Chemical bond change of gibbsite and fumed silica mixture during mechanical activation

Liugang Chen [a], Guotian Ye [a,*], Dayan Xu [a], Lingling Zhu [a], Zhanling Lu [a], Lin Dong [a], Ying Liu [b]

[a] School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China
[b] Center of Analysis and Test, Wuhan University, Wuhan 430072, China

ABSTRACT

Chemical bond changes of gibbsite and fumed silica mixture during mechanical activation were investigated by X-ray powder diffraction (XRD), magic angle spinning nuclear magnetic resonance (MAS-NMR) and X-ray photoelectron spectroscopy (XPS). Crystallinity and intrinsic structural change of the mixture during high-energy milling were examined by XRD. Formation of new Al–O–Si chemical bonds was detected by the changes in Al coordination number of gibbsite in the mixture during milling, and the appearance of new resonance in ^{29}Si NMR spectrum of the ground mixture. The presence of Al–O units in silica framework was demonstrated by the increase of Al 2p binding energy and the decrease of Si 2p binding energy.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Mechanical activation not only decreases the particle size and increases the concentration of structural defects [1], but also introduces the possibility of forming new oxide compounds in the starting materials [2]. In some cases, new compounds may not be formed, but interatomic bonds can be ruptured and rebuilt during grinding [3–5]. However, there are few reports directly providing experimental results of bond-rebuilding of starting materials during mechanical activation.

The purpose of this work is to investigate the chemical bond changes of gibbsite and fumed silica mixture during mechanical grinding. Compared with the silica sources used in the reports [3–5], fumed silica is much finer (5–50 nm in particle size) than fused silica, has much lower density of the surface hydroxyls (1.5–2.5 OH/nm^2) than that of silica gel (4–5 OH/nm^2) [6], and has no OH groups inside its structure compared with silicic acid. So the SiO_2 source used in this work is different in intrinsic structure from those used in the reports [3–5]. In this work, XRD, NMR and XPS were used to monitor chemical bond evolution of the mixture during grinding.

2. Experimental

The starting materials of commercially available gibbsite ($Al(OH)_3$, ≥99% purity, $d_{50}=102.2$ μm) and fumed silica (SiO_2, ≥99.8% purity, specific surface area=380 m^2/g), in a molar proportion corresponding to mullite ($3Al_2O_3 \cdot 2SiO_2$), were mixed for 12 h in ethanol in a rotary mill, using zirconia balls of 5 mm diameter with a balls/powder weight ratio of 3/1. The slurry was dried at 80 °C, crushed and sieved. The mechanical activation was carried out for 40 h, with a vibratory Spex 8000M mixer/mill (Metuchen, NJ) in a stainless-steel cylindrical vial (φ 40 mm × 40 mm), containing one stainless-steel ball (φ 12.7 mm) and 5 g of the starting mixture. The grinding was suspended for 0.5 h after every 0.5 h of milling, to maintain the vial temperature below 50 °C. The vial was air tight during grinding and opened only after it was cooled to room temperature. The mixtures before and after grinding were calcined in air at 1200 °C for 3 h.

^{29}Si and ^{27}Al MAS-NMR spectra of the mixtures were recorded at 9.4 T on a Bruker AVANCE 400WB (AVANCE III 400WB, Bruker Biospin GmbH, Germany) at 79.5 MHz for ^{29}Si and 104.3 MHz for ^{27}Al. The ^{29}Si and ^{27}Al spectra were obtained with rotor spinning rates of 6 kHz and 12 kHz respectively. The ^{29}Si spectra were accumulated using a 90° pulse of 5 μs and a recycle delay of 5 s, and were referenced to kaolinite; the ^{27}Al spectra were accumulated using a 15° pulse of 0.5 μs with a recycle delay of 1 s, and were referenced to an aqueous solution of 1 M $Al(NO_3)_3$. ^{29}Si spectrum of the ground mixture was analyzed using the Jandel "Peakfit" software package until reproducible results were obtained with correlations of r^2 greater than 0.998. The XPS analysis of the mixtures was performed with Kratos XSAM800 spectrometer (Kratos XSAM800, Kratos, Britain), using Mg Kα radiation (1253.6 eV) as the exciting source operated at 12 kV and 16 mA. All the binding energies were referenced to the C 1s line at 284.8 eV. The phases and crystallinity of the mixtures after

* Corresponding author. Tel.: +86 371 6773 9225.
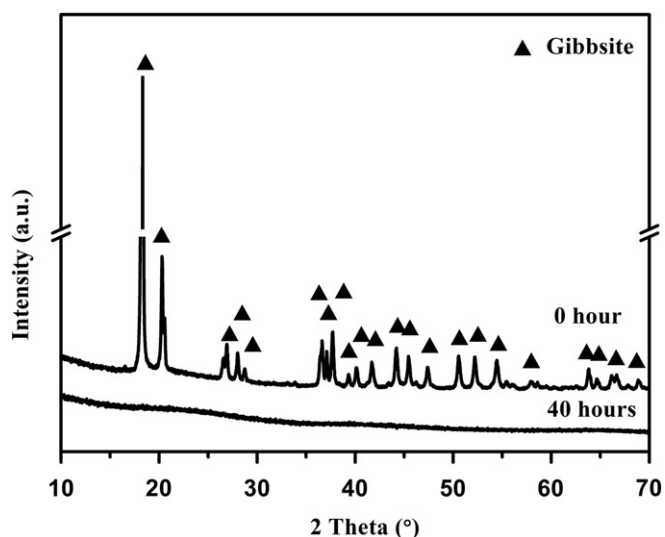 E-mail address: gtye@zzu.edu.cn (G. Ye).

Fig. 1. X-ray diffractometer patterns of the mixtures before and after milling ((▲) gibbsite, powder diffraction file no. 74-1775).

milling and calcination were examined with XRD (X' Pert Pro MPD, Philips, the Netherlands).

3. Results and discussion

Fig. 1 shows the effect of high-energy milling on the crystallinity of the mixtures. It is seen from the figure that all peaks in the starting mixture were related to gibbsite, and no peaks corresponding to SiO_2 were present because fumed silica used is totally amorphous. Milling the mixture for 40 h led to the complete disappearance of all peaks belonging to gibbsite, implying that the crystal structure of gibbsite was ruptured [7], and consequently Al environment in gibbsite might be changed during milling.

The ^{27}Al and ^{29}Si NMR spectra of the mixtures before and after grinding are shown in Fig. 2. The ^{27}Al spectrum of gibbsite in the starting mixture showed a single asymmetric octahedral resonance at about 7.72 ppm with a shoulder at about 0 ppm (Fig. 2a) [8]. Grinding the mixture for 40 h produced a new resonance at 62.07 ppm corresponding to tetrahedral Al–O units
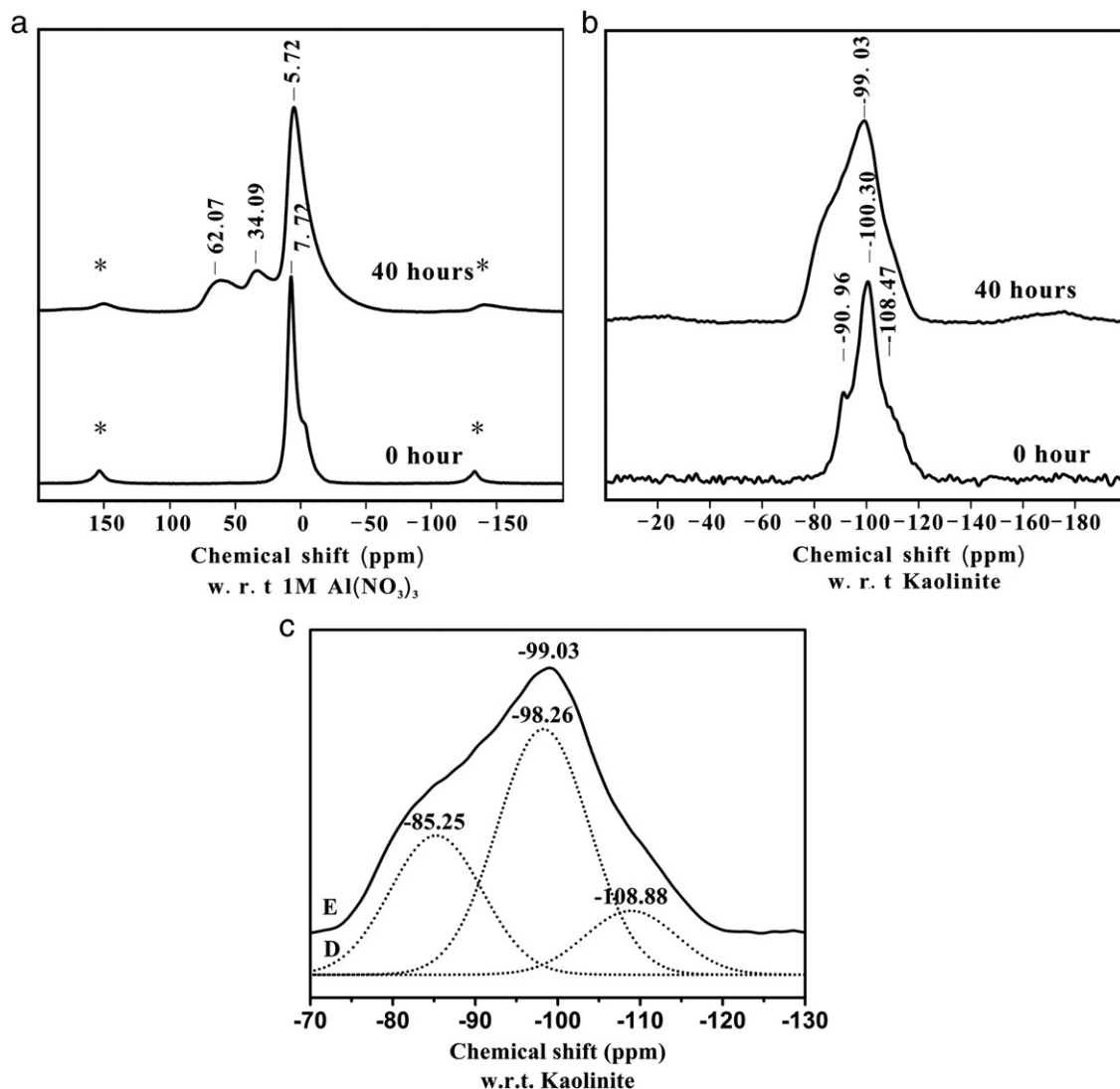

Fig. 2. ^{27}Al and ^{29}Si MAS-NMR spectra of ground and unground mixtures as indicated; (a) ^{27}Al spectra and (b) ^{29}Si spectra (the symbol * in the ^{27}Al spectra represents spinning side band); (c) deconvoluted ^{29}Si spectra of the ground mixture (E: experimental spectrum, D: deconvoluted spectra).

[3,4], and a new resonance at 34.09 ppm (Fig. 2a) due to Al sites with five-fold coordination ("pentahedral" Al sites) [4]. The changed Al coordination number after mechanical grinding means the rupture and rebuilding of Al–O interatomic bonds. The new resonance at 34.09 ppm could also result from distorted four-coordinated Al sites associated with tricluster units [3–5], which may demonstrate formation of Al–O–Si new linkages between gibbsite and fumed silica.

The resonances at −90.96 ppm, −100.30 ppm and −108.47 ppm in ^{29}Si NMR spectrum of the starting mixture (Fig. 2b) were assigned to geminal hydroxyl silicon, single hydroxyl silicon and the Si–O tetrahedral unit in fumed silica respectively [9]. The new resonance at −85.25 ppm in the ground mixture (Fig. 2c) reflected the presence of Si–O units associated with three or four other Al–O units, revealing the formation of new Al–O–Si chemical bonds [3–5]. And the resonance at −98.26 ppm, which was shifted from −100.30 ppm in the starting mixture, might result from Si–O units bonded to one or two other Al–O units [3,4], also revealing the formation of new Al–O–Si linkages.

Fig. 3 demonstrates the changes in the Al 2p and Si 2p binding energy (BE) of the mixtures during high-energy milling. Both the Al 2p and Si 2p XPS spectra of the starting mixture (Fig. 3a) were typical of Al–OH bonds (73.7 eV) [10] of gibbsite and silica units (103.7 eV) [11] of fumed silica respectively. Grinding the mixture for 40 h increased BE of Al 2p from 73.7 eV to 74.4 eV, at the expense of Si 2p BE (decrease from 103.7 eV to 102.3 eV) (Fig. 3b), indicating the formation of Al–O–Si bonds during grinding, because Al is more electropositive than Si [12] and consequently

the presence of Al–O units in silica network would decrease BE of Si 2p and increase that of Al 2p. In fact, the Al 2p BE of 74.4 eV and Si 2p BE of 102.3 eV of the ground mixture were very close to the binding energies for aluminosilicates [13], further confirming the formation of Al–O–Si linkages.
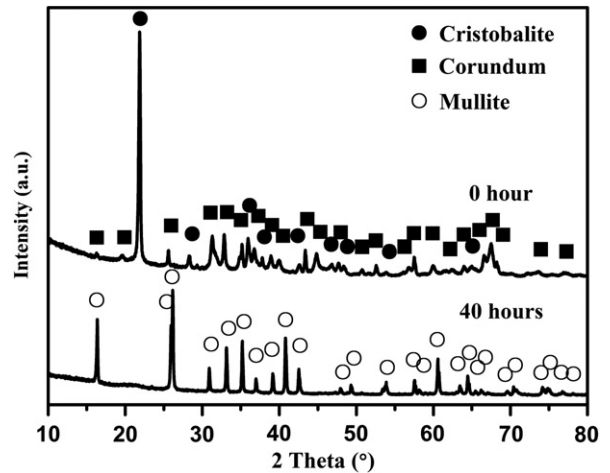
Fig. 4. X-ray diffractometer patterns of ground and unground mixtures fired at 1200 °C for 3 h: ((■) corundum, powder diffraction file no. 86-1410; (●) cristobalite, powder diffraction file no. 77-1317; (○) mullite, powder diffraction file no. 79-1454).
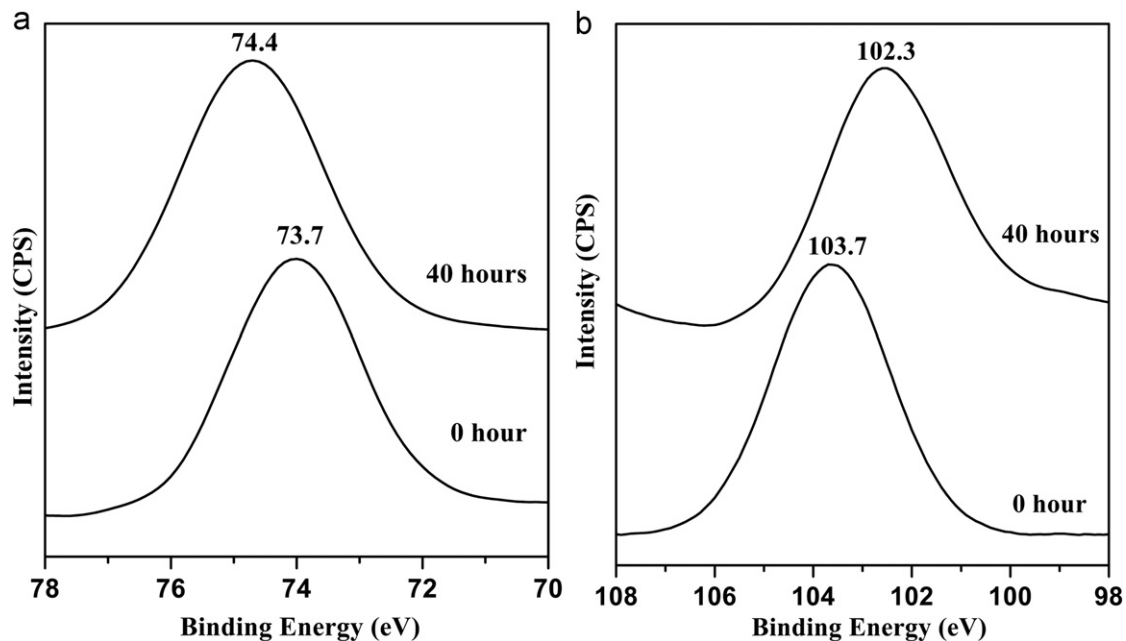
Fig. 3. Al 2p (a) and Si 2p (b) XPS spectra of ground and unground mixtures.

Table 1
Gibbs free energy change of mullite formation at different temperatures.

Temperature (K)	$\Delta G^{\ominus}$ (kJ mo^{-1})[b]				$\Delta G_R^{\ominus}$ (kJ mol^{-1})
	Al(OH)$_3$ (gibbsite)	SiO$_2$ (cristobalite[a])	3Al$_2$O$_3$·2SiO$_2$ (mullite)	H$_2$O	
298	−1305.69	−921.29 (α)	−6901.17	−240.12 (liquid) [16]	614.47
400	−1314.51	−926.41 (α)	−6934.64	−317.84 (gas)	−55.32

[a] The $\Delta G^{\ominus}$ of cristobalite was utilized as $\Delta G^{\ominus}$ of the fumed silica which is not available [14].
[b] The other data of $\Delta G^{\ominus}$ are from Ref. [15].

It is seen from Table 1 that the reaction of $6Al(OH)_{3(s)} + 2SiO_{2(s)} \rightarrow 3Al_2O_3 \cdot 2SiO_{2(s)} + 9H_2O_{(l/g)}$ cannot happen at the room temperature because the Gibbs free energy change ($\Delta G_R^{\ominus}$) of mullite formation is positive at 25 °C (298 K). However, it was estimated that the pressure at the impact sites caused by milling media could reach 3.30–6.18 GPa [17] and the local transient temperature could increase 200–300 °C [18]. As shown in Table 1, $\Delta G_R^{\ominus}$ of mullite formation is negative at and above 127 °C (400 K). Therefore, mullite formation could happen during high energy ball milling as the local temperature of impact sites could be higher than 127 °C [17], revealing that this reacting system is thermodynamically favorable for bond formation during milling.

The XRD patterns of the starting and ground mixtures heated for 3 h at 1200 °C are shown in Fig. 4. After the heat-treatment, the major phases in the starting mixture were corundum and cristobalite, whereas the well-crystallized mullite was presented in the ground mixture, signifying that formation of mullite during the heat treatment was facilitated by the new Al–O–Si bonds generated during grinding, besides the decreased particle/crystal sizes.

4. Conclusions

When the mixture was ground for 40 h, the mixture became totally amorphous, revealing intrinsic structural rupture of gibbsite. Grinding the mixture for 40 h changed the octahedral Al–O units (7.72 ppm) of gibbsite in the starting mixture to tetrahedral (62.07 ppm) and "pentahedral" (34.09 ppm) Al sites, indicating that the coordination number of Al has partially turned from 6 in the starting mixture into 4 and 5 in the ground one. The new resonance at -85.25 ppm in ^{29}Si NMR spectrum of the 40 h ground mixture reflected the presence of the bond of Si with three or four other Al–O units. The increased Al 2p binding energy of 74.4 eV and decreased Si 2p binding energy of 102.3 eV of the 40 h ground mixture were caused by the insert of Al–O units into silica network during grinding, as Al is more electropositive than Si. The changes in Al coordination number, the formation of Si bonded with three or four Al–O units and the presence of the Al–O units in silica framework in the 40 h ground mixture all demonstrate that new Al–O–Si linkages formed during high-energy grinding. As a result, mullite formation during heat treatment was facilitated partly by Al–O–Si linkages created during mechanical activation.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2012.06.103.

References

[1] Ye G, Troczynski T. Mechanochemical activation-assisted low-temperature synthesis of CaZrO₃. J Am Ceram Soc 2007;90:287–90.
[2] Xue J, Wang J, Wan D. Nanosized barium titanate powder by mechanical activation. J Am Ceram Soc 2000;83:232–4.
[3] Temuujin J, Jadambaa TS, Okada K, MacKenzie KJD. Mechanochemical preparation of aluminosilicate precursors from gibbsite–silicic acid mixtures. Mater Lett 1998;36:48–51.
[4] Temuujin J, Okada K, MacKenzie KJD. Characterization of aluminosilicate (mullite) precursors prepared by a mechanochemical process. J Mater Res 1998;13:2184–9.
[5] Temuujin J, Okada K, MacKenzie KJD. Formation of mullite from mechanochemically activated oxides and hydroxides. J Eur Ceram Soc 1998;18:831–5.
[6] Borysenko MV, Gun'ko VM, Dyachenko AG, Sulim IY, Leboda R, Skubiszewska-Zieba J, et al. CVD-zirconia on fumed silica and silica gel. Appl Surf Sci 2005;242:1–12.
[7] MacKenzie KJD, Temuujin J, Okada K. Thermal decomposition of mechanically activated gibbsite. Thermochim Acta 1999;327:103–8.
[8] Vyalikh A, Zesewitz K, Scheler U. Hydrogen bonds and local symmetry in the crystal structure of gibbsite. Magn Reson Chem 2010;48:877–81.
[9] David KM. Differentiating and characterizing geminal silanols in silicas by ^{29}Si NMR spectroscopy. J Colloid Interface Sci 2010;352:163–70.
[10] Kloprogge JT, Duong LV, Wood BJ, Frost RL. XPS study of the major minerals in bauxite: gibbsite, bayerite and (pseudo-)boehmite. J Colloid Interface Sci 2006;296:572–6.
[11] Che J, Xiao Y, Wang X, Pan A, Yuan W, Wu X. Grafting polymerization of polyacetal onto nano-silica surface via bridging isocyanate. Surf Coat Technol 2007;201:4578–84.
[12] Herreros B, He H, Barr TL, Klinowski J. ESCA studies of framework silicates with the sodalite structure: 1. Comparison of purely siliceous sodalite and aluminosilicate sodalite. J Phys Chem 1994;98:1302–5.
[13] Anderson P, Swartz Jr W. X-ray photoelectron spectroscopy of some aluminosilicates. Inorg Chem 1974;13:2293–4.
[14] Turkdogan ET. Physical chemistry of high temperature technology. New York: Academic Press; 1980.
[15] Liang YJ, Che YC. Thermodynamic data handbook of inorganic substances. Shengyang: Northeastern University Press; 1994.
[16] Chase MW. Journal of Physical and Chemistry Reference Data, 4th ed., NIST-JANAF Thermochemical Tables, Monograph 9, 1998.
[17] Shen TD, Koch CC, McCormick TL, Nemanich RJ, Huang JY, Huang JG. The structure and property characteristics of amorphous/nanocrystalline silicon produced by ball milling. J Mater Res 1995;10:139–48.
[18] Davis RM, McDermott B, Koch CC. Mechanical alloying of brittle materials. Metall Mater Trans A 1988;19:2867–74.