally important, and methods for modifying the surface chemical structure are invaluable in improving performance, especially for selective adsorption and catalysis. The complex nature of AC surfaces is well known<sup>4</sup> but the majority of surface modifications have been *via* the oxygen centres using redox chemistry,<sup>4,5</sup> with some reactions reported at aromatic centres.<sup>6</sup> Carbon materials, especially graphite, are efficiently heated by microwaves.<sup>7</sup> Recently, we reported a MAS NMR spectroscopic method for measuring surface energies, which revealed that certain ACs have highly polarisable surfaces<sup>8</sup> with low specific association properties, indicative of a surface rich in C=C bonds but low in O-containing groups. In the light of these observations, we have developed a microwave-assisted method for the direct introduction of various groups onto Norit AC, and compared this with a more traditional bromination–substitution approach (Fig. 1).

According to method A the carbon was activated before use at 150 °C under vacuum and then stirred with Br<sub>2</sub> in THF (15 wt%) at 25 °C for 24 h. After washing with THF and drying under vacuum, the resultant material had a decreased surface area and micropore volume (see Table 1). XPS analysis showed 1.5 atomic% Br at the surface, with two peaks in the Br 3d region at 68.5 and 70.8 eV corresponding to two C–Br environments—close to those observed for brominated fullerene.<sup>9</sup> Thermogravimetric analysis (TGA) showed two peaks at 146 °C (2.9% mass loss) and 190 °C (3.2%), consistent with typical bromination of 0.40 to 0.45 mmol g<sup>-1</sup> of double bonds on the carbon surface. This represents a surface coverage of 1 double bond every 320 Å<sup>2</sup>.

These bromo groups were found to be reactive with water in the presence of sodium carbonate at room temperature. After this hydrolysis reaction, no residual bromine could be detected by XPS,

and the surface oxygen concentration increased. The loading calculated by TGA was 0.9 mmol g<sup>-1</sup>, indicating replacement of both bromo groups. Using a microwave reactor, we were also able to react the unbrominated AC directly with water in the presence of 0.01 M H<sub>2</sub>SO<sub>4</sub> to give a loading of 0.44 mmol g<sup>-1</sup> of OH groups. This loading is half that observed for the bromination reaction, indicating that the same reactive centres are involved, only here the water is added *directly* across the double bond.

It was possible to use the bromination reaction as a stepping stone for further surface modification of the material. In a typical reaction, the brominated AC was reacted with an excess of 1-butylamine with stirring at 50 °C for 24 h. After filtration, the solid was washed with hot THF, hot ethanol and finally 1 : 1 ethanol–water and then dried under vacuum at 200 °C for 12 h to remove any physisorbed species. The material has a somewhat reduced surface area and micropore volume of 505 m<sup>2</sup> g<sup>-1</sup> and 0.26 cm<sup>3</sup> g<sup>-1</sup> respectively. DTG analysis shows two peaks at 310 and 465 °C corresponding to loadings of 0.49 and 0.32 mmol g<sup>-1</sup> respectively. These presumably correspond to the substitution of the two C–Br groups giving two neighbouring amino groups. The methodology was successfully applied to a series of amines and anilines, alcohols and thiols (Table 2). The majority of these materials could be made with consistently high loadings (0.68 ± 0.05 mmol g<sup>-1</sup>) of surface groups that were not displaced at <200 °C. However, longer chain and bulky secondary amines gave lower loadings (>0.2 mmol g<sup>-1</sup>). The reduction in surface area and micropore volume after chemical modification is substantial yet

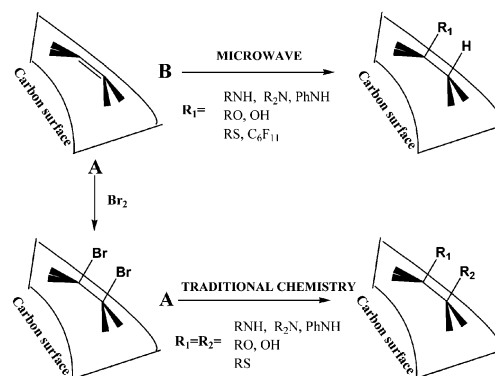


Fig. 1 Modification of unsaturated region of AC surface.

Table 1 Characterisation of samples of activated carbons after modification with Br<sub>2</sub> and H<sub>2</sub>O

	$\Delta O^a$ (atomic%)	$\Delta O^a/\text{mmol g}^{-1}$	Br <sup>a</sup> (atomic%)	$V_{\mu}^d/\text{cm}^3 \text{g}^{-1}$	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$T_D^e/^\circ\text{C}$	Loading/ $\text{mmol g}^{-1}$
Norit	—	—	0	0.41	860	—	—
Norit–Br	–0.6 <sup>b</sup>	—	1.5	0.26	550	146	0.4
						190	0.4
Norit–H <sub>2</sub> O	+0.8	1.1 <sup>c</sup>	0	0.34	700	265	0.5
						335	0.35
Norit–H <sub>2</sub> O <sub>MW</sub>	+0.6	0.47	0	0.38	794	300	0.44

<sup>a</sup> Data from XPS analysis. <sup>b</sup> Observed oxygen content decreases due to loss of SiO<sub>2</sub> from sample. <sup>c</sup> Calculated based on change from brominated material. <sup>d</sup>  $V_{\mu}$  = volume of micropores. <sup>e</sup>  $T_D$  = temperature corresponding to peak on DTG.

**Table 2** Characteristics of the samples of activated carbon (GAC 1240, *ex* Aldrich), after organic group modification

Reagents	Method A				Method B						
	Characteristics of the samples				Reaction conditions			Characteristics of the samples			
	$T_D/^\circ\text{C}$	Loading/ $\text{mmol g}^{-1}$	$S_{\text{BET}}/$ $\text{m}^2 \text{g}^{-1}$	$V_{\mu}/$ $\text{cm}^3 \text{g}^{-1}$	Time/min	$T/^\circ\text{C}$	$W^a/W$	$T_D/^\circ\text{C}$	Loading/ $\text{mmol g}^{-1}$	$S_{\text{BET}}/$ $\text{m}^2 \text{g}^{-1}$	$V_{\mu}/$ $\text{cm}^3 \text{g}^{-1}$
$\text{C}_4\text{H}_9\text{-NH}_2$	310	0.49	510	0.26	50	80	7	415	0.28	663	0.33
	465	0.32									
$\text{C}_6\text{H}_{13}\text{-NH}_2$	320	0.34	525	0.26	50	160	170	470	0.34	610	0.29
	430	0.24									
$\text{C}_8\text{H}_{17}\text{-NH}_2$	330	0.23	470	0.23	30	160	150	475	0.32	590	0.28
	420	0.23									
$\text{C}_{10}\text{H}_{21}\text{-NH}_2$	305	0.22	460	0.23	60	150	80	470	0.31	500	0.25
	475	0.25									
$(\text{C}_4\text{H}_9)_2\text{>NH}$	310	0.15	688	0.33	60	170	130	450	0.14	580	0.29
	445	0.11									
$\text{C}_6\text{H}_5\text{NH}_2$	300	0.36	566	0.27	50	150	40	505	0.20	650	0.32
	420	0.28									
$\text{C}_4\text{H}_9\text{-OH}$	280	0.45	612	0.29	50	140	200	300	0.11	798	0.37
	315	0.31									
$\text{C}_5\text{H}_{11}\text{-OH}$	280	0.47	448	0.22	60	150	140	335	0.46	694	0.34
	325	0.47									
$\text{C}_6\text{H}_{13}\text{-OH}$	280	0.41	474	0.24	60	170	75	355	0.32	700	0.32
	345	0.41									
$\text{C}_5\text{F}_{11}\text{CF}_2\text{-H}$	—	—	—	—	90	90	70	320	0.06	750	0.35
$\text{C}_5\text{H}_{11}\text{-SH}$	328	0.47	490	0.24	60	130	150	350	0.34	630	0.31
	340	0.30									

<sup>a</sup>  $W$  = average power produced by microwave.

independent of the size of the functional group, an observation which suggests that reaction may occur near to the entrance to the micropores, effectively closing them. The regions close to micropores are presumably tightly curved or folded and contain exposed, highly reactive localised double bonds.<sup>10</sup>

While this bromination–substitution method is clearly effective for the formation of new C–N, C–O and C–S surface bonds, it is not an efficient process since it consumes bromine. In the light of the successful microwave addition of water, and the highly polarisable nature of the surface of Norit carbons,<sup>8</sup> we decided to attempt the direct reactions of the same protic reagents with the activated carbon using a microwave reactor.<sup>11</sup>

Under moderate conditions (<100 min, <200 °C) the method proved to be extremely effective with all of the reactants giving moderate to good loadings ( $0.27 \pm 0.03 \text{ mmol g}^{-1}$ ) (Table 2). This is approximately half that produced by the bromination–substitution route: in this case the substrate is added across the double bond. We were also able to use the microwave-assisted method directly to produce new surface C–C groups using relatively acidic C–H compounds:  $\text{C}_6\text{F}_{13}\text{H}$  gave a loading of  $0.06 \text{ mmol g}^{-1}$  (chemisorbed  $\text{C}_6\text{F}_{13}$  groups were observed by  $^{19}\text{F}$  MAS NMR); diphenyl methane reacted in a similar manner ( $0.11 \text{ mmol g}^{-1}$ ). Substantially shorter reaction times (10 min) gave incomplete conversion—for example  $0.14 \text{ mmol g}^{-1}$  for hexylamine. The direct microwave-assisted method gives materials with higher surface areas than the indirect bromination method. Thus with microwave activation we are able to carry out efficient, one-step, solvent-free surface chemical modification to produce a wide range of new surface groups.

In conclusion, we have demonstrated that activated carbons can be chemically modified with a range of functional groups through reaction of localised surface C=C bonds using two complementary methods. Bromination–substitution gives materials with higher

loading but lower surface areas than the microwave reaction. The microwave method allows the direct synthesis of new surface C–C bonds which are not accessible *via* the bromination route.

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- Experimental details: microwave experiments were conducted on a CEM ‘Discovery’ Focused microwave synthesis system, with a cooling flow of compressed air. MAS NMR and XPS spectra were recorded on Brüker DMX 400 and Kratos Analytical X-ray photoelectron spectrometers. To correct for possible deviation caused by electric charge the C1s line at 285.0 eV was taken as an internal standard. TGA was carried out on a Netzsch STA 409 analyser and textural analysis on ASAP 2010 instrument.