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SURFACE ACIDITY OF PYROPHYLLITE AND TALC

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ABSTRACT

Pyrophyllite and talc were shown to have acid sites on their surface, and the
strength and amount of the acidity were much higher for pyrophyllite than talc. The
strength and amount of the acidity of both minerals were not affected by the exchangeable cation species. Water molecules previously adsorbed on the surface

of the minerals lowered both the strength and amount of the acid sites, although the degrees of the decrease were smaller than the case of montmorillonite. When the water was introduced after the adsorption of indicators, the water molecules did not affect both the strength and amount of the acidity.
From above observations, it is suggested that the acidity of pyrophyllite and talc are not attributed to any known origin of the acidity for layer silicates. We concluded that the acidity of pyrophyllite and talc are the Lewis type, and derived
from their nature as electron acceptor due to their 'neutral' layer compositions. The
difference in the acidity between pyrophyllite and talc may come from the difference in
their octahedral cation species.

Key words: pyrophyllite, talc, surface acidity, Hammett indicator method

INTRODUCTION

Layer silicate minerals are known to have acid sites on their surface. Possible origins of the acid sites are: exchangeable hydrogen, water molecules coordinated to exchangeable cations, hydroxyl groups at crystal edges, coordination-unsaturated structural aluminum, and naked exchangeable cations. The former three are Bronsted acid sites, and the latter two are Lewis acid sites. In them, the well known and investigated acidity is the one due to water molecules coordinated to exchangeable cations on expandable layer silicates
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such as montmorillonite. The strength and amount of such acidity are known to be affected by relative humidity (RH) and exchangeable cation species (Mortland and

Raman, 1968; Frenkel, 1974; Henmi and Wada, 1974; Raussell-Colom and Serratosa, 1987).

Pyrophyllite and talc, ideally with no layer charge, are also reported to have acid sites on their surface. Solomon and Rosser (1965) showed that pyrophyllite can catalyze

polymerization of styrene as electron acceptor in the reaction. Solomon and Murray (1972) determined the acid strength of talc to be Ho=+4.0 to +3.3 by Hammett

indicator method (Walling, 1950; Benesi, 1956). However, their findings have drawn little attention, so, the origins and the development mechanisms are not clear for the acid sites

368 D.Y. Wu et al.

of these 'neutral' minerals.

Pyrophyllite and talc are classified into the simplest 2:1 type layer silicate minerals with no layer charge, but these minerals found in nature have trace amounts of isomor-phous substitution sites without exception (Newman and Brown, 1987). Here, it might be possible to attribute the observed surface acidity to the water molecules coordinated to exchangeable cations, similar to montmorillonite. In a preliminary study, however, we found that Na-saturated pyrophyllite showed stronger surface acidity than Na-saturated montmorillonite under a same condition. If the acidity of pyrophyllite is associated with isomorphous substitution sites, Na-montmorillonite should also have comparably strong surface acidity as Na-pyrophyllite.
In this study, we characterized the surface acidity of pyrophyllite and talc with Hammett indicator method under different RHs and cation saturations. The results

obtained suggested that the origin of the acidity of these 'neutral' minerals did not fall into the category of any five origins described above. We concluded that the acidity of these minerals derive from their nature as electron acceptor due to their 'neutral' layer compositions.

EXPERIMENTAL

Standard mineral samples of pyrophyllite (Hiroshima, Japan) and montmorillonite
(Yamagata, Japan) from Clay Science Society of Japan, and rock sample of talc (Liaon-
ing, China) obtained from Nihon Tikagakusha, were used. After grinding, they were
passed through a 60-mesh sieve. For different cation saturations, they were washed with
chloride solutions of Na, Ca, Mg, and Al, then washed with water, ethanol, and acetone,
and air-dried. Hydrogen saturated pyrophyllite and talc were prepared by washing with
0.01 M HCl solution followed by immediate washing with water, ethanol, and acetone,
and air-drying. For montmorillonite, hydrogen saturation was done with hydrogen satur-
ated resin.
For chemical analysis, Na-saturated samples were digested with hydrogen fluoride in
conjunction with aqua regia (Bernas, 1968), and elements were determined by atomic
absorption spectrophotometry. The amount of permanent negative charge was determined
from the amount of Na+ retained by each mineral in equilibrium with mixed solution of
NaCl and HCl of pH-pNa=1.7. Where pNa denotes the negative logarithm of the
concentration of Na+. For clay minerals, when the pH-pNa value of the bulk solution was
less than 2, only permanent negative charges can hold index cation, Na+ (Wada, 1983).
Specific surface area was determined by fitting the amount of N2 adsorbed for BET
equation at -196•Ž after preliminary heating at 160•Ž.
Hammett indicators used in this study are listed in Table 1, with their acidic and basic
colors and pKa values. The smaller the pKa value, the weaker the basicity of the
indicator. Adsorption experiments of the Hammett indicators were done with mineral
samples previously heated at 105•Ž for 16 h. After the heating, each sample was cooled to
room temperature and kept over P2O5 in a desiccator. The mineral samples were then
used for adsorption experiments directly from desiccator (RH=0%) or after equilibration
under various RHs for 48 h. For all combinations of the minerals and indicators, appropriate

Surface Acidity of Pyrophyllite and Talc 369

amounts of benzene and each indicator solution (4 mmol dm-3 in benzene) were added to
the minerals so as to give a series of initial concentrations of 0 to 0.4 mmol dm-3. The
mixtures were then shaken for 12 h at 20•Ž. Preliminary test showed that longer times of
shaking more than 12 h made no increase in the amount of adsorption. After the shaking,
the mixtures were allowed to stand for 30 min, and the optical density of each supernatant
was then determined at the wavelength shown in Table 1. The amount of a indicator
adsorbed was calculated from the difference in the optical densities with and without
mineral sample using Beer's low.
The visible light absorption and reflectance spectrum were determined with HITACHI
U-3500 spectrophotometer. The reflectance spectrum was obtained for each combination
of indicator and mineral sample after adsorption experiment: after decantation of the

TABLE 1. List of Hammett indicators

370 D. Y. Wu et al.

supernatant, the residue was mounted on a quartz glass slide, and air-dried. The reflectance was then determined with Al2O3 powder as a reference material. Spectra of the minerals without the indicators were also obtained and subtracted from the spectra of the mineral-indicator mixtures to obtain the spectra of indicators adsorbed on the minerals.

RESULTS AND DISCUSSION

X-ray powder diffraction patterns (not shown) indicated that trace amounts of kaolin mineral and diaspore were contained in pyrophyllite sample, and small amounts of quartz were contained in pyrophyllite and montmorillonite samples. Elemental composition in Table 2 shows that the pyrophyllite sample contains Fe, Na, K, and Ti in addition to Si and Al, so, small amounts of isomorphous substitution of Si for Al or Al for Fe were suspected. The amounts of permanent negative charge were 8.2, 5.1, and 1128 mmolc kg-1 for pyrophyllite, talc, and montmorillonite, respectively. Specific surface areas deter-mined by N2 were 6.0, 8.4, and 27.1 m2g-1 for pyrophyllite, talc, and montmorilonite, respectively.

Strength of acid sites
Changes in the color of Hammett indicators were judged by naked eye and also by spectrophotometry. Figure 1 shows visible light absorption spectra of butter yellow (pKa=+3.3) in basic form (in pyridine, Figure la) and acidic form (in lactic acid, Figure

TABLE 2. Selected properties of clay mineral samples

Surface Acidity of Pyrophyllite and Talc 371

FIG. 1. Visible light absorption spectra of butter yellow: (a) in pyridine, (b) in lactic acid, (c) adsorbed on H-montmorillonite, and (d) in SiCl4

lb), and that adsorbed on H-montmorillonite (Figure 1c) and in SiCl4 (Figure 1d). Absorption maximum at 420 nm for basic form (yellowish) shifted to 518 nm for acidic form (reddish). The color of butter yellow adsorbed on H-montmorillonite (mostly Bronsted acid) and that in SiCl4 (Lewis acid) were both reddish, and the spectra were similar in their shape and absorption maxima (Figures lc and 1d). This indicated that the distinction between Lewis and Bronsted acid sites of adsorbents was difficult from the

absorption spectra of indicators. Other diazobenzene indicators with pKa values of +1.5 to +5.0 showed similar patterns of spectra as butter yellow, except for their absorption maxima. Three indicators with pKa values less than -3.0 with ketonic functional groups, different from above diazobenzenes, also showed shifts in absorption maxima when the indicators changed from basic to acidic form.
Table 3 shows acid strengths estimated with above Hammett indicators for pyrophyllite, talc, and montmorillonite under different RHs and cation saturation. Montmorillonite showed acidity of H0=+2.0 to +1.5 under RH of 0% and Na saturation, and the acidity increased progressively when saturated with Ca, Mg, Al, and H. The acid strength of montmorillonite was also strongly affected by the water adsorbed on mineral surfaces, RH. These results agree well with the observations reported before (Mortland and Raman, 1968; Frenkel, 1974; Henmi and Wada, 1974; Raussell-Colom and Serratosa, 1987), indicating that the acidity of montmorillonite arises from the dissociation of water molecules coordinated to exchangeable cations.
On the other hand, the acid strength of pyrophyllite and talc were not affected by the exchangeable cation species, and showed Ho values of -5.6 to -8.2 and +1.5 to -3.0 under RH of 0%, respectively. Under RH of 98%, the acid strength of pyrophyllite and talc decreased to H0=-3.0 to -5.6 and +2.0 to +1.5, respectively, but the extents of

372 D. Y. Wu et al.

TABLE 3. Acid strength of minerals in relation to exchangeable cation species and relative humidity (RH)

the decrease were smaller than the case of montmorillonite. It is notable here that the

acid strength of pyrophyllite was strong (HO=-5.6 to -8.2) even under Na-saturation and RH of 53%. Additional test showed that the acidity was maintained up to RH of 81%. Therefore, it is evident that the acidity of pyrophyllite and talc did not derive from water molecules coordinated to exchangeable cations. Because the strength of the acidity due to such water molecules are known to be strongly affected by the exchangeable cation species and RH, as in the case of montmorillonite. The two possible Lewis acid sites, described in INTRODUCTION are also improbable, because these acidities should appear only under dehydrated conditions (Solomon, 1968), and the Lewis acidity due to dehydrated exchangeable cations are also dependent on the cation species.
To eliminate the possible Bronsted acid sites on crystal edges, pyrophyllite was washed with NaOH solution (0.001 M) and 2% Na2CO3. Even after the alkaline treatments, the observed acid strength of pyrophyllite was not changed. Following the alkaline treatments, the possible positive charges on edge aluminol (Al-OH2+) were deprotonated, and the silanol groups with lower pKa values were also deprotonated. In other words, the possible Bronsted acid sites at crystal edges should be eliminated by the treatments. Therefore, it is suggested that the acid sites were not the acidic hydroxyl groups at crystal edges. The inability of alkaline treatment to remove the acid sites suggests the acidity belongs to Lewis type. Because it is believed that only Bronsted sites would be neutralized by alkaline treatments (Hawthorne and Solomon, 1972).

Adsorption isotherms
Adsorption isotherms were obtained for Hammett indicators (pKa=+5.0 to + 1.5) on Na-pyrophyllite, talc, and montmorillonite under RH of 0%. For butter yellow, isotherms on pyrophyllite and montmorillonite saturated with Ca, Mg, Al, and H were also obtained. Figure 2 shows examples of Langmuir plots for methyl red (pKa=+5.0) adsorbed on Na-saturated samples. In the linear form of Langmuir equation,

Surface Acidity of Pyrophyllite and Talc 373

FIG. 2. Examples of Langmuir plots: adsorption of methyl red on Na form of pyrophyllite (Pt), talc (Tc), and montmor-
illonite (Mt) from benzene solutions

C/Y=1/Kb+C/b,

C, Y, b, and K are equilibrium concentration (mmol dm-3), amount adsorbed (mmol kg-1), maximum amount of adsorption (mmol kg-1), and empirical constant, respectively. Langmuir coefficients for all combinations of Hammett indicators and clay mineral samples are shown in Table 4. Obtained r2 values were mostly above 0.99, indicating a monolayer adsorption of these indicators on the surface of the minerals.
It can be seen that the b values for the combination of butter yellow and montmorillonite are strongly dependent on the exchangeable cation species. As described above, acidity of montmorillonite derives mainly from the dissociation of water molecules around the exchangeable cations, so, the greater the polarizing ability of the cation, the more and stronger the acid sites. Thus, as shown in Table 4, the adsorption capacity of montmorillonite for butter yellow decreased in the order: H>Al>Mg>Ca>Na. On the other hand, the adsorption of butter yellow on pyrophyllite was not dependent on the exchangeable cation species (Na, Ca, and Mg). When saturated with Al and H, however, the adsorption capacity of crystal edges increased, because the saturation processes were done under pHs of 2.0 to 2.7; some aluminol groups located at the edges were positively charged, and silanol groups were completely protonated. Therefore, the increase in the adsorption compared to Na, Ca, and Mg saturation may be attributed mainly to the Bronsted acidity at crystal edges of pyrophyllite.
The adsorption capacity of the three minerals was also dependent on adsorbate, the indicators, as shown by the adsorption maxima (b value) of Na-saturated samples (Table

374 D. Y. Wu et al.

TABLE 4. Langmuir parameters for combinations of minerals and Hammett indicators

4). As the pKa of the indicators increased, the b values increased concomitantly. This behavior can be easily explained by the acid-base interactions in the adsorption process. For a given adsorbent, the higher the basicity of the indicator, the more the acid sites which can interact with the indicator.

Amount of acid sites

Visible light reflectance spectra are shown in Figure 3 for butter yellow adsorbed on Na-pyrophyllite and montmorillonite. Both of the spectra showed absorption maxima characteristic of acidic form of the indicators, with some tails towards lower wavelengths. Other spectra for all other Hammett indicators adsorbed on minerals which were acidic in color, showed similar spectra as those in Figure 3. From these results, we concluded that the Hammett indicators adsorbed on minerals are retained almost by acid-base interactions.

Surface Acidity of Pyrophyllite and Talc 375

FIG. 3. Visible light reflectance spectra of butter yellow adsorbed on Na form
minerals: (a) on pyrophyllite under RH of 0%, (b) after soaking the sample
(a) in water for 2 h, (c) on montmorillonite under RH of 0%, (d) after
exposing the sample (c) to RH of 98%

We estimated here the amount of acid sites on mineral surfaces from the maximum

amounts of adsorption (b value in Table 4) for each indicator. A commonly used method
for the estimation of the amount of acid sites on solids, n-butylamine titration method

(Benesi, 1957), was also applied for some samples. Obtained value was, however, larger
than the value estimated from b value for each sample. The cause for the overestimation
may be attributed mainly to the existence of n-butylamine in supernatant solution at the
end-point of titration. Because the adsorption of n-butylamine on minerals has also been
shown to follow Langmuir isotherm, and the equilibrium concentration is not zero when
all acid sites are occupied (Conley and Lloyd, 1971). From the data of b values with
methyl red (pKa=+5.0; the strongest basic indicator used in this study), the amounts of
acid sites were estimated to be 4.7, 1.6, and. 35.4mmol kg-1 for Na-pyrophyllite, talc, and
montmorillonite, respectively. This indicates that there are few acid sites per unit weight
of these minerals with Na-saturation.
Here, if we take into account the specific surface areas of these minerals, and express
the amount of acid sites per unit surface area, the amount of acid sites become considerably
large. In benzene solution, the minerals may have only the external surfaces on which the
relatively large indicator molecules can be adsorbed, so, the effective specific surface
areas of these minerals are considered to be equal to those determined with N2. The
calculated values of the amount of acid sites in ƒÊmolm-2 using specific surface areas were
0.78, 0.19, and 1.26 for pyrophyllite, talc, and montmorillonite, respectively. Further, if
we tentatively assume the effective area of a methyl red molecule to be 100 A2, the

376 D. Y. Wu et al.

calculated percentage of the surface occupied by methyl red molecules were 49, 11, and
76% for Na-saturated pyrophyllite, talc, and montmorillonite, respectively.
However, for H-saturated montmorillonite, the amount of adsorption of butter yellow
was 452 mmol kg-1 (Table 4), and the percentage of the surface occupied by butter yellow
was calculated as 970% under the same assumptions. In this case, the penetration of
butter yellow molecule into the interlamellar space of H-montmorillonite was observed
by X-ray diffraction analysis (not shown). The b value (452 mmol kg-1) was, however,
smaller than the amount of permanent negative charge (1128 mmol kg-1). This difference
may be attributed to the failure of the benzene solution to penetrate all of the interlamellar
space or to a partial conversion of the hydrogen clay to a mixed H, Al-form (Rupert et
al., 1987). Also, in case of Na-montmorillonite, it is possible that the Hammett indicator
molecules penetrated into the interlamellar space. If so, the above value of 76% for Na-
montmorillonite and methyl red become smaller because the effective surface area in
benzene solution should become larger than the value determined by N2 adsorption. This
means further that only a few percentage of Na+ (and water molecules around the Na+)
participated in the adsorption of methyl red in the case of montmorillonite.
Although not shown in this paper, two other pyrophyllite samples were also tested for
the strength and amount of acid sites. Observed acid strengths were the same as the
pyrophyllite sample used in this study under Na-saturation and RHs of 0 and 98% . The
amounts of the acid sites by butter yellow adsorption were different between the three
pyrophyllite samples. The amounts had a correlation with specific surface areas by N2
adsorption rather than the amounts of permanent negative charges.

Effect of water molecules on surface acidity
For the estimation of the effect of water molecules on the amount of acid sites, the
amounts of butter yellow adsorbed on Na-saturated pyrophyllite and montmorillonite
were determined under different RHs. The initial concentration of butter yellow was
fixed at 2•~10-2 mmol dm-3. Table 5 shows the results of this determinations along with
the water contents of the minerals under each RH. For each mineral, decrease in the

TABLE 5. Adsorption of butter yellow and water on Na-saturated pyrophyllite (Pt) and montmorillonite (Mt)

Surface Acidity of Pyrophyllite and Talc 377

amount of adsorption was observed with increase of RH. In case of Na-montmorillonite, the red color due to acidic form of butter yellow disappeared under RH of higher than 93%. This indicates that the strength of all the acid sites on Na-montmorillonite decreases to less than +3.3. Under such RHs, water contents were high (>333 mg g-1), and polarizing forces of the exchangeable cations must be lower for each water molecule (Mortland and Raman, 1968). The amount of butter yellow adsorbed on Na-montmor-illonite became zero also under RH of 93%. On the other hand, the red color of butter yellow on Na-pyrophyllite was maintained up to RH of 100%, and then, 0.36 mmol kg-1 of butter yellow were still retained.
For pyrophyllite, the effect of RH was further estimated on the adsorption of other Hammett indicators. Table 6 shows the amounts of each Hammett indicator adsorbed on

Na-pyrophyllite under RHs of 0% and 98%. In Table 6, the ratios of the adsorption maxima under RHs of 98% and 0% are also listed. The ratio decreased with the decrease of pKa values of the indicators, suggesting that the water molecules acted as Lewis base to disturb the adsorption of Hammett indicator molecules on stronger acid sites. Under RH of 98% , the adsorption amounts became undetectable for indicator whose pKa is +1.5. The maximum acid strength was, however, still HO=-3.0 to -5.6 as shown in Table 3 even under RH of 98%.
Another test for the estimation of the effect of water molecule on the surface acidity, was conducted as follows: butter yellow was first adsorbed on Na-saturated minerals under RH of 0%, and then water molecules were introduced by exposing to RH of 98%

TABLE 6. Adsorption of Hammett indicators on Na-pyrophyllite as affected
by relative humidity (RH)

378 D.Y. Wu et al.

for 48 h or soaking in water for 2 h. Visible light absorption spectra obtained before and after introduction of water molecules are also shown in Figure 3. For Na-montmorillonite, absorption band with peak maximum at 518 nm due to acidic form of butter yellow diminished after exposing to RH of 98% . Notable change in the absorption band was not observed for Na-pyrophyllite even after soaking in water. Na-talc (not shown) also did not show spectral change after introduction of water. Above results indicate, for Na-pyrophyllite and Na-talc, both the amount adsorbed and the adsorption state of butter yellow were not affected by the water molecules introduced afterwards. This fact, together with the results of Tables 5 and 6, further indicates that the hysteresis exists in the competitive adsorption between Hammett indicator and water molecules on pyrophyllite surfaces. Hysteresis in the competitive adsorption on clay mineral surfaces are reported even in the cation exchange reactions between NH4+ and alkaline and alkaline earth metals (Bolt, 1979). The hysteresis may partly be the result of some stabilization of Hammett indicator molecules on pyrophyllite surface. The stabilization may include not only geometrical rearrangements, but also formations of some chamical bondings between pyrophyllite surface and Hammett indicator as a result of electron transfer.

SUMMARY AND CONCLUSIONS

The strength and amount of the acidity of pyrophyllite and talc were not affected by the exchangeable cation species. Water molecules previously adsorbed on the minerals, RH, lowered both the strength and amount of the acidity of these minerals, but the extents of the decrease were smaller than the case of montmorillonite. When the Hammett indicators were adsorbed prior to water, however, the water molecules did not affect both the strength and the amount of acid sites of pyrophyllite and talc. From above results, it is suggested that the acidity of Na-saturated pyrophyllite and talc is not due to any five origins described in INTRODUCTION: acidities from exchangeable hydrogen and hydroxyl groups at crystal edges are excluded by the results of alkaline pretreatment test, and those from water molecules coordinated to exchangeable cations, coordination-unsaturated structural aluminum, and naked exchangeable cations are also excluded by the results of adsorption experiments under different RHs and cation saturations.
We concluded that the origin of the acidity of Na-saturated pyrophyllite and talc is attributed to their nature as electron acceptor (Lewis acidity) which derive from their

'neutral' layer compositions. In other words, the crystals of pyrophyllite and talc themselves
have Lewis acidity, and the basic Hammett indicator molecules were adsorbed on the surfaces of the minerals via electron transfer. One of the possible Lewis acid sites on pyrophyllite and talc sufaces is the octahedral cations (Al or Mg) located at crystal edges. It is suspected that such octahedral cations have ability to accept electrons even when the cation is coordination saturated under relatively high RHs. Another possible adsorption site is the oxygen network of the minerals. Although the oxygen atoms are negatively charged, it may be possible that the octahedral cations accept electrons from basic Hammett indicators via O-Si-O-Al(Mg) bondings. The difference in the strength and amount of the acidity between pyrophyllite and talc may come from the difference in their elemental compositions, that is, their octahedral cation species. Because the difference in elemental compositions means the two minerals are different 'molecule' with each

Surface Acidity of Pyrophyllite and Talc 379

other. Montmorillonite did not show such acidity, although it has similar layer structure to pyrophyllite except for the considerable amounts of isomorphous substitution sites. It may be due to the presence of much negative charges in the structure, even though the negative charges are neutralized by exchangeable cations. Quantum chemical study is necessary and now being conducting to support above speculations; the ability of

pyrophyllite and talc to accept electrons, the Lewis acid sites on the minerals, reasons for the differences in the Lewis acidities between pyrophyllite and talc, and beween pyrophyllite and montmorillonite.

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