

Characterization of diatomaceous silica by Raman spectroscopy

P. Yuan^{a,*}, H.P. He^a, D.Q. Wu^a, D.Q. Wang^a, L.J. Chen^b

^a Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China

^b State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Received 10 November 2003; accepted 13 February 2004

Abstract

The network characteristic of a selection of diatomaceous silica derived from China has been investigated using Raman spectroscopy. Before any thermal treatment of the sample, two prominent bands of 607 and circa 493 cm^{-1} are resolved in the Raman spectra of diatomaceous silica, corresponding to the $(\text{SiO})_3$ -ring breathing mode of D_2 -line and the O_3SiOH tetrahedral vibration mode of D_1 -line, respectively. This is more similar to the pyrogenic silica rather than the silica gel. For the latter, to obtain a $(\text{SiO})_3$ -ring, the sample must be heated between 250 and 450 °C. Significant difference is also found between the diatomaceous silica and other natural silicas, e.g. in the Raman spectra of sedimentary and volcanic opals, neither D_1 nor D_2 band is detected in previous reports.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Diatomaceous silica; Raman spectroscopy; α -Cristobalite

1. Introduction

Opaline minerals have been categorized into three general groups, including Opal-A, Opal-C, and Opal-CT, according to crystallinity and crystal structure [1]. Opal-A is predominantly amorphous. Opal-CT is semicrystalline comprising of crystalline regions of α -cristobalite and α -tridymite. And Opal-C is a well-ordered form of the silicate predominantly in the α -cristobalite form. Diatomaceous silica, the amorphous silica with Opal-A structure, exists in the form of frustule in the natural mineral assemblage of diatomite. Since the diatomaceous silica has properties such as high porosity with strong adsorbability and excellent thermal resistance, diatomite has been widely used as filter aid, catalytic support, biological support, functional filler, and adsorbent, etc. [2–4].

Extensive studies on the crystalline structure of diatomaceous silica and its evolution with thermal treatment have been developed using X-ray crystallography, thermal analysis, infrared (IR) spectroscopy and magic angle spin nuclear magnetic resonance (MAS NMR) [5–8]. To the best of our knowledge, the Raman spectra of diatomaceous sil-

ica have received relatively little attention despite that some Raman spectroscopy studies on synthetic amorphous silica have been reported [9,10].

Our purpose of this work is to investigate network characteristic of diatomaceous silica based on Raman spectroscopy observation. A microprobe Raman technique was used to characterize a selection of diatomite samples derived from China. These samples are compared to amorphous silicas reported previously.

2. Materials and methods

Diatomite samples, collected from Buchang deposit in Haikang county of Guangdong province, and Yuanjiawan deposit in Shengxian county of Zhejiang province, China, are denoted as BP and YP, respectively. A process of water washing and repeated sedimentation was applied to purify the raw samples. The acid washing method that has proved effective [11] was avoided to prevent the sample surface from possible disturbance or reconstruction. The purified samples were dried at 105 °C, then ground to less than 40 μm in mortar and kept in the desiccator for experiment.

The X-ray diffraction patterns of the samples were performed with a D/max-1200 diffractometer with Cu $K\alpha$ radiation under target voltage 40 kV and current 30 mA in a

* Corresponding author. Tel.: +86-20-85290341; fax: +86-20-85290130.

E-mail address: yuanpeng@gig.ac.cn (P. Yuan).

scanning rate of $5^\circ 2\theta \text{ min}^{-1}$. The micromorphology of sample was observed under Hitachi S-3500N scanning electron microscopy (SEM). The specific surface areas of samples were performed with a NOVA-1000 apparatus using nitrogen as adsorbate (BET method).

The Raman studies were performed with a confocal microprobe Raman system (LabRaman I, Dilor SA) equipped with a home-built heating/freezing stage designed to treat the sample in situ. The laser was accurately focused on the surface of diatom shell by the observation of image displayed in the screen. The excitation line was 632.8 nm from a He–Ne laser and the spectra were recorded over 150 scans at a resolution of 2 cm^{-1} .

Powder sample was filled into a micro quartz tube with inner diameter of 2 mm, and the tube was placed in the heating/freezing stage for taking spectra. The in situ thermal treatment, from room temperature (RT) to 650°C , and the process of taking spectra were automatically accomplished. The temperature rising rate was $10^\circ\text{C min}^{-1}$ and the constant time of certain temperature was 5 min. The room temperature is at $23 \pm 1^\circ\text{C}$, and the relative humidity is about 70%.

3. Results and discussion

The SEM result shows that most of diatoms in sample BP belong to the genera *Synedra ulna* (Nitz.) Ehr., with short diameter of 3–15 μm , and long diameter of 40–120 μm . Most of diatoms in sample YP belong to the genera *Melasira granulata* (Ehr.) Ralfs., with diameter of 10–30 μm .

The mineralogical compositions (shown in Table 1) of the two samples, evaluated by their XRD patterns, show that there are only small quantity of quartz and kaolinite impurities in sample BP while sample YP contains considerable quartz and clay impurities after sedimentation. This is consistent with that shown by chemical analysis. As shown in Table 1, sample YP contains more Al_2O_3 than sample BP, which results from clay mineral impurities.

Figs. 1 and 2 show the Raman spectra of samples BP and YP at different thermal treatment temperatures. The wavenumber and assignment of each mode observed are listed in Table 2. The assignments are based on the reports [12,13] on a number of forms of silicates and silicon oxides.

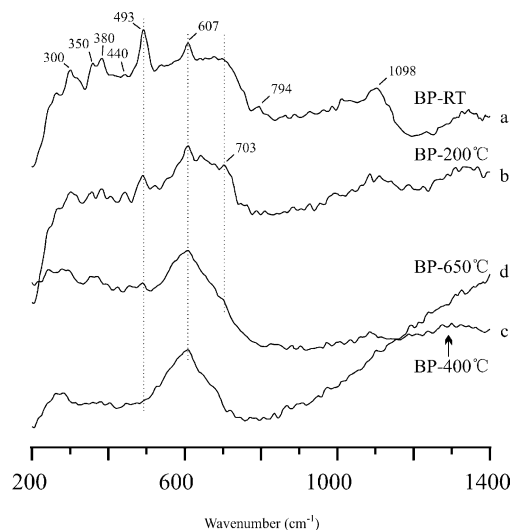


Fig. 1. Raman spectra of BP under thermal treatment conditions.

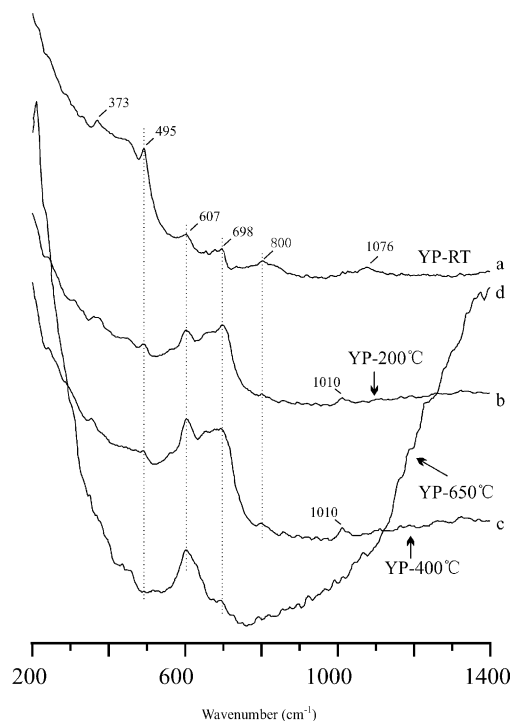


Fig. 2. Raman spectra of YP under thermal treatment conditions.

Table 1
Mineralogical and chemical compositions of diatomite samples (wt.%)

	Diatom shell	Quartz	Kaolinite	Montmorillonite	Illite	Mica	Feldspar	Other impurities
BP	93.2	1.0					4.8	1.0
YP	80.0	4.9	5.3	3.3	2.0	3.0		1.5
	SiO_2	Al_2O_3	Fe_2O_3	Loss	Total	$\text{SA}^a (\text{m}^2 \text{g}^{-1})$		
BP	84.13	1.93	0.72	10.72	97.50	30.9		
YP	74.52	9.64	1.33	9.78	95.27	23.1		

^a SA: specific area.

Table 2
Table of Raman modes of the diatomaceous silica samples BP and YP

Assignments	O–Si–O deformation (silicate impurities)	Unknown	O ₃ SiOH tetrahedral vibration	(SiO) ₃ -ring breathing	Si–O–Si symmetric stretch	Si–O–Si asymmetric stretch
Sample BP	300, 350, 380	440	493	607	703, 794	1098
Sample YP	373		495	607	698, 800	1076

Two prominent bands are observed at 607 and 493 cm⁻¹ in the spectrum of sample BP at room temperature (Fig. 1a). The band at 607 cm⁻¹, corresponding to the defect line of D₂, has been assigned to a (SiO)₃-ring breathing mode [9,14]. The band at 493 cm⁻¹, corresponding to the defect line of D₁, has been assigned to an O₃SiOH tetrahedral vibration mode [9,14]. There exists a second assignment for the D₁-line in the Raman spectra of silica, proposed by Galeener and Geissberger [15], which takes (SiO)₄-ring vibrations as the origin of this band. The spectra of YP series (Fig. 2) are similar to those of BP generally. However, as shown in Figs. 1 and 2, the bands in the spectra of YP, even have the same vibration mode with those in the spectra of BP, have different intensities with small shifts of positions. This reflects the structural difference between diatoms of different genera, possibly resulted from the difference of biomineralization process [5].

With the increase of treatment temperature from room temperature to 650 °C, the intensity of the band at 607 cm⁻¹ increases significantly between 200 and 400 °C, and remains almost constant between 400 and 650 °C (shown in Figs. 1a–d, 2a–d). On the contrary, the intensity of the band at 493 cm⁻¹ decreases simultaneously. This supports the proposal that the D₁-line belongs to a O₃SiOH tetrahedral vibration mode and the D₂-line belongs to a (SiO)₃-ring breathing mode, since the thermal treatment result in the condensation of surface silanols and the formation of three-membered SiO rings [9]. The proposal was also supported by previous report [10], in which Riegel et al. suggested that the absolute intensity ratio D₁/D₂ should be a good indicator of the amount of the hydroxyl groups.

Humbert [14] assumed that if the Q⁴ silicon atom were contained in a three-membered SiO ring, the D₂-line at 607 cm⁻¹ would be observed in the Raman spectra. To obtain a cyclic ring with only three SiO members in a silica gel prepared by a sol–gel process, the sample must be heated between 250 and 450 °C; thus, the Raman shift at 607 cm⁻¹ appears. For the pyrogenic silica, the D₂-line at 607 cm⁻¹ is present before any thermal treatment of the sample. In this sense, the diatomaceous silica is more similar to the pyrogenic silica than the silica gel.

The difference of D₂ band among the pyrogenic silica, silica gel and the diatomaceous silica reflects the variation of their formation conditions. McDonald [16] proposed that the Cab-O-Sil is formed at high temperature, so the rate of rearrangement of silica tetrahedral should be greater than that of precipitated silica, which is formed in solution. The three-membered rings, may have been formed during the

formation process of pyrogenic silica. Since the precipitated silicas do not experience any calcination treatment during the formation process, they have much less chances to form the three-membered rings. The diatomaceous silica, although formed from aqueous solution, shows the presence of some three-membered rings. This might reflect the unique property of diatomaceous silica that formed by a biomineralization process. Recently, Kroger et al. [17] isolated a set of cationic polypeptides (named silaffins) from purified cell walls of the diatom *Cylindrotheca fusiformis* to generate networks of silica nanospheres within seconds when added to a solution of silicic acid. This shows that the diatomaceous silica has some distinguished properties from the other amorphous silica.

Humbert and Burneau [9] studied silica gel powders using both Raman and FTIR spectroscopy and found that strongly H-bonded silanols ($\nu_{\text{OH}} \approx 3500 \text{ cm}^{-1}$) are eliminated at 200 °C. For the same thermal treatment, no three-membered ring contributions appear on the Raman spectra. Between 200 and 400 °C, the groups of weakly bonded silanols, absorbing between 3600 and 3700 cm⁻¹, are dehydroxylated. Simultaneously, D₂-line at 607 cm⁻¹ is obtained in the Raman spectra. D₂ is much increased between 400 and 500 °C, and remains constant between 500 and 600 °C. Based on the evolutions of both the infrared and the Raman spectra, Humbert and Burneau [9] proposed that the three-membered rings come from the condensation between surface silanols which absorb between 3600 and 3700 cm⁻¹ in the infrared spectra, i.e. which are weakly H-bonded.

The preferential dehydroxylation of silanols that interact most strongly with neighbors by H-bond is consistent with the study on the dehydroxylation of silica gel [18,19], which proposed that the stronger the H bond of the silanol is, the more easily condensation occurs. In those studies, however, the 3500 cm⁻¹ band was assigned to the OH vibration mode of the physically adsorbed H₂O, and the OH vibration mode of isolated and H-bonded hydroxyl groups was reported in the range of 3740–3750 cm⁻¹.

For diatomaceous silica, our previous studies by ¹H MAS NMR and DRIFT [6,8,20] have proved the H-bonded hydroxyl groups condense more easily than the isolated ones, and the stronger the hydrogen bond is, the more easily condensation occurs. This is similar to the silica gel mentioned above. The isolated silanols have absorbance at 3745 cm⁻¹ while the H-bonded silanols have absorbance at about 3740 cm⁻¹ in the DRIFT spectra [8,20]. Under the treatment condition of heating in muffle oven for 1 h, the H-bonded silanols has not been dehydroxylated completely

until 1000 °C [20]. However, most of the silanols, corresponding to D₁-line, has been dehydroxylated at 650 °C under in situ treatment condition in this work. Based on the observation that D₂ is much increased between 200 and 400 °C, and remains constant between 400 and 650 °C, it could be presumed that the three-membered rings are mostly resulted from the condensation of the surface silanols between 200 and 400 °C.

Smallwood et al. [21] studied the Raman spectroscopy of sedimentary and volcanic opal samples. Several bands in the spectra of the volcanic opals were found to be consistent with those of α -tridymite. The similarity of the volcanic opal spectra to α -tridymite was believed to be indicative of the presence of α -tridymite. Similarities were also observed between the spectra of the α -tridymite and the sedimentary opals. The most prominent of these similarities was found in the band of 400 cm⁻¹ and a doublet in the 750–850 cm⁻¹ region, which is assigned to bending modes of the Si–O–Si units and symmetric Si–O–Si stretching, respectively. Smallwood et al. [21] proposed that even for the predominantly amorphous opals, some crystallinity is evident. In this work, a band at 794 (for BP) or 800 cm⁻¹ (for YP), corresponding to the symmetric Si–O–Si stretching mode, is also observed in the Raman spectra of diatomaceous silica (Figs. 1a, 2a). This seems to support the suggestion proposed by Smallwood et al. [21]. In the Raman spectra of sedimentary opal and volcanic opal, neither D₁ nor D₂ band is detected [21]. However, both of them are well resolved in the spectra of diatomaceous silica samples of this work. This reflects the difference among opal-structured diatomaceous silica, the sedimentary opal and the volcanic opal.

The number of hydroxyls per unit surface is an important parameter in the description of amorphous silicas. Using CP/MAS NMR spectra, the fractional population of siloxane bond, single silanos and geminal silanol, denoted as Q⁴, Q³, and Q², respectively, could be determined through the relative band areas of the various signals [9,22,23]. Humbert [14] found that the NMR chemical shift of the Q⁴ silicon atom corresponding to the (SiO)₃ ring is located at –106 ppm, different from the other Q⁴ silicon atoms. Consequently, if this type of Q⁴ silicon at –106 ppm were ignored, the Q³ population would be overestimated. The presence of D₂ band in the Raman spectra of diatomaceous silica shows that the silicon circumstance of cyclic trisiloxane ring should be considered in the evaluation of the number of hydroxyls per unit surface.

4. Conclusions

In this study, the network characteristic of diatomaceous silica has been investigated using Raman spectroscopy. Our results show that, even before any thermal treatment of the sample, two prominent bands of 607 and circa 493 cm⁻¹ are detected in the Raman spectra of diatomaceous silica, corresponding to the (SiO)₃-ring breathing mode of D₂-line and

the O₃SiOH tetrahedral vibration mode of D₁-line, respectively. With the increase of heating temperature under in situ condition, the surface silanols are condensed progressively, resulting in the formation of three-membered SiO rings. This is similar to the pyrogenic silica rather than the silica gel. For the silica gel, to obtain a (SiO)₃-ring, the sample must be heated between 250 and 450 °C. There are also some significant differences found between the diatomaceous silica and other natural silicas, e.g. the diatomaceous silica shows the well-resolved D₁ and D₂ band in Raman spectra while sedimentary opal and volcanic opal do not. This unique characteristic of diatomaceous silica might result from the formation process of biomineralization.

Based on the presence of three-membered SiO rings in the diatomaceous silica, the silicon circumstance of cyclic trisiloxane ring should be considered, to avoid the overestimation of the Q³ population in the evaluation of the number of hydroxyls on the surface of diatomaceous silica.

Acknowledgements

Financial support for this work was provided by National Natural Science Foundation (Grant No. 40202006) of China, Natural Science Foundation (Grant No. 021431) of Guangdong Province and Foundation (Grant No. 9911) of State Key Laboratory for Physical Chemistry of Solid Surfaces, China.

References

- [1] J.B. Jones, E.R. Segnit, *J. Geol. Soc. Aust.* 18 (1971) 57–68.
- [2] B. Erdogan, S. Demirci, Y. Akay, *Appl. Clay Sci.* 11 (1996) 55–67.
- [3] P.V. Vasconcelos, J.A. Labrincha, J.M.F. Ferreira, *J. Eur. Ceram. Soc.* 20 (2000) 201–207.
- [4] X. Li, C. Bian, W. Chen, J. He, *Appl. Surf. Sci.* 207 (2003) 378–383.
- [5] F.Y. Wang, H.F. Zhang, *Chin. J. Geochem.* 14 (1995) 140–152.
- [6] P. Yuan, D.Q. Wu, Z.Y. Lin, *Spectrosc. Spect. Anal.* 21 (2001) 783–786 (in Chinese).
- [7] H. Feng, H.F. Zhang, J.G. Guo, L.F. Luo, *Acta Miner. Sinica* 19 (1999) 210–214 (in Chinese).
- [8] P. Yuan, D.Q. Wu, Z. Chen, Z.W. Chen, *Chin. Sci. Bull.* 46 (2001) 1118–1121.
- [9] B. Humbert, A. Burneau, *J. Non-Cryst. Solids* 143 (1992) 75–83.
- [10] B. Riegel, I. Hartmann, W. Kiefer, J. Grob, J. Fricke, *J. Non-Cryst. Solids* 211 (1997) 294–298.
- [11] N. Videnov, S. Shoumkov, Z. Dimitrov, L. Mogilski, L. Brakalov, *Int. J. Miner. Process.* 39 (1993) 291–298.
- [12] K.J. Kingma, R.J. Hemley, *Am. Mineral.* 79 (1994) 269–273.
- [13] P.F. McMillan, G.H. Wolf, in: J.F. Stebbins, P.F. McMillan, D.B. Dingwell (Eds.), *Structure Dynamics and Properties of Silica Melts*, *Rev. Mineral.* 32 (1995) 247–315.
- [14] B. Humbert, *J. Non-Cryst. Solids* 191 (1995) 29–37.
- [15] F.L. Galeener, A.E. Geissberger, *Phys. Rev. B* 27 (1983) 6199–6206.
- [16] R.S. McDonald, *J. Phys. Chem.* 62 (1958) 1168–1178.
- [17] N. Kroger, R. Deutzmann, M. Sumper, *Science* 286 (1999) 1129–1132.

- [18] C.C. Liu, G.E. Maciel, *J. Am. Chem. Soc.* 118 (1996) 5103–5119.
- [19] B.A. Morrow, A.J. Mcfarlan, *J. Am. Chem. Soc.* 96 (1992) 1395–1400.
- [20] P. Yuan, D.Q. Wu, H.P. He, Z.Y. Lin, *Appl. Surf. Sci.* 227 (2004) 30–39.
- [21] A.G. Smallwood, P.S. Thomas, A.S. Ray, *Spectrochim. Acta A* 53 (1997) 2341–2345.
- [22] A.P. Legrand, H. Hommel, J.B. Caillerie, *Colloid Surf. A* 158 (1999) 157–163.
- [23] L. Jelinek, P. Dong, C. Rojas-Pazos, H. Taibi, E. Kovatz, *Langmuir* 8 (1992) 2152–2164.