



Role of hydroxy-aluminosilicate ions (proto-imogolite sol) in the formation of humic substances

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Abstract

Little is known of the role of solution species of soil aluminosilicates in the formation of humic substances. Catalysis by hydroxy-aluminosilicate (HAS) ions, one of the major forms of soluble aluminum and silicon and the precursor of noncrystalline aluminosilicates in acidic natural environments, in catechol humification was investigated in this study by using UV-visible, FTIR, and solid state ^{13}C CP-MAS NMR spectroscopies, X-ray diffractometry, atomic force microscopy, and elemental analysis. Hydroxy-aluminosilicate ions substantially promoted the oxidative polymerization and ring cleavage of catechol, resulting in the formation of black precipitates of humic macromolecules. This abiotic catalysis by HAS ions merits close attention in understanding the formation and related geochemistry of humic substances especially in acidic environments in temperate and subtropical regions. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Sugars, polyphenols, and amino compounds are the main precursors of humic substances in soils and sediments. It was recognized at the beginning of last century that enzymes produced by micro-organisms and plants are directly involved in the formation of humic substances (Stevenson, 1994). Ever since, extensive studies have been carried out to elucidate the principles of biological catalysis (Bollag et al., 1998; Huang et al., 1999; Naidja et al., 1999). However, the biochemistry of the formation of humic substances is still one of the least understood aspects of humus chemistry and one of the most intriguing (Stevenson, 1994). There are different theories and arguments on the pathway of humic substances formation in soils. Besides biotic catalysis, previous research conducted in the last three decades has established that abiotic soil constituents react with organic compounds, analogous to enzyme-mediated transformation, yielding humic substances (Shindo and Huang, 1982, 1984; McBride, 1987; Bollag et al., 1995;

Naidja et al., 1999). Abiotic catalysts, including a series of soil minerals such as clay minerals and metal oxides, promote the transformation of phenolic compounds to humic macromolecules through their oxidative polymerization, ring cleavage, decarboxylation, and/or dealkylation (Wang et al., 1983a; Shindo and Huang, 1984; Huang et al., 1999; Huang, 2000; Majcher et al., 2000).

Recently, some researchers postulated that the accumulation of the residue of partially degraded materials from plants and micro-organisms is one of the important pathways to humic substance formation. Hydrophobic humic components in soil exerted hydrophobic protection towards easily degradable compounds. The associations of apolar molecules deriving from plant degradation and microbial activity incorporate polar molecules, thereby preventing their otherwise rapid microbial degradation, enhancing their persistence in soil, and resulting in the accumulation of humic substances in soils (Piccolo, 1996; Piccolo et al., 1999). This view suggests that humic matter may be composed of polar microdomains surrounded by more hydrophobic components (Spaccini et al., 2000).

The polymerization of polyphenols through abiotic and biotic catalytic processes is one of the important

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pathways to the formation of humic substances (Stevenson, 1994; Huang, 2000). Limited research data show that biotic and abiotic catalysts differ in their capacity to mediate the polymerization of phenolic compounds (Bollag et al., 1995; Naidja et al., 1998; Huang et al., 1999). The ability of abiotic and biotic catalysts to catalyze the transformation should vary with their structural configuration and surface chemistry and the structure and functionality of the phenolic compounds concerned (Huang et al., 1999).

McBride et al. (1988) found that soluble Al increased the rate of oxidation of catechol by O₂, favoring the formation of highly colored solution products in the pH range 5–7 in a reaction period of less than 2 weeks, although no precipitation was observed. Recently, Liu and Huang (2000) reported that the presence of silicic acid and especially hydroxy-Al in solutions substantially promotes the darkening and polymerization of catechol under mild conditions which are very close to natural environments. Hydroxy-Al ions are much more powerful than silicic acid in catechol humification.

Hydroxy-aluminosilicate (HAS) ions are one of the major forms of soluble aluminum and silicon and the precursor of noncrystalline aluminosilicates under acidic (pH < 5.5) environments (Wada and Wada, 1980; Farmer et al., 1979; Lou and Huang, 1988). Although the interactions of HAS ions with soil clay minerals have been investigated (Lou and Huang, 1988, 1994), the role of HAS ions in the formation of humic substances in natural environments remains to be established.

The objective of the present study was to investigate the catalysis of HAS ions in the oxidative polymerization of catechol and the resultant formation of humic substances.

2. Materials and methods

The solution of HAS ions was prepared from 1.0×10^{-1} M AlCl₃ stock solution and 3.56×10^{-3} M mono-silicic acid which was obtained by passing sodium metasilicate solution through a H⁺-form Dowex 50W-X8 ion-exchange resin column. The mixture of these two solutions, with Si/Al molar ratio of 0.55, was titrated with 0.1 M NaOH under continuous stirring at the rate of 0.5 ml min⁻¹ to pH 4.4. A 1 M catechol solution (pH 4.4) was mixed with the HAS solution, bringing the final concentrations of catechol, Al, and silicic acid to 1.0×10^{-1} , 1.8×10^{-3} and 1.0×10^{-3} M, respectively. Both catechol solution and HAS solution alone were also prepared and served as controls. Thimerosal (sodium ethylmercurithiosalicylate) was added into the solutions at 0.02% to prevent the growth of micro-organisms. The solutions in the polypropylene bottles were sealed by Parafilm and shaken at 298.5 K for 10 to 60 days. The growth of micro-organisms was examined by incubating

1-ml suspension or solution obtained at the end of 1-day and 60-day reaction periods in tryptic soy agar (TSA) culture medium at 298.5 K for 1 week.

Small quantities of the reaction solutions or suspensions were removed at the end of 10, 20, 40, and 60-day reaction periods and centrifuged for 25 min at 20,000 *g*. The supernatants were analyzed by UV-visible spectroscopy on a Beckman spectrophotometer (Model DU 650, Beckman Instruments, Inc., Fullerton, CA, USA) in the wavelength range from 350 to 600 nm. The solid product at the end of a 60-day reaction period was dialyzed against deionized distilled water (molecular weight cut off = 1000) and freeze-dried.

The supernatants of the reaction systems at the end of a 60-day reaction period was analyzed by Fourier transform infrared spectroscopy (FTIR) on a Bio-Rad infrared absorption spectrophotometer (Model 3240, Bio-Rad Laboratories, Inc., Philadelphia, Pennsylvania) using a liquid cell. The solid product at the end of a 60-day reaction period and the standard soil HA (IS102H) obtained from the International Humic Substances Society (IHSS) were also examined by FTIR on the same machine using the KBr pellet technique. One milligram of the sample was mixed with 200 mg of KBr for the FTIR analysis. Twenty milligram samples of the solid product and the IHSS standard soil HA were used for the X-ray powder diffraction (XRD) analysis on a Rigaku diffractometer (Rigaku Company, Tokyo, Japan) with Fe-K_α radiation filtered by a graphite monochromator at 40 kV and 130 mA. The X-ray diffractograms were recorded from 4° to 80° 2θ with 0.005° 2θ steps at a speed of 0.5 °2θ per min. The solid state ¹³C nuclear magnetic resonance (NMR) spectra of the solid product and the IHSS standard soil HA were obtained at 90 MHz using magic angle spinning (MAS) and cross polarization (CP) on a NMR spectrometer (Model Avance 360, Bruker Company, Germany) at 301 K by using Fourier transformation. A sweep width setting of 40 kHz was employed to collect 500-point decay curves. Typical values used for parameters involved in CP-MAS NMR analysis were: 7-mm rotor tube, 5.0 kHz spinning rate, 1.5 ms contact time, 1.0 s recycle delay, and 80,000 transients collected. The line broadening for the process of the spectra was fixed at 100 Hz. The CP pulse sequence was used. To reduce the problem of overlapping spinning sidebands with the region of the spectrum occupied by the centrebands, the optimal MAS rate 5.0 kHz was used. The background contributed from empty rotor was subtracted from the signal collected for the sample.

For the atomic force microscopy (AFM) analysis of the precipitate, 5 mg of the solid product and the IHSS standard soil HA were dispersed in 12 ml deionized distilled water by using ultrasonification (Sonifier, Model 350, Danbury, CT) at 150 W for 2 min in an ice bath. The solid product- or IHSS HA-suspension was adjusted to

pH 5.0 with 0.01 M NaOH and HNO₃ and diluted to 15 ml. One drop of the suspension was deposited on a watch glass and air-dried overnight at room temperature (296.5±0.5 K). For the AFM analysis of the solution product, one drop of the supernatant was deposited on a watch glass and air-dried overnight at room temperature. The watch glass was then fastened to a magnetized stainless steel disk (diameter of 12 mm) with a double-sided tape. The 3-dimensional AFM images were obtained under ambient conditions by using a NanoScopeTMIII atomic force microscope (Digital Instruments, Inc., Santa Barbara, CA). The imaging areas were 5×5 μm². The scanner type was 1881 E and the scanner size was 15 μm. A silicon nitride cantilever with a spring constant of 0.12 N/m was used in the contact mode. The scanning rate was 22 Hz. To protect from experimental artifacts, the AFM cantilever was changed frequently. Furthermore, the scanning area and scanning angle were often changed by entering different area and angle parameters to detect the artifacts caused by adhesion of sample particles to AFM tips. The diameter of particles was measured by using *Section* analysis of the AFM based on 30 particles.

The C and H contents of the solid product was measured by a 2400 CHN Elemental Analyzer (Perkin Elmer Corp., Norwalk, CT). The contents of Al, Si, Fe, Mn, Zn, and Cu in the solid product were determined by atomic absorption spectrometry (AAS) on an atomic absorption spectrophotometer (Model 3100, Perkin Elmer Corp., Norwalk, CT) after the sample was digested with HF–HClO₄ mixture. The ash content of the solid product was determined by heating the sample in a muffle furnace at 600 °C for 4 h (Preston and Newman, 1992). Each experiment was conducted in triplicate.

3. Results and discussion

3.1. Characteristics of the liquid phase products

The color of the HAS–catechol system gradually changed from colorless to brown and dark brown as the reaction time increased and the rate of browning was much faster than that of the catechol solution alone. Further, black precipitates were observed in the HAS–catechol system at the end of a 10-day reaction period and the amount of precipitates increased with the increase of reaction time. The color of the catechol solution alone only changed from colorless to slightly brown and no black precipitates were observed even after a 60-day reaction time. The absorbance in the 350–600 nm range of the supernatant of the HAS–catechol system was much higher than that of the catechol solution alone at the same reaction time (Fig. 1), revealing that HAS substantially enhanced catechol darkening and promoted the polymerization of catechol at a slow rate

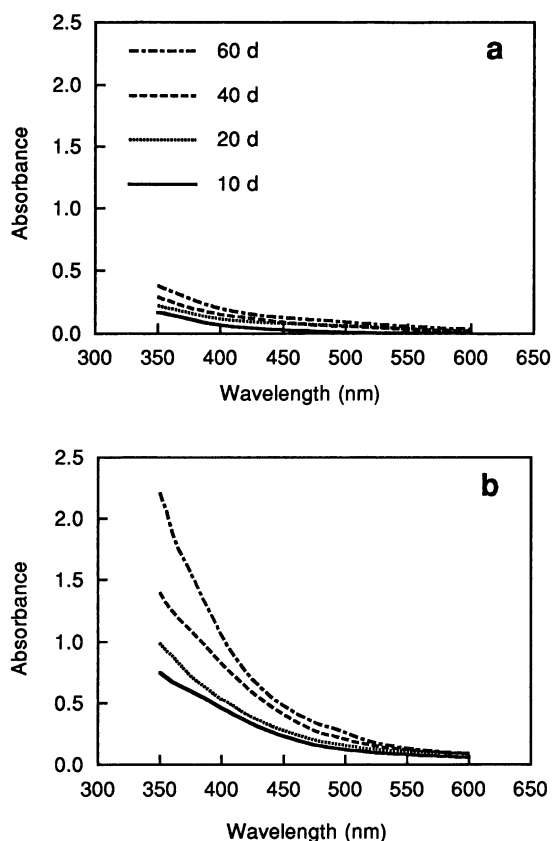


Fig. 1. Absorption spectra in the range of 350–600 nm of (a) catechol solution and (b) the supernatant of the HAS–catechol system at the end of various reaction periods.

of O₂ supply (the reaction vessel was sealed by Parafilm), room temperature, and a low pH value (4.4). The increase in the absorbance of the supernatant of the HAS–catechol system at lower wavelengths with the increase of reaction time was more pronounced, compared with that at higher wavelengths (Fig. 1). This suggests that the black precipitates predominantly resulted from the catechol-derived polymerized materials with higher molecular weights. No microbial growth was detected in the reaction system at both the beginning of the reaction and the end of a 60-day reaction period, indicating that the nature of the reaction was abiotic processes.

The AFM images of the catechol solution, HAS solution and the supernatant of HAS–catechol system at the end of a 60-day reaction time after air-drying are presented in Fig. 2. A 60-day aged catechol solution alone after air-drying was predominantly present as massive materials with a few spheroidal particles (Fig. 2a). These spheroidal particles were attributed to the catechol-derived humic molecules formed by the slow auto-oxidation of catechol in the presence of dissolved O₂. After air-drying, the HAS solution formed layers of

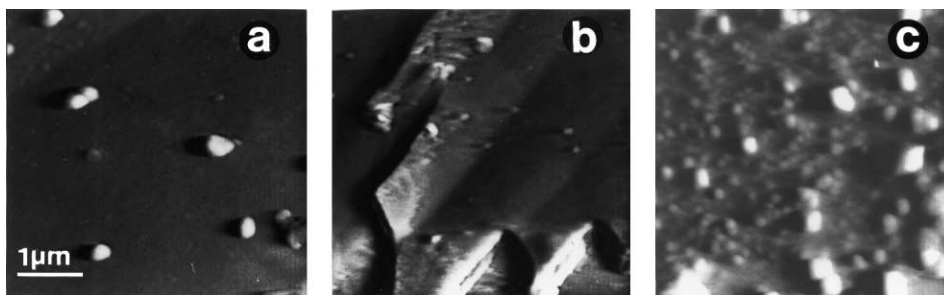


Fig. 2. Atomic force micrographs of the air-dried (a) catechol solution alone, (b) HAS solution alone, and (c) supernatant of the HAS-catechol system after 60-day aging. The scale is the same for (a) to (c).

precipitates (Fig. 2b). By contrast, a large amount of spheroidal particles and their aggregates were observed in the HAS-catechol supernatant at the end of a 60-day reaction period after air-drying (Fig. 2c). This further revealed that HAS ions substantially catalyzed catechol polymerization. The diameter of the spheroidal particles in the HAS-catechol reaction system after air-drying ranged from ca. 80 to 600 nm (Fig. 2c), which were much larger than that (ca. 50–150 nm) of the spheroidal particles of the IHSS standard soil HA (Liu and Huang, 1999). These spheroids larger than the standard soil HA apparently resulted from the aggregation, during the air-drying process, of the catechol-derived humic molecules and their complexation with HAS ions.

Five absorption bands at 1279, 1386, 1460, 1503, and 1636 cm^{-1} were observed in the difference FTIR spectrum between the supernatant of the HAS-catechol system and catechol solution alone at the end of a 60-day reaction period (Fig. 3). The band at 1279 cm^{-1} was attributed to the vibration of aromatic ethers ($\text{O}-\text{CH}_2$) (MacCarthy and Rice, 1985) and OH deformation of COOH (Stevenson, 1994). The band at 1386 cm^{-1} was from OH deformation and C–O stretching of phenolic OH, C–H deformation of CH_2 and CH_3 groups, and COO^- antisymmetric stretching (Stevenson, 1994). The band at 1460 cm^{-1} was due to the bending vibration of

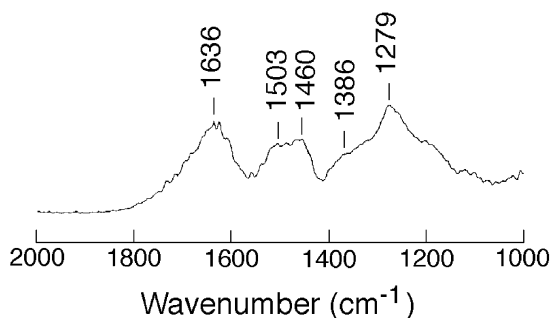


Fig. 3. Difference FTIR spectrum between the catechol solution and the supernatant of the HAS-catechol reaction system at the end of a 60-day reaction period.

aliphatic C–H groups (MacCarthy and Rice, 1985; Stevenson, 1994). The absorption band at 1503 cm^{-1} was from stretching vibrations of aromatic C=C bonds (Juo and Barber, 1969). The absorption bands at 1636 cm^{-1} was attributed to the vibration of the carboxylic groups COO^- and aromatic C=C double bond conjugated with C=O groups (MacCarthy and Rice, 1985). These absorption bands indicate that the solution reaction product in the HAS-catechol system was significantly different from the catechol solution alone at the same reaction time. The data indicates that the presence of HAS ions promoted the ring cleavage of catechol, resulting in the formation of aliphatic fragments.

3.2. Characteristics of the solid phase products

The IHSS standard soil HA and the non-purified precipitate formed in the HAS-catechol system were analyzed by solid state ^{13}C CP-MAS NMR spectroscopy under the same instrumental conditions. Since the solid product of HAS-catechol system was not purified, the organic C content was diluted by the precipitated HAS (Table 1). The intensity and broadness of the signals in the NMR spectrum of the in situ solid product

Table 1
Element contents of the solid product of the HAS-catechol system at the end of a 60-day reaction period (g/kg)^a

C	H	O	Al	Si	Fe	Mn	Cu	Zn	Ash
487.2 (590.1) ^b	28.6	334.2	101.2	48.8	n.d. ^c	n.d.	n.d.	n.d.	174.4

^a The standard error of the contents was less than 5%

^b The numbers in the parentheses are the element concentration after deashing. Based on the 500 g organic C kg^{-1} humic polymers (Wang et al., 1983b), the yield of humic polymers in the solid product was estimated to be 70.1 mg in the system studied, which was higher than the yield of humic polymers (55.0 mg) in the solid product in the hydroxy-Al-catechol system (Liu and Huang, 2000).

^c Not detectable. The detection limit for Fe, Mn, Cu, and Zn was, respectively, 0.025, 0.0125, 0.005, 0.002 g kg^{-1} .

and those of the IHSS standard soil HA are not identical as expected. Further, the existing literature shows that humic substances from different sources exhibit similar chemical shifts but may differ substantially in the relative intensity of chemical shifts (Krosshavn et al., 1990; Malcolm and MacCarthy, 1991; Schnitzer, 1991). Therefore, the chemical shifts, i.e., the kinds of functional groups of the IHSS standard soil HA and the in situ solid product of the HAS–catechol system can be compared. In the present study, the IHSS standard soil HA was used as a reference for investigating the kinds of functional groups of C of the in situ solid product which was not fractionated. Some similar chemical shifts were observed for these two samples (Fig. 4). The chemical shifts at 26 and 31 ppm in the NMR spectrum of the standard HA (Fig. 4a) and 33 ppm in that of the precipitation product of the HAS–catechol system (Fig. 4b) were due to paraffinic structures (CH, CH₂, and CH₃) (Bortiatynski et al., 1996). The relative higher intensity at 33 ppm of the HAS–catechol system indicates that HAS ions substantially promoted the cleavage of the ring structure and the formation of single-bonded carbons from double-bonded carbons of catechol. This is further corroborated by the chemical shifts at 58 (carbons in CH₂OH groups and polysaccharides), 72 (aliphatic C bonded to OH in alcohols, carbohydrates, esters and ethers), and 105 ppm (carbons in –O–CH₂–O– groups, or acetal or ketal) of the precipitation product (Fig. 4b). These chemical shifts were consistent with the chemical shifts at 57, 73, and 103 ppm of the standard HA (Fig. 4a). The chemical shifts at 117 (protonated aromatic carbons), 131 (unsubstituted and alkyl-substituted aromatic carbons), 146 and 152 (aromatic carbons substituted by oxygen, aromatic ether, phenol), and 171 ppm (carboxyl carbons and ester groups) (Wershaw, 1985; Stevenson, 1994) of the NMR spectrum of the precipitates formed in the HAS–catechol system (Fig. 4b) are similar to the chemical shifts observed in the standard soil HA obtained from the IHSS (Fig. 4a). However, compared with the precipitation product of the HAS–catechol system, the chemical shifts at 117 and 146 ppm are absent and the intensity of the chemical shift at 152 ppm is much weaker in the case of the standard soil HA. The presence of the chemical shift at 171 ppm (Fig. 4b) caused by the carboxylic carbons and/or esters provides evidence of the formation of carboxyl groups in the HAS–catechol system. Previous reports (Hatcher et al., 1985; Preston and Newman, 1992; Stevenson, 1994; Preston, 1996) show that soil HAs, FAs, and humins have very similar chemical shifts of ¹³C NMR spectra, although the proportion of some chemical shifts is different. The ¹³C NMR spectra of HAs show significantly less carbohydrate carbons and greater concentrations of aromatic carbons relative to paraffinic carbons (Hatcher et al., 1985). However, the proportion of chemical shifts also varies with the source

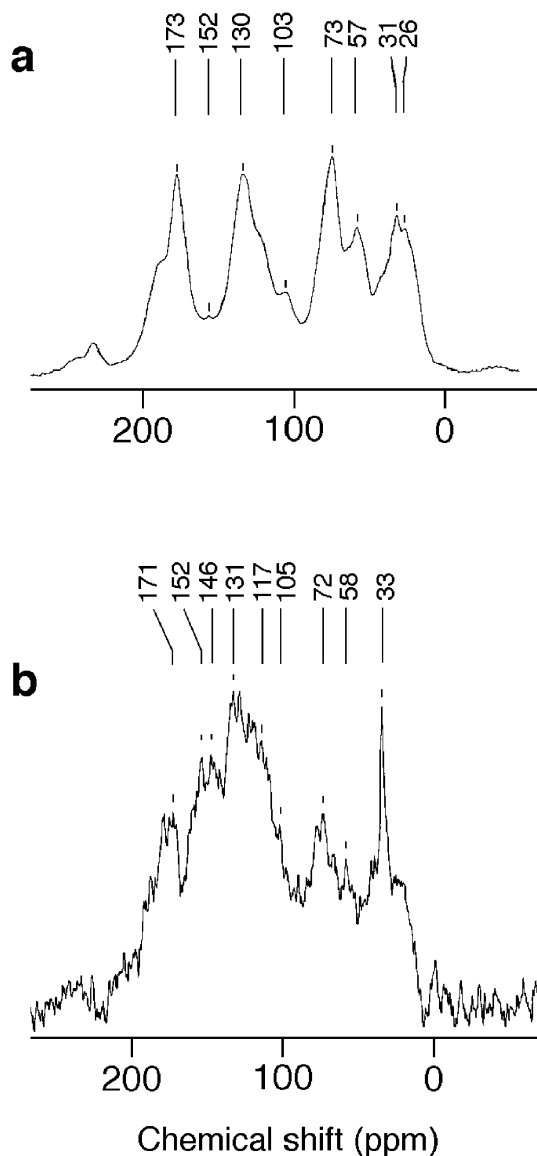


Fig. 4. Solid state ¹³C CP–MAS NMR spectra of (a) the IHSS standard soil HA and (b) the precipitation product of the HAS–catechol reaction system at the end of a 60-day reaction period. Spectrum (b) is the result of the analysis of the in situ sample which was composed of HAS and humified materials, not fractionated, and the C content was diluted by HAS present in the precipitate.

of humic substances (Krosshavn et al., 1990; Malcolm and MacCarthy, 1991). The precipitation product of the HAS–catechol system was not purified, not fractionated, and the in situ sample was analyzed by ¹³C NMR in the present study. In spite of this, the chemical shifts in the ¹³C NMR spectrum of the precipitation product of the HAS–catechol system remarkably resemble those of the IHSS standard soil HA.

The AFM images show that the precipitation product of the HAS–catechol system consisted of small spheroidal particles; some of these spheroidal particles coated bigger plate particles (Fig. 5b). These small spheroids (Fig. 5b) were very similar to the spheroids of the IHSS standard soil HA observed under the same conditions (Fig. 5a). The diameter of the spheroids in the precipitation product of the HAS–catechol system and that of the standard HA ranged from 40 to 171 nm with the average of 88 nm and from 50 to 150 nm with the average of 85 nm, respectively. The bigger plate particles were apparently the precipitates formed from HAS ions. The C content of the in situ precipitation product of the HAS–catechol system was 487.2 g C kg⁻¹ (Table 1). After de-ashing, the C content was 590.1 g C kg⁻¹, which is very close to the C content of the IHSS standard soil HA (581.3 g C kg⁻¹). Further, 95% of the black precipitates dissolved in 0.5 M NaOH, indicating that the vast majority of the humic substances formed was not humin. The Si and Al contents of the precipitation product of the HAS–catechol system were, respectively, 48.8 and 101.2 g kg⁻¹ with a Si/Al molar ratio of 0.48 which is very close to that of imogolite. In addition, coprecipitation of some of the HAS ions with catechol-derived humic substances resulted in the presence of a considerable amount of Si in the precipitation product of the HAS–catechol system. Humic and fulvic acids, extracted from soils and sediments, contain considerable quantities of inorganic constituents as indicated by the ash content and the presence of Si and Al as the predominant metal constituents (Stevenson, 1994). Griffith and Schnitzer (1975, 1976) found that Al and Si were, respectively, the first and second predominant elements in the ashes of purified FA extracted from tropical volcanic soils. Fotiev (1971) also found that the ash content of fulvic acid which was formed by decomposition of vegetation and animal remains was predominantly Si, Al and Fe. Since the complexation between silicon and polyphenols such as catechol is much weaker than that between Al and polyphenols ($\log K_{\text{Si-catechol}} = -12.42$ and $\log K_{\text{Al-catechol}} = -6.0$ at 25 °C and $I = 0.1$) (Martell et al., 1998), besides binding

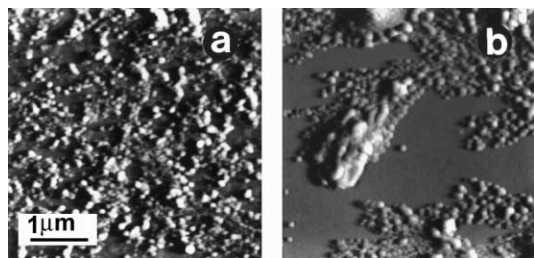


Fig. 5. The atomic force micrographs of (a) the IHSS standard soil HA and (b) the precipitation product of the HAS–catechol system at the end of a 60-day reaction period. The scale is the same for (a) and (b).

to fine clay mineral grains, the presence of significant amounts of silicon (ca. 20–60 g kg⁻¹) in natural humic substances (Griffith and Schnitzer, 1975, 1976; Stevenson, 1994) may be attributed to complexation of humic substances with HAS ions.

The FTIR spectrum of the solid products formed in the HAS–catechol system was also similar in certain aspects to that of the IHSS standard soil HA (Fig. 6). The absorption bands at 3238–3253 cm⁻¹ (Fig. 6) were attributed to the OH stretching from adsorbed water and phenolic and alcoholic OH groups in the solid product. The weak absorption band at 2922 cm⁻¹ (Fig. 6a) and the weak shoulder at 2922 cm⁻¹ (Fig. 6b) were from stretching vibrations of aliphatic C–H bonds in methyl and/or methylene units (MacCarthy and Rice, 1985). The decrease in the intensity of the band at 2922 cm⁻¹ in the precipitate of the HAS–catechol system was probably due to the complexation of HAS ions with humic macromolecules. Previous research showed that the band at about 2900 cm⁻¹ of soil HA disappears after retreating the sample to sodium salt (Stevenson, 1994). The absorption band at 2331 cm⁻¹ was due to the vibrations of CO₂. The absorption band at 1721 cm⁻¹ in the standard soil HA (Fig. 6a) was attributable to the C=O stretching vibration, due mainly to the carboxyl groups. However, only a shoulder band at 1715 cm⁻¹ of the precipitation product of the HAS–catechol system was observed (Fig. 6b). The NMR spectrum of the precipitate of the HAS–catechol system shows a significant fraction of carboxylic carbon between 165 and 190 ppm (Fig. 4b). However, the FTIR band at 1721 cm⁻¹ of humic substances greatly varies with the sample treatment. For example, a humic acid extracted from a Mollisol has strong bands at 1600 and 1720 cm⁻¹, whereas its sodium salt only has a weak shoulder at 1700 cm⁻¹ and the band at 1600 cm⁻¹ shifted to 1580 cm⁻¹ (Stevenson, 1994). The complexation of HAS ions with humic macromolecules formed in the HAS–catechol system apparently leads to some alteration of the FTIR spectrum. The bands at 1613 cm⁻¹ (Fig. 6a) and 1599 cm⁻¹ (Fig. 6b) were assigned to aromatic C=C double bonds conjugated with C=O and/or COO⁻ (MacCarthy and Rice, 1985). The absorption band at 1464 cm⁻¹ (Fig. 6b) is attributed to the bending vibration of aliphatic C–H groups (MacCarthy and Rice, 1985). The absence of this band in the FTIR spectrum of the IHSS standard soil HA (Fig. 6a) suggests that some simple aliphatic fragments were formed in the HAS–catechol system. The band at 1390 cm⁻¹ (Fig. 6a and b) was attributed to the O–H bending vibrations of alcohols or carboxylate groups (MacCarthy and Rice, 1985). The absorption bands at 1221–1275 cm⁻¹ may be due to the C–O stretching vibration and OH bending deformations from carboxyl groups. The absence of the absorption band at 2612 cm⁻¹ (due to COOH vibration) and much lower intensity of the band at 1715 cm⁻¹ in

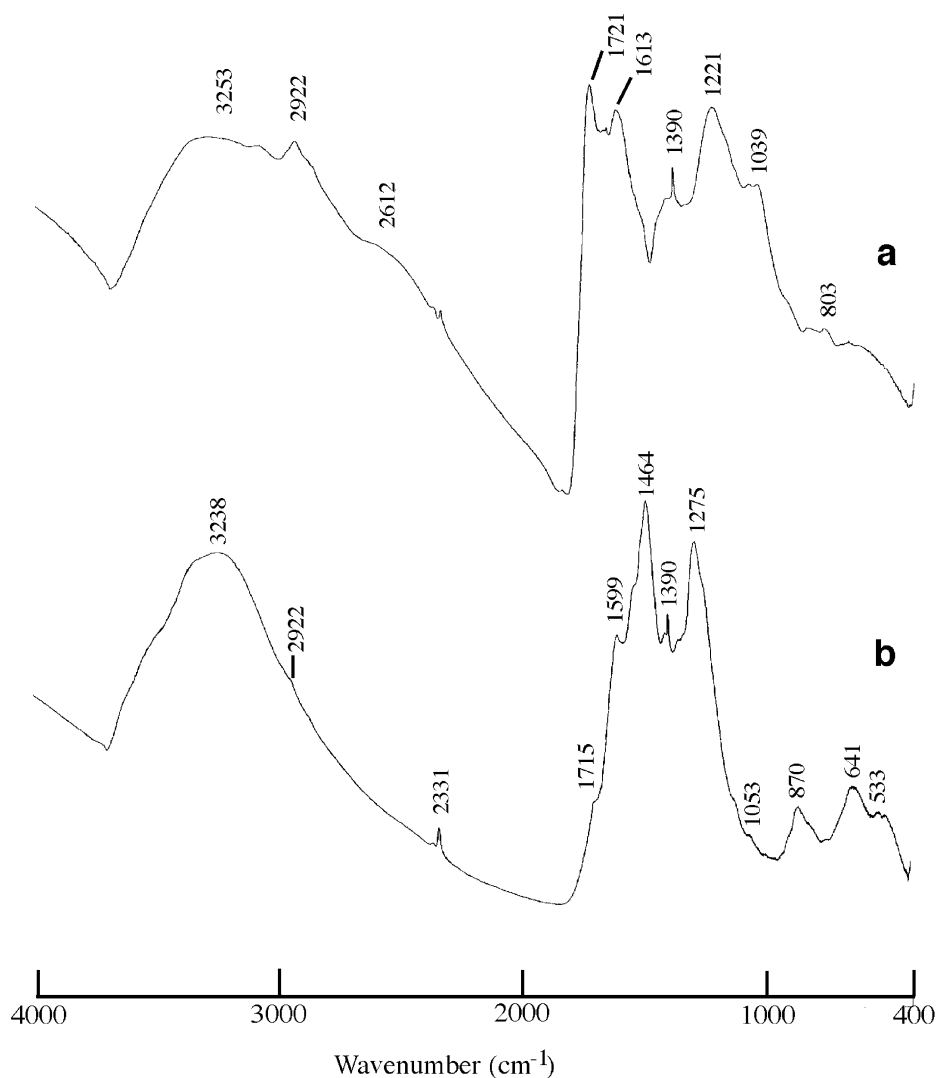


Fig. 6. FTIR spectra of (a) the IHSS standard soil HA and (b) the precipitation product of the HAS-catechol system at the end of a 60-day reaction period.

the FTIR spectra of the precipitation product of the HAS-catechol system (Fig. 6a and b) indicate that less COOH functional groups were probably present in the precipitate of the HAS-catechol system compared with the IHSS standard soil HA. The absorption bands at 1039–1053 cm^{-1} were assigned to C–O stretching of polysaccharide-like substances and Si–O vibrations of the silicate impurities. The IHSS standard soil HA contains 8.8 g ash kg^{-1} HA. The weak band at 803 cm^{-1} of the standard soil HA (Fig. 6a) was probably due to the metal-oxygen vibrations of some metal impurities. The more pronounced bands at 533–870 cm^{-1} of the precipitation product of the HAS-catechol system were attributable to the Al–O vibrations (van der Marel and Beutelspacher, 1976) of the coprecipitated Al with

humic macromolecules as revealed by the substantial Al content of the solid product of the HAS-catechol system (Table 1).

Several workers have used X-ray analyses for elucidating the chemical structure of humic substances (Tokudome and Kanno, 1965; Kodama and Schnitzer, 1967; Schnitzer et al., 1991). The XRD patterns of HAS usually show a broad peak near 3.5 Å, whereas those of FAs show broad peaks near 4.5 Å (Schnitzer et al., 1991). The 3.5-Å peak is also referred to as the G band and is ascribed to tightly condensed C in HA nuclei, that is, mainly aromatic C. By contrast, the 4.5-Å peak, often referred to as the γ band, is associated with C occurring mostly in side chains, which are less tightly packed and are considered to be primarily aliphatic. The

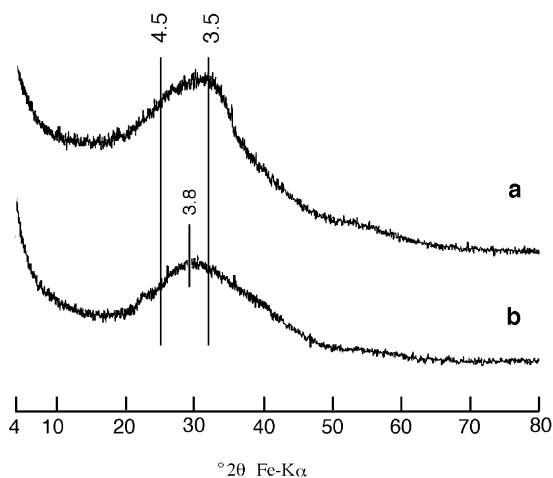


Fig. 7. X-ray powder diffractograms of (a) the IHSS standard soil HA and (b) the precipitation product of the HAS–catechol system at the end of a 60-day reaction period.

X-ray diffraction patterns of the IHSS standard soil HA and the precipitation product of the HAS–catechol system are presented in Fig. 7. Although a broad peak appeared in both XRD patterns, the X-ray pattern of the IHSS standard soil HA shows the relatively high intensity of the peak at 3.5 Å (Fig. 7a). However, the ^{13}C NMR spectrum of the HAS–catechol solid product shows a relatively higher peak intensity of aromatic C to aliphatic C compared with the IHSS standard soil HA (Fig. 4). The XRD broad peaks of amorphous humic substances make it very difficult to interpret, especially quantitatively, to elucidate the aromatic and aliphatic C of humic substances only based on XRD patterns. Not all of humic substances show the two peaks at 3.5 and 4.5 Å (Pollack et al., 1971; Matsui et al., 1984). The HA extracted from black peats shows a broad peak at 3.85 Å (Pollack et al., 1971). Matsui et al. (1984) also reported that HAs may have a stronger peaks at 4.1 Å than that at 3.5 Å. Further, the XRD pattern of HAs varies with the treatment of the samples. When HCl-pretreated HAs were further treated with Na-amalgam, the peak at 3.5 Å of the recovered HA moved to 3.8 Å (Matsui et al., 1984). Therefore, the broad peak in the region from 4.5 Å to 3.5 Å of the precipitation product of the HAS–catechol system (Fig. 7b) suggests that the precipitation product may have the nature of both HAs and FAs and/or the complexation of HAS ions with humic macromolecules may result in the shift of the peak from 3.5 Å of HA to 3.8 Å.

3.3. Catalytic mechanisms of HAS ions in catechol humification

The solid state ^{13}C NMR (Fig. 4) and FTIR data (Fig. 6) indicate the ring cleavage and oxidation of

catechol catalyzed by HAS and the resultant formation of aliphatic C and carboxylic groups. The formation of a dark colored solution as indicated by UV-visible spectra (Fig. 1) and the spheroidal particles in the AFM images (Figs. 2 and 5), the increase of the formation of black precipitates with the reaction time, the ash-free organic C content of the solid product (Table 1), and the XRD data (Fig. 7) clearly show the polymerization of catechol catalyzed by HAS ions. The results obtained from the spectroscopies, X-ray diffraction, and elemental analysis indicate that HAS has the ability to catalyze the transformation of catechol to humic substances.

The catalytic effectiveness of a metal ion depends upon its ability to complex with ligands and shift electron density and molecular conformation in the ways favorable for the reaction (Stone and Torrents, 1995). The complexation of HAS ions with catechol has not been reported. However, based on the complexation of Al and Si with catechol (Iler, 1979; MacBride et al., 1988; Martell et al., 1998; Liu and Huang, 2000) and the data obtained in the present study, a mechanism for the catalytic effect of HAS ions on the humification of catechol is proposed (Fig. 8). Catechol acts as a hard Lewis base and Al and Si of HAS ions are hard Lewis acids. Hydroxy-aluminosilicate ions can complex with catechol through Al–O and Si–O bond formation. The electronegativity values of Al, Si, H, and O are, respectively, 1.61, 1.90, 2.20, and 3.44 (Huey, 1983). Therefore, when Al or Si replaces H in catechol, the electron cloud delocalizes around the Al–O and Si–O bonds from phenolic oxygen into the π -orbital bonding formed from the overlaps between the 2p orbitals of the C atoms of the aromatic ring, thus apparently accelerating the formation of semiquinone free radicals and their coupling to form polycondensates. The semiquinone free radicals formed appeared to be partially transformed, through ring cleavage, to aliphatic fragments, resulting in the development of carboxyl groups and subsequent decarboxylation and CO_2 release. The polycondensates and aliphatic fragments formed were associated with the precipitates and also present in the supernatant as revealed by the formation of the dark supernatant and the black precipitates.

4. Conclusions

The results obtained in the present study show that HAS ions, which are the most common solution species of Al and Si in acidic soils in temperate to subtropical regions (Wada and Wada, 1980; Farmer et al., 1979; Lou and Huang, 1988), substantially promoted the humification of catechol. This finding is of fundamental significance in understanding the abiotic formation and related geochemistry of humic substances in acidic

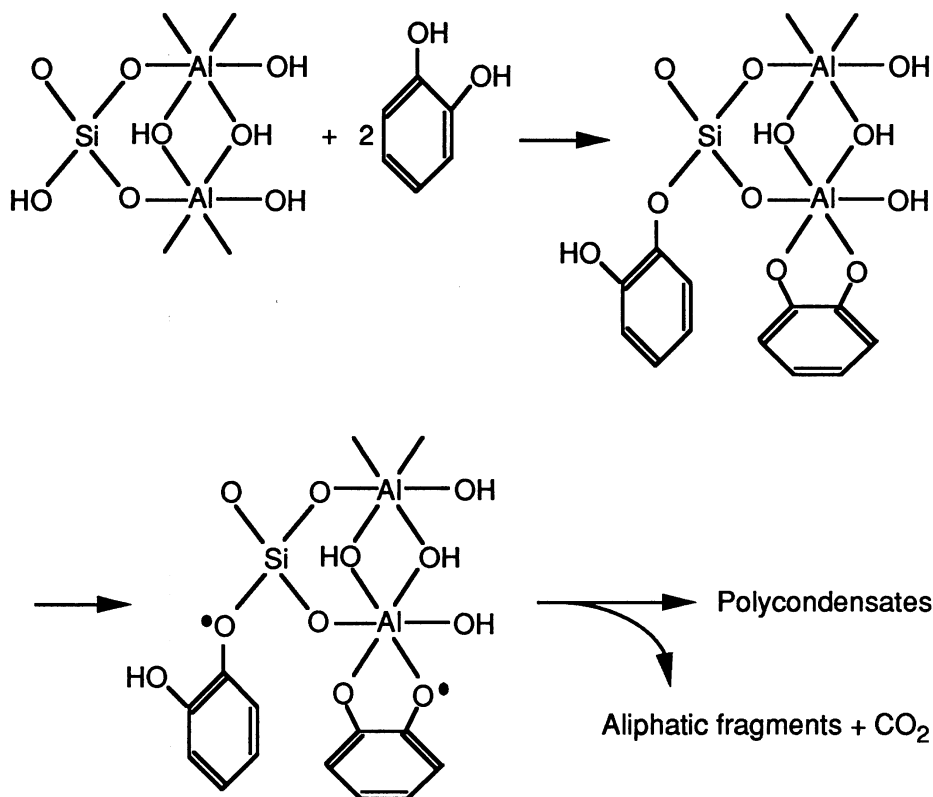


Fig. 8. Proposed mechanism for the catalysis of HAS ions in catechol humification.

environments. The incorporation of some HAS ions into the structure of humic substances during their formation may provide an explanation for the presence of substantial amounts of Al and Si as impurities in humic substances extracted from soils and sediments.

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