Chemical Structure of Si–O in Silica Fume from Ferrosilicon Production and Its Reactivity in Alkali Dissolution

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As an environmentally hazardous waste, silica fume was considered as a potential alternative for cement and SiO₂ production. The structure of Si–O was highly relevant to the reactivity of Si conversion for efficient utilization. In this study, the characteristic and chemical structure of Si–O in silica fume were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). Deconvolution of XPS and FTIR spectra into elementary profiles was carried out to analyze the structural components. As a result, the valence state, bonding structure and elementary unit in the Si–O network of silica fume were determined. Then, the reactivity silica fume with alkali solution was studied involving the effects of NaOH concentration and temperature. The staged kinetics behavior was associated with the structure of Si–O bonds, and the activation energies were determined. The results thus provided fundamental information for the utilization of silica fume for SiO₂ production and geopolymer.

KEY WORDS: silica fume; ferrosilicon; industrial solid waste; Si–O structure; alkali dissolution; staged kinetics.

1. Introduction

With the rapid development of the steelmaking industry, there is a great demand for ferrosilicon used as deoxidizing agent.¹⁾ Ferrosilicon is produced by carbothermal reduction of silica and iron oxide with carbon in an electric arc furnace. During the production of ferrosilicon, a large amount of silica fume was generated as a type of dust waste.²⁾ It was estimated that 2 million tons/year of silica fume was generated in China.³⁾ Silica fume is a highly effective pozzolanic material due to its large specific surface area and high amorphous silica content.^{4,5)} It has been used in geo-materials by combining with fly ash of coal combustion as a partial substitute of Portland cement, showing several advantages in terms of mechanical performance and durability.^{6–8)} Silica fume of sub-micro size is an active component which can react with Ca(OH)₂ to produce the calcium silicate hydrate C–S–H (gel) phase. In the alkali-activated reaction, silicate reactive materials are rapidly dissolved into alkaline solution to form free SiO₄ tetrahedral units. During the polycondensation reaction, the tetrahedral units are linked in an alternate manner to form amorphous geopolymers, and OH[−] in Ca(OH)₂ is released to afford alkali for the dissolution of –Si–O–Si– structure.^{9–11)}

The addition of silica fume can modify the microstructure of hydrated pastes due to the formation of denser and lower-porosity, compact C–S–H.^{11,12)} Silica fume also can be recycled as Si resource for Na₂SO₃ and SiO₂ material production.^{13–15)} Ultrafine hydrophobic precipitated silica (nano-silica) was obtained from silica fume by carbonation process and surface modification.^{13,14)} The Si component in silica fume was leached by NaOH and transferred to Na₂SiO₃. Then Na₂SiO₃ solution was carbonated by CO₂ to produce nano-silica.

About 80% of Si was recycled, and the purity of SiO₂ produced was 95%.¹⁴⁾ High silica microporous zeolite was synthesized by a hydrothermal method using silica fume as Si source, which exhibited high purity structure and a large surface area.¹⁵⁾ During the hydrothermal reaction, silica fume and Al source (Al₂(SO₄)₃·18H₂O) were gradually dissolved in NaOH to form monovalent monomers with negative charge (Si(OH)₃O[−], Al(OH)₄[−]).¹⁵⁾

As a key factor for efficient utilization, the reactivity of Si component depended on the physicochemical structure of Si–O network. A better understanding of the structure and its effect on the reactivity behavior was beneficial to improve the utilization of silica fume. Generally, silica fume was non-crystalline material with disordered network structure based on silicon-oxygen tetrahedra [SiO₄].^{2,3,5)} However, the microstructure of Si–O network was still not analyzed in detail, which was highly relevant to the hydra-

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tion and alkali dissolution reactivity.

Therefore, in this study the chemical microstructure, especially Si–O bonds and bridging oxygen structure, of Si–O network in silica fume was characterized by XPS and FTIR. In order to estimate the type and the contribution of structural components, the spectra of Si and O were deconvoluted into elementary profiles. Then, the alkali dissolution reactivity of silica fume was examined using an isothermal kinetics method, and the kinetics parameters were determined based on the experimental data.

2. Experimental Section

2.1. Materials

The silica fume (SF) samples used in this study were provided by Ordos Metallurgy Group Corporation in Inner Mongolia, China. The samples were collected from a bag-type dust separator installed in an electric arc furnace gas cleaning system. The phase and chemical composition of silica fume were listed in **Fig. S1** and **Table S1**, respectively. Silica fume was amorphous, exhibiting only a very broad scattering peak. The main chemical component (in oxide form) was SiO₂ (96.97 wt%). The granulometric distribution analysis of silica fume was shown in **Fig. S2**. The mean particle size was about 4.5 μm. The BET surface area was about 23 m²/g. NaOH with analytical grade (>97%) was provided by Beijing Chemical Reagents Company.

2.2. Characterization

2.2.1. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS, AXISULTRA-DLD, Japan) was performed to determine the chemical states of Si and O present in silica fume. The Al Kα (1 486.6 eV) line was used for the X-ray source. The peak positions for binding energy of samples were corrected by considering the charging effect. A binding energy of 284.7 eV was assumed for the C 1 s peak maximum in correcting for surface charging. PeakFit v4.12 software (SeaSolve Software Inc.) was used for fitting and deconvolution of Si 2p and O 1 s spectrum.

2.2.2. FTIR Spectroscopy

Fourier transform infrared spectrometer (FTIR, NICOIET-470, USA) was used to determine the chemical bonding of Si–Si and Si–O. The FTIR spectra of the silica fume sample were recorded over the range of 4 000–400 cm^{−1} using the KBr pellet technique. The spectral resolution was 1 cm^{−1}. Each measurement was taken at three different spots to eliminate the heterogeneity of the sample. ORIGIN 8.5 software was used for fitting and deconvolution of FTIR spectrum.

2.3. Alkali Dissolution Reactivity and Kinetic

The silica fume samples were dissolved by NaOH solution (5–20 wt%) at a constant temperature (50–80°C) in a 250 mL Jacketed PMMA reactor. The solid-liquid ratio and the stirring speed were 1:10 (g/mL) and 300 rpm, respectively. Then the samples of the solution were taken out by an adjustable volume pipette at a certain time interval, and each sampling volume was 0.25 mL (solution volume change was

ignored). The sampling solution was transferred into a 25 mL volumetric flask and was diluted to 25 mL by deionized water. After the centrifugal separation, the concentration of Si of the upper clear liquid was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer OPTIMA 3000, USA). Finally, the conversion degree of Si (η) was calculated using the equation as followed:

$$\eta = \frac{C_{\text{Si}} \cdot V_F \cdot \frac{V_R}{V_S}}{m_0 \omega} \times 100\%$$

where C_{Si} is the concentration of Si in the volumetric flask (g/L). V_F , V_R , V_S are the volume of the volumetric flask, the Jacketed PMMA reactor and the sampling solution (L), respectively. m_0 is the mass of silica fume (g). ω is the mass fraction of Si in the silica fume (wt%).

3. Results and Discussion

3.1. Chemical Structure of Si–O in Silica Fume

3.1.1. XPS Spectra

The XPS analysis was used to identify the different states of Si and O on the surface of silica fume. The wide-scan spectrum of XPS analysis is shown in **Fig. S3**. The Si 2p spectrum ranging from 94 to 108 eV is shown in **Fig. 1**. Asymmetry and broadening observed in Si 2p spectra were because of the existence of different Si environments. XPS curve was subjected to peak fitting using PeakFit v4.12 software. The Si 2p spectrum was deconvoluted into four elementary components (Gaussian type) at 103.8, 102.7, 101.4, and 100.5 eV (**Table 1**). It is well known that some interme-

Fig. 1. XPS spectra of Si 2p for silica fume. (Online version in color.)

Table 1. Fitting parameters obtained from XPS spectra of Si 2p for silica fume.

Binding energy (eV)	Structure	FWHM (eV)	Peak area	Contribution (%)
103.8	Si–O ₄ (Si ⁴⁺)	2.0	5 811	27.4
102.7	Si–Si–O ₃ (Si ³⁺)	1.9	5 113	24.1
101.4	Si ₂ –Si–O ₂ (Si ²⁺)	1.9	4 506	21.3
100.5	Si ₃ –Si–O (Si ¹⁺)	2.1	5 753	27.2

diolate silicon oxide states exist at the SiO_2/Si interface region during Si oxidation. These intermediate silicon oxide states have the same tetrahedral structure as Si-O_4 (Si^{4+} oxidation state, ~ 103.5 eV). However, in amorphous silica oxide, O atom can be replaced partly by Si to form the tetrahedra: Si-Si-O_3 (Si^{3+} oxidation state), $\text{Si}_2\text{-Si-O}_2$ (Si^{2+} oxidation state) and $\text{Si}_3\text{-Si-O}$ (Si^{1+} oxidation state) with binding energies of 100.7, 101.5 and 102.5 eV, respectively.^{16–18)} As the oxygen content of silicon oxide increased, the binding energy increased from 99.3 to 103.7 eV. Therefore, in this study the binding energies at 103.8, 102.7, 101.4, and 100.5 eV were assigned to Si-O_4 , Si-Si-O_3 , $\text{Si}_2\text{-Si-O}_2$, and $\text{Si}_3\text{-Si-O}$, respectively. The proportion of Si in different states was calculated by integrating the peak area. It was found that the contents of Si^{+4} , Si^{+3} , Si^{+2} , and Si^{+1} were 27.4%, 24.1%, 21.3%, and 27.2%, respectively. Silica fume was generated by re-oxidation of Si and SiO vapor during Si production.^{2,3)} Because the vapor was rapidly cooled and condensed, the solidified oxide layer inhibited further oxidation of Si and SiO by O_2 . Some lower valence Si (Si and SiO) still existed in silica fume. Therefore, silica fume was the mixture of silica oxides with different oxidation states.

As shown in **Fig. 2**, the O 1s spectra from 527 to 539 eV were asymmetrical and broadening, suggesting that different chemical environments for oxygen existed in silica fume. The O 1s spectrum was deconvoluted into three elementary components (Gaussian type) at 530.7, 532.9 and 534.8 eV (**Table 2**). In the SiO_2 structure, the bridging oxygen connected two Si atoms to form a more stable state Si-O-Si and thus had a lower binding energy than non-bridging oxygen. The energy difference between bridging and non-bridging oxygen was about 1.3 eV.¹⁹⁾ Therefore, the binding energies

Fig. 2. XPS spectra of O 1s for silica fume. (Online version in color.)

Table 2. Fitting parameters obtained from XPS spectra of O 1s for silica fume.

Binding energy (eV)	Structure	FWHM (eV)	Peak area	Contribution (%)
534.8	Si-O-O-Si Peroxy bridge	2.5	54 053	24.8
532.9	Si-O Non-bridge oxygen	1.9	38 406	17.6
530.7	Si-O-Si Bridge oxygen	2.4	125 349	57.6

at 530.7 and 532.9 eV were assigned to the bridging oxygen and the non-bridging oxygen, respectively. The higher binding energy component at 534.8 eV may be due to structural defects similar to the peroxy bridge Si-O-O-Si .¹⁹⁾ The proportions of different states of oxygen were calculated by integrating the peak area, as shown in **Table 2**. It was found that the major elementary unit was the bridging oxygen, indicating high structural symmetry and bonding degree in the Si-O network. The unsaturated Si-O bonds (non-bridging oxygen) were considered as one of the causes for amorphous SiO_2 .²⁰⁾ However, the proportion of this structure was relatively small (17.6%). Therefore, it was inferred that the non-crystallizing of silica fume was attributed to the atom arrangement in the Si-O network.

3.1.2. FTIR Spectra

As shown in **Fig. 3(a)**, the bands at 486 cm^{-1} and 805 cm^{-1} were assigned to the bending vibration of O-Si-O and symmetric stretching of Si-O-Si , respectively. The strong band at $950\text{--}1360\text{ cm}^{-1}$ belonged to the asymmetric stretching modes of Si-O bonds, which was deconvoluted into five elementary bands (Lorentzian type) as shown in **Fig. 3(b)** and **Table 3**. The SiO_2 and silicate structure were composed of a series of elementary units of $[\text{SiO}_4]$ tetrahedron, Q_n , where n is number of bridge oxygen around

Fig. 3. FTIR spectra of silica fume: (a) $400\text{--}4000\text{ cm}^{-1}$ region; (b) Deconvolution of $900\text{--}1400\text{ cm}^{-1}$ region. (Online version in color.)

Table 3. Fitting parameters obtained from FTIR spectra (900–1 400 cm⁻¹) of silica fume.

Band position (cm ⁻¹)	Structure	Si–O–Si angle (°)	FWHM (cm ⁻¹)	Peak area	Contribution (%)
1 063.3	Si ₂ O ₆ ⁶⁻ (Q ₂)	134.3	74.8	1 640.6	20.9
1 129.0	Si ₂ O ₅ ⁴⁻ (Q ₃)	164.7	66.8	3 366.9	42.8
1 172.2	SiO ₂ (Q ₄)	115.8	54.1	1 172.7	14.9
1 206.5	Si–O–Si ring	125.8	47.8	975.0	12.4
1 238.4	Si–O–Si ring	136.9	44.8	711.4	9.0

[SiO₄].²⁰⁾ The elementary unit was formed by the polymerization of [SiO₄] tetrahedron. The FTIR vibrational modes of silica fume were associated with the structural configurations of Si–O bonds. As the polymerization of [SiO₄] tetrahedron increased, the number of bridge oxygen increased. The absorption bands at 1 063.3, 1 129.0 and 1 172.2 cm⁻¹ were associated to the asymmetric stretching modes of the Si–O bonds of the Q₂, Q₃ and Q₄ units, respectively.¹⁸⁾ These bands shifted to higher wavenumbers because of the variation of Si–O bond angles.^{21,22)} The proportions of the Q_n units were calculated by integrating the peak area. As shown in Table 3, the major elementary unit was Q₃, indicating a high degree of polymerization of [SiO₄]. Based on the distribution of Q₂, Q₃ and Q₄, the content of non-bridge oxygen was calculated to be 21.4%, which was in accord with the result of XPS.

The bands at >1 200 cm⁻¹ were assigned to the local vibration absorption of Si–O due to the impurity oxygen.^{21–23)} In this structure, O atoms (bridge oxygen) were inserted in the lattice of Si as a bridge to connect the neighboring Si atoms, leading to the formation of Si–O–Si interconnecting rings in the Si–O network. The Si–O–Si rings also included the peroxy bridge structure as mentioned in section 3.1.1. As the number of bridge oxygen increased, the bands of Si–O shifted to higher wavenumbers due to the stronger Si–O bonds in the Si–O–Si rings. According to the positions of the maximum of elementary components (*w*) in FTIR spectrum, the mean values of Si–O–Si bond angles (*θ*) can be calculated:^{21,22)}

When 1 010 cm⁻¹ < *w* < 1 140 cm⁻¹

$$w = (2\pi c)^{-1} \left[\frac{2}{m} \left(\alpha \sin^2 \frac{\theta}{2} + \beta \cos^2 \frac{\theta}{2} \right) \right]^{\frac{1}{2}} \dots\dots\dots (1)$$

When 1 140 cm⁻¹ < *w* < 1 300 cm⁻¹

$$w = (2\pi c)^{-1} \left[\frac{2}{m} \left(\alpha \sin^2 \frac{\theta}{2} + \beta \cos^2 \frac{\theta}{2} + \gamma \right) \right]^{\frac{1}{2}} \dots\dots\dots (2)$$

where *m* is the mass of oxygen atom (2.657 × 10⁻²⁶ kg); *α* and *β* are the central and non-central force constants (610 and 100 N/m, respectively²¹⁾); *γ* is a constant (181.82 N/m²²⁾); *c* is the velocity of light (2.997 × 10⁸ m/s). As listed in Table 3, the distribution of Si–O–Si angles in the structural units of silica fume was rather wide (115.8° < *θ* < 164.7°) due to mixing of the different types of elementary units. It indicated that the structural ordering of Si–O network decreased.^{21,22)} The Si–O–Si bond angle of the Q₄ unit was

Fig. 4. The effect of NaOH concentration on the conversion degree of Si (70°C). (Online version in color.)

115.8°, which was close to the theoretical value of 109.5°. Therefore, the Q₄ unit was the orderly [SiO₄] tetrahedron in SiO₂ crystalline structure. However, the proportion of this structure was relatively small (only 14.91%). As a result, the structure of silica fume was predominantly amorphous and disordered.

3.2. Alkali Dissolution Reactivity of Silica Fume

3.2.1. Effects of NaOH Concentration

The effect of NaOH concentration on the conversion degree of Si was investigated when the reaction temperature was 70°C. The conversion degree of Si increased with increasing the NaOH concentration (Fig. 4). When the NaOH concentration was 5 wt%, the conversion degree of Si was lower (only 50%). When the NaOH concentration was increased from 5 to 10 wt%, the conversion degree of Si increased notably up to about 70%. However, when the NaOH concentration was higher than 10 wt%, the conversion degree of Si was almost unchanged and reached about 70–75%. As the NaOH concentration increased, the activity of OH⁻ increased. The interaction between OH⁻ and amorphous SiO₂ was stronger, and thus it was easier for OH⁻ to be absorbed on the surface of SiO₂. As a result, the dissolution of amorphous SiO₂ was enhanced. However, when the NaOH concentration was higher than 10 wt%, the ionic strength (*I*) was increased significantly, and the activity coefficient (*γ*) was decreased.²⁴⁾ Thus, the increase of the OH⁻ activity was small. In addition, the viscosity of NaOH solution also increased, limiting the diffusion of OH⁻. Therefore, the conversion degree of Si was increased slowly.

3.2.2. Effects of Reaction Temperature

The effect of reaction temperature on the conversion degree of Si was investigated from 50 to 80°C. The NaOH concentration was 10 wt%. At the same reaction time, the conversion degree of Si increased with increasing the temperature especially at the early stage (less than 400 min). At the reaction time of 200 min, for example, the conversion degree of Si increased notably from about 46.3% at 50°C up to 74.4% at 70°C (Fig. 5). But when the temperature was >70°C, the conversion degree of Si increased only from

Fig. 5. The effect of reaction temperature on the conversion degree of Si (NaOH=10 wt%). (Online version in color.)

74.4% at 70°C to 76.6% at 80°C, and the increasing speed declined significantly. The results indicated that increasing temperature enhanced the dissolution of silica fume in NaOH solution. The rise in temperature of the leaching system increased the mobility of ions and thereby enhancing the interaction between ions of solid and liquid phase. Thus, when the temperature was up to 70°C, the conversion degree of Si increased notably because the reaction rate and diffusion was enhanced. At temperatures >70°C, the reagents had been almost fully activated, and thus the changes of reaction rate and the Si conversion degree were not remarkable.

3.2.3. Kinetics Models

In order to deduce the reaction mechanism and determine the kinetics parameters, the most probable kinetics model is evaluated corresponding to the kinetics data. It is usual to postulate a kinetics model and the rate-determining step for reaction based on the experimental observations. Therefore, this paper tried to present a kinetics model for the alkali dissolution of silica fume.

Kinetics analysis of thermally stimulated reactions is traditionally expected to produce an adequate kinetics description of the process in terms of the reaction model and of the Arrhenius parameters using a solid-solid kinetics equation:^{25,26)}

$$\frac{dX}{dt} = k(T)f(X) \quad \text{..... (3)}$$

where X is the conversion degree of reaction, t is the reaction time, T is the reaction temperature, $f(X)$ is the reaction model, $k(T)$ is the kinetics rate constant, which is given as:

$$k(T) = k_0 \exp\left(\frac{-E}{RT}\right) \quad \text{..... (4)}$$

By taking the logarithm and rearranging it, one can obtain:

$$\ln k(T) = \ln k_0 - \frac{E}{RT} \quad \text{..... (5)}$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), k_0 is the pre-exponential factor, E is the apparent activation energy. For reaction kinetics under isothermal conditions, Eq. (3)

can be analytically integrated to yield:

$$G(X) = \int_0^X \frac{dX}{f(X)} = k(T)t \quad \text{..... (6)}$$

where $G(X)$ is the integral form of the reaction model. By combining Eqs. (3)–(5), the kinetics rate constant [$k(T)$] can be obtained from the slope of linear regression of $G(X)$ and t at different temperatures using a reasonable kinetics model [$G(X)$]. Then By plotting $\ln k(T)$ versus the reciprocal of reaction temperature ($1/T$) according to Eq. (5), the apparent activation energy and pre-exponential factor can be obtained by the slope and the intercept of linear regression, respectively.

3.2.4. Model Evaluation

In order to evaluate the kinetics model and the rate-controlled mechanism, the kinetics data (X versus t) were needed. Thus, the effect of the reaction time on the conversion degree of Si was examined from 50°C to 80°C (NaOH = 10 wt%) (Fig. 5). The results indicated that the conversion degree of Si increased with the reaction time. At 50–60°C, the conversion degree of Si increased rapidly from 0 to 300 min and reached a maximum at about 350 min. At 70–80°C, the conversion degree of Si increased rapidly from 0 to 100 min and reached a maximum at about 120 min. In the process of alkali dissolution, the following three steps occurred in succession: (1) Diffusion of OH^- from the NaOH solution through the liquid film to the surface of silica fume; (2) Reaction on the surface between OH^- and silica fume; (3) Diffusion of reaction products (SiO_3^{2-}) from the surface of the solid through the liquid film back into the NaOH solution. Because the reaction product was the soluble SiO_3^{2-} , the reacting particle shrank during reaction and finally disappeared, and the size of particles was changing with time. There was no solid product layer formed, and thus internal diffusion in the solid particles did not contribute any reaction resistance. Therefore, the alkali dissolution reaction of silica fume suited to a shrinking-core model for unchanging size. When the reaction was controlled by chemical reaction between OH^- and silica fume, the dissolution process of mono-sized particles was predicted based on the shrinking core model. The integral form of the reaction model [$G(X)$] was expressed as:²⁷⁾

$$G(X) = 1 - (1 - X)^{\frac{1}{3}} \quad \text{..... (7)}$$

Substituting Eq. (7) into Eq. (6), the model equation was expressed as:

$$1 - (1 - X)^{\frac{1}{3}} = k(T)t \quad \text{..... (8)}$$

where X is the conversion degree.

Due to the very small size of silica fume (average diameter < 100 nm) according to SEM observation result (Fig. S4), the mass transfer coefficient of the liquid film was in the Stokes law regime and was inversely proportional to the particle size.²⁷⁾ Therefore, when the reaction was controlled by the diffusion of OH^- through the liquid film, the integral form of the reaction model [$G(X)$] was expressed as:²⁷⁾

$$G(X) = 1 - (1 - X)^{\frac{2}{3}} \dots\dots\dots (9)$$

Substituting Eq. (9) into Eq. (6), the model equation was expressed as:

$$1 - (1 - X)^{\frac{2}{3}} = k(T)t \dots\dots\dots (10)$$

According to the kinetics data in Fig. 5, it was found that none of the one-step process models $(1 - (1 - X)^{1/3})$ and $1 - (1 - X)^{2/3}$ fitted the data. The plot of $1 - (1 - X)^{2/3}$ versus t showed an excellent linear relation when the conversion degree was $X < 0.35$. However, the regression of $1 - (1 - X)^{1/3}$ versus t was straight-line when the conversion degree was $0.35 < X < 0.6$. Therefore, it was inferred that the process of alkali dissolution was multi-stepped. The rate controlling mechanisms at $X < 0.35$ and $0.35 < X < 0.6$ were diffusion through the liquid film and chemical reaction, respectively. In order to obtain the kinetics parameters, substituting the data of the conversion degree of Si into Eqs. (7) and (9), the values of $1 - (1 - X)^{2/3}$ and $1 - (1 - X)^{1/3}$ can be calculated. According to Eqs. (8) and (10), the values of kinetics rate constant, $k(T)$, were determined from the slope obtained a regression line by plotting $1 - (1 - X)^{2/3}$ and $1 - (1 - X)^{1/3}$ versus t at different temperatures as shown in Figs. 6(a) and 7(a). The values of $\ln k(T)$ also were calculated by taking

the logarithm of $k(T)$. Subsequently, the apparent activation energy and pre-exponential factor were obtained from the slope and intercept by linear regression of $\ln k(T)$ with the reciprocal of reaction temperature ($1/T$) in the Arrhenius equation (Eq. (5)).

According to the data from Fig. 5, the plots of $1 - (1 - X)^{2/3}$ and $1 - (1 - X)^{1/3}$ with t at different temperatures are depicted in Figs. 6(a) and 7(a), respectively. The values of $k(T)$ were obtained from the slope of a linear regression between $G(X)$ and t . Regression analysis showed that the correlation coefficients for all the fittings were > 0.99 , which supported a good linear relation between $G(X)$ and t . That is, the staged model (Eqs. (8) and (10)) fitted the kinetics data. Therefore, it was indicated that our assumption about the kinetics model was reasonable. Then the value of $-E/R$ was obtained from the slope of a linear regression between $\ln k(T)$ and $1/T$. The apparent activation energies (E) at $X < 0.35$ and at $0.35 < X < 0.6$ were calculated as 42.22 ± 3.03 and 78.06 ± 4.27 kJ/mol, respectively (Figs. 6(b) and 7(b)).

In the process of alkali dissolution, OH^- groups adsorbed the surface Si atoms, increasing its electronic density and weakening the Si-O bonds.²⁸⁻³¹ And the depolymerization of Si-O-Si bonds increased the reactivity of the neighboring Si atom due to the creation of surface Si-OH groups.²⁸ In the early stage of the reaction, the increase of dissolution rate was attributed to the reactive high energy sites on the

Fig. 6. Kinetics analysis of alkali dissolution ($X < 0.35$): (a) The plot of $1 - (1 - X)^{2/3}$ against reaction time at different temperature; (b) The plot of $\ln k(T)$ and $1/T$. (Online version in color.)

Fig. 7. Kinetics analysis of alkali dissolution ($0.35 < X < 0.6$): (a) The plot of $1 - (1 - X)^{1/3}$ against reaction time at different temperature; (b) The plot of $\ln k(T)$ and $1/T$. (Online version in color.)

surface of silica fume. These high energy sites were associated with the distorted Si–O–Si bonds and low-coordinated Si atoms.^{28,31)} As discussed in Section 3.1, the proportion of the unsaturated Si–O bonds (Q_2 , Q_3 units and the peroxy bridge structure) accounted for 42.45%. The bond angles of Q_2 (134.3°) and Q_3 (164.7°) were deviated largely from the stable value of tetrahedron (109.5°). Si–O–Si bonds were distorted, and thus the strength of Si–O was weakened. Besides, non-bridging oxygen, especially the peroxy bridge structure (Si–O–O–Si), also resulted in a loose structure of the Si–O network to disintegrate. Therefore, Si–O bonds of non-crystalline SiO_2 in silica fume were easier to be broken by OH^- . It was reasonable to consider that the dissolution rate at $X < 0.35$ was much greater than the OH^- diffusion rate in liquid film. However, in the later stage of the reaction ($0.35 < X < 0.6$), most of amorphous SiO_2 with distorted Si–O bonds was dissolved. The residue was mainly crystalline SiO_2 with the orderly $[\text{SiO}_4]$ tetrahedron unit (Q_4). The dissolution rate was much slower than that in the early stage of the reaction. Consequently, the rate controlling step was the chemical reaction between OH^- and SiO_2 . A similar activation energy value (82 ± 6 kJ/mol) was reported for the dissolution of SiO_2 aerogel in NaOH at $15\text{--}56^\circ\text{C}$.²⁸⁾ It also suggested that the assumption of the rate-controlling step was reasonable. Finally, the alkali dissolution kinetics model of silica fume was established. The kinetics equation was expressed as:

$$1 - (1 - X)^{\frac{2}{3}} = 62\,380 \exp\left(-\frac{4\,957.39}{T}\right) t \quad (X < 0.35)$$

$$1 - (1 - X)^{\frac{1}{3}} = 91\,422 \exp\left(-\frac{9\,388.41}{T}\right) t \quad (0.35 < X < 0.6)$$

..... (11)

4. Conclusions

In this paper, the structural characterization by several analytical techniques was carried out in order to analyze the chemical structure of Si–O bonds in silica fume for developing the recycling methods. XPS analysis showed the presence of Si^{+4} , Si^{+3} , Si^{+2} , and Si^{+1} . Silica fume was a mixture of silicon oxides with multiple valence states. The structures of bridging, non-bridging and the peroxy bridge (Si–O–O–Si) oxygen existed in the Si–O bonding. The FTIR spectra showed that the elementary units of Q_2 , Q_3 , Q_4 and Si–O–Si rings constituted the Si–O network in silica fume. The distribution of Si–O–Si angles in the structural units was wide ($115.8^\circ < \theta < 164.7^\circ$). The proportions of the non-bridging oxygen and the ordered $[\text{SO}_4]$ structure were small. Therefore, the non-crystallizing of silica fume was attributed to the Si–O–Si atom arrangement (bond angles).

For alkali dissolution reactivity, the kinetics model was divided into two stages. When the conversion degree was < 0.35 , the rate controlling step was the diffusion of OH^- through the liquid film, and the apparent activation energy was 42.22 ± 3.03 kJ/mol. When the conversion degree was $0.35 < X < 0.6$, the rate controlling step was the chemical

reaction of OH^- with Si–O, and the apparent activation energy was 78.06 ± 4.27 kJ/mol. The obtained data provided useful information as an important base for the further studies of utilizing silica fume.

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Supporting Information

Details about XRD, XRF, XPS data and particle size distribution of the silica fume sample are given in Figs. S1, S2, S3, S4 and Table S1 in Supporting Information.

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