doi:10.1246/cl.2010.424

Preparation of Nonporous Carbon-based Sorbent from Sucrose

Deyi Zhang,* Heming Luo, Yi Wang, and Huixia Feng
College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, P. R. China

(Received January 13, 2010; CL-100037; E-mail: xixizhang@lut.cn)

A nonporous carbon-based sorbent was obtained by partial carbonization of sucrose utilizing the dehydration effect of concentrated sulfuric acid. The BET specific surface area of the reported sorbent only is $0.6\,m^2\,g^{-1}$, but it exhibits excellent adsorbability. Differently from active carbon, oxygen groups, such as hydroxy groups and carboxyl groups, are main active adsorption sites of the reported sorbent.

Since the end of the 18th century, the adsorbability of lignose has been known, and various carbon-based materials, such as active carbon, porous graphite, and carbon molecular sieves, have been extensively used for potable and waste water treatment, respirators, air and gas purification.[1,2] In recent years, the production of carbon-based sorbents from a range of low-cost precursors, mainly industrial or agricultural by-products, has received increasing attention.[3,4] Sucrose, acting as the carbon source, has been utilized to prepare active carbon,[5] ordered mesoporous carbons,[6] and carbon-coverd function materials, such as TiO_2/carbon composite[7] and $LiFePO_4$/carbon composite.[8] In the fabrication process, it is crucial to carbonize and activate the sucrose at high temperature, which would destroy the oxygen groups on the surface of carbon-based materials and consume large amounts of energy.

In this letter, a nonporous carbon-based sorbent (NCS) was prepared by partial carbonization of sucrose utilizing the dehydration effect of sulfuric acid. Sucrose was partial carbonized in 98% sulfuric acid at ambient temperature followed by oxidation with hot concentrated sulfuric acid under vacuum. The preparation of NCS does not require carbonization at high temperature and activation is unnecessary. As a secondary process, oxidation reactions were performed in vacuum, hydroxy groups were oxidized to carboxyl groups or carbonyl groups without any overoxidation to carbon dioxide, which created the possibility of preserving oxygen groups on the surface of prepared sorbent.

According to the process described below the nonporous carbon-based sorbent was prepared. Briefly, 5 g of sucrose was dissolved in 3 mL of H_2O, after which 9 mL of 98% H_2SO_4 was added dropwise at ambient temperature. The mixture was stirred for 5 min and then maintained at 120 °C for 1 h, after which it was transferred to a vacuum drying oven and heated at 230 °C for 6 h at 0.06 MPa. Finally, the sample was directly cooled to ambient temperature under vacuum. A black nonporous carbon-based sorbent powder then was obtained.

Figure 1 shows the XPS spectrum of NCS. The analysis results show that the surface components of NCS are mainly carbon and oxygen, the O1s/C1s composition ratio is higher then 0.35:1. These results indicate that there is an abundance of oxygen groups on the surface of prepared sorbent.

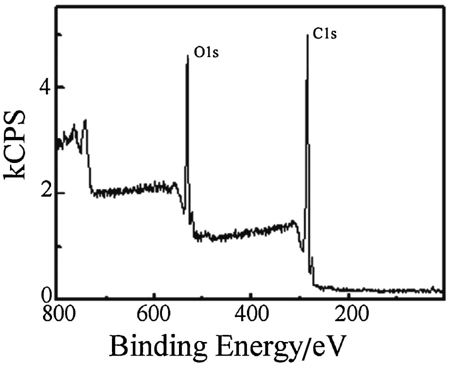


Figure 1. XPS spectra of NCS.

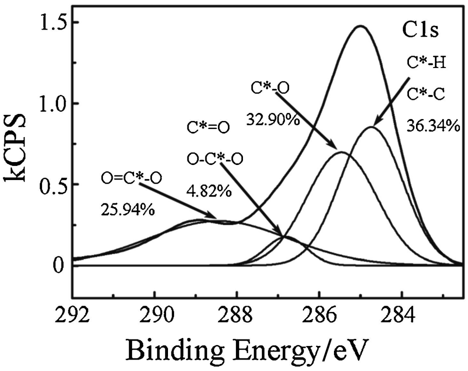


Figure 2. Curve fit of C1s photoelectron peak of NCS.

The high-resolution XPS C1s spectrum of NCS (Figure 2) shows several relatively well-resolved peaks corresponding to carbon atoms in different chemical environments. So, it is resolved into four individual component peaks representing graphitic carbon (C–C, B.E. = 284.7 eV) as the major peak, hydroxy/ether groups (C–O, B.E. = 285.5 eV), carbonyl groups (C=O, B.E. = 286.8 eV), and carboxyl groups (COOH, B.E. = 288.4 eV).[9–11] The results show that hydroxy groups and carboxylic groups are the main oxygen groups on the surface of prepared sorbent.

Figure 3 shows the FT-IR spectrum of NCS. The presence of oxygen groups is evidenced by the bands at 3000–3700 cm^{-1} (a wide band attributed to O–H stretching vibrations in hydroxy or carboxyl groups), 1720 cm^{-1} (C=O vibrations corresponding to carbonyl, quinone, ester, or carboxyl) and 1000–1300 cm^{-1} (C–O stretching vibrations in hydroxy, ester, or ether and O–H bending vibrations).[12,13] Moreover, the presence of aliphatic structures is suggested by the band at 3000–2815 cm^{-1}, which corresponds to stretching vibrations of aliphatic C–H.[14] The presence of hydroxy groups and aliphatic structure illustrates that carbonization of sucrose by sulfuric acid is incomplete, a great number of sucrose molecule fragments with numerous

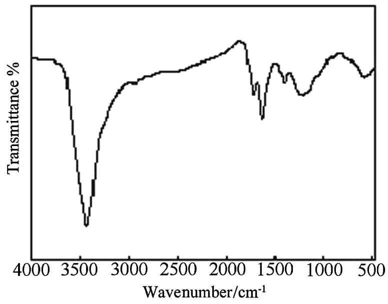
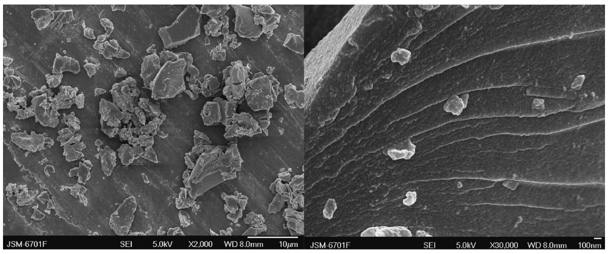


Figure 3. FT-IR spectrum of NCS.



(a) ×2000 **(b)** ×30.000

Figure 4. SEM images of NCS at different magnification.

hydroxy groups are still present on the surface of prepared sorbent. The presence of carboxylic groups and carbonyl groups indicates that hydroxy groups could be oxidized to carboxyl groups or carbonyl groups by hot concentrated sulfuric acid under vacuum.

Figure 4 shows a SEM image of NCS. The prepared sorbent shows an irregularly shaped mass with particle size in the range of 1–10 μm. There is not any apparent pore structure on the surface of prepared sorbent. At much greater magnification, the surface of prepared sorbent displays apparent grooves, which are possibly resulting in the corrosion by hot sulfuric acid of carbonaceous surface.

Table 1 lists the Cr(VI) and Methylene Blue (MC) adsorptive capacity of the prepared nonporous carbon-based sorbent (NCS), active carbon (AC), superactive carbon (SAC), and carbon black (CB). These data show that the prepared sorbent shows greater Methylene Blue adsorptive capacity than active carbon, Cr(VI) adsorptive capacity can reach about 60.3% of the capacity of active carbon. There are not any apparent pore structures on the surface of prepared sorbent, but it still exhibits excellent adsorbability, especially for cationic organic dye, Methylene Blue. The results could indicate that the prepared sorbent has a different adsorption mechanism than active carbon.

Figure 5 shows the possible formation mechanism of the nonporous carbon-based sorbent. Sucrose is partial carbonized by 98% H_2SO_4 due to dehydration. A great number of sucrose molecule fragments on which still remain abundant hydroxy groups embedded on the surface. Through further dehydration reaction between the hydroxy groups in the sucrose molecule fragments, carbon particles are connected to each other, and a carbon particles network is formed. At middle temperature in vacuum, some hydroxy groups on the surface are oxidized to carboxyl groups or carbonyl groups by hot concentrated sulfuric acid.[15] Vacuum conditions create the possibility of controlling the extent of oxidation and preserving oxygen groups on the surface of prepared sorbent. Differently from active carbon, the oxygen groups are the main active adsorption sites of the nonporous carbon-based sorbent.

Table 1. Adsorptive capacity of different sorbents

Sorbents	Cr(VI) adsorptive capacity/mg g^{-1}	MC adsorptive capacity/mg g^{-1}
NCS	5.90	453.09
AC	9.79	329.64
SAC	12.24	494.36
CB	3.18	35.09

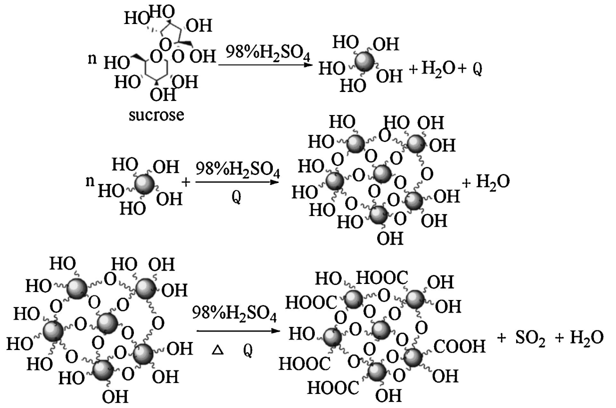


Figure 5. Formation mechanism of NCS.

In conclusion, the prepared nonporous carbon-based sorbent has inappreciable specific surface area but still exhibits excellent adsorbability due to abundant oxygen groups on the surface and could be used as a substitute for activated carbon for heavy metal ion and organic dye adsorption treatment in waste water.

We acknowledge the National Science Council, Gansu, for financially supporting this research under Contracts Nos. 3ZS062-B25-027, 0809DJZA011, and ZSO21-A25-028-C.

References

1 F. D. Shire, B. McEnaney, *Energeia* **1991**, *2*, 1.
2 E. Matisová, S. Škrabáková, *J. Chromatogr., A* **1995**, *707*, 145.
3 J. M. Dias, M. C. M. Alvim-Ferraz, M. F. Almeida, J. Rivera-Utrilla, M. Sánchez-Polo, *J. Environ. Manage.* **2007**, *85*, 833.
4 O. Ioannidou, A. Zabaniotou, *Renewable Sustainable Energy Rev.* **2007**, *11*, 1966.
5 C. Scherdel, G. Reichenauer, *Carbon* **2009**, *47*, 1102.
6 K. Böhme, W. Einicke, O. Klepel, *Carbon* **2005**, *43*, 1918.
7 S.-M. Yun, K. Palanivelu, Y.-H. Kim, P.-H. Kang, Y. S. Lee, *J. Ind. Eng. Chem.* **2008**, *14*, 667.
8 H. Liu, J. Xie, K. Wang, *J. Alloys Compd.* **2008**, *459*, 521.
9 Y. Xie, P. M. A. Sherwood, *Chem. Mater.* **1990**, *2*, 293.
10 Z. Yue, W. Jiang, L. Wang, S. D. Gardner, C. U. Pittman, Jr., *Carbon* **1999**, *37*, 1785.
11 S. Yun, K. Palanivelu, Y. Kim, P. Kang, Y. Lee, *J. Ind. Eng. Chem.* **2008**, *14*, 667.
12 M.-N. Pons, S. L. Bonté, O. Potier, *J. Biotechnol.* **2004**, *113*, 211.
13 B. Saha, M. Streat, *Ind. Eng. Chem. Res.* **2005**, *44*, 8671.
14 R. K. Sharma, J. B. Wooten, V. L. Baliga, X. Lin, W. G. Chan, M. R. Hajaligol, *Fuel* **2004**, *83*, 1469.
15 T. P. Goldstein, Z. Aizenshtat, *J. Therm. Anal. Calorim.* **1994**, *42*, 241.