Radio Frequency Plasma-Induced Hydrogen Bonding on Kaolinite

Hui Ming*,† and Kaye M. Spark‡,§

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia, and University of Queensland, P.O. Box 1123, Gatton, Qld 4343, Australia

The radio frequency (RF) plasma-modified surfaces of kaolinite were investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and deuteration techniques to determine the nature of RF plasma-induced surface functional groups, the altered sites in the lattice, and interaction mechanism between RF plasma and the surface of the kaolinite. It has been concluded that the RF plasma-induced infrared (IR) vibration absorption bands at 2805, 3010, and 3100 cm^{-1} are attributable to the stretching vibration of hydrogen-bonded hydroxyl groups, and the band at 1407 cm^{-1} is attributable to the bending vibration of (HO−)Al−O or (HO−)Si−O groupings with hydrogen-bonded hydroxyl groups. Structural alteration occurred on both the surface and subsurface region of the kaolinite during RF plasma treatment. Further structural alteration or adjustment was also observed on well-modified and well-deuterated kaolinite. There are two types of OD bands visible in the DRIFT spectra of this kaolinite, one type which decreased rapidly as a function of time in moist air, and the other which remained unchanged during the measurement. Furthermore, the appearance of broad IR bands at 3500−3100 cm^{-1} as a result of deuteration is evidence of structural disturbance by RF plasma treatment lattice deuteration. An RF plasma-induced hydrogen bonding model on the surface of the kaolinite is proposed.

Introduction

In a previous study, RF plasma-modified Georgia kaolin was investigated by X-ray photoelectron spectroscopy (XPS) and DRIFT.[1] The RF plasma treatment on kaolinite was found to be an intense bombardment process with limited surface sputtering. The process resulted in four new major IR absorption bands associated with the surface of RF plasma-treated kaolinite, located at 1407, 2805, 3010, and 3100 cm^{-1}. Additional small or unresolved new IR bands were also visible in the vicinity of these regions. The new IR bands were concluded to arise from the presence of new functional groups formed as a result of the plasma treatment. The intensity of the IR absorbance of these RF plasma-induced functional groups was found to be dependent on the period of plasma treatment and the energy applied but generally independent of the nature of the gas used for the plasma treatment. However, the nature of these functional groups was not able to be determined from that study.

Attribution of the new IR bands to possible reaction between either the plasma gas and the surface of the solid during plasma treatment, or a residual gas with the plasma-activated kaolinite surface were both ruled out. Instead it was concluded that the new RF plasma-induced IR bands were associated with surface bonding alterations such as functional group rearrangements as a result of plasma treatment.[1] As only the vibrations of the groups in the surface (interface between solid and gas) and immediate subsurface regions of a solid (surface region which is affected by the bombardment) can be measured using IR spectroscopy, the major RF plasma-induced IR bands (1407, 2805, 3010, and 3100 cm^{-1}) are most likely concerned with surface and immediate subsurface group activity.

Hydrocarbon contamination of the surface of the kaolinite is one possible explanation of the observed plasma-induced IR absorbances as it is difficult to eliminate all hydrocarbon contamination during the treatment. The types of hydrocarbon groups which absorb in the infrared vibration frequency ranges include C−H and Si−R (where R is an organic group).[2−10] The bending vibrations (ν_b) of C−H and Si−R (Si−C−) are often observed in the vicinity of 1400 cm^{-1}. However, for common types of hydrocarbon contamination, alkyl groups would also be expected to be present which would give rise to several sharp stretching vibration bands in the 2850−3050 cm^{-1} region due to CH$_x$ related sp^2 and sp^3 stretching vibration.[7] As they were not observed, the possibility that hydrocarbons are a source of the plasma-induced IR bands is low.

A second, and more promising explanation for the observed plasma-induced IR bands is that they arise from O−H groups, which can be present as part of the kaolinite structure or associated with water adsorbed from air moisture. The OH groups from loosely absorbed water molecules will give bands at 3435 cm^{-1} (stretching vibration) and 1630 cm^{-1} (bending vibration). This bending vibration often gives rise to multicomponent bands in the region 1600−1650 cm^{-1}. Absorbances for monomeric unassociated (vapor) H$_2$O molecules are found at 3756 and 1595 cm^{-1} and those for liquid H$_2$O molecules are found at 3455 and 1645 cm^{-1}.[3,10] Free (i.e., no hydrogen bonding involved) O−H vibrations normally result in stretching vibrations (ν_s) and bending vibrations at 3700−3500 and 1300−1200 cm^{-1}, respectively.[8,11] In contrast, when the O−H group is involved in hydrogen bonding, these vibration modes can be shifted to 3400−1700 and ~1400 cm^{-1}, respectively, due to the change in force constant;[12−20] the stronger the hydrogen

* Author to whom correspondence should be addressed at Centre for Advanced Manufacturing Research, University of South Australia, Mawson Lakes, SA 5095, Australia. Fax: 61 8 8302 5292. E-mail: hui.ming@unisa.edu.au.
† Ian Wark Research Institute, University of South Australia.
‡ University of Queensland.
§ E-mail: kaye.spark@uqg.uq.edu.au.

bonding, the greater the observed shift. Other IR features of hydroxyl group involved with hydrogen bonding are broadened stretching vibration bands with enhanced intensity.[12-20] Variation in the material with hydrogen bonding, such as temperature, concentration, solvent, and some physical properties, can also affect the IR spectrum of the sample.[12-20] The characteristics of plasma-induced functional groups on kaolinite are broadened bands with a low ν_s which fit the characteristic of hydrogen-bonded hydroxyl groups.

The nature of OH functional groups in kaolinite can be studied using both direct and indirect deuterium exchange, i.e., intercalation−deuteration.[21-33] The deuterium-substituted labile hydrogen exhibits vibrational absorption bands in the IR spectra shifted in frequency by a factor of approximately $1/\sqrt{2}$ from the bands associated with the un-deuterated sample.[2] This technique is able to distinguish the site of the hydroxyl groups in the lattice of the kaolinite as the surface hydroxyl groups readily exchange with deuterium to produce deuteroxyl groups,[11,29,31-33] but to achieve the deuteration of lattice hydroxyl groups on kaolinite requires hydrothermal conditions.[21,23-33] The aim of this study was to determine the site of the O−H groups on the surface or in the lattice of the kaolinite responsible for the plasma-induced IR bands by using controlled deuterium exchange conditions such as temperature, pressure, and time.

Experimental Section

The well-crystalline kaolinite, Georgia kaolin Hydrite PX (Georgia), was obtained from the Georgia Kaolin Company. The general characteristic of the product has been described in a previous study.[1]

The chemicals used in this study were all A. R. grade except for KBr which was dried Spectroscopic Grade (Merck). Ar used for plasma treatment was a high-purity gas from BOC Gases and the water used in the plasma study was Milli-Q water (Reagent grade water system, Millipore Corporation, Bedford, MA). The purity of deuterium oxide (Aldrich) was 99.9%.

The plasma reactor used in this study has been described elsewhere.[1] The operation conditions for D_2O or Ar plasma treatment were the following: power input 50 W, radio frequency 0.41 MHz, pressure 2×10^{-1} Torr, and gas flow-rate of 4 standard cubic centimeters per minute (sccm). As soon as the D_2O plasma treatment was completed, the sample was left in the plasma chamber in the same vapor until the pressure of the chamber reached equilibrium with that in the D_2O reservoir. Ar was then slowly admitted into the chamber to bring it up to atmospheric pressure. As soon as the sample was removed from the chamber, it was immediately mixed with KBr and transferred to a DRIFT cell for IR measurement.

The DRIFT spectra were recorded using a Magna-IR 750 infrared spectrometer (Nicolet Instrument) with a diffuse reflectance accessory (Spectra Tech.), a KBr beam splitter, and a liquid nitrogen cooled MCT/B detector. Purified compressed air was continuously flushed through the instrument compartment to remove moisture and carbon dioxide. The IR spectra were scanned between 400 and 4000 cm^{-1}. All samples were measured at 25 °C in absorbance mode at 4 cm^{-1} resolution. A commercial software, OMNIC (Nicolet Instrument), was used for data acquisition and spectra analyses. The kaolinite was mixed with KBr to give 5 wt % samples and KBr was used as a background. Most samples were allowed to equilibrate in the DRIFT cell compartment for 5 min prior to analysis to avoid interference from absorbed water vapor. However, the spectra for the time-resolved scans were recorded at predetermined time intervals to observe the changes in DRIFT spectra as a function of time. To further identify hydroxyl groups with hydrogen bonding, cryogenic-time-resolved scans was used to detect variation in intensity of IR absorption bands as a function of temperature and time. The sample holder filled with a KBr/kaolinite sample was placed in contact with a metal block which was partially immersed into liquid nitrogen for a few minutes to achieve equilibrium temperature, and then transferred to the DRIFT compartment for measurement.

The in situ surface deuteration of kaolinite was conducted using an FTS-65 infrared spectrometer (BIORAD) with a diffuse reflectance accessory (Spectra Tech.) mounted with an environmental chamber (model 0030-102). A TDGS detector with KBr window was used for collecting spectra. The 5% kaolinite sample mixed with KBr was sealed in an environmental chamber, put under vacuum for 30 min while heating at 120 °C to eliminate possible absorbed water, and then cooled to room temperature under vacuum. Ar was bubbled through D_2O into the chamber for 30 min to achieve H−D exchange equilibrium and then the chamber was again put under vacuum to remove all unexchanged species in the gas phase. Ar was bubbled through H_2O to the chamber for 15 min to reverse the exchange process. Finally, the system was put under vacuum again to remove water vapor.

The D−H exchange under hydrothermal conditions was conducted in a heated, sealed Pyrex tubing. For this analysis, 0.3 g of sample was placed in a 10 mm long Pyrex borosilicate glass tube (8 mm o.d., 4 mm i.d.) with one end sealed. The precalculated amount of D_2O was added to the tube under Ar in a glovebox so that at the specified temperature, the vaporized D_2O would generate the desired pressure. The sample was fast frozen in liquid N_2 and sealed by oxygen torch. The Pyrex vessel was placed into a furnace at ambient temperature. The temperature of the sample was raised gradually to the desired temperature and left there for a period of time. At end of the deuterium exchange, the sample was cooled to ambient temperature and transferred to a dried glovebox under dried Ar. The Pyrex tubing was broken, stored in a desiccator, and pumped down to remove water vapor. The dried sample was ground and mixed with KBr before being transferred to the DRIFT spectrometer for immediate analysis.
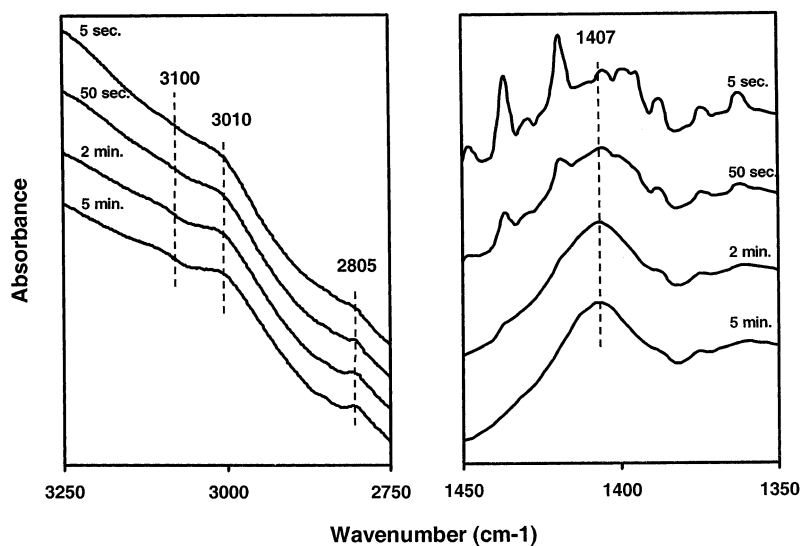
Results

Assignment of IR Bands of Kaolinite. There are a large number of studies using a variety of infrared- or Raman-related techniques investigating the assignment of the observed IR absorption bands of kaolinite in the group frequency region.[3-6,25-40] Although there are some doubts regarding the sources of some combination or overtone bands and noninherent lattice bands of kaolinite, the assignments of most of the individual IR bands of the kaolinite are reasonably well understood.[6,22] A summary of absorption bands observed in the IR spectra of this kaolinite, together with published assignments of these bands, is displayed in Table 1.

Due to varying crystallinity and impurities in natural kaolinites, not all bands listed in Table 1 are visible in the IR spectra of a particular sample of kaolinite.[6,21,37,39] For example, the Georgia kaolin studied in this work had no bands at 3600 and 880 cm^{-1}; these are visible if the kaolinite has Fe^{3+}-substituted Al^{3+} in the octahedral sheet of the lattice.[37] Conversely, the 3435 cm^{-1} band, which was generally regarded as the OH stretching vibration of loosely adsorbed water molecules, is not always visible in the IR spectra of kaolinites but is apparent in that of the Georgia kaolin.[3] There appears to be no definitive

TABLE 1: Possible Assignment of Group Frequency in the DRIFT Spectra of Kaolinite

band (cm^{-1})	possible assignment	ref.
3694	O−H stretch-inner surface hydroxyls with the dipole at right angles to the basal plane (in phase vibration), coupled with 3667 cm^{-1} band	[3,4,6,30,31,33]
3684	O−H stretch-uncoupled inner surface hydroxyls. Raman active	[21, 37]
3669	O−H stretch-inner surface hydroxyls with the dipole at right angles to the basal plane (180° out of phase vibration), coupled with 3692 cm^{-1} band	[3,4,6,31,33]
3653	O−H stretch of the inner surface hydroxyl group lying close to the plane of the sheet	[3,4,6,31,33]
3620	O−H stretch-inner hydroxyl with the dipole inclined toward empty octahedral sites	[3,4,6,30,31]
3600	OH stretch vibration of AlFe^{3+}OH groupings resulting from Fe^{3+}-for-Al substitution in the octahedral sheet of the kaolinite structure if Fe^{3+} isomorphous substitution occurred	[6,39]
3435	O−H stretch of molecular water on the surface	[3][a]
2705, 2670	difference band, small to very small, $\nu_{3620} - \nu_{916} \approx \nu_{2705}$, $\nu_{3692} - \nu_{1020} \approx \nu_{2670}$	[22]
2342	atmospheric CO_2	[2,3]
2227, 2146	combination bands, very small, $2\nu_{1113} \approx \nu_{2227}$, $\nu_{1022} + \nu_{1113} \approx \nu_{2146}$	[22]
1931, 1823,	combination bands, $\nu_{1022} + \nu_{915} \approx \nu_{1931}$, $2\nu_{915} \approx \nu_{1823}$	[21,22,40]
1757, 1725	combination band, small	[40]
1653	OH bending vibration from H_2O absorbed	[2,9]
1635	OH bending vibration from H_2O absorbed	[2,3,9]
1540	combination band, very small, $\nu_{535} + \nu_{1009} \approx \nu_{1544}$	b
1472	combination band, very small, $\nu_{467} + \nu_{1009} \approx \nu_{1476}$	b
1400	combination band, very small, $\nu_{973} + \nu_{432} \approx \nu_{1400}$	b
1113	Si−O stretch	[3,4,37]
1110	Si−O stretch	[3,4]
1022	Si−O−Si stretch	[3,4,21,40]
1009	Si−O−Al stretch	[3,4,21]
937	O−H deformation of Al−O−H inner hydroxyl group	[3,4,6,21,32,35]
915	O−H deformation of Al−O−H inner surface hydroxyl group	[3,4,6,21,35,40]
880	OH bending vibration of AlFe^{3+}OH groupings resulting from Fe^{3+}-for-Al substitution in the octahedral sheet of the kaolinite structure if Fe^{3+} isomorphous substitution occurred	[3,6,39]
795	Si−O−Al stretch and OH translation	[3,4,6,35]
753	Si−O−Al stretch and surface hydroxyl translation	[3,4,6,35]
693	Si−O−Al stretch and OH translation	[3,4,35]
646	Si−O−Al deformation	[3,35]
535	Si−O−Al^{VI} deformation	[3,4,28,35]
467	Si−O deformation	[3,4,28,35]
431	Si−O deformation	[3,4,28]
416	Si−O deformation	[4]

a Assignment of this band will be discussed later. *b* There bands present in all natural occurred kaolinites with very weak intensities.

Figure 1. A time-resolved DRIFT scan of a prior plasma treated (5 h) Georgia kaolin.

data in the literature on IR bands resulting from RF plasma treatment.

Time-Resolved Study of the Formation of RF Plasma-Induced IR Bands. A previous study has shown that the intensities of RF plasma-induced IR bands associated with kaolinite at 3100, 3010, 2805, and 1407 cm^{-1} are increased as a function of time of plasma treatment.[1] Some of the time-resolved DRIFT spectra of the kaolinite after plasma treatment (multiple spectra taken between 5 and 340 s, since the sample

was placed in DRIFT cell for measurement) are displayed in Figure 1. The normalized spectra of the scans indicate that the increases in IR intensities of these four bands are a combined variation between a receding baseline and ascending new bands. The receding baseline was attributed to the removal of loosely adsorbed water from the surface of the kaolinite in the DRIFT cell during IR measurement because raw Georgia kaolin showed a similar but lesser degree of receding trace without emerging new IR bands. The greater receding baseline for the plasma-
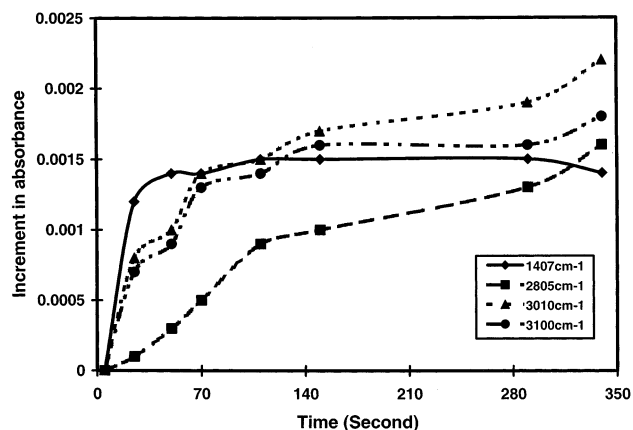
RF Plasma-Induced Hydrogen Bonding on Kaolinite

J. Phys. Chem. B, Vol. 107, No. 3, 2003 **697**

Figure 2. The increment in intensity as a function of time of selected IR bands from the results shown in Figure 1.

treated samples is possibly linked to the increase in intensity of the IR-induced bands.

The corresponding increment in intensity of four plasma-induced IR bands in Figure 1 is shown in Figure 2. The increase in the intensity of the 1407 cm^{-1} band occurred mostly over the first minute but changed little in the following few minutes over which the time-resolved scans were taken. In contrast, the intensity of the other three bands (2805, 3010, and 3100 cm^{-1}) continued to increase for around 150 s. Therefore, although these bands appear concomitantly in the IR spectra as a result of the plasma treatment, the differing time-dependent behavior indicates that the source of the vibration for the band at 1407 cm^{-1} is not the same as that for the other bands in this group.

Temperature Dependence of RF Plasma-Induced IR Bands. One of the primary means of verifying the presence of hydrogen bonding in a material is to observe the frequency and intensity changes in the IR spectra of the material as a result of decreasing the temperature.[12−17,19,20] The change in temperature causes a shift in equilibrium of a variety of polymeric forms of hydrogen-bonded species, each with a characteristic vibration frequency and absorption coefficient.[13] Two plasma-treated kaolinite samples (5 h and 10 min in Ar plasma, respectively), pre-cooled with liquid nitrogen were scanned separately a number of times over the time period in which each of them was allowed to defrost freely in a DRIFT cell.

The DRIFT spectrum taken 5 s after placement in the DRIFT cell of the pre-cooled kaolinite, which had been treated in Ar plasma for 5 h, showed two greatly enhanced new IR bands at ∼3250 and ∼3385 cm^{-1}, while the bands previously associated with plasma treatment, 3100, 3010, and 2805 cm^{-1}, were no longer apparent (Figure 3A). As the sample increased in temperature to ambience over the following few minutes, the intensity of the two new bands decreased rapidly and the former plasma-induced IR bands gradually became more apparent. There was no observable change in the region around the 1407 cm^{-1} band during this process.

For kaolinite treated under Ar plasma for 10 min, the DRIFT spectra of the pre-cooled kaolinite sample (Figure 3B) showed a similar behavior with respect to the presence of a new band at ∼3250 cm^{-1} and possibly a new band in the ∼3385 cm^{-1} region, and absence of plasma-induced IR bands as it increased in temperature to ambience. However, the enhanced intensity of the new bands in this sample was much smaller than those of the sample plasma-treated for 5 h. These two experiments confirm that the plasma-induced IR bands at 2805, 3010, and 3100 cm^{-1} are hydrogen-bonded surface functional groups, and are most likely hydroxyl groups.

The intensity and frequency of the plasma-induced IR band at 1407 cm^{-1} was not affected by temperature which implies that this band is not likely to be directly associated with the bending vibration of hydrogen-bonded surface functional groups. However, as this band is always present on plasma-treated kaolinite concomitantly with these hydrogen-bonded functional groups, the formation of the functional group attributed to the 1407 cm^{-1} band may be structurally related to the formation of the hydrogen-bonded functional groups.

In Situ Deuterium Exchange of Ar Plasma-Treated Kaolinite. To further verify the nature of the surface functional groups responsible for plasma-induced IR bands and their location on the kaolinite, the plasma-treated kaolinite was deuterated with D$_2$O at room temperature, and then rehydrated with H$_2$O to observe the changes in IR frequency of hydroxyl groups and plasma-induced IR bands. For the kaolinite treated under Ar plasma for 5 h, the only change in the DRIFT spectra as a result of in situ deuterium exchange was a minor reduction in intensity of the plasma-induced IR bands. As in situ deuteration at room temperature can only replace hydrogen on the surface of the kaolinite, the small reduction in intensity of the IR bands may be attributed to the hydroxyl groups on the surface (basal surface and edge surface) of the kaolinite.[8,11] The estimated surface hydroxyl to bulk hydroxyl group ratio of the kaolinite is considerably less than 1% which means that even if all the hydroxyl groups on the surface of the kaolinite were exchanged by deuterium, the intensity of OD bands would be still too small to be distinguishable.

As none of the plasma-induced functional groups were significantly affected by in situ deuterium exchange at ambient temperature, it implies that they must be situated below the surface where they are not able to be affected by this type of deuteration.

Deuterium Oxide Plasma Treatment of Kaolinite. D$_2$O plasma treatment on Georgia kaolin was used as an alternative means to understand the nature of the plasma-induced functional groups on the kaolinite. This technique involves surface deuteration of kaolinite conducted during D$_2$O (vapor) plasma treatment. Because the plasma-generated ions are continuously bombarding the surface of the kaolinite under a reasonably good vacuum, it was possible that this technique could result in a more extensive H−D substitution of kaolinite than that achieved in the results presented in the previous experiment.

The DRIFT spectra taken immediately after the D$_2$O plasma treatment showed that besides the regular plasma-induced IR bands observed as a result of Ar plasma treatment, there were new bands at 2726, 2702, 2677, and a shoulder at ∼2650 cm^{-1}. It is apparent from the isotopic shift ν_{OH}/ν_{OD} expected during this process of 1.355−1.366, that these bands are the OD bands related to the OH bands at 3695−3620 cm^{-1}. From the results in Table 2, the extent of the D−H exchange is relatively low during D$_2$O plasma treatment.[30,31,33] The plasma-induced OH bands in the 3100−2800 cm^{-1} region would be expected to shift to the 2300−2050 cm^{-1} region after deuterium substitution but this was not observed. Hence, D$_2$O plasma treatment of kaolinite was not found to be a suitable method to distinguish the nature and site of plasma-induced hydrogen-bonded surface functional groups.

Hydrothermal Deuterium Exchange of RF Plasma-Treated Kaolinite. Previous studies have shown that significant deuteration of subsurface lattice hydroxyl groups of kaolinite requires high temperature, high pressure, and a very long contact time, or indirect deuteration such as intercalation.[23−33] In this study hydrothermal deuteration on kaolinite, treated in Ar plasma
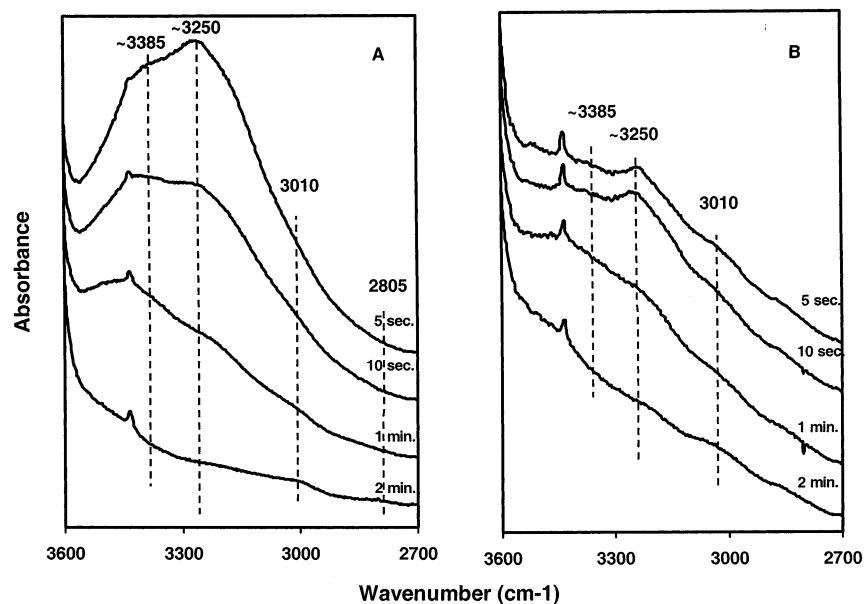
Figure 3. Time-resolved DRIFT scans of plasma-treated Georgia kaolin after removal from the cooling chamber (−196 °C); (A) Georgia kaolin plasma treated for 5 h; (B) Georgia kaolin plasma-treated for 10 min.

TABLE 2: Comparison of Various Deuteration Techniques on Georgia Kaolin

technique	sample	experiment conditions	extent of deuteration		inherent OH(OD) bands			hydrogen-bonded OH(OD) bands		
			S_{OD}/S_{OH}	$S_{OD}/(S_{OH}+S_{OD})\%$	ν_{OH}	ν_{OD}	ν_{OH}/ν_{OD}	ν_{OH}	ν_{OD}	ν_{OH}/ν_{OD}
in situ deuteration	Ar plasma-treated Georgia kaolin for 5 h	ambient, ~1 Torr, 30 min	0	0	N/A	N/A	N/A	N/A	N/A	N/A
D$_2$O plasma treatment	Ar plasma-treated Georgia kaolin for 5 h	~100 °C, 0.2 Torr, 5 h	0.0816 (0.0763)[a]	7.54 (7.09)	3695	2726	1.355	3100	0	N/A
					3669	2702	1.358	3010	0	N/A
					3654	2677	1.365	2805	0	N/A
					3620	2650	1.366			
hydrothermal deuteration	Ar plasma-treated Georgia kaolin for 5 h	~150 °C, 10 atm, 3 days	0.243	20.0	3695	2731	1.353	3100	0	N/A
					3669	2722	1.348	3010	0	N/A
					3654	2698	1.354	2805	0	N/A
					3620	2673	1.354			
hydrothermal deuteration	Georgia kaolin	~300 °C, 30 atm, 5 days	0.890	47.1	3695	2723	1.353			
					3669	2711	1.355			
					3654	2697	1.355			
					3620	2671	1.355			
hydrothermal deuteration	Ar plasma-treated Georgia kaolin for 5 h	~300 °C, 30 atm, 5 days	1.33	57.1	3693	2727	1.354	3430[b]	N/A	N/A
					3670	2710	1.354	3370	N/A	N/A
					3653	2698	1.354	3230	N/A	N/A
					3620	2671	1.355		2422[c]	1.280
					939	719	1.306		2350	1.281
					915	689	1.328		2260	1.241
hydrothermal deuteration	Ar plasma-treated Georgia kaolin for 10 min	~300 °C, 30 atm, 5 days	1.21	54.8	3695	2727	1.355	3370	N/A	N/A
					3670	2709	1.355	3240	N/A	N/A
					3654	2698	1.354			
					3620	2671	1.355			
					939	719	1.306			
					915	688	1.330			

[a] The figure in bracket was obtained after the sample had been exposed in air for 4 days. [b] These IR bands were not a direct result of plasma treatment. [c] ν_{OH} was taken value of plasma-induced IR bands at 3100, 3010, and 2805 cm^{-1}.

for 5 h, was initially conducted at 150 °C, 10 atm, for 3 days. About 20% D−H exchange on OH groups exhibiting bands at 3690−3620 cm^{-1} took place as a result of this process with no detectable D−H exchange in Al−OH bending vibration at 935 and 915 cm^{-1} (Table 2). Furthermore, the plasma-induced IR bands were still visible and no corresponding D−H substituted OD bands were observed in the 2700−3300 cm^{-1} region.

As a result of increasing hydrothermal deuteration conditions to 300 °C at 30 atm for 5 days, the extent of deuteration of Georgia kaolin with similar plasma treatment was increased to approximately 60% (Table 2). The time-resolved scans of the DRIFT spectra are shown in Figure 4 and some enlarged regions

of these scans are displayed in Figure 5. The intensities of the OH-related vibration bands in the region A at 3690−3620 cm^{-1} and region B at 937, 915 cm^{-1} were reduced due to isotopic substitution, and the corresponding OD bands in region A′ at 2726−2671 cm^{-1} and in region B′ at 720, 688 cm^{-1} were increased as shown in Figure 4. The intensity of both the OH and OD bands of these bands did not alter during the time period associated with the time-resolved scans. This kind of behavior was also observed for hydrothermally deuterated Georgia kaolin which had not undergone plasma treatment. This type of deuteration is attributed to the D−H exchange in bulk structure of the kaolinite.
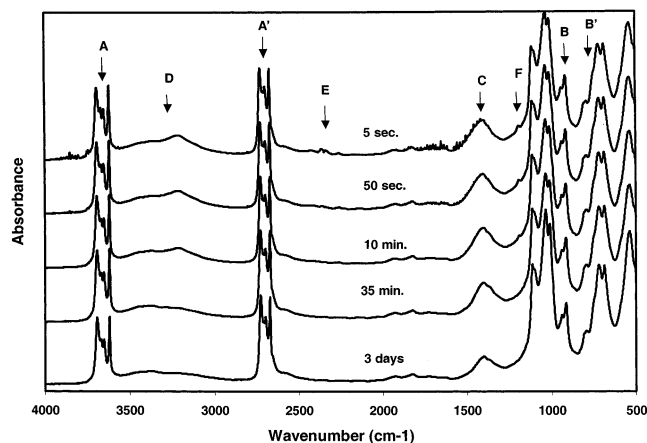
RF Plasma-Induced Hydrogen Bonding on Kaolinite

J. Phys. Chem. B, Vol. 107, No. 3, 2003 **699**

Figure 4. Time-resolved DRIFT scan of Ar plasma-treated (5 h) Georgia kaolin after intense hydrothermal deuteration (300 °C, 30 atm for 5 days).

In contrast to these bands at A, A′, B, and B′ regions, some other bands arising from this intense hydrothermal deuteration of the plasma-treated kaolinite showed a reduction in intensity as a function of time during time-resolved scans. As these bands lost intensity by coming in contact with moisture but remained unchanged in dry air, water vapor in air must be interacting with these functional groups on the deuterated kaolinite. This implies that D−H exchange must be taking place during this process and these diminishing IR bands are OD-related vibration bands. This type of band is visible in three separate IR regions 2900−3500, 2200−2500, and 1192 cm $^{-1}$ (regions D, E, and F in Figures 4 and 5). The band in region F at 1192 cm $^{-1}$ was attributed to OD bending vibration due to substitution of O−H at the 1640 cm $^{-1}$ region.

2800−3200 cm $^{-1}$ Region of RF Plasma-Induced IR Bands. The three bands at 2422, ∼2350 (which was obtained by subtracting the overlapped CO_2 band with Georgia kaolin undergoing deuteration without plasma treatment), and 2260 cm $^{-1}$ (region E in Figures 4 and 5) showed a reduction in intensity over the time period of the time-resolved scans. Assuming a frequency shift of $\nu_{OH}/\nu_{OD} = 1.35$ as a result of the deuteration, the corresponding OH bands of these three bands should be located at 3267, 3172, and 3051 cm $^{-1}$, respectively. These values are about 150−250 cm $^{-1}$ higher than those of plasma-induced OH bands found in the 3100−2800 cm $^{-1}$ region. Plasma-induced IR bands were neither evident immediately after hydrothermal deuteration of the plasma-treated kaolinite nor visible at the conclusion of the time-resolved scans. The inverse relationship in the presence of these two sets of bands indicates that the bands at 2422, ∼2350, and 2260 cm $^{-1}$ are most likely the three deuterium-replaced OH bands responsible for the plasma-induced IR bands at 3100, 3010, and 2080 cm $^{-1}$, respectively.

1407 cm $^{-1}$ Region of RF Plasma-Induced IR Band. In contrast to the above observed reduction of the intensity of IR-induced OH bands, the hydrothermal deuteration on plasma-treated Georgia kaolin significantly enhanced the intensity of 1407 cm $^{-1}$ band. This enhancement was accompanied by the addition of two unresolved bands at ∼1345 and ∼1385 cm $^{-1}$ on the shoulder of the 1407 cm $^{-1}$ band (region C in Figures 4 and 5). As there was no observed band of the deuterated plasma-treated kaolinite at 1042 cm $^{-1}$ (which would be the position of the deuterated 1407 cm $^{-1}$ if this band was directly associated with an OH group), it implies that the 1407 cm $^{-1}$ band does not belong to a bending vibration of a hydroxyl group. From

the results here and in previous results above, this band is more likely to be associated with a lattice vibration which arises from structural disturbance as a result of the plasma treatment and is further affected by structural disturbance during hydrothermal deuteration of the kaolinite. The enhanced 1407 cm $^{-1}$ band was relatively unchanged in intensity during the time-resolved scans but the intensity did decrease slightly after 3 days in air.

The 1407 cm $^{-1}$ band could arise from the bending vibration of either Al−O or Si−O associated with the gibbsite layer or the siloxane layer, respectively. Although the bending vibration of both bonds is usually visible in IR spectra at about 1000 cm $^{-1}$, an enhanced electronegativity of the atoms in the neighborhood of Al and Si as a consequence of the plasma-induced changes, such as forming hydrogen bonding, could shift this vibration mode to a higher wavenumber region.[2,3]

Deuteration-Induced Functional Groups on RF Plasma-Treated Kaolinite. The new bands in the IR spectra, at 3214 and 3363 cm $^{-1}$, behaved similarly to the three OD bands at 2422, ∼2350, and 2260 cm $^{-1}$, with respect to reduction in intensity with time during the time-resolved scans of the DRIFT spectra after intense deuteration (region D in Figures 4 and 5). The contour of both bands is broad. These features are typical characteristics of hydrogen-bonded hydroxyl groups.[12] A possible explanation for these new bands is that they are due to an intermediate hydrogen-bonded OH group associated with structure adjustments as a result of the hydrothermal deuteration. It was shown in a previous study[1] that the surface structure of plasma-treated kaolinite is altered during intensive plasma particle bombardment. It is possible that as a result of deuteration, these altered structures of kaolinite could be further altered due to D−H exchange, resulting in the temporary formation of a new form of OH bonding on the surface of kaolinite. As the H−D exchange reverses when the deuterated sample is in contact with air, these temporary OH bonds are broken and the surface of the plasma-treated kaolinite reverts to the original structure following plasma treatment.

Beside the bands at 3363 and 3214 cm $^{-1}$, there are shoulder bands in region D at ∼3430 cm $^{-1}$ (Figures 4 and 5). This shoulder band was initially overshadowed by these bands at 3363 and 3214 cm $^{-1}$, but became apparent as the latter bands decreased in intensity with time after the sample was in contact with air. Similar hydrothermal deuteration of Georgia kaolin without plasma treatment, did not produce these types of IR bands in its DRIFT spectra. It is concluded that the formation of these bands on the surface of the kaolinite is an indirect result of plasma treatment on kaolinite. Similar to the two neighboring bands at 3363 and 3214 cm $^{-1}$, the band at ∼3430 cm $^{-1}$ also exhibits typical characteristics of a hydrogen-bonded functional group with a downward trend in frequency and broadening in contour.[12,13]

As three IR bands at 3100, 3010, and 2805 cm $^{-1}$ have been described as plasma-induced hydrogen-bonded hydroxyl group, these new bands at 3363, 3214, and ∼3430 cm $^{-1}$ should be described as deuteration-induced IR bands on RF plasma-treated kaolinite. It is noted that some of the deuteration-induced IR bands still remained even after rehydration of deuterated kaolinite. The hydrothermal deuteration on RF plasma-treated kaolinite not only resulted in D−H exchange in the lattice of the kaolinite, but also from this study it appears to result in a solid-state reaction, or further surface reconstruction of the kaolinite which has previously been modified by plasma treatment.

DRIFT spectra of a kaolinite which has been hydrothermally deuterated under the same conditions as the previous sample,
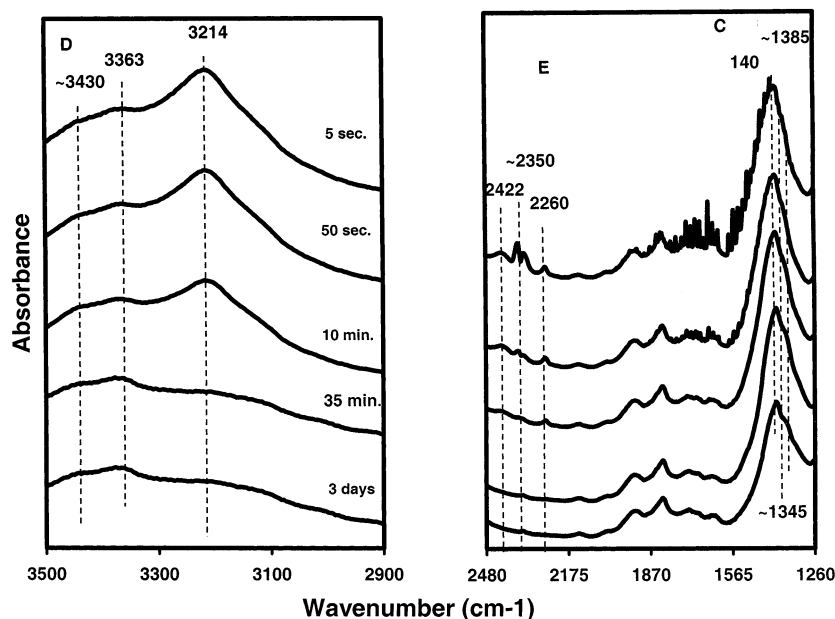
Figure 5. Detailed view of newly merged IR bands in regions D, E, and C of Figure 4.
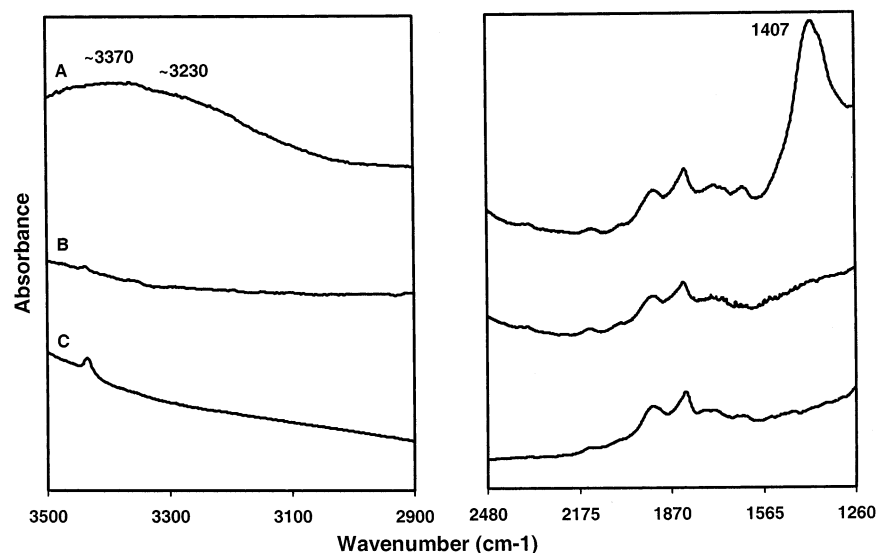

Figure 6. Comparison study of DRIFT spectra of several Georgia kaolin. (A) Intense hydrothermal deuterated (300 °C, 30 atm for 5 days) Georgia kaolin treated in Ar plasma for 10 min. (B) Intense hydrothermal deuterated (300 °C, 30 atm for 5 days) Georgia kaolin without plasma treatment. (C) Untreated Georgia kaolin.

but which had received 10 min of plasma treatment prior to deuteration, exhibited some features observed in the previous sample, including inherent lattice-replaced OD bands at A′ and B′ regions, the greatly enhanced 1407 cm^{-1} band, and newly formed broad bands at ~3370 and ~3230 cm^{-1} (trace A in Figure 6). However, neither of the OD bands at 1200 and 2200–2500 cm^{-1} in Figures 4 and 5 is visible for this sample, nor does the intensity of IR bands vary as a function of time in air as exhibited for the 5 h plasma-treated sample.

To directly compare the significance of prior plasma treatment on the changes in the IR spectra as a result of this type of hydrothermal deuteration, Figure 6 also includes the corresponding spectra of severely hydrothermal-deuterated Georgia kaolin, which has been subjected to no plasma treatment, and raw Georgia kaolin without any plasma treatment or hydrothermal deuteration. In the previous study,[1] it was observed that the intensity of plasma-induced IR bands on the surface of kaolinite which had undergone 10 min plasma treatment is more than 50% of that for the sample which had undergone 5 h plasma treatment. The DRIFT spectra of 10 min and 5 h plasma-treated samples displayed quite large differences in enhancement of plasma-induced IR bands at low temperature (Figure 3). Here, the hydrothermal deuteration on the samples also demonstrates a significantly different behavior in formation of variable IR bands. It is therefore apparent that, although the intensity of plasma-induced IR bands on Ar plasma-treated kaolinite between 10 min and 5 h of process is not greatly different, the qualitative difference in the resultant surface characteristics between these samples undergoing deuteration is quite significant.

A summary of the results for the deuterium exchange-related experiments is given in Table 2. The isotopic shifts of most of the stretching vibration bands are consistent with $\nu_{OH}/\nu_{OD} = 1.353–1.355$, except for the severe deuteration of plasma-treated kaolinite for 5 h. The extent of deuteration among the plasma-treated samples was generally increased as more severe condi-

RF Plasma-Induced Hydrogen Bonding on Kaolinite

J. Phys. Chem. B, Vol. 107, No. 3, 2003 **701**

tions were applied for deuterium exchange. The difference in extent of deuteration between well- (longer time) plasma-treated kaolinite and untreated kaolinite was about 10% even though the hydrothermal deuteration for all samples was conducted under the same conditions. A previous study has concluded that well crystalline materials are poorly deuterated, whereas materials with a loose, easily accessible disordered structure are the easiest.[3] Although the initial form of these three samples were all well crystalline Georgia kaolin, structural damage on Georgia kaolin as a result of RF plasma bombardment is significant.[1] This explains the observed extent of deuteration of three kaolinites, from high to low, of well plasma-treated > poorly plasma-treated > untreated Georgia kaolin.

Discussion

The time-resolved scans of RF plasma-treated kaolinite have shown that variation of the intensity of the plasma-induced lattice band 1407 cm^{-1} is not consistent with those of plasma-induced hydrogen-bonded hydroxyl bands at 3100, 3010, and 2805 cm^{-1}. The intensity of the latter bands has continuously increased for several minutes since the start of the time-resolved scan (Figures 1 and 2). This implies that the moisture absorbed on the surface of the kaolinite affects the formation of plasma-induced hydrogen-bonded hydroxyl groups. The infrared region 2700−3500 cm^{-1} is the summation of a receding baseline and ascending new bands of hydrogen-bonded hydroxyl groups. The receding baseline in the IR trace is actually the result of removal of loosely hydrogen-bonded absorbed water vapor.[3,8,11] It appears that the surface of the plasma-treated kaolinite is in equilibrium between removal of loosely hydrogen-bonded absorbed water and formation of plasma-induced hydrogen-bonded hydroxyl groups. The initial surface of the plasma-treated kaolinite was probably covered with absorbed water when exposed to the air, which produce a weak broad IR band at 2700−3500 cm^{-1}.[3,10] After the sample was placed in the DRIFT cell in which dry air continuously flushed over the surface of the kaolinite, weakly bonded water vapor would be rapidly removed from the surface of the sample changing the surface sorption state of the kaolinite. This kind of behavior implies that the surface bonding structure of plasma-treated kaolinite is in a "reversibly self-adjustable" state.

Kaolinite is a layered aluminosilicate consisting of both a siloxane basal plane and a gibbsite basal plane. The structural characteristics of the siloxane layer can be regarded as a continuous network of Si−O 12-member rings and the gibbsite layer as a network of Al−O 12-member rings (Figure 7, structures A and B, respectively). The internal −OH and −O− groups between the siloxane layer and gibbsite layers are connected with both basal layers to form a repeatable AlSi$_2$O$_3$ six-member ring (Figure 7, structure C). Of these three types of structures, both the 12-member gibbsite layer ring (structure B) and six-member cross layer ring (structure C) are directly involved in bonding with hydroxyl groups. No hydroxyl group is linked directly to the siloxane layer. The 3620−3670 cm^{-1} bands in the kaolinite IR spectra resulted from the intrinsic vibration of hydroxyl groups which showed little hydrogen bonding nature.[8] The wavenumber of the RF plasma-induced IR bands associated with hydrogen bonding on the surface and subsurface region of RF plasma-treated kaolinite is much lower, which implies the formation of much stronger hydrogen bonding.[14] Such a low wavenumber for hydrogen bonding is generally an indication that intramolecular hydrogen bonding is formed inside the material. This implies that intrinsic hydroxyl group bonding in kaolinite must be broken to permit the
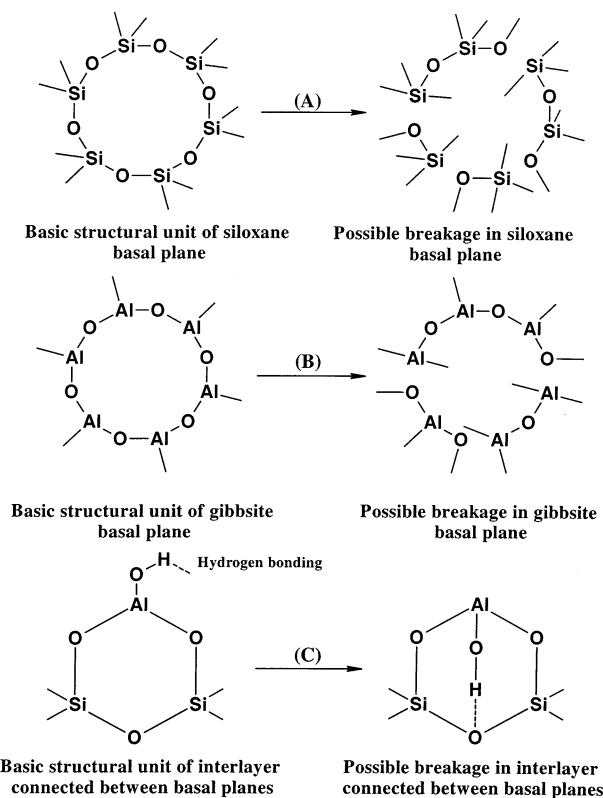

Figure 7. Three types of basic structural units of kaolinite and their possible alterations as a result of plasma treatment.

formation of new forms of hydroxyl groups during plasma treatment.

Previous results suggested that slight surface structural damage on the surface of the kaolinite occurs during the plasma treatment.[1] Spectroscopic evidence has indicated that the damage results in reconstruction of surface hydroxyl groups involved in hydrogen bonding. As hydroxyl groups in kaolinite structure are bonded with either the 12-member gibbsite layer ring or the six-member cross layer ring, breaking either structure will be essential to release hydroxyl groups from old bonding sites to the new. As the new form of hydroxyl bonding is established, new IR adsorption bands become evident. If the new form of hydroxyl group primarily comes from the gibbsite layer, the 12-member Al−O ring would break as a large molecular ring is often structurally unstable. In contrast, if the new form of hydroxyl group was associated with the interlayer structure, the AlSi$_2$O$_3$, this six-member ring may be less likely to be altered as a six-member ring structure is much more stable. And such a structure may also be beneficial to the formation of hydrogen bonds because the oxygen in the six-member ring could form intramolecular hydrogen bonds with ring-associated hydroxyl groups to form another relatively stable six-member cross ring (Figure 7, structure C). The latter structure appears more realistic in explaining the results observed in this study, although neither bonding model could be ruled out until further experimental evidence is available.

Besides being associated with the plasma-induced IR bands (2805, 3010, and 3100 cm^{-1}) arising from hydrogen-bonded hydroxyl groups, the bonding vibrations from Si−O or Al−O are also the most likely source of the IR band at 1407 cm^{-1}. This band does not appear to involve hydrogen bonding because its IR intensity was basically unchanged during the low-temperature DRIFT analysis, and the IR vibration frequency did not alter as a result of hydrothermal deuteration. However, the alteration in the lattice during hydrothermal deuteration

caused the intensity of this band to increase and the appearance of new shoulder bands at a lower wavenumber.

Because the formation of plasma-induced hydroxyl groups takes place in both the surface and the subsurface regions, it would be expected that the sites of initial impact by the plasma ions, i.e., the surface itself, would be the first to form these functional groups, with sites in the shallow subsurface region taking longer and those in the deep subsurface region, the longest. The plasma-induced functional groups on kaolinite which had been treated for 10 min with Ar plasma, are most likely formed on the surface or may also include isolated spots in which the shallow subsurface region is affected. With the more extensive 5 h plasma treatment, more structural bonds would be broken and more plasma-induced hydroxyl groups are created in the shallow and deep subsurface region of the kaolinite, ultimately leading to the whole subsurface region or near-subsurface region being affected. As the coverage of partially freed hydroxyl groups increases so does the continuity of hydrogen bonding, eventually forming a network of bonding which can be further stabilized by a cooperatively bonded hydrogen-bond to form an energetically favorable finite or infinite hydrogen bond chain.[19,20] The difference in the formation of hydrogen bonding from isolated or continuous forms could explain the observed different behavior of both the cryogenic DRIFT scan experiment and the severe hydrothermal deuteration on plasma-treated kaolinites for periods between 10 min and 5 h, although the intensity of plasma-induced IR bands is different but not significant.

Conclusion

The variety of deuteration on Georgia kaolin with or without plasma treatment has confirmed that surface modification on kaolinite occurred both on the surface and in the subsurface region. The new IR bands at 2805, 3010, and 3100 cm^{-1} are attributed to stretching vibration of the hydrogen-bonded hydroxyl groups that resulted from RF plasma action. The new IR band at 1407 cm^{-1} is attributed to the bending vibration of Al$-$O($-$OH) or Si$-$O($-$OH) associated with hydrogen-bonded hydroxyl groups. Severe hydrothermal deuteration on plasma-treated kaolinite not only substituted OH groups in the lattice involved with hydrogen bonding but also caused further disturbance on the partially plasma-altered kaolinite structure. During hydration in air for severely deuterated kaolinite, some inner structure self-adjustment had taken place.

References and Notes

(1) Ming, H.; Spark, K. M.; Smart, R. St. C. *J. Phys. Chem. B* **2001**, *105* (16), 3196−3203.

(2) Socrates, G. *Infrared characteristic group frequencies tables and charts*, 2nd ed.; John Wiley & Sons: New York, 1994.

(3) Marel, H. W. van der; Beutelspucher, H. *Atlas of infrared spectroscopy of clay minerals and their admixtures*; Elsevier: New York, 1976.

(4) Lazarev, A. N.; *Vibrational spectra and structure of silicates*; English Translation by Archard, G. D.; Farmer, V. C., Ed.; Consultants Bureau: New York, 1972.

(5) Farmer, V. C. *The infrared spectra of minerals*; Mineralogical Society: London, 1974.

(6) Russell, J. D.; Fraser, A. R. *Clay Mineralogy−spectroscopic and chemical determinative methods*, 1st ed.; Wilson, M. J., Ed.; Chapman & Hall: New York, 1994; pp 11−67.

(7) McGuire, G. E. *Handbook of deposition technologies for films and coatings science, technologies and applications*, 2nd ed.; Bunshah, R. F., Ed.; Noyes Publications: Park Ridge, NJ, 1994; pp 763−821.

(8) Hair, M. L. Infrared spectroscopy in surface chemistry; Marcel Dekker: New York, 1967.

(9) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The handbook of infrared and Raman characteristic frequencies of organic molecules*; Academic Press: New York, 1991.

(10) Nyquist, R. A.; Kagel, R. O. *Infrared spectra of inorganic compounds (3800−45 cm^{-1})*; Academic Press: New York, 1971.

(11) Little, L. H. *Infrared spectra of adsorbed species*; Academic Press: New York, 1966.

(12) Sheppard, N. *Hydrogen bonding*; Hadzi, D., Thompson. H. W., Eds.; Pergamon Press: Elmsford, NY, 1959; pp 85−105.

(13) Pimentel, G. C.; McClellan, A. L. *The hydrogen Bond*; W. H. Freeman and Company: New York, 1960.

(14) Hamilton, W. C.; Ibers, J. A. *Hydrogen bonding in solids methods of molecular structure determination*; W. A. Benjamin Inc.: Reading, MA, 1968.

(15) Vinogradov, S. N.; Linnel, R. H. *Hydrogen Bonding*; VNR Company: New York, 1971.

(16) Kollman, P. A.; Allen, L. C. *Chem. Rev.* **1972**, *3* (72), 283−303.

(17) Novak, A. *Struct. Bonding* **1974**, *18*, 177−215.

(18) Bellamy, L. J. *The infrared spectra of complex molecules, II*; Chapman and Hall: New York, 1980.

(19) Jeffrey, G. A.; Saenger, W. *Hydrogen bonding in biological structures*; Springer-Verlag: New York, 1991.

(20) Jeffrey, G. A. *An introduction to hydrogen bonding*; Oxford University Press: New York, 1997.

(21) Michaelian, K. H.; Bukka, K.; Permann, D. N. S. *Can. J. Chem.* **1987**, *65*, 1420−1423.

(22) Frost, R. L.; Johansson, U. *Clays Clay Miner.* **1998**, *46*, 466−477.

(23) McAuliffe, C. D.; Hall, N. S.; Dean, L. A.; Hendricks, S. B. *Proc. Soil Sci. Soc. Am.* **1947**, *12*, 119−123.

(24) Faucher, J. A.; Thomas, H. C. *J. Phys. Chem.* **1955**, *59*, 189−191.

(25) Romo, L. A. *J. Phys. Chem.* **1956**, *60*, 987−989.

(26) Roy, D. M.; Roy, R. *Geochim. Cosmochim. Acta* **1957**, *11*, 72−85.

(27) Stubican, V.; Roy, R. *Z. Kristallogr.* **1961**, *115*, 200−214.

(28) Stubican, V.; Roy, R. *J. Phys. Chem.* **1961**, *65*, 1348−1351.

(29) Fripiat, J. J.; Toussaint, F. *J. Phys. Chem.* **1963**, *67*, 30−36.

(30) Ledoux, R. L.; White, J. L. *Science* **1963**, *143*, 244−246.

(31) Ledoux, R. L.; White, J. L. *Science* **1964**, *145*, 47−49.

(32) Wada, K. *Clay Miner.* **1967**, *7*, 51−61.

(33) Rouxhet, P. G.; Samudacheate, N.; Jacobs, H.; Anton, O. *Clay Miner.* **1977**, *12*, 171−180.

(34) Frost, R. J.; Van der Gaast, S. J. *Clay Miner.* **1997**, *32*, 471−484.

(35) Frost, R. L.; Vassallo, A. M. *Clays Clay Miner.* **1996**, *44*, 635−651.

(36) Frost, R. L. *Clay Miner.* **1997**, *32*, 65−77.

(37) Michaelian, K. H. *Can. J. Chem.* **1986**, *64*, 285−289.

(38) Grim, R. E. *Clay mineralogy*, 2nd ed.; McGraw-Hill: New York, 1968.

(39) Mendelovici, E.; Yariv, S.; Villalba, R. *Clay Miner.* **1979**, *14*, 323−331.

(40) Nguyen, T. T.; Janik, L. J.; Raupach, M. *Aust. J. Soil Res.* **1991**, *29*, 49−67.