Evidence for C–C bond cleavage by H_2O_2 in a mesoporous CMK-5 type carbon at room temperature

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We reported an evidence for C–C bond cleavage by milder oxidizing agent H_2O_2 in a mesoporous CMK-5 type carbon at room temperature.

Porous carbons are solids with a high carbon content, usually in a nongraphitic state. Due to their high surface area and surface reactivity, they usually also contain substantial amounts of oxygen and hydrogen. These materials normally have high surface area and porosity, to some extent tunable pore size, and large pore volume. Carbon materials are considered as chemically inert under various harsh reaction conditions, *i.e.* they are stable in strongly acidic or basic environments, and withstand high temperature treatment in non-oxidative atmosphere. Therefore, porous carbon materials find many applications as adsorbents, catalyst supports and electrode materials.[1]

However, the hydrophobic nature of as-made highly porous carbons is disadvantageous with respect to access of water, which is necessary for many applications. Therefore, the surface of a porous carbon material often needs to be modified to create surface functional groups which increase the hydrophilic (acid or base) properties and facilitate the interaction with guest species.

Porous carbon with oxygen or nitrogen containing functional groups can be directly synthesized *via* a pyrolysis process by using oxygen or nitrogen rich precursors.[2] However, the most frequently used method to generate surface oxygen is oxidative treatment. This may include gas phase reactions (air or oxygen plasma) or liquid phase reactions (NaOCl, H_2O_2, HNO_3, or H_2SO_4 solution).[3] Oxidation through partial gasification usually results in substantial carbon loss and causes changes in surface area and pore size distribution. Nitric acid treatment produces the highest concentration of surface oxygen groups, especially carboxylic acid groups. Sodium hypochlorite and H_2O_2 as milder oxidizing agents rather favor phenol groups instead of lactone and carboxylic acid groups. The porous structure of a porous carbon normally remains almost unchanged after H_2O_2 treatment.[4]

Since their discovery in 1999,[5] ordered mesoporous carbons have gained much attention due to their fascinating regular structure, high surface area, narrow pore size distribution, and many promising applications. Modification of the surface chemistry of such materials, however, has so far only been studied to a minor extent.[6] Ordered mesoporous carbon of the CMK-5 type can be described as a hexagonal packing of carbon tubes. It has very interesting properties, such as very high surface area, bimodal porosity and is promising as a catalyst support.[7] In order to explore the possibility of modifying the surface of such carbon types, we have been using the mild oxidizing agent H_2O_2 with the goal to introduce oxygen-containing groups and thus to improve the hydrophilicity, while maintaining the pore structure. Surprisingly, CMK-5 carbon loses its ordered structure after treatment with H_2O_2 (30 wt%) at room temperature, even after only a few minutes of treatment. This indicated that H_2O_2 reacts strongly with the CMK-5 carbon under cleavage of part of the C–C bonds, leading to a structural collapse. In the following, we report a more detailed study of this degradation, based on characterization of the materials with powder X-ray diffraction (XRD), nitrogen sorption, transmission electron microscopy (TEM) and gas chromatography (GC).

CMK-5 carbons were prepared according to published procedures.[8] Briefly, furfuryl alcohol containing oxalic acid as the polymerization catalyst was infiltrated into the pores of the SBA-15 template *via* incipient wetness impregnation. In order to prepare CMK-5 carbon with tunable pore wall thickness, the concentration of furfuryl alcohol was adjusted by adding trimethylbenzene as diluting agent, as reported in Table 1. FA was polymerized at 60 °C and then 80 °C, followed by carbonization at 850 °C for 4 h in nitrogen. CMK-5 carbons were generated after leaching out the silica template with HF(aq) solution. The solid residue was recovered by filtration, washing with distilled water and acetone, and drying at 90 °C overnight. Samples were named as CMK-5/*x*, where *x* is from 1 to 3. In comparison, CMK-5/4 was prepared from Al/SBA-15 as the template. Textural properties of these samples are given in Table 1.

0.5 g of CMK-5 carbon was treated with hydrogen peroxide by adding 10 ml of H_2O_2 (30 wt%) dropwise to the carbon powder on a filter. Immediately, foam is formed, probably resulting from

Table 1 The synthetic conditions and texture parameters of CMK-5 carbons before and after H_2O_2 treatment

Sample	C_{FA} (vol%)	S_{BET}/ $m^2\ g^{-1}$	V_{tot}/ $cm^3 g^{-1}$	a/nm	D_{wall}/ nm	m_{loss} (%)
CMK-5/1	40	2025	2.00	9.9	1.4	13
CMK-5/2	60	1590	1.50	10.1	1.7	45
CMK-5/3	70	1338	1.19	10.0	1.8	40
CMK-5/4	70	1496	1.4	10.0	1.8	43
CMK-5/1- H_2O_2		692	0.43			
CMK-5/2- H_2O_2		212	0.18	—	—	
CMK-5/3- H_2O_2		239	0.20	—	—	
CMK-5/4- H_2O_2		589	0.48	—	—	

[a] C_{FA}: concentration of furfuryl alcohol in trimethylbenzene; S_{BET}: specific surface area calculated by the BET method; V_{tot}: total pore volume at p/p_0 = 0.99; a: unit cell parameter. D_{wall}: pore wall thickness of a mesoporous carbon; m_{loss}: weight loss of the CMK-5 carbons after H_2O_2 treatment.

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decomposition of the hydrogen peroxide. After washing with water and acetone on the filter, the dried carbon was characterized by small angle XRD. The XRD patterns show that the ordered structure of CMK-5 disappears after H_2O_2 treatment. This is obviously due to the treatment with H_2O_2, and indicates that the H_2O_2 reacts with CMK-5 carbon, leading to substantial damage of the carbon structure. These experiments were repeated many times, always with the same result. However, the attack on the carbon structure is dependent on the concentration of the H_2O_2 solution. Treatment at concentrations below 15 wt% leaves the CMK-5 structure intact.

In order to study in more detail the processes occurring during reaction between CMK-5 carbon and H_2O_2 solution, the following experiments were performed: Batches of 0.7 g each of CMK-5 carbon with different pore wall thickness (Table 1) were impregnated with 15 ml of H_2O_2 (30 wt%) in a glass bottle at room temperature and maintained under static conditions. The cap of the glass bottle has a small hole for pressure release since gaseous products are formed. After 30 days, the clear supernatant solution was carefully decanted into another bottle. This bottle was heated to 100 °C in order to release volatile compounds into the gas phase, and the headspace was subjected to GC analyses. The remaining carbon powders were dried at 90 °C for 2 days, and labeled CMK-5/*x*-H_2O_2, where *x* ranges from 1 to 4, corresponding to the original samples.

CMK-5 carbons before and after H_2O_2 treatment were characterized by XRD. As shown in Fig. 1(a), the original CMK-5 carbon shows well-resolved (100), (110), (200), (210) and (300) reflections, indicating that the samples have an ordered structure with 2-D hexagonal symmetry. After H_2O_2 treatment, the well-resolved reflections (Fig. 1 (b)) disappear for all CMK-5 samples, regardless of their wall thickness, indicating the loss of structural order under the treatment conditions. From the XRD results, one can conclude that CMK-5 carbon is chemically rather reactive, being easily attacked by H_2O_2. This is very different compared to the reaction between conventional activated carbon and H_2O_2, where the structure and textural properties of the activated carbon is almost completely maintained.[4]

In order to further investigate how the pore structure and textural properties of the CMK-5 carbon were changed, CMK-5 carbons before and after H_2O_2 treatment were characterized using nitrogen sorption (ASAP2010, Micromeritics). The isotherms are presented in Fig. 2, where the isotherms of CMK-5/1 and CMK-5/3 are not shown because they are quite similar to that of CMK-5/2. The corresponding pore structure parameters, including BET surface areas, total pore volumes and unit cell parameters are compiled in Table 1. The nitrogen sorption isotherms of the parent samples are essentially of type IV with a pronounced hysteresis loop, corresponding to published results. As seen in Table 1, the samples exhibit very high BET surface areas and large pore volumes. After H_2O_2 treatment, the carbons show nitrogen sorption isotherms with a completely different shape, *i.e.* the capillary condensation step has completely vanished and the total amount adsorbed is reduced very strongly. This indicates that the mesopore system is completely destroyed by the hydrogen peroxide treatment. This is also reflected in Table 1, where the BET surface area and pore volume of CMK-5 decreases significantly after the H_2O_2 treatment, by a factor of about 2.5–7.5 compared to the parent carbons. CMK-5 carbon consists of interconnected tubes with pores inside the tubes and in between the tubes, and surface area inside the tubes and on the external surface of the carbon tubes. If only the interconnections of the tubes were destroyed by the H_2O_2 treatment, the surface area of the CMK-5 carbon should not decrease too strongly, since then the intra-tube surface area and pore volume would still be maintained. The strong loss of pore volume and surface area indicates, that major changes of the pore structure occur, affecting not only the connections of the tubes, but the carbon tubes themselves. Combining the results from XRD and nitrogen adsorption, one can conclude that the structure of CMK-5 is damaged drastically by the H_2O_2 treatment.

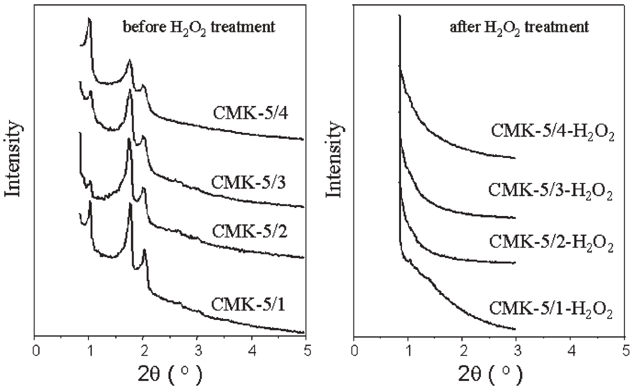

Fig. 1 XRD patterns of CMK-5 carbons before and after H_2O_2 treatment.

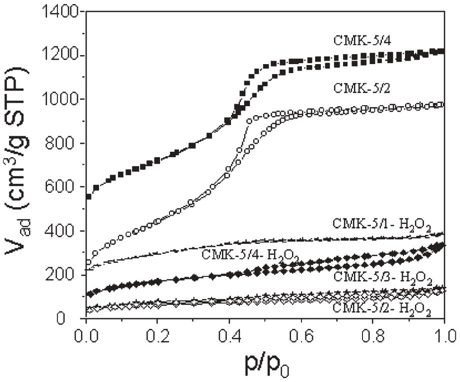

Fig. 2 Nitrogen sorption isotherms of CMK-5 carbons before and after H_2O_2 treatment. For clarity, the isotherms of CMK-5/4 and CMK-5/1-H_2O_2 are offset vertically by 300 and 100 cm^3 g^{-1} STP, respectively.

TEM studies further corroborate these conclusions. Fig. 3a shows high-resolution TEM images of the CMK-5/1. One can see well-defined pores parallel to each other. The white lines are corresponding to the mesopores generated in the space previously occupied by the walls of the SBA-15 template. The brighter features in the middle of the dark lines correspond to the intra-tube voids. Fig. 3b, c, and d display high-resolution TEM images of CMK-5/1 after H_2O_2 treatment. As seen from Fig. 3b, after H_2O_2 treatment, the global particle shape is maintained. However, the well-defined pore structure is completely destroyed. Careful examination of the sample by TEM reveals that in some parts of the sample residual order is still present, but these regions are estimated to correspond to less than 5% of the total sample

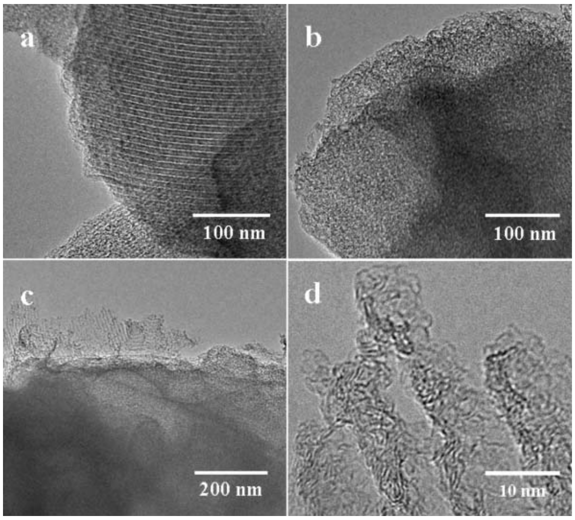

Fig. 3 TEM images of CMK-5/1 before (a) and after H_2O_2 treatment (b, c and d).

volume. Closer inspection of the data in Table 1 suggests that samples with different wall thickness and surface area are differently affected by the H_2O_2 treatment. So far, no clear correlation could be identified, but this aspect is worthy of further, more detailed investigation.

As reported in a previous study,[9] ordered mesoporous carbons can maintain an ordered structure even in boiling 5 M aqueous solution of NaOH, KOH, or H_2SO_4 over a week, showing strong resistance to attack by acids and bases. Thus, capillary pressures developed during the drying of the sample cannot be responsible for the destruction of the structure, but instead it has to be attributed to the oxidative attack. Since conventional porous carbon does not show a corresponding change of the structure and texture after treatment with hydrogen peroxide, the reactivity of the CMK-5 type carbon must be attributed to its unique structure, *i.e.* the interconnected tubes and the very thin carbon walls (less than 2 nm). In general, the surface of graphitic carbon consists of two types of crystalline planes, the basal planes and the edge planes. The unsaturated bonds at the edges of the graphitic layer planes are very reactive and form functional groups with suitable foreign atoms. For CMK-5 carbon, the framework consists of nanosized amorphous carbon fragments, which are cured in part and cross-linked extensively (see Fig. 3d). They may have a higher fraction of not fully coordinated carbon atoms on the edges of the carbon layers, resulting in increased chemical reactivity. In the presence of H_2O_2 molecules, the links between adjacent amorphous carbon fragments may be cleaved into smaller species, thus leading to collapse of the whole structure. This hypothesis is supported by the GC analysis of the headspace. The GC measurements show that after H_2O_2 treatment a mixture of various C_4 to C_8 species is present, the identity of which could not be established as yet. It is highly improbable that these species are residual organic compounds left in the CMK-5 material. The CMK-5 carbon was obtained after carbonization at 850 °C, followed by acid treatment, water and acetone washing, and prolonged drying, which should remove all residual volatile organic compounds. The headspace was analyzed for five samples, with the results for all five samples being very similar. Although the identity of the C_4–C_8 species could not be established so far, their formation shows that the reaction of the CMK-5 carbon with H_2O_2 is very pronounced, leading not only to degradation of the structure, but even to the oxidative formation of small organic molecules.

In addition to the formation of small organic molecules after hydrogen peroxide treatment, the samples lose a substantial fraction of their mass (Table 1). The mass losses after H_2O_2 treatment are in the range of 13–45wt% depending on the parent materials. It cannot be fully excluded, that some small fractions of the material were lost during the decantation, but the decanted solutions were clear to the naked eye, so that it seems improbable, that a substantial part of the weight loss can be attributed to decantation of small particles. Full mass balancing, taking into account all products, was not possible so far, since the bubbling due to the decomposition of the hydrogen peroxide solution after contact with the carbon makes quantification of released gases very difficult. In addition, it is not easy to analyze the liquid phase, since the residual hydrogen peroxide can damage the column of the GC. However, work is under way to establish a full mass balance of the process. Nevertheless, the substantial weight loss supports the interpretation, that the CMK-5 carbon is oxidatively degraded under partial formation of small organic molecules.

In summary, we have demonstrated that 30 wt% H_2O_2 solution can break C–C bonds in CMK-5, leading to structural collapse, the formation of small organic molecules and substantial weight loss. These surprising results suggest that nanostructured carbons such as CMK-5 may have a much more reactive surface than conventional porous carbons, which are considered to be rather inert solids with respect to H_2O_2 treatment. We are presently investigating methods for modifying the surface properties of CMK-5 type carbons and related materials while maintaining their structural integrity.

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