

NOTES

^1H MAS NMR spectra of hydroxyl species on diatomite surface

YUAN Peng^{1,2}, WU Daqing¹, CHEN Zhong³,
CHEN Zhiwei³, LIN Zhongyu³,
DIAO Guiyi¹ & PENG Jinlian¹

1. Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China;

2. State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China;

3. College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China;

Correspondence should be addressed to Wu Daqing (e-mail: Daqingwu@gig.ac.cn)

Abstract High spinning speed ^1H magic-angle spinning nuclear magnetic resonance (^1H MAS NMR) was used to detect surface hydroxyl groups of diatomite, which include isolated hydroxyl groups and hydrogen-bonded hydroxyl groups, and water adsorbed on diatomite surface that include pore water and hydrogen-bonded water. The corresponding proton chemical shifts of above species are ca. 2.0, 6.0–7.1, 4.9 and 3.0 respectively. Accompanied by thermal treatment temperature ascending, the pore water and hydrogen-bonded water are desorbed successively. As a result, the relative intensities of the peaks assigned to protons of isolated hydroxyl groups and hydrogen-bonded hydroxyl groups increase gradually and reach their maxima at 1000°C. After 1100°C calcination, the hydroxyl groups that classified to strongly hydrogen-bonded ones and the isolated hydroxyl groups condense basically. But some weakly hydrogen-bonded hydroxyl groups may still persist in the micropores.

Keywords: diatomite, surface hydroxyl groups, ^1H MAS NMR, thermal treatment.

Diatomite is natural amorphous silica engendered by deposition of diatom skeleton. It is formed by closest packing of hydrous SiO_2 spheres and is classified as opal-A mineralogically. Diatomite possesses abundant pores that consist of pores in diatom shell and nanomicropores between SiO_2 spheres. For its high porosity with strong adsorbability and its excellent thermal resistance, diatomite are used for filter-aids, catalytic support, adsorbent and functional filler^[1].

High temperature calcination is a key step to produce diatomite filter-aids and catalytic support. Accordingly, previous studies were focused on the high temperature phase transformation of diatom shell in which amorphous silica crystallized from disorderly opal to orderly α -cristobalite^[2–4]. Nevertheless, much attention has been paid to the applications of diatomite in the field of novel absorbent and functional support recently, as a result more and

and more researches are developed to study the interface reaction related to diatomite and adsorbed species^[1, 5–7]. In interface reactions, such as surface absorption, catalysis, surface coordination, etc., surface hydroxyl groups play essential roles^[8]. Consequently, developing researches on surface hydroxyl species of diatomite and on their transformation under thermal treatment conditions are the base of interface reaction research, and it will have deep significance for improving the application of diatomite.

IR spectrometry is a useful measure to study surface hydroxyl groups. However, it is difficult to distinguish different surface hydroxyl species of diatomite because the O-H vibration frequency (ca. 3745 cm^{-1}) of surface isolated hydroxyl groups and H-bonded hydroxyl groups are analogical. On the other hand, diatomite prefers to adsorb water for its high porosity, thereby in IR spectra the peak of strongly H-bonded hydroxyl groups is overlapped by the broad peak (with middle wavenumber at ca. 3500 cm^{-1}) that assigned to the adsorbed water and then is difficult to be discerned^[9]. In this study, by high spinning speed (11kHz) ^1H MAS NMR, high-resolution spectrum was obtained to explore the changes of hydroxyl species on diatomite surface under different thermal treatment conditions.

1 Materials and methods

Diatomite sample was collected from Puchang deposit in Haikang County of Guangdong Province, China. After being washed, it was separated by sedimentation and dried at 100°C, then ground to less than 40 μm by hand. The micromorphology of sample was observed under a Hitachi S-3500N Scanning Electron Microscopy (SEM). The results showed that most of diatoms belong to the *Pinnularia* species with a diameter ranging from 10 to 20 μm . The intrusive mercury method was used to measure a pore structure, and a macropore structure with a diameter ranging from 50 to 100 nm and a micropore structure with a diameter of 10–20 nm was found in the sample.

The XRD analysis revealed that the sample had a typical opal structure. There were no quartz peaks detectable in the spectrum, but some weak peaks attributed to kaolinite were observed. Chemical analysis showed that its main composition included SiO_2 (82.95%) (wt.), loss (7.93%), Al_2O_3 (5.75%) and Fe_2O_3 (1.41%). The content of Al_2O_3 is appreciably higher than normal because of the presence of kaolinite in sample.

The phase transformation from amorphous silica to α -cristobalite was proved at 1150°C by previous studies^[3]. Thereupon we chose the thermal treatment temperature ranging from 200°C to 1100°C to study the hydroxyl group changes on diatomite surface. A ceramic pot with about 500 mg diatomite was placed in a programmed temperature-controlled muffle oven for thermal treatment. The temperature rising speed was 5°C/min and the con-

stant time of certain thermal treatment temperature was 60 min. After thermal treatment, the sample was transferred into a weighing bottle and sealed quickly, and then were kept in the desiccator.

The ^1H MAS-NMR spectra were recorded on a Varian Unity pulse-300 spectrometer with Larmor frequency of 299.951 MHz at room temperature. High pure nitrogen gas was introduced as both driving gas and bearing gas to obtain 11 kHz (unless specially noted hereafter) magic-angle spinning speed. The detector was purged by nitrogen gas and the rotor was dried under vacuum condition to eliminate proton background peaks of water. The powdered sample was packed into an outer diameter 5 mm Si_3N_4 rotor. A 5 μs excitation pulse with 20° flip angle and 2s' recycle delay was used to accumulate ca. 600 scans. The chemical shift δ of proton was referenced to tetramethylsilane (TMS).

2 Results

Fig. 1 shows ^1H MAS NMR spectra of diatomite samples under different thermal treatment conditions. Spectrum 1 and spectrum 2 were taken respectively with spinning speed of 7 and 11 kHz after samples exposed in air with relative humidity of about 60% for 10 h. In both spectra there are a strong sharp peak at $\delta 4.9$ and a relatively weak peak at $\delta 7.1$ (fig. 1, spectra 1 and 2). The latter is weaker in spectrum 1 than in spectrum 2. In the spectrum of sample calcined at 200°C (fig. 1, spectrum 3),

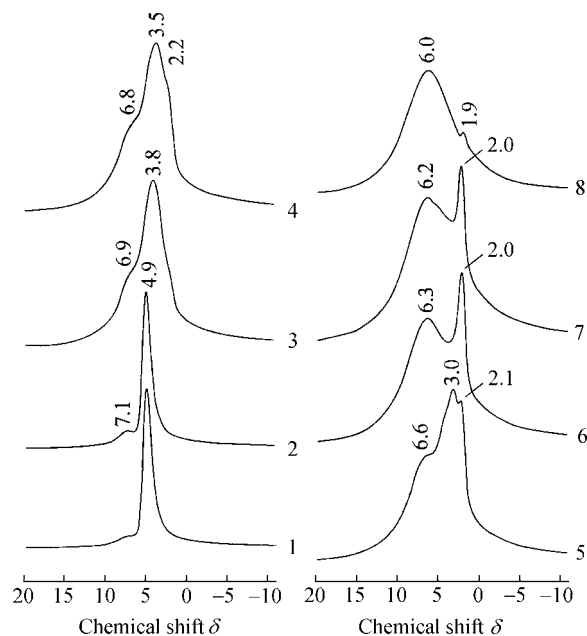


Fig. 1. ^1H MAS NMR spectra of hydroxyl groups on diatomite surface under thermal treatment conditions. 1, Sample exposed in air for 10 h, 7 kHz MAS speed; 2, same as in 1, 11 kHz MAS speed; 3, calcined at 200°C for 60 min; 4, calcined at 400°C for 60 min; 5, calcined at 650°C for 60 min; 6, calcined at 900°C for 60 min; 7, calcined at 1000°C for 60 min; 8, calcined at 1100°C for 60 min.

the $\delta 4.9$ peak shifts to $\delta 3.8$ and the $\delta 7.1$ peak shifts to $\delta 6.9$ accompanied by intensity increasing. When calcination temperature is up to 400°C (fig. 1, spectrum 4), the intensity of peak at $\delta 6.8$ continues to increase and the $\delta 3.8$ peak shifts to $\delta 3.5$. Besides, there appears a relatively weak shoulder peak at $\delta 2.2$. In the spectrum of sample calcined at 650°C (fig. 1, spectrum 5), the $\delta 6.8$ peak shifts to $\delta 6.6$ and becomes stronger slightly. Meanwhile, the $\delta 3.5$ peak shifts to $\delta 3.0$ accompanied by intensity decreasing. The $\delta 2.2$ peak shifts to lower shielding appreciably with intensity ascending obviously. As calcination temperature is up to 900°C , the $\delta 3.0$ peak disappears and the $\delta 6.6$ peak shifts to $\delta 6.3$ accompanied by intensity heightening (fig. 1, spectrum 6), and it presents as a very wide peak. The intensity of this peak keeps on increasing after 1000°C calcination (fig. 1, spectrum 7), but the intensity of $\delta 2.0$ peak is not changed basically. In the spectrum of sample calcined at 1100°C (fig. 1, spectrum 8), the $\delta 6.2$ peak shifts to $\delta 6.0$ with its intensity decreasing. The $\delta 2.0$ peak shifts to $\delta 1.9$, and still can be discerned though its intensity is weakened drastically.

3 Discussion

In terms of previous research on synthetical amorphous silica (Cab-O-Sil, silica gel, etc.), surface hydroxyl groups of silica have been classified according to their coordination (single and geminal silanols were bonded to a $^3\text{Q}(\text{OH})$ or $^2\text{Q}(\text{OH})$ silicon, respectively) and whether they are hydrogen-bonded or not (isolated and H-bonded hydroxyl groups). And the H-bonded hydroxyl groups can be further divided by the strength of hydrogen bond^[10–15]. Water adsorbed on the surface consists of pore water that resulted from capillarity effect and water that bonded to surface hydroxyl groups with hydrogen bond.

Although the proton chemical shifts of those hydroxyl groups vary with species of silica, they show some rules as a whole. The proton chemical shift δ of isolated hydroxyl groups is sharp and is located at ca. 2.0 generally. Because of the formation of hydrogen bond, the proton chemical shift of hydrogen-bonded hydroxyl groups moves to lower shielding that ranges from $\delta 3$ to $\delta 8$ relatively to that of isolated silanols, and presents as a wide peak. The geminal hydroxyl groups are very limited in quantity and prefer to form hydrogen bonds with each other, thus in the spectra of ^1H MAS NMR their proton chemical shift is difficult to be distinguished from that of hydrogen-bonded hydroxyl groups. The ^1H - ^{29}Si CP/MAS NMR, however, can distinguish geminal hydroxyl groups^[16]. The position of proton chemical shift δ of pore water is at about 5.0 with settled relatively. The proton chemical shift of water hydrogen-bonded to surface hydroxyl groups is within the range from $\delta 3.0$ to $\delta 3.5$.

The sharp peak at $\delta 4.9$ is assigned to water adsorbed to surface (fig. 1, spectrum 2), which consists of both H-bonded water and pore water, and the latter is the pri-

NOTES

mary component. Nevertheless, there is only a single peak in the corresponding spectrum because there occurs the rapid proton exchange between protons of the two water species^[15]. It is likely that the sample has high water content and then the quick and random movements of water molecules average the ^1H - ^1H dipolar interactions to some extent and make the peak sharp. In accordance with previous research on amorphous silica^[13,15], the weak wide peak at $\delta 7.1$ was attributed to H-bonded hydroxyl groups. Between H-bonded hydroxyl groups there exist intense dipolar interactions that are hard to be completely eliminated by MAS. Furthermore, these H-bonded hydroxyl groups are various: they include outer surface hydroxyl groups, inner surface hydroxyl groups and interparticle ones, etc. As a result, the peak is wide and its position varies with the species of silica in a relatively large scale ($\delta 3.0$ — 8.0). So far, the fine ^1H MAS NMR spectra of H-bonded hydroxyl groups are still difficult to be obtained. Our MAS experimental results (fig. 1, spectra 1 and 2) show that the intensity of $\delta 7.1$ wide peak with 11 kHz spinning speed is stronger than that with 7 kHz spinning speed evidently. Those results suggest that high-speed magic-angle spinning may be a useful way to eliminate the line-broadening effect resulting from ^1H - ^1H dipolar interactions between the protons of H-bonded hydroxyl groups. There are no peaks of isolated hydroxyl groups at ca. $\delta 2.0$ (fig. 1, spectrum 2), which indicates that isolated hydroxyl groups are hydrogen-bonded to water molecules basically at that time. In this aspect, diatomite is analogous to silica gel but not to fumed silica Cab-O-Sil, on whose surface there exist "true" isolated hydroxyl groups inaccessible to water^[10].

After 200°C calcination, the $\delta 4.9$ sharp peak moves to $\delta 3.8$ and becomes wider. The result indicates that most of pore water is desorbed at 200°C and it is consistent with the results of wide-line NMR and thermal analysis^[17]. The $\delta 3.8$ chemical shift results from the proton exchange between the hydrogen-bonded water whose proton chemical shift is at 3.0 — 3.5 and the small quantity of remaining pore water whose proton chemical shift is at ca. 5.0 . When the treatment temperature goes up, adsorbed water is desorbed continuously and this peak gradually shifts to $\delta 3.0$, which is the proton chemical shift position of H-bonded water (fig. 1, spectra 3—5). After 900°C calcination, it disappears, indicating that adsorbed water was desorbed exhaustively and the critical temperature of dehydration is within the range from 650°C to 900°C .

In the spectrum of sample calcined at 400°C , there is a distinct shoulder peak at $\delta 2.2$, actually it appeared as the sample was calcined at 200°C , but at that time the peak is so weak that it is almost invisible. The peak can be assigned to isolated hydroxyl groups. After 200°C calcination, a small quantity of H-bonded water is desorbed and as a result this peak emerges. Accompanied by H-bonded water desorbed continuously, the amount of

isolated hydroxyl groups increase and its peak intensity enhances gradually. Because the dipolar interactions between protons of isolated hydroxyl groups are relatively weak, they are prone to be averaged by magic-angle spinning and therefore the peak is sharp. When the temperature is up to 900°C , the intensity of this peak reaches its maximum. That identifies with the thorough dehydration of H-bonded water. The peak intensity gets unchanged as the temperature rises to 1000°C but decreases drastically after 1100°C . This indicates that isolated hydroxyl groups are condensed and dehydrated on large scale.

Accompanied by thermal treatment temperature rising from 200°C to 1000°C , the $\delta 7.1$ wide peak that was assigned to protons of hydrogen-bonded hydroxyl groups moves to $\delta 6.2$ and its intensity increases gradually (fig. 1, spectra 3—7). The shift of peak reflects the property difference of different-strength H-bonded hydroxyl groups under thermal treatment conditions. Analogous to silica gel and fumed silica studied previously, the proton chemical shift of hydrogen-bonded hydroxyl groups of diatomite varies with the strength of hydrogen bond, the stronger the hydrogen bond is, the more intense the proton chemical shift moves to lower shielding^[13]. Under thermal treatment conditions, strongly H-bonded hydroxyl groups are easier to condense than the weakly H-bonded ones. By this reason, the $\delta 7.1$ wide peak moving to higher shielding indicates that the condensation of strongly H-bonded hydroxyl groups takes place first at about 200°C . And the peak intensity of H-bonded hydroxyl groups gets more and more intense along with dehydration of them. Furthermore, some originally non-H-bonded hydroxyl groups bond to each other after they were desorbed the hydrogen-bonded water. As a result, the content of H-bonded hydroxyl groups ascends and the intensity of peak becomes stronger. After 1000°C calcination, the $\delta 6.3$ peak just slightly shifts to $\delta 6.2$, that indicates condensation of strongly hydrogen-bonded hydroxyl groups finished by and large. However, the peak of weakly hydrogen-bonded hydroxyl groups becomes more intense slightly. It shows that their quantities continue to rise and most of them are not condensed. As the temperature reaches 1100°C , the $\delta 6.2$ peak moves to $\delta 6.0$ with intensity descending (fig. 1, spectrum 8). It may be the result of condensation of considerable but not all weakly hydrogen-bonded hydroxyl groups. As for silica with micropores (that is to say, pores with a diameter ranging from several to tens nanometer) structure, Bogdan^[14] considered that the H-bonded hydroxyl groups that exist on the inner wall of micropores arranged closer and hence preferred to form H-bonded hydroxyl groups. Generally, the condensation temperatures of them are relatively high and thus these H-bonded hydroxyl groups were attributed to weakly hydrogen-bonded hydroxyl groups. Because the sample studied in this work bear micropores with a diameter ranging from 10 to 20 nm, it can be deduced that most of the remaining

weakly hydrogen-bonded hydroxyl groups exist in these micropores.

Moreover, it is necessary to note that the proton peak of structural silanols of kaolinite composition does not appear in the ^1H MAS NMR spectra. It may be because the content of kaolinite is so low that its proton peak is hard to be discerned in the spectra.

4 Conclusions

The results of ^1H MAS NMR research show that proton chemical shifts of isolated hydroxyl groups, hydrogen-bonded hydroxyl groups and pore water, hydrogen-bonded water are at ca. 2.0, 6.0—7.1, 4.9 and 3.0—3.5 respectively. Along with thermal treatment temperature rising, pore water and hydrogen-bonded water are described successively, as a result the intensities of peaks attributed to protons of isolated hydroxyl groups and H-bonded hydroxyl groups increase and reach their maximum at 1000 °C. After 1100 °C calculation, the strongly hydrogen-bonded hydroxyl groups are condensed and dehydrated thoroughly and so are most of isolated hydroxyl groups, but weakly H-bonded hydroxyl groups that exist in micropores are not condensed completely under that condition.

Acknowledgements This work was supported by the Guangdong Provincial Natural Science Foundation (Grant No. 980748), the Foundation of the State Key Laboratory for Physical Chemistry of Solid Surfaces in Xiamen University (Grant No. 9911) and the President Foundation of Guangzhou Institute of Geochemistry, the Chinese Academy of Sciences.

References

1. Yuan, P., Wu, D. Q., Present situation in applications of diatomite in fields of some products with high additional value and related fundamental research, *Journal of Mineral and Petrology* (in Chinese), 2000, 20(1): 101.
2. Calacal, E. L., Whittemore, O. J., The sintering of diatomite, *American Ceramic Society Bulletin*, 1987(2): 1.
3. Wang, F. Y., Zhang H. F., Feng, H. et al., A mineralogical study of diatomite in Leizhou Peninsula, *Chinese Journal of Geochemistry*, 1995, 14(2): 140.
4. Feng, H., Zhang, H. F., Guo, J. G. et al., ^{29}Si MAS NMR spectroscopic study of diatomite, *Acta Mineralogica Sinica* (in Chinese), 1999, 19(2): 210.
5. Yang, Y. X., Wang, J. X., Yang, Z. et al., A study on the mechanism of the adsorption of urokinase on the local diatomite, *Acta Chimica Sinica* (in Chinese), 1994, 52: 670.
6. Chen, R. S., Yang, Y. X., Hou, Q. T., Progress of study on local diatomites and their new application, *Chemical Industry Times* (in Chinese), 1997, 11(5): 54.
7. Wang, X. Q., Gao, S., Yu, L. X. et al., Synthesis of porphyrin nanometer material by a new method, *Journal of Chinese Universities* (in Chinese), 1998, 19(6): 854.
8. Wu, D. Q., Diao, G. Y., Wei, J. F. et al., Surface function groups and surface reactions of minerals, *Geological Journal of China Universities* (in Chinese), 2000, 6(2): 225.
9. Yuan, P., Wu, D. Q., Ling, Z. Y. et al., Study on surface hydroxyl species on diatomite using drift spectroscopy, *Spectroscopy and Spectral Analysis* (in Chinese) (in press).
10. Morrow, B. A., Mcfarlan, A. J., Surface vibrational modes of hydroxyl groups on silica, *Journal of American Chemical Society*, 1992, 96: 1395.
11. Koretsky, C. W., Sverjensky, D. A., Salisbury, J. W. et al., Detection of surface hydroxyl species on quartz, γ -alumina, and feldspars using diffuse reflectance infrared spectroscopy, *Geochim. Cosmochim. Acta*, 1997, 61: 2193.
12. Bronnimann, C. E., Zeigler, R. C., Maciel, G. E., Proton NMR study of dehydration of the silica gel surface, *Journal of American Chemical Society*, 1988, 110(7): 2023.
13. Liu, C. C., Maciel, G. E., The fumed silica surface: a study by NMR, *Journal of American Chemical Society*, 1996, 118: 5103.
14. Bogdan, A., Kulmala, M., Gorbunov, B. et al., NMR study of phase transitions in pure water and binary $\text{H}_2\text{O}/\text{HNO}_3$ films adsorbed on surface of pyrogenic silica, *Journal of Colloid and Interface Science*, 1996, 177: 79.
15. Caillierie, J. B., Aimeur, M. R., Kortobi, Y. E., Water adsorption on pyrogenic silica followed by ^1H MAS NMR, *Journal of Colloid and Interface Science*, 1997, 194: 434.
16. Hamdan, H., Muhid, M., Endud, S. et al., ^{29}Si MAS NMR, XRD and FESEM studies of rice husk silica for the synthesis of zeolites, *Journal of Non-crystalline Solids*, 1997, 211: 126.
17. Li, X. A., Feng, H., Zhang H. F. et al., NMR study of water in diatomite, *Acta Mineralogica Sinica* (in Chinese), 1999, 19(2): 154.

(Received December 1, 2000)