



## Research paper

## Defects in structure as the sources of the surface charges of kaolinite

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## ABSTRACT

The sign and magnitude of the surface charge govern the particle interactions and hence determine the physical properties of dispersions. The present work is to evaluate the distortions, isomorphic and broken surface bond as the sources of the permanent or variable surface charges of kaolinite. The theoretical permanent charge density ( $\sigma_{cc}$ ) was calculated by XRF. The experimental permanent charge density ( $\sigma_p$ ) and variable charge density ( $\sigma_v$ ) were obtained by the method of potentiometric titration. The degree of broken bonds ( $D_{b,b}$ ) of Al–O–Al and Si–O–Si at the side of kaolinite structure were characterized by the numbers and strength of surface hydrogen in <sup>1</sup>H MAS NMR, absorbance of Al–OH or Si–OH in FTIR and edge fractures in FESEM. The surface area was measured by N<sub>2</sub> adsorption–desorption. The defects such as basal z corrugation ( $\Delta z$ ), tetrahedral rotation angles ( $\theta$ ) and octahedral flattening angles ( $\psi$ ) were obtained by the XRD rietveld refinement. The negative  $\sigma_{cc}$  or  $\sigma_p$  of three samples KA, KB and KC are 0.012, 0.007 and 0.009 C·m<sup>-2</sup> or 0.24, 0.19 and 0.22 C·m<sup>-2</sup>, respectively.  $D_{b,b}$  of three samples are  $D_{b,b-KA} > D_{b,b-KC} > D_{b,b-KB}$ . The  $\sigma_v$  depend on the degree of the broken bonds at edges of kaolinite and can be affected by pH significantly. The negative variable charge density at alkaline condition decreased with the increase of the degree of broken bonds at the side of kaolinite structures. Surface charges of kaolinite come from the defects such as isomorphic substitutions and broken bonds Al–O–Al and Si–O–Si. The distortions in structure e.g.  $\Delta z$ ,  $\theta$  and  $\psi$  may not directly create the surface charges.

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## 1. Introduction

For kaolinite colloidal particles possessing permanent charges and variable charges, the sign and magnitude of the surface charge govern the particle interactions (Gupta and Miller, 2010; Gupta et al., 2011) and hence determine the physicochemical properties of dispersions (e.g. rheological properties (Au and Leong, 2013), their stability against coagulation, floating, adsorption (Tribe et al., 2012), and viscosity) in many industries such as paper (Cunha et al., 2006), the soil (Jiang et al., 2011), drilling slurries, dewatering (Mpofu et al., 2003), and oil sand (Jiang et al., 2010). Until now, many authors have been investigated the factors affecting the surface charges (Yukselen and Kaya, 2011), the methods to measure the charges (Piccinini et al., 2013) and the sources of charges (Tombácz and Szekeres, 2006). The factors affecting the surface properties of kaolinite include pH, additives (e.g. electrolytes, ionic liquids and minerals) (Markiewicz et al., 2013; Alkan et al., 2005), temperature (Torres Sánchez and Tavani, 1994) and pressure (Rodríguez and Araujo, 2006). Various procedures have been used for the determination of surface charges of kaolinite. They generally rely on ion adsorption, potentiometric titration, electrophoretic mobility

(zeta potential) measurements and structural formula method (Khawmee et al., 2013; Kosmulski, 2012).

A kaolinite layers, with the ideal chemical composition of Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, consists of a silica tetrahedral surface corresponding to the (001) basal plane and an aluminum hydroxide octahedral surface corresponding to the (00 $\bar{1}$ ) basal plane as shown in Fig. 1 (Bish and Dreele, 1989). The kaolinite particles have (010) and (110) edge surfaces which are generated as a result of broken covalent bonds. Kaolinite has a heterogeneous surface charge (Tombácz and Szekeres, 2006). It is traditionally believed that the (001) and (00 $\bar{1}$ ) basal plane surfaces of kaolinite particles are negatively charged due to isomorphic substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in the silica tetrahedral layer and Mg<sup>2+</sup> for Al<sup>3+</sup> in the alumina octahedral layer, whereas the edge surface ((010) and (110) plane surfaces) carries a positive or negative charge depending on the pH of the system (Schroth and Sposito, 1997).

Uniform distribution of surface charge are assumed for chemical compositions, morphologies, particle sizes, grains, surface areas (Hu and Liu, 2003; Du et al., 2010; Liu et al., 2014a, 2014b). The degrees of isomorphic substitution and edge surface site are different; therefore the layer charge density and variable charge density of clay minerals show high variety. Liu et al. calculated the surface charge densities and surface potentials of selected phyllosilicate surfaces from AFM surface force measurements. The silica faces of clay minerals follow the constant surface charge model because of isomorphous substitution in

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## Nomenclature

$\sigma_{cc}$	theoretical permanent charge density or constant charge ( $\text{mol} \cdot \text{g}^{-1}$ or $\text{C} \cdot \text{m}^{-2}$ )
$D_{b, b}$	degree of broken bonds
$z$	$z$ atomic position of basal oxygen
$\Delta z$	basal $z$ corrugation
$\theta$	tetrahedral rotation angles ( $^\circ$ )
$\psi$	octahedral flattening angles ( $^\circ$ )
$\zeta$	zeta potentials (mV)
$\Gamma_{\text{H}^+}$ and $\Gamma_{\text{OH}^-}$	adsorption amounts of $\text{H}^+$ or $\text{OH}^-$ ( $\text{mol} \cdot \text{g}^{-1}$ )
$\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}$	adsorption amounts of $\text{H}^+$ and $\text{OH}^-$ at some pH value ( $\text{mol} \cdot \text{g}^{-1}$ )
$w$	oven-dried kaolinite samples weight
$N_{A, \text{sample}}$	amounts of acid added to the kaolinite dispersion (mol)
$N_{A, \text{blank}}$	amounts of acid added to the blank solution (mol)
$F$	Faraday constant ( $96,485 \text{ }^\circ\text{C} \cdot \text{mol}^{-1}$ )
$SSA_m, SSA_t$	experimental and theoretical specific surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )
$R_p, R_{wp}$	profile residual and weighted profile residual
$X$	layer charge of mineral ( $\text{mol} \cdot \text{mol}^{-1}$ )
$M_{FW}$	crystal formula weight of mineral ( $\text{g} \cdot \text{mol}^{-1}$ )
$\sigma_T$	total net surface charge density ( $\text{mol} \cdot \text{g}^{-1}$ )
$R$	ideal gas constant ( $8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )
$T$	absolute temperature (K)
$\varepsilon$	dielectric constant of medium
$n$	electrolyte concentration ( $\text{mol} \cdot \text{L}^{-1}$ )
AFM	atomic force microscope
XRD	powder X-ray diffraction
XRF	X-ray fluorescence spectroscopy
FTIR	Fourier transform infrared
$^1\text{H MAS NMR}$	$^1\text{H}$ magic angle spinning nuclear magnetic resonance
FESEM	field emission scanning electron microscope
ICSD	The Inorganic Crystal Structure Database
BET	Brunauer–Emmett–Teller method
Peakfit	a software for fitting spectra
IEP	isoelectric points
PZSE	point of zero salt effect
$OI$	order index of kaolinite based on FTIR
$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$	vibration bands at $3695 \text{ cm}^{-1}$ , $3668 \text{ cm}^{-1}$ , $3652 \text{ cm}^{-1}$ , $3620 \text{ cm}^{-1}$ and $914 \text{ cm}^{-1}$
$\delta$	chemical shifts in $^1\text{H MAS NMR}$ spectra (ppm)
$S$	relative percentage of integrated areas at some chemical shift (%)
$r^2$	determination coefficient (%)
$\alpha, \beta, \gamma, a, b, c$	structure parameters of unit
$\varepsilon_0$	permittivity of free space ( $8.854 \times 10^{-12} \text{ }^\circ\text{C} \cdot \text{V}^{-1} \cdot \text{mol}^{-1}$ )
$e$	electric charge ( $1.6021 \times 10^{-19} \text{ C}$ )
$\sigma_p$	permanent charge density ( $\text{mol} \cdot \text{g}^{-1}$ )
$\sigma_v$	variable charge density ( $\text{mol} \cdot \text{g}^{-1}$ )

the silica tetrahedral layer (Liu et al., 2014a, 2014b). Additional polar sites, mainly octahedral Al–OH and tetrahedral Si–OH groups, are situated at the broken edges and expose hydroxyl-terminated planes of clay layers (Johnston and Tombácz, 2002). The amphoteric sites are conditionally charged, and so either positive or negative charges, depending on the pH, can develop on the O faces and at the edges by direct  $\text{H}^+$ / $\text{OH}^-$  transfer from aqueous phase (Hu and Liu, 2003). Zhang et al. (2014) found that different particle size, morphology and structural defects of four kaolinite samples are attributed to the broken bonds of Al–O–Si, Al–O–Al and Si–O–Si and the Al substitution for Si in tetrahedral sheets. Aung et al. (2015) researched that  $\text{Na}^+/\text{H}^+$  selectivity coefficient depends strongly on the particle morphology, and considered that the

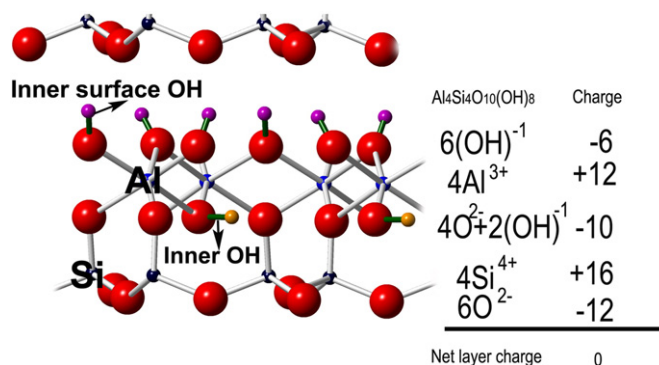


Fig. 1. Kaolinite structure and calculation of net layer charge X.

specific surfaces of lateral sites and adsorption site density identified by crystallography for the difference faces (010), (110), ( $1\bar{1}0$ ) presented in the synthesized kaolinites. Here, we will research the surface charges of different kaolinite for paper coating collected from the world and try to study the effect of defects and broken bonds on the surface charges.

The aim of the present work is to evaluate the surface charges of kaolinite from the sources of isomorphous and broken surface bond to create the permanent and pH-dependent charges. Three classical kaolinite samples for paper coating were collected from America, Brazil and China. The theoretical permanent charge density was achieved by the chemical compositions measured by XRF. The experimental permanent density and variable density were obtained by the method of potentiometric titration. Zeta potentials of dispersions were also analyzed as comparative. The defects in microstructures such as basal  $z$  corrugation ( $\Delta z$ ), tetrahedral rotation angles ( $\theta$ ) and octahedral flattening angles ( $\psi$ ) were obtained by the rietveld refinement of kaolinite from XRD data. The broken surface bonds, shape, thickness of kaolinite particles were analyzed by  $^1\text{H MAS NMR}$ , FTIR and FESEM.

## 2. Experimental

### 2.1. Materials

Kaolinite samples KA and KC were products for paper coating bought from the Imerys Minerals (USA) and Maoming City of Guangdong Province of China, which were denoted as KA and KC. Kaolinite KB was collected from clay mine about 30 miles north of Manaus city near the Amazon river in Brazil and purified in a laboratory.

### 2.2. Characterization

#### 2.2.1. XRD

The X-ray powder diffraction profiles of three classical kaolinite powders were recorded using Ni-filtered  $\text{CuK}\alpha$  radiation from Bruker AXS D8-Focus X-ray analyzer operated at 40 kV and 40 mA. The step-scan data was recorded for the entire angular range of  $10^\circ$ – $80^\circ$  (increment  $0.01$  and scan speed  $6 \text{ s}/0.01^\circ$   $2\theta$ ). The structure of kaolinite (non-hydrogen atoms only) was refined in space C1. The atomic coordinates of kaolinite in ICSD card number 68,697 were used as starting parameters to refine kaolinite samples.

#### 2.2.2. XRF

Chemical compositions of kaolinite samples were measured by XRF (Axios<sup>advanced</sup>, PAN analytical Netherlands).

#### 2.2.3. Zeta potential

Before zeta potential and potentiometric titration, kaolinite samples were stirred and washed by deionized water, centrifuged in a centrifuge, dried at 383 K an oven, and then grinded in an agate mortar.

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