Quantification of Surface Sites of Ideally Shaped Particles

이상적인 외형을 가진 입자의 표면원자 수계산법

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ABSTRACT : Surface sites and areas of particles are geometrically calculated for the cubic structures to investigate how the surface sites vary with the variation of morphology and particle size. The numbers of surface site and area become smaller when the particles become equi-dimensional shape. The ratios of surface site to surface area are almost constant except the case of anion of fluorite structure. The ratios of the number of surface site to area are almost constant regardless of particle size except the size of up to 5 to 10 times of the unit cell dimension. This quantification method can be used to obtain data related to the surface reaction.

요약 : 입자의 모양과 크기의 변화에 따라 표면에 노출된 원자수의 변화를 알아보기 위해서, 이상적인 외형을 갖는 입자에 대해 표면 원자수의 계산법을 제시하였다. 같은 부피의 입자의 경우, 기하학적으로 이미 예견되듯이, 입자의 3변이 모두 같아질수록 표면의 원자수가 작아진다. 그러나, 입자/표면적 비율은 입자의 모양에 관계없이 거의 일정하다. 단 형석구조의 음이온은 예외이다. 또 입자의 크기에 따른 표면 원자수/표면적 비율은 단위포의 5~10배 크기 이상에서는 거의 일정하다. 이러한 계산법은 임의의 크기의 입자가 이상적인 외형을 가질 때 표면 원자수와 표면적을 구하는 방법으로 사용될 수 있으므로, 표면 반응 연구의 각종 변수를 얻을 때 유용하게 쓰인 수 있다.

INTRODUCTION

Quantification of surface sites is very important in the interface reaction. The information of surface sites can be used in calculating the reaction rate and adsorption isotherm, etc.. The rate of surface reaction is usually expressed as moles $\cdot$ cm^{-2} $\cdot$ sec^{-1}. Total moles of chemical species released or grown or adsorbed over some period of time are divided by surface area to obtain the kinetic rate constant. The total surface area, defined as the area measured in a Brunauer-Emmet-Teller (BET) method (Brunauer et al., 1938; Adamson, 1982; Gregg and Sing, 1982), is still used. Much has been written about the difference between total surface area and "reactive" surface area (Aagaard and Helgeson, 1982; Helgeson et al.,

1984). All the ions present in the surface do not react, but only some of them react. They are called "surface reactive sites".

Surface sites can be estimated from the geometry of the mineral structure (Lasaga, 1990). Significant discrepancies are present on the dissolution rates, and there is no rate model which is generally accepted. Rate measurements at pH 5 range from 10^{-8} to 10^{-14} mol $\cdot$ m^{-2} $\cdot$ s^{-1} (Brantley and Chen, 1995).

Various attempts have been made to know the relationship between the particle shape and the surface area using K (=volume shape factors (α_v) / surface shape factor (α_s)). (Groves, 1978; Gregg and Sing, 1982). The problem of surface topography such as kinks, edges etc. and kinetics were nicely developed by the transition state theory and Monte Carlo simulation (Jackson, 1967; Blum and Lasaga, 1987; Lasaga; 1990).

In this study, surface site and surface area with respect to only particle shape and size, are geometrically treated to quantify the ideally shaped particles.

EVALUATION OF SURFACE SITE OF PARTICLES

Though every particle has different habit, only orthogonally shaped particles are considered here for simplicity in calculating surface exposed atoms. The numbers of surface exposed sites vary with the unit cell types. Primitive cubic (PC), body-centered cubic (BCC), face centered cubic (FCC), halite-structure, and fluorite-structure (Fig. 1) were used to study the relationship between the surface area and the number of surface exposed sites.

To calculate the surface exposed atoms, we constructed a 3×3 transformation patterns of
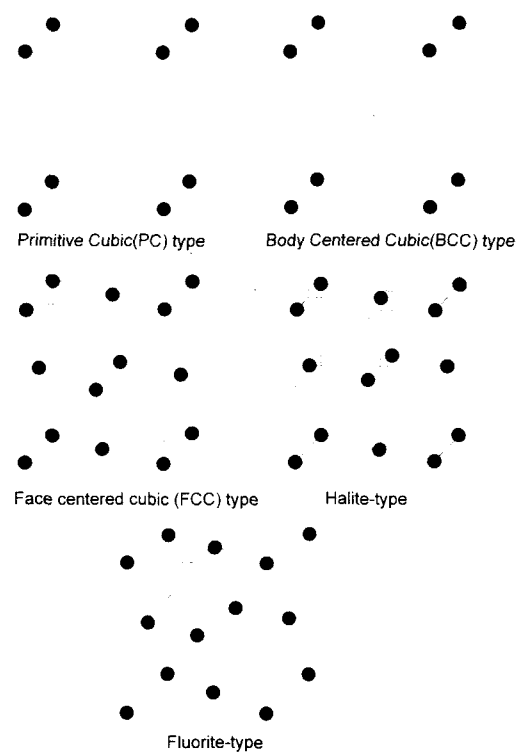
Primitive Cubic(PC) type   Body Centered Cubic(BCC) type

Face centered cubic (FCC) type   Halite-type

Fluorite-type

Fig. 1. Five cubic unit cell structures used in calculating surface sites.
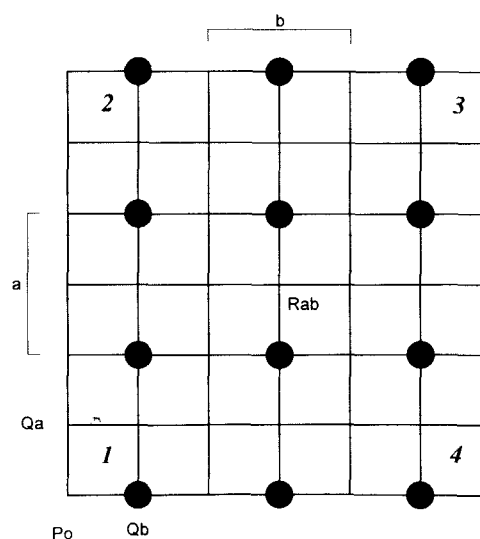
Fig. 2. The arrangement of atoms in the ab-plane of the external sites.

Table 1. Types of weight values and their notation.

Weight	Type*	Notation	Location
1/3	P	Po, Uab_i, Ubc_i, Uca_i (i = 1~4)	Corner
	U		Face
1/2	Q	Qa, Qb, Qc	Edge
	V	Vab_L, Vab_R, Vab_T, Vab_B etc.	Face
1	R	Rab, Rbc, Rca	Face
	W	Wab_I, Wbc_I, Wca_I	

* P, Q and R denote external type and U, V, W internal type.

crystal planes (Fig 2). According to the characteristics of the exposed atoms, we classified the types of weight values of exposed atoms and denoted proper notation as in Table 1. Weight value of 1/3 means that it is commonly shared by other planes, namely it is located in the corner of the unit cell structure. Similarly weight value 1/2 and 1 are located in the edge and face of the plane, respectively.

The followings are basic assumption to calculate number of sites on the surface of the particle. This is somewhat different from the calculation of the unit cell content and the coordination number (Bloss, 1971).

(1) Number of sites is calculated on the basis of the unit cell structure.

(2) Number of site is allocated to 1 if site is on the faces, 1/2 on the edges and 1/3 on the corners. These 1, 1/2, 1/3 are referred to weight value (W_v) and their notations are defined as in Table 1.

(3) The unit cell and crystal structure were largely based on Klein and Hurlbut (1985) and Cullity(1978).

The surface sites are composed of two types; one is originally present on the surface, external sites (E) and the other is exposed outward from the interior out of the crystal, internal sites (I). Therefore, the total number of surface sites, $S_{<xyz>}$, of the particles can be written,

$$S_{<xyz>} = E_{<xyz>} + I_{<xyz>} \qquad (1)$$

where $E_{<xyz>}$ and $I_{<xyz>}$ are the number of external surface sites and internal sites of the particle having the xa, yb and zc dimension, respectively. a, b and c are the unit cell dimension.

Evaluation of External Sites

The number of site is calculated on the basis of the 3×3 transformation patterns (Fig. 2 and 3). Po is number of sites in the corner, Qa, Qb and Qc are in the a-, b- and c-edges and Rab, Rbc and Rca are in the ab-, bc- and ca-face, respectively.

Number of external sites, E_{xy}, on the surface xy is

$E_{xy} = \underline{4\ (Po/3)}$
  increment in the corner
 + $\underline{Rab \cdot xy}$
  increment from the face
 + $\underline{2\ (x \cdot Qa/2)}$
  increment in the a
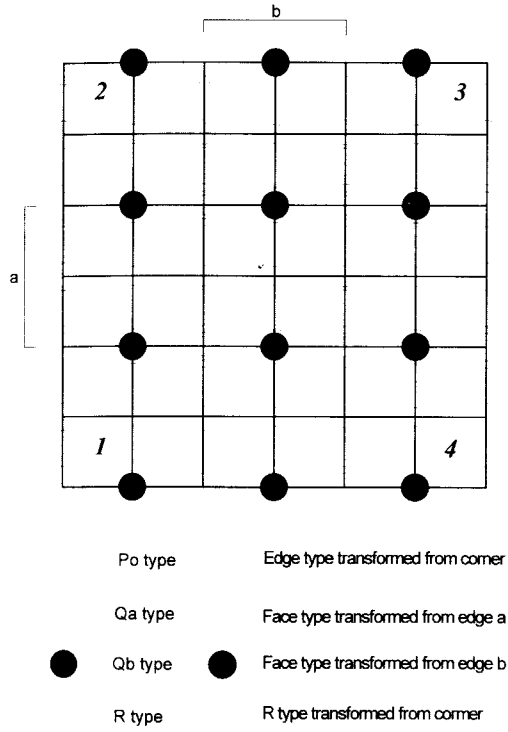
Fig. 3. 3×3 transformation pattern of sites in ab-plane of the external sites.

$$+ \; \underline{2 \; [(x-1) \cdot \; Po/2]}$$
addition from the corner to a
$$+ \; \underline{2 \; (y \cdot \; Qb/2)}$$
increment in the b
$$+ \; \underline{2 \; [(y-1) \cdot \; Po/2]}$$
addition from the corner to b
$$+ \; \underline{y(x-1) \cdot Qb} + \underline{x(y-1) \cdot Qa}$$
addition from b and a to the face on expanding x and y, respectively
$$+ \; \underline{(x-1)(y-1) \cdot Po}$$
addition from the corners to the face on expanding xy
$$= (Po + Qa + Qb + Rab) \; xy + Po/3$$

$$(2)$$

Similarly,

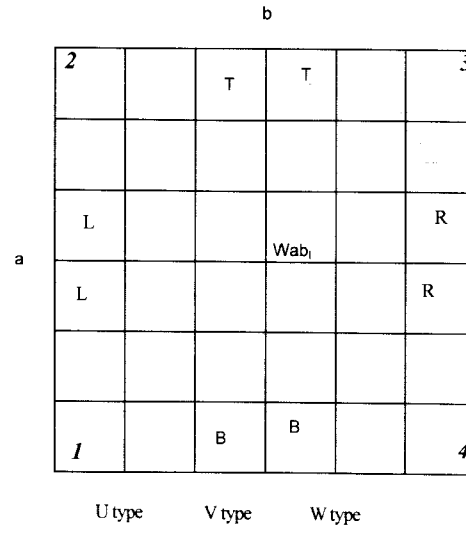$$E_{yz} = (Po + Qb + Qc + Rbc) \; yz + Po/3 \qquad (3)$$

Fig. 4. 3×3 transformation pattern of ab-plane of the internal sites. T and B : the sites at the top and bottom, respectively. L and R : the sites at the left and right, respectively.

$$E_{zx} = (Po + Qc + Qa + Rca) \; zx + Po/3 \qquad (4)$$

The above equations mean that number of external sites is the sum of increment from xy, yz, and zx in the translational vector of the unit cell. As a result, from the equations (2), (3) and (4), number of external sites of particles, $E_{<xyz>}$, having dimension of xa, yb and zc is,

$$E_{<xyz>} = 2 \; (E_{xy} + E_{yx} + E_{zx}) \qquad (5)$$

Evaluation of Number of Internal Sites

The interior sites may be exposed toward the surface if the bond length of interior sites reaches outward the unit cell boundary. The general distribution of the internal sites is presented in the 3×3 transformation pattern (Fig. 4).

The notations used in internal sites are defined as followings;

i ; the 1st, 2nd, 3rd and 4th corner.

L and R ; the sites at the left and right side edge, respectively.

T and B ; the sites at the top and bottom of the edge, respectively.

I ; the sites in the ab-, bc- and ca-inner face, respectively.

Number of external sites, I_{xy}, on the surface xy is,

$$I_{xy} = \sum_{i=1}^{4} (Uab_i/3 + Vab_i/2 + Wab_i)$$

increment at the corner

$+ \underline{Wab_I\ (x\text{-}2)(y\text{-}2)}$

increment in the inner face ab

$+ \underline{(Vab_L/2 + Wab_L)\ (x\text{-}2)}$

increment of L in x

$+ \underline{(Vab_R/2 + Wab_R)\ (x\text{-}2)}$

increment of R in x

$+ \underline{(Vab_T/2 + Wab_T)\ (y\text{-}2)}$

increment of T in y

$+ \underline{(Vab_B/2 + Wab_B)\ (y\text{-}2)}$ (6)

increment of B in y

In the same manner,

$$I_{yz} = \sum_{i=1}^{4} (Ubc_i/3 + Vbc_i/2 + Wbc_i)$$

$+ Wbc_I\ (y\text{-}2)(z\text{-}2)$

$+ (Vbc_L/2 + Wbc_L + Vbc_R/2 + Wbc_R)\ (y\text{-}2)$

$+ (Vbc_T/2 + Wbc_T + Vbc_B/2 + Wbc_B)\ (z\text{-}2)$ (7)

$$I_{zx} = \sum_{i=1}^{4} (Uca_i/3 + Vca_i/2 + Wca_i)$$

$+ Wca_I\ (z\text{-}2)(x\text{-}2)$

$+ (Vca_L/2 + Wca_L + Vca_R/2 + Wca_R)\ (z\text{-}2)$

$+ (Vca_T/2 + Wca_T + Vca_B/2 + Wca_B)\ (x\text{-}2)$ (8)

Wab_I, Wbc_I and Wca_I denote all the innermost sites in the 3x3 transformation pattern, for example, $Wab_I = 5$ in this case (Fig. 4).

Number of external sites, $I_{<xyz>}$, having dimension of xa, yb and cz is written,

$$I_{<xyz>} = 2\ (I_{xy} + I_{yz} + I_{zx})$$ (9)

Surface Sites of Particles Having Cubic Unit Cell

Number of surface sites depends upon the kinds of the unit cells. Here, primitive cubic

Table 2. Variables of surface site of ab plane for the cubic structure.

Weight type		Unit cell type*				
Location	Notation	PC	BCC	FCC	NaCl	CaF₂
External	Po	1	1	1	-1	1
	Qa	0	0	0	+1	0
	Qb		0	0	+1	
	Rab	0	0	1	-1	1
Internal	Uab_i	0	0	0	0	-1
	Vab_i	0	0	0	0	-2
	Wab_i	0	0	0	0	-1
	Vab_L	0	0	0	0	-2
	Vab_R	0	0	0	0	-2
	Wab_L	0	0	0	0	-2
	Wab_R	0	0	0	0	-2
	Vab_T	0	0	0	0	-2
	Vab_B	0	0	0	0	-2
	Wab_T	0	0	0	0	-2
	Wab_B	0	0	0	0	-2
	Wab_I	0	0	0	0	-4

* Minus sign is used to distinguish between cation and anion.

(PC), body centered cubic (BCC), face centered cubic (FCC), halite-structure, and fluorite-structure (Fig. 1) are taken into consideration to know the relationship between the surface area and number of sites.

The parameters in calculating number of surface site for the cubic unit cell are written in Table 2.

Putting those parameters in Table 2 into equations (2) to (9), the result for the PC is,

$$E_{xy} = xy + 1/3, \quad E_{yz} = yz + 1/3,$$
$$E_{zx} = zx + 1/3 \tag{10}$$

As E_{xy}, E_{yz} and E_{zx} exist doubly in the unit cell, number of surface sites for PC, $S_{<xyz>PC}$, is,

$$S_{<xyz>PC} = 2 (E_{xy} + E_{yz} + E_{zx})$$
$$= 2 (xy + yz + zx) + 2 \tag{11}$$

Similarly,

$$S_{<xyz>BCC} = 2 (xy + yz + zx) + 2 \tag{12}$$
$$S_{<xyz>FCC} = 4 (xy + yz + zx) + 2 \tag{13}$$
$$S_{<xyz>Halite} = \frac{4 (xy + yz + zx)}{cations}$$
$$+ \frac{4 (xy + yz + zx) + 2}{anions} \tag{14}$$

$$S_{<xyz>Fluorite} = \frac{4(xy+yz+zx) + 2}{cations}$$
$$+ \frac{8(xy+yz+zx) - 8(x+y+z) + 8}{anions} \tag{15}$$

The variation of number of the surface sites as the shape of particle changes can be obtained if we let xyz=constant in equation (11) to (15).

The morphology of flake, slab, cube, columnar, rod and fibrous is arithmetically derived
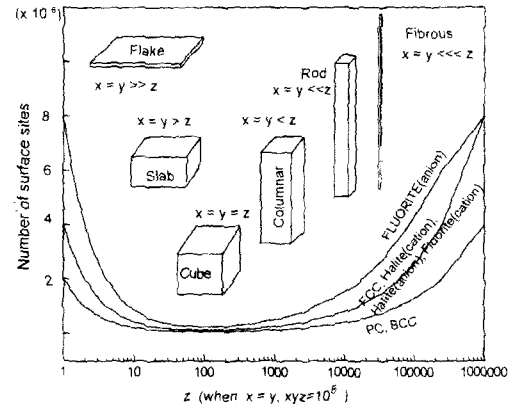

Fig. 5. Number of surface sites for the different shapes of isovolumetric particles when $xyz=10^6$.

and arbitrarily determinated when $xyz=10^6$ (Fig. 5). The characteristics of the surface sites in relation to the morphology are; (i) The number of surface sites becomes smaller as the shape tends to have equi-dimensional lengths. (ii) The number of surface sites increases in the order of PC≈BCC < FCC ≅ halite(cation) ≅ halite(anion) ≅ fluorite(cation) < fluorite(anion) as a factor of 1, 2.0 and 3.96 for the cube morphology.

Surface Area of Particles

Total surface area of particles, $A_{<xyz>}$, having xa, yb and zc dimension, and axial angles α, β, and γ is,

$$A_{<xyz>} = 2 (xyab \sin\gamma + yzbc \sin\alpha + zxca \sin\beta) \tag{16}$$

According to the unit cell dimension of the relevant crystal, the a values were chosen 2.5, 2.86, 3.56, 5.607 and 5.46 Å for PC, BCC (α-Fe), FCC(β-Fe), halite structure and fluorite structure, respectively. Variation of the surface
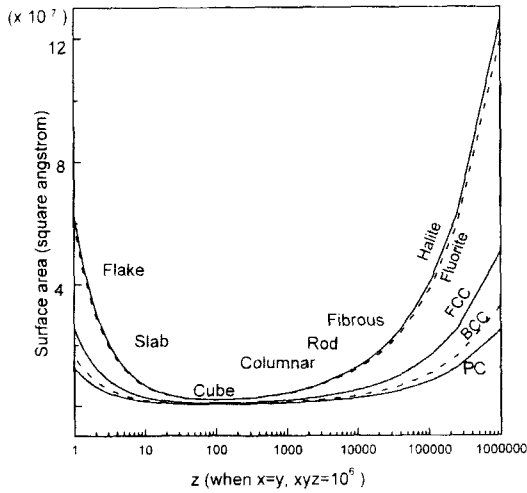
Fig. 6. Surface area for the different shapes of isovolumetric particles when $xyz=10^6$. Unit cell dimensions are described in the text.

area in relation to crystal morphology is shown in Fig. 6. The surface area also decreases as all three x, y and z get closer values to each other.

Site Density

$SD_{<xyz>}$, the site density of particles having xa, yb and zc dimension, is written,

$$SD_{<xyz>} = S_{<xyz>} / A_{<xyz>} \qquad (17)$$

The site density is almost constant regardless of the crystal habit in the isovolumetric particles except anion of fluorite (Fig. 7). But it varies with the different unit cell structures ranging roughly $6 \sim 18 \cdot 10^{14}$ sites/cm^2, which is similar to other's value of 10^{15} sites/cm^2 (Lasaga, 1990; ller, 1979). Even though the shapes of particles are different, the site density has the same value in the isovolumetric particles except the anion of fluorite-structure
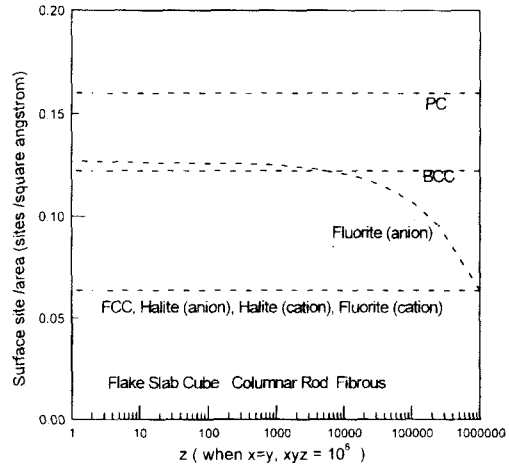
Fig. 7. Surface site density for the different shapes of isovolumetric particles when $xyz=10^6$.

showing a decreasing value with increasing z. These constant values suggest that theoretically there is no distinction of site densities among the ideally shaped particles. It is notable that in extreme fibrous shape the site density decreases approximately half the value of the other shape.

Variation of Site Density according to Particle Size

The number of surface sites/area is almost constant regardless of the particle size except the extremely fine particles which range only up to 5 to 10 times of the unit cell dimension. (Fig. 8). Furthermore, the anion of fluorite shows different trends compared with others. The difference of surface site/area is within the range of 1.5 times or so. Also, Parks (1990) found surface roughness is independent of grain size. Therefore, the reason of fast reaction rate due to small particle size may be ascribed to the different state of individual site on the surface. The change of weight value, namely,
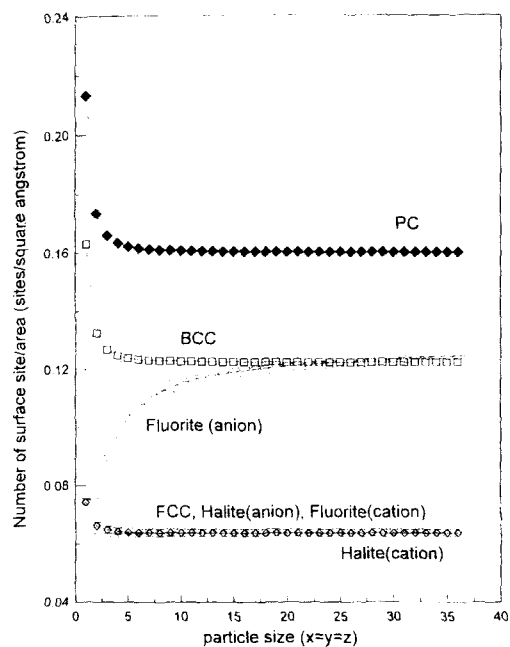
Fig. 8. Variation of number of surface site/area according to the particle size.

the number of unbound bond-bridges may affect the reaction rate.

CONCLUSION

Though the site density and adsorbable site do not exactly coincide, the variation of site density depending upon size and shape is very important in the rate equation. The fibrous, rod, flake and slab have large amounts of surface sites, and higher surface energy than cube, therefore they tend to lower surface energy consuming "reactive" sites to form cube or sphere. This explains why micro-equigranular grains are ubiquitous in the natural sedimentary environment (Philpotts, 1990).

The site density, total sites present on the surface per unit area, is distinguished from the "adsorbable or reactive site" which mean the

sites potentially reactive on the surface. The latter is measured in the laboratory using a BET or other methods (Gregg and Sing, 1982). We developed a method of getting the general number of surface sites in terms of variation of shape and size for the ideally shaped particles in this study. This method will be utilized in obtaining the number of surface sites for the randomly shaped particles. The result can be widely used in surface reaction, especially in adsorption study.

ACKNOWLEDGEMENTS

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